PRATIMA BAJPAI

BIERMANN'S HANDBOOK OF PULP AND PAPER

RAW MATERIAL AND PULP MAKING

VOLUME 1
THIRD EDITION

BIERMANN'S HANDBOOK OF PULP AND PAPER: RAW MATERIAL AND PULP MAKING

THIRD EDITION

PRATIMA BAJPAI
Consultant Pulp & Paper
Kanpur, India

ELSEVIER

Elsevier
Radarweg 29, PO Box 211, 1000 AE Amsterdam, Netherlands
The Boulevard, Langford Lane, Kidlington, Oxford OX5 1GB, United Kingdom
50 Hampshire Street, 5th Floor, Cambridge, MA 02139, United States

Copyright © 2018 Elsevier Inc. All rights reserved.

No part of this publication may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, recording, or any information storage and retrieval system, without permission in writing from the publisher. Details on how to seek permission, further information about the Publisher's permissions policies and our arrangements with organizations such as the Copyright Clearance Center and the Copyright Licensing Agency, can be found at our website: www.elsevier.com/permissions.

This book and the individual contributions contained in it are protected under copyright by the Publisher (other than as may be noted herein).

Notices
Knowledge and best practice in this field are constantly changing. As new research and experience broaden our understanding, changes in research methods, professional practices, or medical treatment may become necessary.

Practitioners and researchers must always rely on their own experience and knowledge in evaluating and using any information, methods, compounds, or experiments described herein. In using such information or methods they should be mindful of their own safety and the safety of others, including parties for whom they have a professional responsibility.

To the fullest extent of the law, neither the Publisher nor the authors, contributors, or editors, assume any liability for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions, or ideas contained in the material herein.

Library of Congress Cataloging-in-Publication Data
A catalog record for this book is available from the Library of Congress

British Library Cataloguing-in-Publication Data
A catalogue record for this book is available from the British Library

ISBN: 978-0-12-814240-0

For information on all Elsevier publications visit our website at
https://www.elsevier.com/books-and-journals

ELSEVIER
Book Aid International
Working together
to grow libraries in
developing countries
www.elsevier.com • www.bookaid.org

Publisher: Joseph P. Hayton
Acquisition Editor: Kostas KI Marinakis
Editorial Project Manager: Michelle W. Fisher
Production Project Manager: Mohanapriyan Rajendran
Designer: Mark Rogers

Typeset by TNQ Books and Journals

"Dedicated to my beloved parents & family"
For their love, endless support, encouragement & sacrifices

Contents

1. Introduction and the Literature

2. Wood and Fiber Fundamentals

3. Wood and Fiber—Growth and Anatomy

4. Softwood Anatomy

5. Hardwood Anatomy

6. Wood Fiber Anatomy and Identification

7. Properties of Wood

8. Wood-Based Products and Chemicals

9. Calculations of Wood, Paper, and Other Materials

10. Nonwood Fiber Use in Pulp and Paper

11. Raw Material Preparation

12. Pulping Fundamentals

13. Pulping Calculations

14. Production of Dissolving Grade Pulp

15. Pulp Washing

16. Pulp Cleaning, Screening, and Fractionation

17. Kraft Spent Liquor Recovery

18. Alternative Chemical Recovery Processes

19. Pulp Bleaching

20. Hexenuronic Acid and Their Removal

21. Bleaching and Pulp Properties Calculations

22. Purification of Process Water in Closed-Cycle Mills

23. Fiber From Recycled Paper and Utilization

24. Pulp Bioprocessing

25. Forest Biorefinery

Preface to the Third Edition

The second edition, *Handbook of Pulping and Papermaking*, authored by Dr. Biermann was published in 1996 and has proven to be very successful. As many important technological developments have taken place during the last two decades, Elsevier decided to publish the third edition and approached me to work on it. The third edition is split into two books: *Biermann's Handbook of Pulp and Paper: Raw Material and Pulp Making* and *Biermann's Handbook of Pulp and Paper: Paper and Board Making*.

Biermann's Handbook of Pulp and Paper: Raw Material and Pulp Making is a comprehensive reference for industry and academia covering the entire gamut of pulping technology. This book provides a thorough introduction to the entire technology of pulp manufacture and features chapters covering all aspects of pulping from wood handling at the mill site through pulping, bleaching, and pulp drying. It also includes a discussion on bleaching chemicals, recovery of pulping spent liquors, regeneration of chemicals used, and the manufacture of side products. The secondary fiber recovery and utilization and current advances such as organosolv pulping and attempts to close the cycle in bleaching plants are also included. Hundreds of illustrations, charts, and tables help the reader grasp the concepts being presented.

This book is a valuable tool for specialist in the field, researchers, teachers, and students for enlarging their horizon on pulp manufacturing. This book will provide professionals in the field with the most up-to-date and comprehensive information on the state-of-the-art techniques and aspects involved in pulp making. It has been updated, revised, and largely extended. Alongside the traditional aspects of pulping and papermaking processes, this book also focuses on biotechnological methods, which is the distinguishing feature of this book. It includes wood-based products and chemicals, production of dissolving pulp, hexenuronic acid removal, alternative chemical recovery processes, forest products biorefinery. The most significant changes in the areas of raw material preparation and handling, pulping, and recycled fiber have been included. A total of 11 new chapters have been added. This handbook is essential reading for all chemists and engineers in the paper and pulp industry.

I am very much grateful to Dr. Biermann for bringing the first and second edition of this book under the titles of *Essentials of Pulping and Papermaking* and *Handbook of Pulping and Papermaking*, respectively. These books were designed primarily as a teaching tool and also found wide use by industry. I am thankful to Dr. Kostas Marinakis, Senior Acquisition Editor, Elsevier, for inspiring me to work on the third edition.

I am grateful for the help of many people and companies (Andritz, Valmet, Acrowood, Peterson Pacific Corporation, FEECO International, GLV, Kadant, Stora Enso) for providing information on their products. I am thankful to various publishers/organizations—Tappi press; Taunton press; Forest Products Engineers Association; RISI; IEA Bioenergy; APPITA; PAPTAC; Wiley

VCH Verlag GmbH & Co; Forestnet.com; Walter De Gruyter GmbH & Co. KG, Berlin; Pulp and Paper, Canada; FAO, United Nations; Paperonweb; Smithers PIRA. My special thanks to Dr. Jean Paris from Western Ontario, Canada, for providing information on forest biorefinery; Dr. Paul Janze, Advanced Biomass Consulting Inc., Langley, BC, Canada, for providing information on Disc Screens; Mr. Lari Lammi (Valmet) and Mrs. Sirpa Välimaa, Technical Customer Service Manager, Stora Enso, for providing information on dissolving pulp; Michael Spreadbury from Peterson Pacific Corporation for providing information on Chippers; and Lucas Lippel from Lippel, Brazil, for providing information on Silos.

Pratima Bajpai
Kanpur, India

Preface to the Second Edition

The first edition of this book, under the title of *Essentials of Pulping and Papermaking*, was designed primarily as a teaching tool and also found wide use by industry as a current source of information. The second edition of this work retains the first 20 chapters with only minor alterations. To increase the dual use of this work, it has been expanded to include key areas of paper chemistry and optical properties, wood and fiber anatomy, paper use, and processing equipment, including a useful pump troubleshooting guide. The comprehensive nature of the work now merits the modified title of *Handbook of Pulping and Papermaking*.

The first 11 chapters of this book are introductory in nature for beginning students and workers in the field who desire some knowledge of the entire mill. The remainder of the book provides detailed information on topics central to the production and use of paper. Throughout, numerous references lead the reader to further information.

Several areas, such as pulp bleaching, environmental issues, and papermaking chemistry, are changing so rapidly that the reader will need to consult current journals to stay abreast of these fields. Nevertheless, this work provides the background and context for the improvements the industry is realizing in these areas.

I am grateful for the help of many people who provided information and figures and who reviewed portions of the manuscript. The information on clay was supplied by F. Camp Bacon, Jr. of Evans Clay Co.; Stuart Pittman of Thiele Kaolin Co.; Robert F. Hurst of Huber Clay; and John A. Manasso of Dry Branch Kaolin Co.

Mankui Chen provided material on transportation safety. R.L. Krahmer and A.C. VanVliet provided most of the macroscopic cross-sectional photographs of woods in Chapters 26 and 27.

Gary Vosler of Willamette Industries reviewed the section on corrugated containers. Fred Green and Carter P. Hydrick of Keystone International, Inc. provided information and figures on valves. Kelly Lacey provided the figure of a progressing cavity pump.

Todd Chase reviewed material for clarity. Reviews of selected material were provided by Kevin Hodgson and Richard Gustafson, University of Washington, and Mahendra Doshi, Doshi and Associates, although the author is solely responsible for any deficiencies in the text.

Christopher J. Biermann
Oregon State University
Oregon, USA

Preface to the First Edition

It is said that "if you give a man a fish, he eats for a day; if you teach a man to fish, he eats for a lifetime." This adage represents the entire aim of science, that is, to characterize or explain as wide a range of phenomena or conditions as possible with the least number of rules. In short, science generalizes to as large a degree as possible. To memorize a formula that applies to only one set of conditions is no more learning science than giving a man a fish is teaching him how to fish. Yet many cultures, including our own, continue to teach by requiring memorization of rules or formulas. Students wind up learning formulas they do not understand with little idea of the underlying assumptions on which they are based (and conditions to which they apply.) The result is students who show very little imagination and extension of thought to solve new problems, which is the very essence of science. The author has seen students with a great deal of tenacity, but not creativity, spend hours upon hours late into the night attempting to find a solution to a problem by searching dozens of books, rather than attempting to solve it by thinking it through, using their own internal resources.

This book stresses concepts and gives a series of problems to demonstrate the understanding of the concepts rather than just the memorization of "facts"; the difference results in the molding of a mind into that of a scientist in preference to molding a mind into an insignificantly small, unreliable database.

I hope instructors who use this book make the tests open book—after all, life in the mill is open book—there is no point in teaching any other way. Some of the problems in this book are deliberately irrelevant to anything one might encounter in reality to demonstrate the wide applicability of certain techniques and to discourage the student from trying to find a reference book to solve the problem. Frequent "curve balls" are included to keep one thinking in terms of the "big picture"; that is, when problem-solving in a mill, one is not going to have all the necessary information delivered on a silver platter. It is important to figure out what information is required, what information is at hand, and where to obtain the remainder of the information to solve a problem. Often it is not what we do not know, but rather what we *think* we know that is *not* true, that causes us problems.

This book is designed as an educational tool for pulp and paper science courses and a reference book to those in industry. It is a scientific reference concentrating on principles of pulp and paper processes rather than the multitudinous types of equipment available to carry out these processes. TAPPI Standard Methods are emphasized, but many of the TAPPI Standards give references to related methods such as those of ASTM, CPPA, SCAN, ISO, and APPITA.

Material is presented roughly in the same order as material flows through the pulp and paper mill. The first section of the book covers fundamentals, and the later sections cover more advanced treatments. It is impossible to present so much information on so many diverse areas and supply all of the necessary background in each section without undue duplication. Also, one does not like to burden the novice with details only important to a few investigators. It is appropriate to use the extensive index as the ultimate, alphabetical guide to this volume to find all of the material available on a particular topic.

The author welcomes your comments regarding this book and suggestions for teaching aids.

Christopher J. Biermann
Oregon State University
Oregon, USA

Acknowledgments

The author wishes to thank all of the people and companies who contributed information, photographs, and other help. Special thanks to the Pope and Talbot mill in Halsey, Oregon; the James River mill in Halsey, Oregon; the James River mill in Camas, Washington; and the Boise Cascade Corporate Research Center in Portland, Oregon, for providing valuable help. The sketches by the late John Ainsworth were used with generous permission of the Thilmany Paper Division of International Paper Co.

Stephen Temple of Black Clawson was instrumental in providing information and figures of his company's equipment, as were Bonny Rinker of Andritz Sprout-Bauer, Inc.; Barbara Crave and Elaine Cowlin of Beloit Corp.; Henry Chen of James River Corp. in regard to Crown Zellerbach Corp. material; Robert Gill of Pfizer, Inc.; Manuel Delgado of Straw Pulping Technology; R. H. Collins of Kamyr, Inc.; Jody Estabrook of Fiberprep; Maria Krofta of Krofta Eng. Corp.; Steven Khail of Manitowoc Eng. Co.; Garth Russell of Sunds Defibrator; and many others who provided information for this book.

Alfred Soeldner took many of the excellent scanning electron micrographs that are shown in this volume. An extensive resource of notes in the OSU pulp and paper files was used in this work; contributions to these files were made by Walter Bublitz, James Frederick, Jr., Philip Humphrey, and others, although it was not always clear who supplied any given information. Alton Campbell, University of Idaho, contributed a copy of his class lecture notes, which were helpful to this work. Michael Haas, Longview Fibre, contributed a set of the books prepared for the Pulp and Paper Manufacturing Technology Program offered through Lower Columbia College. Andre Caron, National Council of Air and Stream Improvement, supplied information concerning environmental regulations and control. Myoungku Lee prepared the index and assisted with many aspects of this work. Troy Townsend and Jinfeng Zhuang reviewed much of the manuscript.

Victor Hansen reviewed the paper machine wet-end section and contributed much information on water removal on flat wire machines.

Special acknowledgment is made to the late Kyosti Sarkanen who inspired me to start this project, sent copies of his class lecture notes to me, and was to have collaborated on this work. The editorial and production staff at Academic Press contributed substantially to this work. One could not ask for a more reasonable publisher.

Additional recognition is given to Jerry Hull, my right-hand man who runs my laboratory when I am not to be found for days at a time, for numerous suggestions of research activities and comments on this work, and editorial help on the manuscript. I would especially like to thank my wife, Lora Jasman, M.D., for numerous suggestions and editorial help.

Many other people have been involved in the review process but must remain publicly unthanked, as they remain unknown to me.

This book was typeset from WordPerfect 5.1. Many of the drawings were done with Generic CADD 5.0. Many of the chemical structures were drawn with Wimp2001. Many graphs were drawn with QuattroPro 3.0. The original copy was printed on a Hewlett Packard LaserJet 4 with CG Times font.

A conscientious effort has been made to include trademarks when cited in the text. Any omission is unintentional, and I welcome notification of any oversights.

The inclusion of color plates has been made possible by the generous support of the following companies and organizations:

The Black Clawson Company
Contributors to Oregon State University
Pacific Section Tappi
Rhône Poulenc
Specialty Chemicals
Basic Chemicals
Willamette Industries, Incorporated

Abbreviations

2,3,7,8-TCDD 2,3,7,8-Tetrachlorodibenzo-p-dioxin
2,8-DCDD 2,8-Dichlorodibenzo-p-dioxin
ABS Acrylonitrile—butadiene—styrene terpolymer
AFPA American Forest and Paper Association
AKD Alkyl ketene dimer
AOX Adsorbable organic halides
API American Paper Institute (now AFPA)
APMP Alkaline peroxide mechanical pulping
APP Alkaline peroxide pulping
AQ Anthraquinone
ASA Alkenyl succinic anhydride
ASB Aerated stabilization basin
ASTM American Society for Testing and Materials
AZC Ammonium zirconium carbonate
BAT Best available technology
BCT Box compression test
C2S Coated two sides
CCT Corrugated crush test
CMC Carboxy methyl cellulose
CMT Concora medium test
CSF Canadian Standard Freeness
CTMP Chemithermomechanical pulp
DCS Dissolved and colloidal substances
DCS Distributive control system
DDJ Dynamic drainage (Britt) jar
DP Degree of polymerization
ECF Elemental chlorine-free
ECT Edge crush test or edgewise compression test
EDAX Energy dispersive X-ray analysis
EDTA Ethylenediaminetetraacetic acid
EGSB Expanded granular sludge blanket
EMC Equilibrium moisture content
EO Ethylene oxide
EPA Environmental Protection Agency
EPP Epoxidized polyamine—polyamide
ESP Electrostatic precipitator
FAS Formamidine sulfinic acid
FBB Folding boxboard
FCG Fine ground carbonate
FCT Flat crush test
FDA Food and Drug Administration
FGCC Fine ground calcium carbonate
FPAR First-pass ash retention
FPR First-pass retention
FSP Fiber saturation point
GCC Ground calcium carbonate
GP Gel permeation
GPC Gel permeation chromatography
GSM Grams per square meter
HLB Hydrophilic—lipophilic balance
HMWT High molecular weight
HPLC High-performance liquid chromatography
HST Hercules size tester
HSWO Heatset web offset
HW Hardwood
HWC High weight coated
IC Internal circulation
IPC Institute of Paper Chemistry
ISA Ionic strength adjuster
LCL Lower control limit
LMWT Low molecular weight
LVDT Linear variable differential transformer
LWC Lightweight coated
MBBR Moving bed biofilm reactor
MC$_{GR}$ Moisture content on wet weight basis
MC$_{OD}$ Moisture content on ovendry basis
MD Machine direction
MF Melamine formaldehyde
MG Machine glazed
MOW Mixed office waste
MSDS Material safety data sheet
MT Metric ton
MWC Medium weight coated
NCASI National Council for Air and Stream Improvement
NCR No carbon required
NIR Near-infrared
NIRS Near-infrared spectroscopy
NMRS Nuclear magnetic resonance spectroscopy
NPSH Net positive suction head
NPSHA Net positive suction head available
NPSHR Net positive suction head required
NSPS New Source Performance Standards

NSSC Neutral sulfite semichemical
OCC Old corrugated container
OCR Optical character recognition
OMG Old magazine
ONP Old newspaper
PAC Polyaluminum chloride
PAM Polyacrylamide
PCC Precipitated calcium carbonate
PDADMAC Poly(diallyldimethylammonium chloride)
PE Polyethylene
PEI Polyethylenimine
PEO Polyethylene oxide
PGW Pressure groundwood
PID Proportional−integral−derivative
PM Paper machine
PO Propylene oxide
PFI Paper and Fiber Research Institute
Ppm Parts per million
Ppq Parts per quadrillion
Ppt Parts per trillion
Psi Pounds per square inch
PUR Polyurethane resin
PVC Polyvinyl chloride
RCF Recycled carbon fiber
RCT Ring crush test
RH Relative humidity
RTDs Resistance−temperature detectors
SBR Styrene-butadiene rubber
SCR Silicon-controlled rectifier
SCT Short-span compression test
SEC Size Exclusion Chromatography
SEM Scanning electron microscopy
SMA Styrene maleic anhydride
SPC Statistical process control
SQC Statistical quality control
TAPPI Technical Association of the Pulp and Paper Industry
TCF Totally chlorine-free
TOC Total organic carbon
TOCl Total organically bound chlorine
TQC Total quality control
TQM Total quality management
TRS Total reduced sulfur
TSS Total suspended solids
UASB Upflow anaerobic sludge blanket
UCL Upper control limit
UF Urea-formaldehyde
ULWC Ultra-lightweight coated
UM Useful Method
UV Ultraviolet
UVS Ultraviolet spectroscopy
WRV Water retention value

CHAPTER

1

Introduction and the Literature

1.1 GLOBAL PULP AND PAPER INDUSTRY

The pulp and paper industry is one of the largest industries in the world. It supplies paper to over 5 billion people worldwide. Originally, papermaking was a slow and labor-intensive process. Today pulping and papermaking are driven by capital-intensive technical equipment and high-tech and high-speed paper machines that produce rolls of paper at a speed that may reach 2000 m/min and with a web width that may exceed 8 m. Paper is essentially a sheet of cellulose fibers with a number of added constituents, when necessary, to affect the quality of the sheet and its fitness for the intended end use.

Paper is an important material, used daily for many purposes worldwide. The global production of paper and cardboard stood at approximately 407 million metric tons in 2015. More than half of that production was attributable to packaging paper, whereas almost one-third was attributable to graphic paper. It has been estimated that global paper consumption in 2020 will amount to 500 million tons (Fig. 1.1). This means growth of about 1.6% a year. Global consumption of paper has increased by almost half since 1980. The world's three largest paper-producing countries are China, the United States, and Japan. These three countries account for half of the world's total paper production, whereas the leading paper importing and exporting countries are Germany and the United States. Tables 1.1–1.4 show top five paper- and paperboard-producing countries, wood pulp–producing countries, recovered paper-producing/collection countries, and non-wood pulp–producing countries, respectively (FAO, 2015).

In a study conducted by (RISI is the best positioned and most authoritative global source of forest products information and data.) RISI (Annual Review of Global Pulp and Paper Statistics, 2015), global paper and paperboard production advanced 1.0% in 2014 to reach a new record level of 406.5 million tons, in spite of a continuous decline in North America and Europe. Positive growth in the cases of packaging and tissue grades continued to counteract the retreat in global graphic paper production. China has maintained the top position for both production and demand of total paper and paperboard since

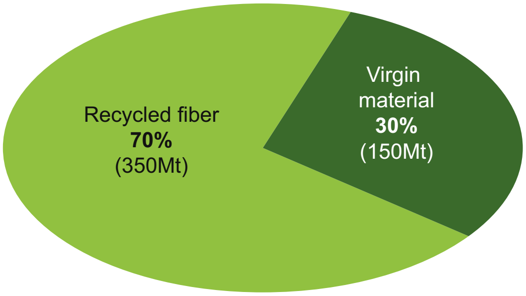


FIGURE 1.1 2020 scenario: 500 million tons paper produced with 70% recycled fiber.

Biermann's Handbook of Pulp and Paper: Raw Material and Pulp Making
https://doi.org/10.1016/B978-0-12-814240-0.00001-X

TABLE 1.1 Top Five Paper- and Paperboard-Producing Countries (Million Metric Ton in 2014)

Paper and Paperboard				
	Production	**Imports 1000 m**	**Exports**	**Apparent Net Consumption (ANC)**
World	406,295	105,522	110,597	401,220
China	111,150	4497	6656	108,991
USA	72,397	9485	11,598	70,283
Japan	26,228	1810	1514	26,524
Germany	22,602	10,693	13,211	20,084
India	14,961	2326	572	16,715

FAO (2015).

TABLE 1.2 Top Five Wood Pulp—Producing Countries (Million Metric Ton in 2014)

Wood Pulp				
	Production	**Imports 1000 m**	**Exports**	**Apparent Net Consumption (ANC)**
World	175,622	58,713	59,069	175,266
USA	49,368	5353	7732	46,989
Brazil	17,813	424	12,043	6194
Canada	17,590	331	9912	8009
Sweden	11,622	395	3484	8533
Finland	10,450	408	3136	7721

FAO (2015).

TABLE 1.3 Top Five Recovered Paper-Producing/Collection Countries (Million Metric Ton in 2014)

Recovered Paper				
	Production	**Imports 1000 m**	**Exports**	**Apparent Net Consumption (ANC)**
World	225,106	57,404	56,965	225,545
China	53,788	29,882	1042	82,628
USA	47,328	706	19,586	28,448
Japan	21,751	35	4261	17,525
Germany	15,221	3989	2543	16,667
Korea Rep.	8333	1543	555	9321

FAO (2015).

TABLE 1.4 Top Five Nonwood Pulp—Producing Countries (Million Metric Ton in 2014)

Other Fiber Pulp				
	Production	**Imports 1000 m**	**Exports**	**Apparent Net Consumption (ANC)**
World	12,338	546	519	12,366
China	6799	41	82	6759
India	1995	4	1	1998
Spain	828	7	17	818
Pakistan	370			370
USA	320	23	84	259

FAO (2015).

2009, whereas the United States remained in the second place. China accounted for 25% of global demand and 26% of global production of total paper and paperboard in 2014. The leading companies of the forest, paper, and packaging (FPP) industry as of 2015 were International Paper and Kimberly-Clark, both based in the United States. The US paper industry earned around 96.1 billion US dollars of annual revenue in 2015. In 2016, International Paper generated more than 21 billion US dollars of revenue, whereas Kimberly-Clark made around 18.2 billion US dollars. Other leading paper industry companies include Asia Pulp & Paper from Indonesia, Svenska Cellulosa from Sweden, Stora Enso and UPM-Kymmene from Finland, and Oji Paper and Nippon Paper Group from Japan.

The global paper and pulp mills industry has contracted slightly over the past 5 years, primarily because of the transition to digital media and paperless communication across the most developed economies (www.ibisworld.com/industry/global/global-paper-pulp-mills.h). The manufacturing booms in several emerging markets have partially compensated the decline by driving increased demand for paper used in packaging materials. The industry is now shifting its focus toward packaging materials and sanitary products that are its two most promising segments for growth. Industry revenue is expected to resume slow expansion over the next 5 years, although the growth in developing markets will surpass revenue increases in Europe and the United States. A global paper market study, "World Paper Markets up to 2030," conducted by Pöyry, reports that the world's demand for paper and paperboard is expected to grow to 482 million tons in 2030, but North America will experience reduced demand (www.midlandpaper.com/global-paper-and-pape). This equals an overall increase of 1.1% per year, with variations by grade. Particularly, the graphic paper market is facing enormous challenges, and the increasing digitalization is reducing demand for newsprint and other printing papers and also uncoated and coated wood-containing and wood-free papers. According to Pöyry's study, the demand for containerboards, cartonboards, and tissue paper will grow up to 2030. This is driven by increasing packaging requirements in emerging markets, booming e-commerce, and the growing demand for convenience food and consumer goods brands. The annual consumption of packaging material and tissue/hygiene products will thus increase by up to 2.9%. Focusing on regional growth markets, it can be found that the demand for paper continues to grow in the emerging markets, such as China and India. This is because of the urbanization, the increasing population, and the development of a new middle class. On the other hand, in Japan, Western Europe, and North America, the demand will decrease by around 0.8% per year up to 2030. "Since 1950 the production of paper has continually grown." According to Timo Suhonen from Pöyry Management Consulting, the last 5–6 years were very challenging for the global paper industry, particularly for companies in western markets. Pöyry experts forecast a strong need for structural changes in the paper industry. Particularly in western Europe, the experts find an urgent requirement for further capacity reductions. The industry must take a more disciplined approach as to the capacity expansions after the markets in the emerging Asian regions have become more mature. Industry consolidation, acquisitions, mergers, and alliances start making more sense there, too. Earlier, exits from the graphic paper industry sometimes turned to entries into the packaging paper and paperboard sector through a conversion of the machines. However, for multisector companies, this move would probably be the least painful one and should be decided on a case-by-case basis.

The global paper and printing market has been estimated at 1270 billion US dollars. It dropped down −6% in 2015 versus 2014 and is expected to drop once again this year due to sales decreasing by −2% (www.eulerhermes.com/economic-research/sector-risks/Global-Paper-Report). The upstream pulp sector continues to survive with a reduction in demand globally. Over 2015, most regions observed pulp production and prices reducing on average, particularly leading producers China (−2% year by year) and Brazil, down by 2.5% because of an annual high in 2012. The downstream sector does not appear to fare better, with no end in sight for long-term reduction in graphic paper. Asia, which accounts for 45% of total paper and paperboard demand, can hardly makeup for slow demand from either Western Europe or slowing down Latin America. This situation appears most challenging in Europe because of the strong dollar, which weighs down on European pulp buyers. Furthermore, there is growing competition from digital devices (much tougher than in Asia), which leads to plant closures. Corrugated papers and tissue are the only two prominent subsectors still on a positive path, owing to a rising demand for e-commerce packaging.

According to Smithers Pira, UK, based on recent trends, the sector will experience a period of sustained growth of up to 6% annually through 2017. This is expected to result in a global market of more than 30 million tons with an approximate value of $70 billion (www.packagingdigest.com/.../demand-grows-for-paperboard-with-some). Globally, the per capita paper consumption for Europe is 129 kg, Australia 116 kg, Asia 45 kg, and China 75 kg (www.printweek.in). In India, on the other hand, the per capita paper consumption is 9 kg, against 22 kg in Indonesia, 25 kg in Malaysia, and 75 kg in China. North Americans still consume more paper per capita, upward of 500 lbs. annually, than anyone else on earth (Environmental Paper Network, 2007, 2011). The global average stands at 58 kg. This shows that there is a lot of headroom for growth in India. From a demand point of view, every 1 kg incremental per capita consumption results in additional demand of more than 1 million ton a year (www.business-standard.com). Besides, policy factors also have a major role to play in the growth of the paper industry in India. The government's sustained focus on literacy, increased consumerism, and expansion in organized retail are expected to positively affect paper consumption and demand in India. Digital media has a lot of ground to cover, at least as far as penetration is concerned, particularly in the rural areas. Paper consumption is being encouraged; it is an established business. What was heartening was although there were several challenges, the packaging side of the segment is continuing to grow. In the last 5 years, the Indian paper sector has invested about INR 20,000 crore on capacity enhancement, technology upgrading, and acquisitions. Now, the companies in the pulp and paper sector are seeking to improve their balance sheets. The sector is eager to expand capacity further, but the decisions in this regard will depend on how soon companies can improve their financials. The Indian paper industry accounts for about 3% of the world's production of paper. The estimated turnover of the industry is INR 50,000 crore (USD 8 billion) approximately, and its contribution to the exchequer is around INR 4500 crore. The industry provides employment to more than 0.5 million people directly and 1.5 million people indirectly.

Most of the paper mills are in existence for a long time, and hence present technologies fall in a wide spectrum ranging from oldest to the most modern. The mills use a variety of raw materials, viz. wood, bamboo, recycled fiber, bagasse, wheat straw, rice husk, etc. In terms of share in total production, approximately 24% are based on wood, 65% on recycled fiber, and 11% on agro-residues. The geographical spread of the industry and market is mainly responsible for regional balance of production and consumption.

India is the fastest growing market for paper globally, and it presents an exciting scenario; paper consumption is poised for a big leap forward in sync with the economic growth. The futuristic view is that the growth in paper consumption would be in multiples of GDP, and hence an increase in consumption by 1 kg per capita would lead to an increase in demand of 1 million tons.

1.2 INTRODUCTION TO PULP AND PAPER MANUFACTURING

The availability of writing material has always gone hand in hand with the development of society. The earliest medium for writing was the stone tablet. Egyptians invented papyrus around 3000 BC. Papyrus is made by crisscrossing thin sections of the papyrus reed, which is ubiquitous in the marshy delta of the Nile River. Papyrus is held together by natural glues within the reed when pressure is applied. The papyrus was smoothed by rubbing with smooth stones. Around 200 BC parchment, the tanned skin of sheep or goats was developed. Parchment is now a high-quality grade of paper made from

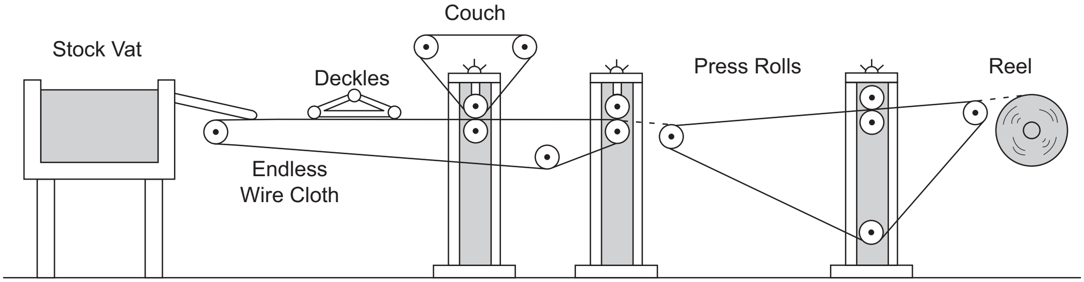


FIGURE 1.2 Diagram of Bryan Donkin's paper machine, c.1804. *Redrawn from J. Ainsworth,* Papermaking, *1957 Thilmany Paper Co., with permission.*

vegetable fibers. The invention of paper is credited to Ts'ai Lun of China, who, in AD 105, worked on a papyrus substitute by decree of Emperor Hoti. Within 20 years, he had paper from the bark of mulberry trees that was treated with lime, bamboo, and cloth. The Chinese considered paper as a key invention and kept this a closely guarded secret for over five centuries until the technology slowly made its way westward. The Arabs captured a Chinese city containing a paper mill in the early 700s and from this started their own papermaking industry. Paper was first made in England in 1496. The first US mill was built in 1690, the Rittenhouse mill, Germantown, Pennsylvania. The development of the paper machine is the most important milestone of the industry. Louis Robert, working at the paper mill owned by Ledger Didot, made his first model of the continuous paper machine in 1796 near Paris. The first model was very small and made strips of paper about as wide as tape. He received a French patent for his machine in 1799, at the age of 37, based on drawings he had submitted. Shortly after being awarded the patent, he began construction based on these drawings. Development of the paper machine was led by the two Fourdrinier brothers, Henry and Sealy, who, in 1801, bought one-third interest in the British patent rights of Robert's machine. They hired Bryan Donkin who took 3 years to develop the first practical paper machine, which was in operation at Two Waters Mill, Hertz, England, in 1804. A sketch of this machine is shown in Fig. 1.2. Donkin's company continued to manufacture and improve the Fourdrinier Machine for many years. His company supplied most of the early Fourdrinier Machines throughout the world. At about the same time, John Dickinson, a colleague and friend of Donkin, was working on his cylinder machine, which was refined in 1809. In fact, Dickinson and Donkin contributed important ideas to each of these machines. For example, in 1817, John Dickinson became the first person to mention steam-heated drying cylinders. He used cast iron cylinders complete with stationary siphon tubes. In 1820, Thomas Crompton added dryer felts using single-tier dryer. Double-tier dryers soon followed. Crompton studied textile drying, which may have provided the thought for using dryer felts. Drying cylinders and cylinder arrangements have not changed appreciably in concept, since this time. The dandy roll was patented in 1825 by the two brothers John and Christopher Phipps of Kent county. They made rolls from 4 to 12 in. (10–30 cm) in diameter. Some people claim that John Marshall may have been the first person to make a "riding roller," and he began manufacturing them in 1826. M. Canson of Annonay, France, put a suction box under the wire of his Fourdrinier Machine in 1826, as had already been done on the cylinder machine but kept this as a secret. In 1828, George Dickinson received a patent for a machine that, among many other things, had the forerunner of the suction roll. It was, however, about 80 years later, with the invention of the cycloidal vacuum pump, those suction rolls were used in the wet end or press section. In 1829, John Dickinson used a reverse press with double felting to decrease the two-sidedness of paper. In fact, many of the important inventions of the paper machine were discovered within the first three decades of Robert's invention. With the invention of the paper machine, the amount of paper that could be produced was soon limited by the fiber supply because cotton was the main constituent in paper. During the mid-19th century, the technology for converting wood to pulp suitable for paper was developed. With a plentiful supply of pulp available, the amount of paper production was then closely related to improvements in paper machine speeds and widths. The production of paper in the United States increased by a factor of 10 in the 19th century and almost 50 in the 20th century. Paper production in developed countries seems to be limited once again by fiber supply. Gone are the days when huge logs went directly to pulp mills as shown in Fig. 1.3. Much roundwood is obtained from precommercial thinning using skidders to drag them to the roadside as shown in Fig. 1.4. In the Northwest United States, wood prices are high enough that some mills are now pulping construction wastes, pallets, and other materials that are chipped. Even chemical pulping of old corrugated boxes is practiced in some parts of the world to stretch fiber resources. Fig. 1.5 gives the steps in making paper for a present-day mill. Regardless of the method of making paper, whether by machine or by hand, there are some common steps that are shown in Fig. 1.6. In principle, paper is made by pulping, to separate and clean the fibers; beating and refining the fibers; diluting to form a thin fiber slurry; suspended in solution; forming a web of fibers on a thin screen; pressing the web to increase the density of the material; drying, to remove the remaining moisture; finishing, to provide a suitable surface for the intended end use.

Pulp and paper are made from cellulosic fibers and other plant materials, although some synthetic materials may be used to impart special qualities to the finished product. Most paper is made from wood fibers, but rags, flax, cotton linters, and bagasse (a sugar cane residue) are also used in some papers. Used paper is also recycled, and after purifying and sometimes deinking, it is often mixed with virgin fibers and reformed again into paper. Other products

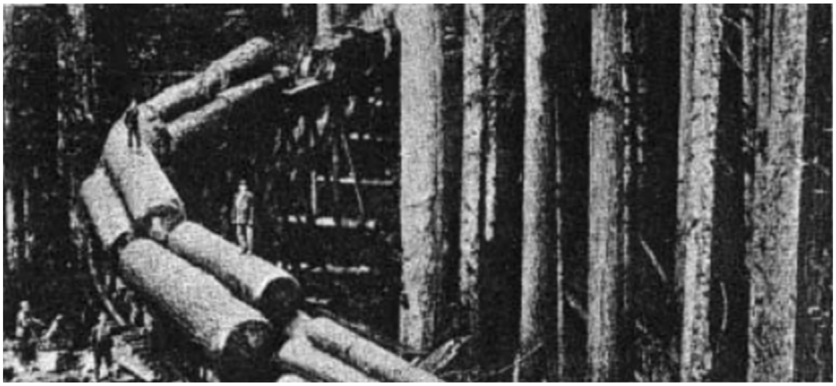


FIGURE 1.3 Pulp logs leaving the forest. *Reprinted from* History and Description of Paper Making, *©1939 Crown Zellerbach Corp., with permission.*

FIGURE 1.4 Skidders drag small trees from the forest so that the remaining trees can grow faster. *Reprinted from* Making Pulp and Papery *©1967 Crown Zellerbach Corp., with permission.*

made from wood pulp (cellulose) include diapers, rayon, cellulose acetate, and cellulose esters, which are used for cloth, packaging films, and explosives. Wood is composed of cellulose, lignin, hemicellulose, and extractives. Cellulose comprises about 50% of wood by ovendry weight. This constituent is of primary interest in papermaking. Lignin cements the wood fibers together. It is a complex organic chemical. Its structure and properties are not fully understood. It is largely burned for the generation of energy used in pulp and paper mills. As the chemistry of lignin becomes better understood, what is now mostly a waste product used for fuel (some is converted to chemical products), it could become a valuable feedstock for new chemical products. The objective of pulping process is to remove as much lignin as possible without sacrificing fiber strength, thereby freeing the fibers and removing impurities that cause discoloration and possible future disintegration of the paper. Hemicellulose plays an important role in fiber-to-fiber bonding in papermaking. Several extractives are contained in wood but do not contribute to its strength properties; these too are removed during the pulping process. The fiber from nearly any plant or tree can be used for paper. However, the strength and quality of fiber, and other factors that can complicate the pulping process, varies among tree species. In general, the softwoods yield long and strong fibers that impart strength to paper and are used for boxes and packaging. Hardwoods, on the other hand, generally have shorter fibers and therefore produce a weaker paper, but one that is smoother, more opaque, and better suited for printing. Both softwoods and hardwoods are used for papermaking and are sometimes mixed to provide both strength and printability to the finished product.

The manufacturing of paper or paperboard can be divided into several process steps (Table 1.5). Paper production is mainly a two-step process in which a fibrous raw material is first converted into pulp, and then the pulp is converted into paper. The harvested wood is first processed so that the fibers are separated from the unusable fraction of the wood, the lignin. Pulp making can be done mechanically or chemically. The pulp is then bleached and further processed, depending on the type and grade of paper that is to be produced. In the paper factory, the pulp is dried and pressed to produce paper sheets. Postuse, an increasing fraction of paper and paper products, is recycled. Nonrecycled paper is either landfilled or incinerated.

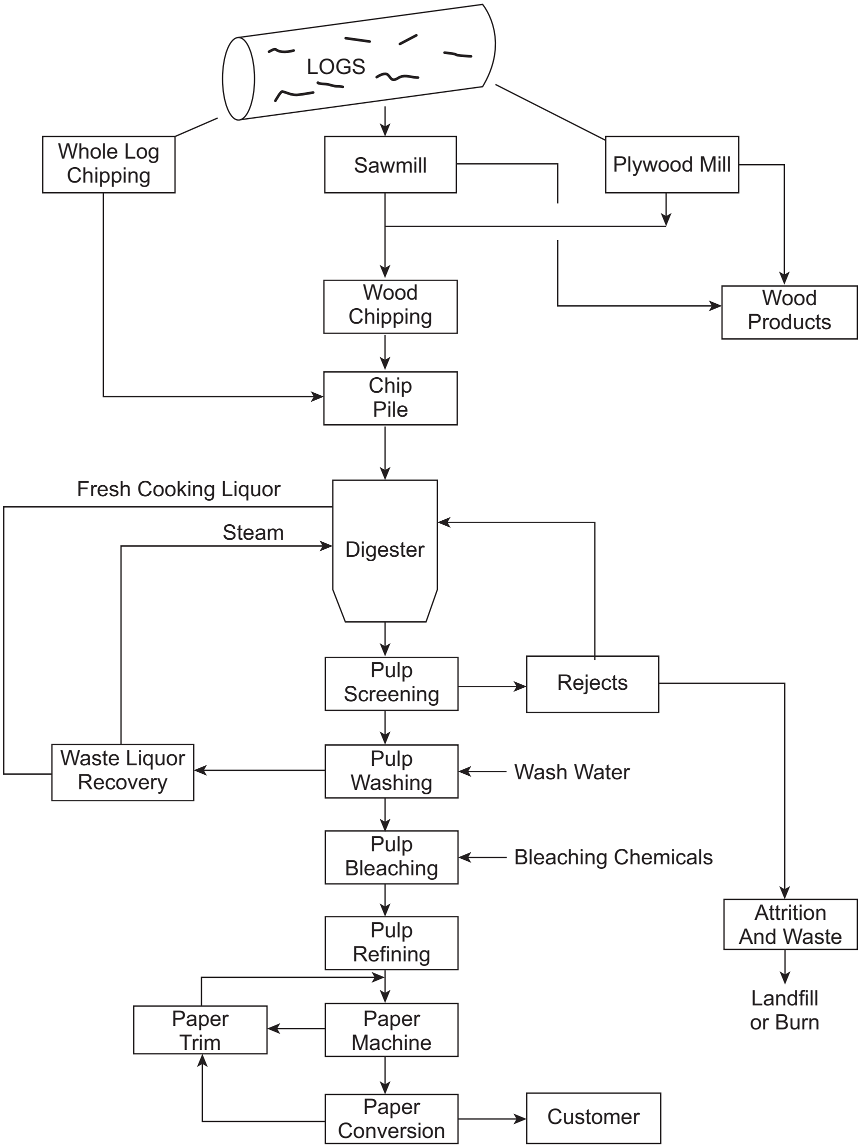


FIGURE 1.5 An overview of chemical pulping and papermaking processes. *Courtesy of W. Bublitz.*

1.3 INTRODUCTION TO THE LITERATURE

It is very important to be able to access articles in the scientific literature in particular subject areas. Information is one of the most underused resources in the pulp and paper industry. The information in original research papers and other references can be used to solve many problems and questions that arise in pulp and paper mills. If you are not aware of a particular journal or reference book mentioned in this chapter or

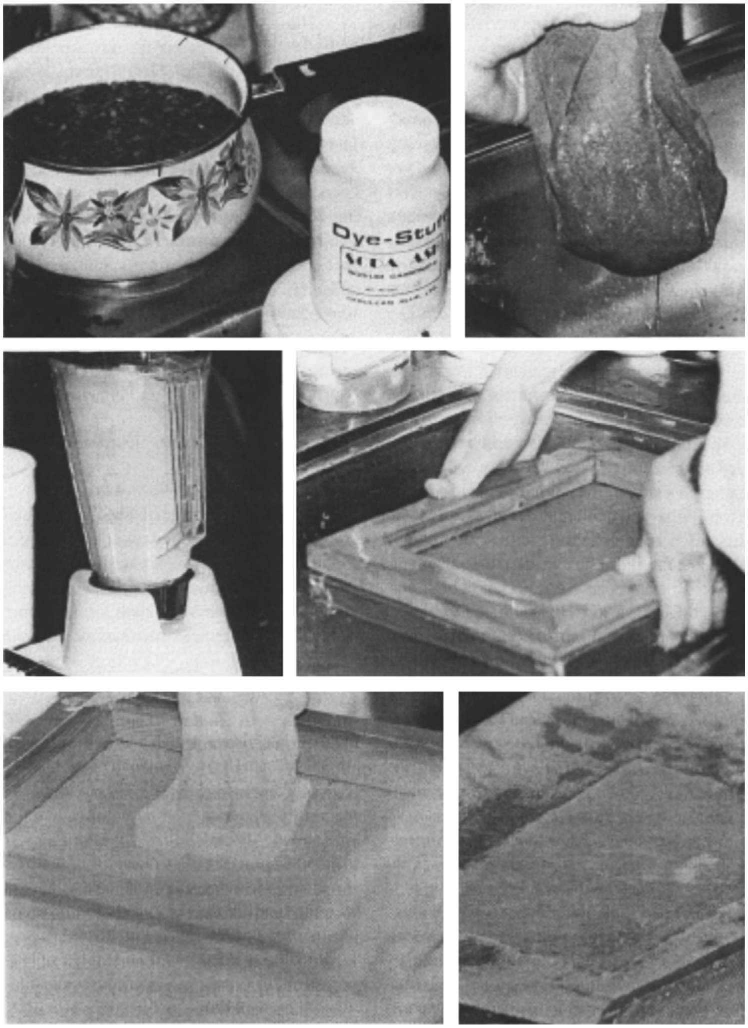


FIGURE 1.6 The basic steps to papermaking. The fiber source is pulped (and bleached for white papers); the pulp is washed; the pulp is refined to ensure that the fibers are separated from each other and to roughen the surface for better fiber bonding; a paper web is formed from a dilute pulp slurry letting most of the water dram by gravity; additional water is pressed from the web; and the remaining free water is removed by evaporation to give the product.

how it is used, be sure to ask your librarian for assistance. Many libraries can obtain copies of articles or books, which they do not have in the library, through interlibrary loan programs. The lists in this chapter are by no means exhaustive; however, some of the more routinely used references are included. The literature can be divided into the primary literature and the secondary literature. The primary literature consists of patents, journal articles, and proceedings of meeting presentations. This is the most current information and the most difficult to access. One can keep abreast of only a few journals. To fully use this resource, one should periodically

TABLE 1.5 Process Steps Involved in the Manufacturing of Pulp and Paper

Process Steps
Raw Material Preparation
Debarking
Chipping and Conveying
Pulping
Chemical Pulping
Sulfate Process
Sulfite Process
Semichemical Pulping
Mechanical Pulping
Stone Ground Wood Pulping
Refiner Mechanical Pulping
Thermomechanical Pulping
Chemithermomechanical Pulping
Recycled Paper Pulping
Chemical Recovery
Evaporation
Recovery Boiler
Recausticizing
Calcining
Bleaching
Mechanical or Chemical Pulp Bleaching
Stock Preparation and Papermaking
Preparation of Stock
Dewatering
Pressing and drying
Finishing

conduct library searches with the abstract indices in areas of critical importance to a mill. For example, if a mill is considering conversion to alkaline papermaking, one would want to obtain as much current information as possible on the subject to save downtime during the conversion. The primary literature is never obsolete. Indeed, it is often important to go back to the primary literature to check the source of equations, tables, etc. used in the secondary literature. Often, on investigation of an original article, one learns that information that has become widespread is being used under inappropriate conditions.

The secondary literature is information that is summarized in books, monographs, reference books, and so forth. It tends to be older and may be outdated; however, it is usually the best source to get background information in a particular field. If one considers articles (and other references) in specialized fields with applicability to pulp and paper, such as corrosion, process control, simulation, and so forth, to be useful, then the importance of abstract indices to access the literature becomes obvious. One should not rely on merely the pulp and paper journals; many important advances to pulp and paper technology are merely modifications of technologies that are well established in other disciplines.

Online Computer Searches

Literature searches using computer terminals is quite common and convenient. Virtually, any computer with a modem can be used from any location once an account is setup with a vendor. Most libraries have facilities for doing literature searches from computers and would probably know what sources to use for the pulp and paper industry. This information is also available from other sources (Steelhanmier and Wortley, 1992). It is recommended that some time be spent with thorough manual searching of 1 or 2 years with abstract indices when searching a new topic, especially a topic outside of one's normal activities. This is helpful to learn what keywords are most effective so that important work will not be overlooked. One should also be familiar with the pulp and paper literature before getting overly accustomed to using computer-aided searches of the literature.

1.4 ABSTRACT INDICES

Abstract Bulletin of the Institute of Paper Science and Technology

The most complete abstracting service of research directly related to pulp and paper is the *Abstract Bulletin, Institute of Paper Science and Technology* that is published monthly, in addition to an annual index. It is available online for computer searching. Before 1989, it was the *Abstract Bulletin of the Institute of Paper Chemistry*.

Chemical Abstract Index

The *Chemical Abstract Index* is a comprehensive abstract bulletin covering all areas of chemistry and chemical engineering. It is extremely useful for getting current information on all aspects of chemical problems, affecting the pulp and paper industry. Author, subject, chemical, and chemical formula indices are available to find abstracts. Indices cover a 6-month period; collective indices cover 10 volumes, corresponding to 5 years.

Scientific Citations Index

The principal use of the *Scientific Citations Index* is to keep track of the articles cited in the primary scientific literature. For example, suppose Dr. I. M. First published an article in 1988, and the citation for that article appeared in the *Literature Cited* section of an article published in *Tappi J.* in January, 1990 by Ms. U. R. Second. Under First, I. M. in the 1990 *Citations Index* (not the *Source Index*), one would find that U. R. Second cited the article of I. M. First. This is a useful form of feedback to determine the significance of a particular scientific publication. In some fields, there are a few key authors whose work is usually cited. By determining who cited these authors, one can find some of the most recent work.

1.5 TECHNICAL AND TRADE JOURNALS

Nordic Pulp and Paper Research Journal

This journal publishes about 40 high-quality, fundamental, original research papers per year.

(Arbor Pub. AB, Stockholm, Sweden, appears quarterly.) This journal started to publish research papers at about the same time (in 1986) the long-standing *Svensk Papperstidning* ceased publishing research papers.

Journal of Pulp and Paper Science

This journal also publishes high-quality, fundamental, original research papers per year (Technical Section, Canadian Pulp and Paper Association, Montreal, Quebec, appears bimonthly).

Tappi Journal

This journal publishes high-quality, original research papers per year. It also includes industry news, summaries of TAPPI conferences, advertisements, and other topics (TAPPI, Norcross, Georgia, appears monthly). Because of the sheer number of articles published, this is often a useful source to collect some of the current information on a technical subject. By using the annual index in the December issue, several years of this magazine can be rapidly checked for articles on a particular subject. References cited in those articles will give further information, although not necessarily the most current information.

Other Pulp and Paper Research Journals

Pulp and Paper Canada publishes high-quality, original research articles annually in addition to industry news, feature articles, advertisements, and so forth (Southam Business Information and Communications Group Inc., Don Mills, Ontario, published monthly).

Appita Journal publishes high-quality, original research papers annually in addition to industry news, features, advertisements, and so forth (Technical Association of the Australian and New Zealand Pulp and Paper Industry, Inc., Parkville, Victoria, appears bimonthly).

Paperi ja Puu-Paper and Timber publishes original research, review, and feature articles annually along with departments and other news items (Toimitusjohtaja, Helsinki, Finland, 10 issues annually).

Progress in Paper Recycling appears quarterly since late 1991 and contains research articles and practical, useful articles in paper recycling (Doshi & Associates, Appleton, Wisconsin).

Other Research Journals

There are many other journals that have original research articles on pulping, fiber modification, and other chemical subjects applicable to the pulp and paper industry. Some of these include *Journal of Wood Chemistry and Technology* (Marcel Dekker, Inc., appearing quarterly since 1981), *Wood Science and Technology* (Springer-Verlag, the journal of the International Academy of Wood Science, appears quarterly), *Wood and Fiber Science* (Society of Wood Science and Technology, Madison, Wisconsin, appears quarterly), *Holzforschung* (Walter de Gruyter, appears bimonthly), *Mokuzai Gakkaishi* (Japan Wood Research Society, appears monthly), and the *Forest Products Journal* (Forest Products Research Society, Madison, Wisconsin, 10 issues annually). These journals are essentially confined to research articles.

Trade Journals or Magazines

Other pulp and paper journals have industry news, feature articles, and advertisements, on a wide variety of issues in pulp and paper presented in a relatively nontechnical fashion. Many are available without charge to industry personnel. *Paper Age* is published monthly (Global Publications, Inc., Westwood, New Jersey). *Pima Magazine* is published monthly and is designed for mill management (Paper Industry Management Association, Arlington Heights, Illinois). *American Papermaker* (A/S/M Communications, Inc., Atlanta, Georgia) is published monthly. It was published in four editions by region of the United States from 1987 to 1992; before 1987 it was published as *Southern Pulp and Paper*. *International Papermaker* is published quarterly as of late 1992. Other magazines include *Pulp and Paper Magazine* (Stockholm, Sweden, published quarterly) and *Pulp & Paper Journal* (Maclean Hunter Ltd., Toronto, Ontario, 11 issues per year).

Pulp & Paper (the international version is *Pulp & Paper International, PPI*) is published monthly and is a very good source of current industry production figures for North America (Miller Freeman Publications, San Francisco, California). (In November 1986, the *Paper Trade Journal* ceased publication and was incorporated into *Pulp & Paper*.) It has about 6 to 10 articles in each issue, which focus on one or two topics in addition to feature articles that might be on any topic. The focus of a given month does not change much from year to year, so this is often an **excellent source for general, up-to-date information** on a given topic.

1.6 REFERENCE BOOKS

PaperWorld

This highly recommended, five volume reference (in addition to the General Index and World Atlas) covers the international pulp and paper industry. Each volume is divided into five parts covering (1) pulp and paper industry, (2) exporters and importers, (3) suppliers (for example, machines and chemicals), (4) associations, and (5) trade press. Names, addresses, and phone numbers are given in most cases (Birkner & Co., Hamburg, Germany).

Lockwood-Post's Directory

The *Lockwood-Post's Directory* lists pulp and paper mills, converting mills, and suppliers with information on personnel, types and amounts of products produced, water, wood and power usages, equipment, etc. by state or province for the United States and Canada, respectively. It is updated annually (*1990 Lockwood-Post's Directory*, Miller Freeman Publications, Inc., New York, N.Y. 1990).

Pulp & Paper Fact Book

This 426-page reference book lists production by grades, sales, prices, and historical trends of companies for each grade. It is updated annually (*1990 North American Fact Book*, Miller Freeman Publications, Inc., San Francisco, CA 1990).

Tappi Test Methods, Tappi Useful Methods

This two-volume set contains standardized test procedures for everything from wood chips to containers and coated paper, including many raw materials used in these processes. Volume 1 covers fibrous materials, pulp testing, and paper and paperboard testing. Volume 2 covers nonfibrous materials, container and structural materials testing, and testing practices. These test methods are used throughout the industry to insure quality control and comparability of results. Other countries have similar sets of testing procedures that are mentioned later (*Tappi Test Methods*, TAPPI, Atlanta, Georgia, 1991. In 1992, it was published as a single volume). *Tappi Useful Methods* is a supplement of additional methods that have not been as thoroughly reviewed as the official test methods.

Tappi Technical Information Sheets

This three-volume set contains data sheets on densities of solutions, troubleshooting and other guides, inspection reports, tables, figures, glossaries, etc. (*Technical Information Sheets*, TAPPI, Atlanta, Georgia, 1989).

Standard Testing Methods

This contains a series of standardized test methods and data sheets of use to the pulp and paper industry. It is similar to the two previously listed references put out by TAPPI Press but contains tests of the CPPA (*Standard Testing Methods*, Technical Section, Canadian Pulp and Paper Association, Montreal, Quebec). *Pulpwoods of the United States and Canada*, a two-volume set (Volume 1, conifers; Volume 2, hardwoods), lists tree species, their silvics, wood properties, and general pulping characteristics with references. It includes the commercial species of North America. This information is increasingly important as pulp mills look to alternate species as wood fiber supplies become more difficult to obtain (*Pulpwoods of the United States and Canada*, 3rd edition. Institute of Paper Chemistry, Edited by Isenberg, I.H., revised by Harder, M.L., and L. Louden, Appleton, Wisconsin, 1981).

Wood Handbook

This is a general handbook on the physical, mechanical, electrical, thermal, and other properties of wood and wood composites (*Wood Handbook: Wood as an Engineering Material*. Agriculture Handbook number 72, Washington, DC: U. S. Dept. of Agriculture; revised 1987).

1.7 TEXTBOOKS

Handbook for Pulp and Paper Technologists

This resource of pulp and paper technology includes numerous illustrations. It is weak in the theoretical and practical sides of the field and slightly dated but strong on the equipment aspect (*Handbook for Pulp and Paper Technologists*, Smook, G.A., Joint Textbook Committee of the Paper Industry, CPPA, Montreal, Quebec or TAPPI, Atlanta, Georgia, 1982. 395 p.). *Pulp and Paper: Chemistry and Chemical Technology*, a four-volume set, gives a comprehensive look at the chemistry of pulp and paper technology. It is not heavily illustrated, nor does it give much detail on equipment descriptions, but neither of these detract from its purpose. It is a useful reference book, a good starting point for detailed information on many topics in pulp and paper (*Pulp and Paper: Chemistry and Chemical Technology*, Casey, J.P., Ed., Wiley-Interscience, New York, N.Y. 1980, 1980, 1981, 1983 vol. 1–4, respectively. 2609 p. total). Topics are as follows:

1. Wood chemistry, pulping and bleaching
2. Papermaking and environmental control
3. Chemical additives, paper properties and analysis
4. Coating and converting

Wood Chemistry: Fundamentals and Applications

This book is a fundamental volume on wood chemistry of very high relevance to the pulp and paper industry. It covers the chemistry of wood and bark components, pulping and bleaching chemistry, chemistry of cellulose plastics and other derivatives (derived from dissolving pulp), and carbohydrate chemistry (*Wood Chemistry: Fundamentals and Applications*, Sjostrom, E., Academic Press, New York, 1981. 223 p.; 2nd edition, San Diego, 1993).

Textbook of Wood Technology

Volume 1—structure, identification, uses, and properties for the commercial woods of the United States and Canada—is very useful. Extensive micrographs and descriptions by wood species also make it an important reference book. Because the cost of wood is now about 20%–40% of the final product (although quite variable) and can be expected to increase as a percentage with more competition for this resource, knowledge about wood becomes very important (*Textbook of Wood Technology Vol 1*, 3rd edition, Panshin, A.J., and C. deZeeuw, McGraw-Hill Book Company, New York, N.Y., 1970. 705 p.).

Handbook of Pulp, Two-Volume Set

This book published by Wiley (two-volume set) has been edited by Dr. Herbert Sixta, head of the cellulose and viscose research department at Lenzing AG in Austria. Alongside the traditional aspects of pulping processes, pulp used in industry and paper pulps, this book describes all pulping processes used for paper and paperboard manufacturing, as well as waste liquor treatment, pulp bleaching and environmental aspects, while also covering pulp properties and applications.

Handbook of Paper and Board

This book published by Wiley has been edited by Herbert Holik. This handbook describes the manufacturing processes of various types of papers, recovered paper treatment, and the quality and economical aspects. More than 20 authors contribute a variety of viewpoints, one of the many features of this book. They give a concise description of the fascinating art and technology of papermaking, providing lay readers, students, politicians, and others with the latest information on current technologies. The second edition of this book has been also published in 2013. It has been updated, revised, and largely extended in depth and width, including the further use of paper and paperboard in converting and printing.

Papermaking Science and Technology Book Series

TAPPI currently partners with the Forest Products Engineers based in Finland. As part of their partnership, they offer the Papermaking

Science and Technology book series featuring 20 volumes that cover the entire paper manufacturing process from wood raw material to end product. Books are available in print or convenient PDF downloads. This series is ideal to train new employees in the company or as a reference guide for the experienced workforce. The Papermaking Science and Technology series is also an excellent textbook resource for universities and colleges.

Others

Other textbooks are still useful if somewhat dated. These include *Pulping Processes*, Rydholm, S.A., Interscience, New York, 1965 (corrected version, 1967) 1269 p.; *Handbook of Pulp and Paper Technology*, Britt, K.W., Reinhold, Publishing Corp., New York, 1964, 537 p.; the two-volume set *Pulp and Paper Science and Technology*, Libby, C.E., McGraw-Hill, New York, 1962, 436 and 415 p., respectively; *Paper and Paperboard, Kline, I.E.*, Miller Freeman, San Francisco, 1982, 232 p. (2nd ed., 1991, 245 p. and, except for updated statistics, very similar to the first edition); *Pulp Technology and Treatment for Paper*, Clark, J.d'A., Miller Freeman, San Francisco, 1978, 751 p. (2nd ed., 1985, 878 p., which includes nominal updating of some fundamentals such as mechanical pulping); and the three-volume set *Pulp and Paper Manufacture*, 2nd ed., MacDonald, R.G., Ed., McGraw-Hill, New York, 1969 (769, 542, and 655 p., respectively) listed below.

1. The Pulping of Wood
2. Control, Secondary Fiber, Structural Board, Coating
3. Papermaking and Paperboard Making Work on the 3rd edition of the *Pulp and Paper Manufacture series* (*with* 7 × 10 in. format) began in 1983.

Although generally informative, they often lack continuity, making them difficult for newcomers to use. The titles are as follows:

1. Properties of Fibrous Raw Materials and Their Preparation for Pulping, 1983, 174 p.
2. Mechanical Pulping, 1987, 281 p.
3. Secondary Fiber and Nonwood Pulping, 1987, 266 p.
4. Sulfite Pulping and Technology, 1985, 352 p.
5. Alkaline Pulping, 1989, 637 p.
6. Stock Preparation and Nonfibrous Additives, 1992, 316 p.
7. Paper Machine Operations, 1991, 693 p.
8. Coating, Converting and Specialty Processes, 1990, 386 p.
9. Mill Control and Control Systems: Quality & Testing, Environmental, Corrosion, Electrical, 1992, 386 p.
10. Process Control & Information Systems, 1993.

1.8 CHEMISTRY REFERENCE BOOKS

Merck Index

The *Merck Index* contains data on over 10,000 chemicals, drugs, and biologicals with information on synonyms, formula, structure, elemental composition, commercial manufacture, toxicity, uses, physical properties, and solubilities in various solvents. It is updated approximately every 8 years, with the 11th edition appearing in 1989 and available online for computer searches. There are also tables on subjects such as pH indicators and buffer solutions, conversion factors, abbreviations, and names of organic chemistry reactions (*The Merck Index*, eleventh edition, Merck & Co., Inc. Rathway, N.J., 1989).

Handbook of Chemistry and Physics

This is a widely used, extensive collection of information that is revised annually. It is divided into sections containing mathematical tables, properties of the elements, inorganic compounds and organic compounds, general chemistry, and physical constants (*Handbook of Chemistry and Physics*, 70th edition, 1989—1990, Weast, R.C., Ed., CRC Press, Boca Raton, Florida, 1989).

Lange's Handbook of Chemistry

The *Handbook of Chemistry* contains tables of mathematical statistics, fundamental constants, conversion factors, atomic and molecular structures, physical constants of inorganic and organic compounds (crystalline form, refractive index, melting and boiling points, density, and selected solubilities), analytical chemistry (activity coefficients, equilibrium constants, pH measurements, gravimetric factors, etc.), electrochemistry, spectroscopy (X-ray, NMR, IR), thermodynamic properties (enthalpies and Gibbs free energies of formation, entropies, and heat capacities of compounds and elements), and physical properties (solubilities, vapor pressures, melting and boiling points, viscosity, dipole moments, etc.). This handbook is revised approximately every 6 years (*Lange's Handbook of Chemistry*, thirteenth edition. Dean, J.A., Ed., McGraw-Hill Book Co. New York, N.Y., 1985).

Perry's Chemical Engineers' Handbook

Although most of the information covered in this extensive reference is related to engineering rather than chemistry, this is an extremely useful reference book for topics such as thermodynamics, corrosion, reactor design, distillation, process control, and evaporation in the area of chemical engineering. Information on virtually any unit operation used by the pulp and paper industry can be found in this book (*Perry's Chemical Engineering Handbook*, sixth edition. Perry, R.H. and D.W. Green, editors, McGraw-Hill Book Co., New York, N.Y., 1984).

1.9 OTHER REFERENCES

This list of references does not include the many books, bibliographies, conference proceedings, and other sources of information available in specific areas of pulp and paper. To locate these, one should obtain a *Publications Catalog* from TAPPI Press (Atlanta, Georgia), a *Bibliographic Series List* from the Institute of Paper Science and Technology [Atlanta, Georgia, and formerly the Institute of Paper Chemistry (Appleton, Wisconsin)], a list of Pulp and Paper Technical Books available from the Technical Section of the Canadian Pulp and Paper Association, or similar resources. There are many reports of the US Department of Agriculture Forest Product Laboratory (FPL) in Madison, Wisconsin, that are not well known. The early summary publication that includes bibliographies of FPL reports and journal publications of the FPL staff is useful to access much of the early work of this laboratory. The reference to this information is Report No. 444, List of publications on pulp and paper, August, 1960, 58 pp. Semiannual lists are available as well on the work done at the FPL. Some of these reports contain pulping and papermaking studies on wood species that may become commercial in the future as fiber becomes more and more difficult to obtain.

1.10 ANNOTATED BIBLIOGRAPHY

Steelhammer, LC. and B. Wortley, The computer connection, *PIMA Mag*. 75(5):40-41(1992). This brief article lists several of the vendors of computer literature searches with their addresses and phone numbers.

Clapperton, R.H., *The Paper-making Machine, Its invention, Evolution and Development*, Pergamon Press, New York, 1967, 365 p. (Out of print.) This work is easy reading and made interesting by the diagrams and photographs. A section includes biographies of early papermakers, including L. Robert, L. Didot, J. Gamble, H. Fourdrinier, J. Hall, J. Dickinson, Escher Wyss, and J. Voith. As I read this, I soon find myself vicariously looking over the shoulders of the great inventors as they first design and assemble

their machines. This was an important source of information for the text above and is my favorite reference on the history of the paper machine.

Smith, D.C., History of Papermaking in the United States (1691—1969), Lockwood Pub. Co., New York, 1970. 693 p.

Hunter, D., *Papermaking, The History and Technique of an Ancient Craft*, 2nd ed,. Alfred A. Knope, New York, 1943. 611 p., with over 317 photographs and diagrams. Dard Hunter came from a long line of papermakers and printers. His writings on the history of papermaking are well known, and a papermaking museum, once housed at the Massachusetts Institute of Technology, but now at the Institute of Paper Science and Technology, is named after him.

Hunter, D., *Papermaking Through Eighteen Centuries*, William Edwin Rudge, New York, 1930. 358 p. This work deals with early methods of papermaking and includes numerous sketches and pictures of old techniques.

Rudlin, B., *Making Paper - A Look into the History of an Ancient Craft*, Vallingby, Sweden, 1990, 278 p., with 16 color plates (8 leaves) of contemporary, artistic, handmade papers using a variety of vegetable fibers. This work covers both handmade paper and machine-made paper.

Sixta, H. (Ed.) (2006). Handbook of Pulp. WILEY-VCH Verlag GmbH & Co. KgaA, Weinheim Germany, pp. 69—107, (Chapter 3).

This is a comprehensive handbook dealing with the traditional aspects of pulping processes. It describes all pulping processes used for paper and paperboard manufacturing, as well as waste liquor treatment, pulp bleaching and environmental aspects, while also covering pulp properties and applications.

Gullichsen J (2000). Fiber line operations. In: Gullichsen, J., Fogelholm, C.-J. (Eds.), Chemical Pulping—Papermaking Science and Technology: Book 6A. Fapet Oy, Helsinki, Finland. This book deals step by step, why and how things are done to obtain fibers from wood by chemical pulping. This book combines science and technology in a way that allows both students and mill engineers to benefit from learning about modern fiber lines, while increasing their awareness of the challenges and opportunities involved in research and in the design and operation of new pulp mills.

Hubbe, M.A., 2005. Paper, Kirk-othmer Encyclopedia of Chemical Technology. John Wiley & Sons Inc. https://doi.org/10.1002/0471238961.1601160512251405.a01.pub2. http://www3.interscience.wiley.com/

Annual Review of Global Pulp and Paper Statistics, 2015. Available from: www.risiinfo.com/risi.../annual-review-global-pulp-paper-statistics.htm

Environmental Paper Network, 2007. The State of the Paper Industry 2007. Retrieved from: http://environmentalpaper.org/state-of-the-paper-industry-2007.php.

Environmental Paper Network, 2011. The State of the Paper Industry 2011. Retrieved from: http://environmentalpaper.org/state-of-the-paper-industry-2011.php.

US EPA, 1998. Pulp and Paper NESHAP: A Plain English Description. Available from: www.epa.gov/ttnatw01/pulp/guidance.pdf.

Bajpai P (2017). Pulp and Paper Industry 1st Edition ELSEVIER Inc. USA

FAO (2015) FAO yearbook of forest products. www.fao.org

EXERCISES

Sources of Information

1. In 1981 and 1982, some articles on carbohydrate analysis came out of the

laboratory of G. D. McGinnis. Using the *Chemical Abstracts*, find one or two citations for these articles.

2. Once again, using the *Chemical Abstracts*, find the references for some recent articles on silylation (trimethylsilylation) of carbohydrates (monosaccharides). How would you find some of the more important references in this field without looking through every single *Chemical Abstract* index over the last 30 years?

CHAPTER

2

Wood and Fiber Fundamentals

2.1 BARK AND WOOD

Bark

Bark (Fig. 2.1) is the outermost layer of tree trunks and branches that protects the tree from its environment. It comprises about 10%–20% of the tree stem and has complex anatomy and chemistry. Bark is a contaminant in the wood supply used for making pulp because it decreases the quality of pulp proportional to its level of contamination. There is very little usable fiber in bark (mostly because of the very small size of the fibers in bark), and it consumes chemicals during pulping and bleaching stages; furthermore, it causes dark specks in the final paper product. The relatively high level of *nonprocess elements* (impurities) such as silica and calcium interfere with chemical recovery processes. For the pulp industry, typical bark tolerances in wood chips are 0.3%–0.5% although the kraft process is more tolerant than the other pulping processes. Bark removed from wood is usually burned as a fuel. Whole tree chipping in the forest (a practice some argue will become important in the future as it gives a higher yield of wood chips) requires cleaning of the chips before pulping to remove bark, dirt, needles or leaves, twigs, etc.

Chemically, bark typically consists of about 10%–30% extractives (depending on the species and extraction procedures), 15%–45% cellulose, 15%–40% lignin, and the remainder is other carbohydrates (termed polyoses that are similar to the hemicelluloses) and tannins (condensed polyphenolic compounds). Bark, especially the outer bark, may contain waxy materials called suberin and cutin, which are polyesters of dicarboxylic acids with C-16 to C-24 structures and bifunctional alcohols among other molecules.

The distinction between lignin and other polyphenolic compounds is not always possible. The bark of a few tree species is used as a source of tannins due to the high extractives and polyphenolic compounds. Tannins are used commercially for dyes, astringents, and leather tanning. The fuel value of bark is about 18.6–25.6 MJ/kg (8000–11,000 Btu/lb) of ovendry bark. The ash content of softwood bark is about 0.5%–4%, whereas hardwood bark is about 1%–6%. The ash is primarily calcium (80%–94% of the cations) and potassium (2%–7% of the cations) salts of oxalates, silicates, and phosphates. The effect of moisture content on the fuel value is described later in this chapter.

Physically, bark usually has a basic specific gravity between 0.40 and 0.65. There are a variety of bark layers, but mature bark is loosely divided into the inner bark (consisting of living phloem tissue) and outer bark (consisting of dead rhytidome tissue).

Biermann's Handbook of Pulp and Paper: Raw Material and Pulp Making
https://doi.org/10.1016/B978-0-12-814240-0.00002-1

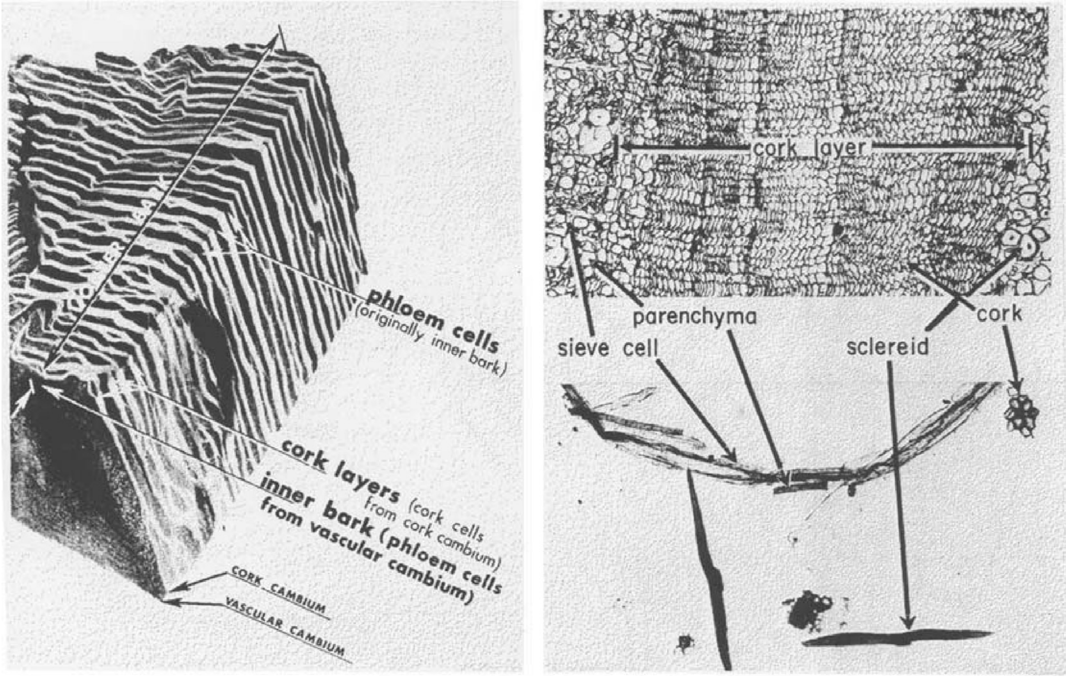


FIGURE 2.1 The anatomy of Douglas fir bark including three-dimensional view of whole bark (left), cross section of bark (upper right), and isolated fibers (lower right). *Courtesy of R.L. Krahmer.*

Wood

Technically, wood is xylem tissue, which arises from the cambium (inner bark) of trees and shrubs and consists of cellulose, hemicellulose, lignin, and extractives, hence a lignocellulosic material. Its function is support of the crown and conduction of water and minerals from the roots to the leaves of a tree. Sapwood is the outer part of the trunk and contains some living cells. Heartwood is found in the center of older trees, contains only dead cells, and is generally drier than sapwood. Each annual growth ring contains earlywood (sometimes called springwood), which is laid down in the early part of the growing season (spring and summer) and is characterized by large cells with thin cell walls, and latewood (sometimes called summerwood), which is characterized by small cells and thick cell walls. Fig. 2.2 shows the gross structure of wood, and Table 2.1 shows the function and characteristics of woody tissues.

The inner portion of wood in a tree eventually dies with a corresponding deposition of extractives, the process of heartwood formation. Heartwood is more difficult to pulp than sapwood. The moisture content of sapwood is high as the wood is normally saturated with water, but with heartwood formation, the moisture content decreases, with air replacing some of the water. Some hardwoods, such as the white oaks, but not the red oaks, form tyloses in the vessels during heartwood formation, which greatly reduces the permeability of the wood to fluid flow. For this reason, white oaks are impermeable and suitable for wine barrels, whereas red oaks are quite permeable and unsuitable for barrels. In many species the heartwood is obviously darker than the sapwood; in other species the presence

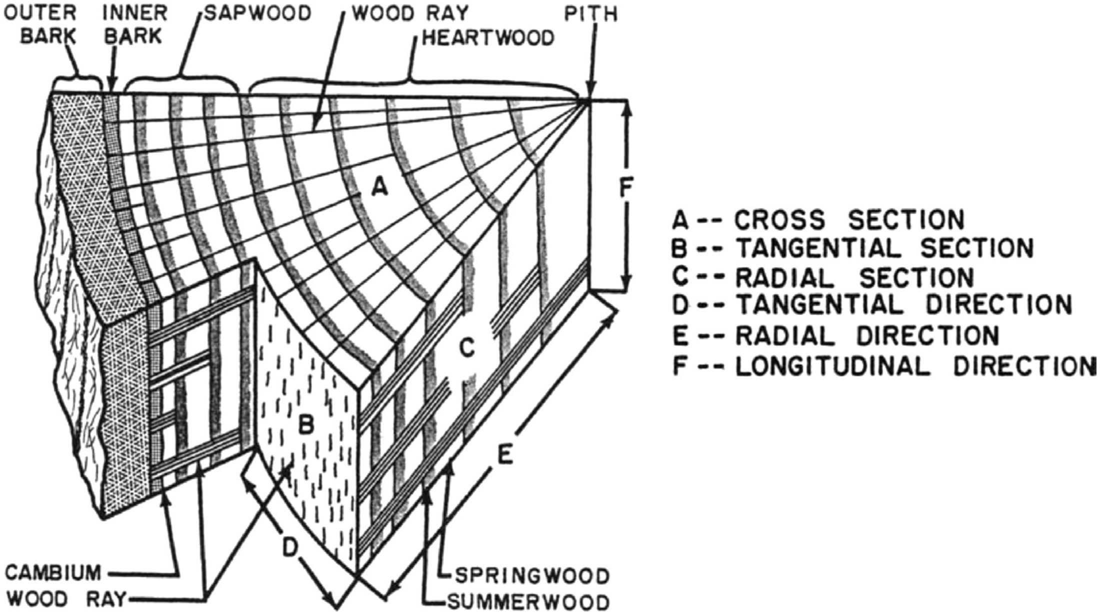


FIGURE 2.2 Gross structure of a softwood stem cross section. *Reprinted from W.I. West, Wood Pole Conference, Corvallis, Ore., Mar. 21, 1960, with permission.*

TABLE 2.1 The Function and Characteristics of Various Tree Stem Tissue

Tissue	Function
Outer bark	Physical and biological protection
Phloem (inner bark)	Conduction of food up and down the stem
Vascular cambium	Thin layer of cells giving rise to all the wood and inner bark fibers; the tree stem grows outward
Rays	Storage and lateral food movement from the phloem to the living cells of the cambium and sapwood
Pith	The center of the tree; from the apical meristem
Growth ring	1 year's growth of wood
• Earlywood • Latewood	Low-density wood designed for conduction of water High-density wood for strength to support the tree
Sapwood	Conduction of sap (water, soil nutrients) up to the leaves
Heartwood	Provides strength to support the crown; often relatively low moisture content in softwoods
Juvenile wood	The first 10 growth rings surrounding the pith; usually low density and relatively short fibers

of starch in sapwood allows it to be distinguished from heartwood by a test with iodine.

Some of the important pulping variables of wood and wood chips are as follows:

1. Moisture content: percentage of water reported relative to dry or wet wood weight
2. Specific gravity: the density of wood material relative to the density of water
3. Tension and compression strength properties
4. Bark content
5. Chemical composition: cellulose, hemicellulose, lignin, and extractives
6. Length of storage: amount of decay and extractives content
7. Chip dimensions
8. Wood species

The moisture content of wood is an important factor because one pays for wood on an ovendry basis, which represents the actual amount of wood material present. Often it is desirable to have a low moisture content to reduce the energy requirements to chemically pulp the wood and reduce transportation costs, but there is little that can be done to control the moisture content of wood sources. The wood density and wood chip bulk density (including air between the wood chips) are also important in determining the amount of wood material one purchases and in determining digester charge levels.

The properties of wood (or chips from wood) depends on growth factors such as the location of the tree from which it came and its location within the tree. For example, the average fiber length typically increases gradually as the first 50 inner growth rings are formed, and fibers are longest in wood 10–20 ft above the ground. For this reason, there is some concern about the properties of wood harvested from short-rotation wood plantations or forests that have trees with high amounts of juvenile wood, the wood made during the first 10 years after a stem forms. Trees growing on wet, warm, and sunny locations are fast growing and have coarse, stiff fibers, whereas trees growing on dry, cold, and less sunny locations are slow growing and have fine, dense fibers.

Softwoods

Woods, or trees, from the gymnosperms, a subdivision of the division spermatophytes (plants with seeds), are known as softwoods. Gymnosperms are also called conifers or evergreens. These trees retain their needles (leaves) in winter. Softwoods are characterized by relatively simple wood anatomy consisting of 90%–95% longitudinal fiber tracheids 2.5–7 mm long and 25–60 μm wide, 5%–10% ray cells, and 0.5%–1.0% resin cells. Fig. 2.3 shows a wood cube from cypress.

All wood fibers have many similar structural and chemical features. Fig. 2.4 shows a typical softwood fiber. The S2 layer is generally the

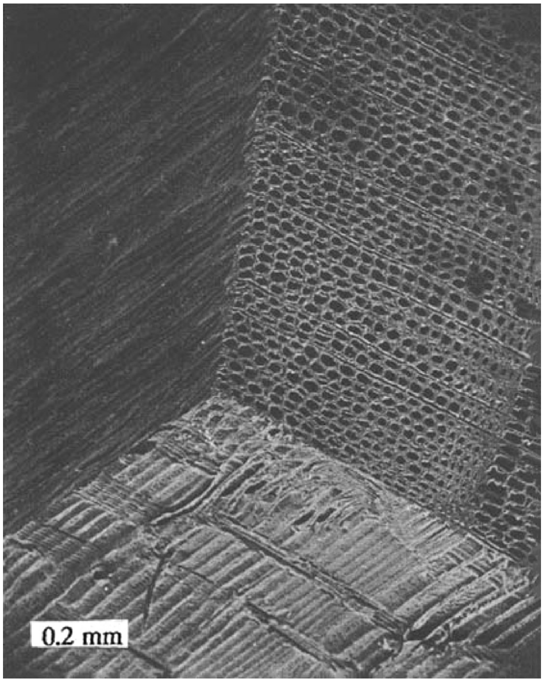


FIGURE 2.3 Scanning electron micrograph (SEM) of a cypress heartwood cube.

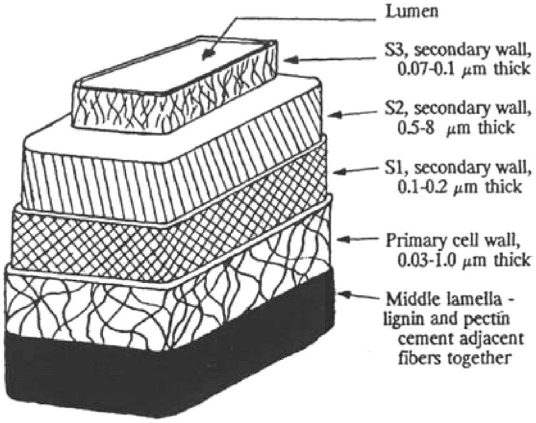


FIGURE 2.4 A mature softwood fiber. *Adapted from U.S. For. Ser. Res. paper FPL-5, 1963.*

thickest layer of the fiber, and its effect dominates the overall properties of the fiber. In this layer, the cellulose microfibrils are oriented at about 10–30 degrees from the main longitudinal axis of the fiber. This gives the fiber a higher tensile strength in this direction compared with the radial or tangential directions. Fibers do not shrink and swell appreciably in the longitudinal direction, whereas there is very high shrinkage in the other two directions. The microfibril angle is discussed further in regard to fiber strength in Section 2.7.

Softwood Fiber Length and Coarseness

Most softwood fibers average 3–3.6 mm in length. Some notable exceptions are three of the four southern pines: longleaf, shortleaf, and slash pines at 4.6–4.9 mm; sugar pine at 5.9 mm; western larch at 5.0 mm; sitka spruce at 5.9 mm; redwood at 7.0 mm; Douglas fir at 3.9 mm; and bald cypress at 6.2 mm. Fiber coarseness (the mass per chain of fibers 100 m long) is typically 18–30 mg/100 m (data from Pulpwoods of the United States and Canada, 1980).

Hardwood

Woods, or trees, from the angiosperms, a subdivision of the division spermatophytes, are known as hardwoods. Hardwood trees are also called broadleaves or deciduous. These trees lose their leaves in winter. Hardwoods have complex structures, including vessel elements, fiber tracheids, libriform fibers, rays cells, and parenchyma cells. The fibers of hardwoods are on the order of 0.9–1.5 mm long, leading to smoother paper of lower strength, compared with softwood fibers. The morphology of hardwoods is much more complex than that of softwoods. The cellular composition is 36%–70% fiber cells, 20%–55% vessel elements, 6%–20% ray cells, and about 2% parenchyma cells by volume. Fig. 2.5 shows the structure of red oak.

Pits

Chemical pulping of wood depends on the ability of cooking liquor to flow through the wood. Fibers in wood have numerous openings between each other on their radial surfaces that are known as pits or pit pairs. In the living sapwood, they allow for the movement of liquids up and down the length of the tree. (The swelling of wood above a pH of 10–12 during alkaline pulping increases the tangential and radial permeability drastically.) The type of pit will depend on the fiber type in which the pits are found. The most common type is the bordered pit that occurs between two adjacent tracheids of softwoods. The exact nature of a bordered pit depends on the species of wood. Pits are the only intercellular channels for conduction of liquids in softwood tracheids, which make them important in wood pulping and treatment with preservatives. In softwoods, the bordered pits become aspirated during heartwood formation; that is, the pit membrane is displaced to one side of the pit chamber allowing the torus to seal the aperture, which effectively stops the flow of liquids through the pit. This

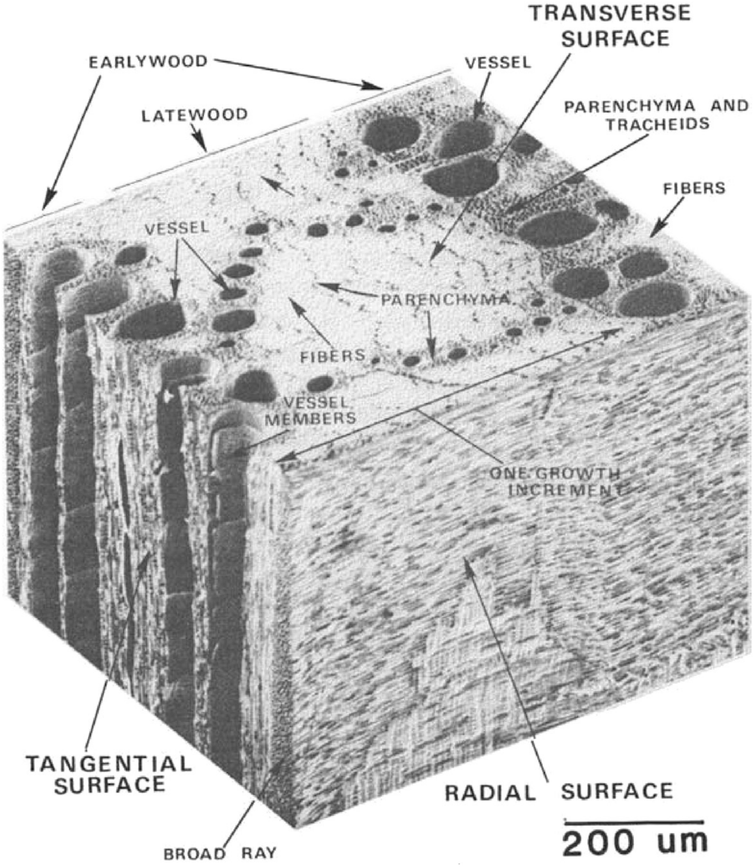


FIGURE 2.5 Red oak hardwood. *From C.W. McMillin and F.G. Manwill,* The Wood and Bark of Southern Hardwoods. *USDA Rep. SO-29, 1980.*

condition is known as pit aspiration and occurs whenever wood is air or kiln dried. This is one reason dried softwood does not pulp well.

Knots

A knot is the base of a branch that starts from the trunk or a large limb of the tree. The wood grows around the base of the branch and gives rise to several types of knots that influence the pulping and pulp characteristics of the material. For example, if the branch dies, the trunk will continue to form around the branch, encasing the entire branch stub, including the bark. Eventually there will be no trace of the knot from the exterior tangential surface. If the branch continues to live, the branch wood and trunk wood are then continuous. Knots are harder, more dense, often more resinous, and more difficult to pulp than the normal wood. Knots often remain unpulped after chemical pulping operations and decrease the screened pulp yield.

Reaction Wood

Trees under physical stresses such as the weight of heavy branches or leaning trunks produce wood that reacts to these stresses and is known as reaction wood. In practice, there is little one can do about the presence (or absence) of reaction wood, but it is usually not present in large amounts.

Angiosperms (hardwoods) produce tension wood, which is usually located on the upper side of branches or leaning trunks where the wood is under a tension force. Tension wood has fewer vessels, and those are of smaller diameter, a thick gelatinous layer in the cell wall on the lumen side and a higher cellulose content than normal wood. Tension wood produces pulp with higher yield but with lower strength, than normal wood, which makes it well suited for dissolving pulps.

Gymnosperms (softwoods) form compression wood on the lower side of branches or leaning trunks, where the wood is under a compression force. Compression wood tends to have a higher proportion of latewood, higher lignin content, higher density, and higher hardness compared with normal wood, making it less suited for pulping. TAPPI Standard T 267 has photographs and methods for compression wood identification.

Moisture Content (Wet or Green Basis), MC_{GR}

The moisture content based on the wet weight of material is used in pulp and paper mills for wood, as well as most other raw materials such as pulp, paper, and fillers. It represents the amount of water in wood as a fraction of the wet weight of wood. If no subscript is used, one can generally assume that the moisture content is on a wet basis in the pulp and paper literature. The weight of water is determined by weighing the wood before and after drying at 105°C. The green-basis moisture content of freshly cut wood is typically 50% but can vary from about 30% to 60%.

$$MC_{GR} = \frac{\text{mass } H_2O \text{ in wood}}{\text{wet wood mass}} \times 100\%$$

A measure of the moisture content of wood based on the ovendry (an obsolete term is bone-dry) weight of wood is used by wood scientists and foresters. It represents the amount of water in a wood sample divided by the ovendry weight of wood material. The ovendry weight is obtained by drying the wood to constant weight at 103–105°C (217–221°F). Freshly cut wood has an ovendry basis moisture content on the order of 100% although it varies from about 45% to 150%.

$$MC_{OD} = \frac{\text{mass } H_2O \text{ in wood}}{\text{ovendry wood mass}} \times 100\%$$

Solids Content

The solids content is a measure of the solid material in wet samples such as wood, pulp, and paper. The term *consistency* is used instead of solids content in pulp slurries.

$$\text{solids content} = 100\% - MC_{GR}$$

$$\text{solids content} = \frac{\text{ovendry sample mass}}{\text{wet sample mass}} \times 100\%$$

Solid Wood Density

Solid wood density is a measure of the dry weight of wood per unit volume of green wood. Because wood contracts about 8%–15% on a volume basis as it is dried below 30% moisture, it is important to specify the moisture content at which the volume was measured. Typical units are lb/ft^3 g/cm^3, or kg/m^3.

Specific Gravity

Specific gravity is the (unit less) ratio of the *solid wood density* to the density of water at the same temperature. The solid wood density may be determined using the green volume, the ovendry volume, or intermediate volumes. This is notable as wood shrinks about 8%–15% as it dries. The *basic specific gravity* always uses the green volume. [The density of water at 20°C (68°F) is 62.4 lb per cubic foot, 1 g per cc, or 1 metric ton per cubic meter.] Softwoods have typical specific gravities of 0.35—0.50 g/cc on a green volume basis but can vary from 0.29 to 0.60 among North American commercial species; hardwoods have typical specific gravities of 0.35—0.60 on a green volume basis but can vary from 0.30 to 0.90 among the North American commercial species. Balsa wood, used in model building, has a basic specific gravity of 0.16, whereas ironwood is 1.05. The specific gravity of the cell wall material is 1.50. Note that (using appropriate units): Specific gravity of wood × Density of water = Solid wood density.

Wood Decay and Other Deterioration

At ambient temperatures and suitable pH conditions, wood can decay in the presence of moisture and oxygen. In temperate environments, decay leads to much more loss of structural wood than is caused by termites. Wood in the form of logs kept under a water sprinkler (Fig. 2.6) or immersed in water (Fig. 2.7) tends to decay slowly. Although water may seem to promote decay, under these conditions, available oxygen is low in concentration due to air displacement by water, limiting decay. Keeping wood in any form below 20% moisture content prevents decay, but it is generally impractical to dry wood for pulping, and dry wood usually does not pulp well because liquor penetration is more difficult.

Wood chip piles, as a rule of thumb, lose 1% per month due to decay and chemical oxidation. Fig. 2.8 is a summary of wood deterioration in chip piles from Fuller (1980).

Wood deterioration begins by respiration of living parenchyma cells of the wood rays. This increases the temperature and accelerates bacterial and fungal decay. Heating above 45—55°C (115—130°F) is mostly due to chemical oxidation (especially of extractives), as most bacteria and fungi will not grow well at these temperatures. Temperatures above 55°C (130°F) lead to severe

FIGURE 2.6 Logs stored under a water sprinkler to keep oxygen out and thereby prevent decay. *The photo was taken at Mary's River Lumber in Philomath, Oregon, and is courtesy of Susan Smith.*

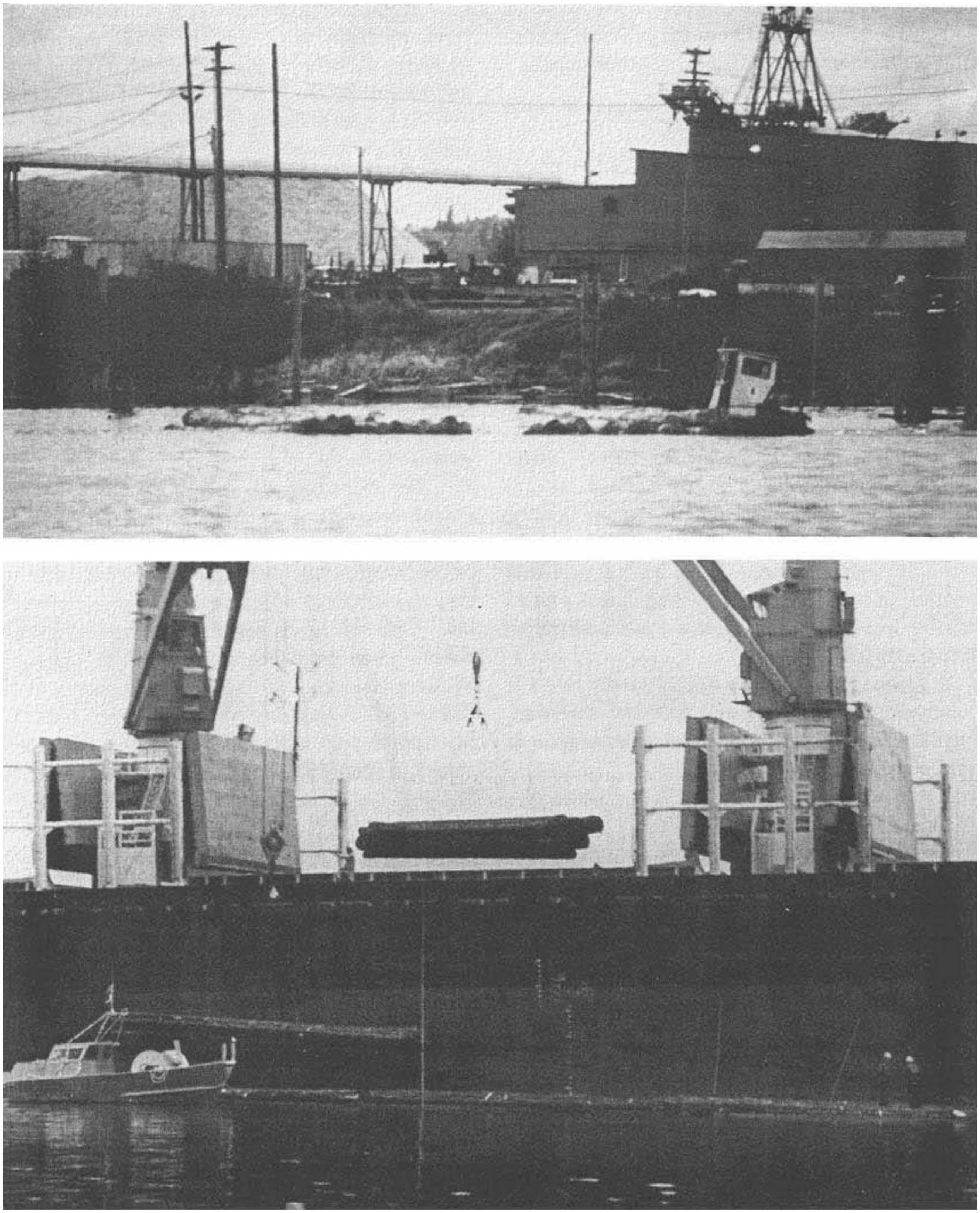


FIGURE 2.7 Logs for export on the Columbia River in the northwest U.S. Keeping wood in water decreases decay and makes for easy handling and transportation in rafts.

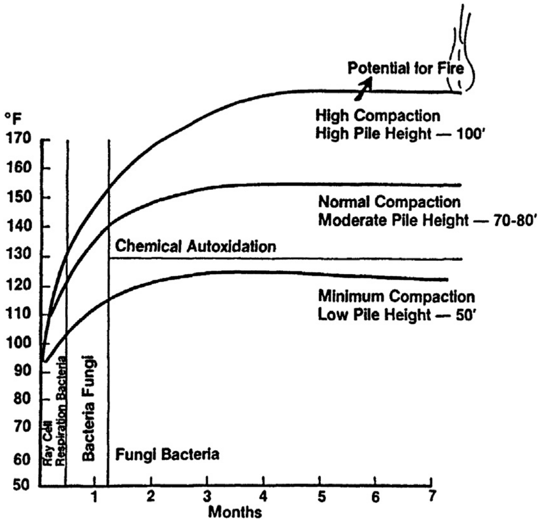


FIGURE 2.8 Deterioration in wood chip piles. *©1985 TAPPI. Reprinted from Fuller (1985) with permission.*

losses on pulping. Degradation can be limited by keeping piles below 50—60 ft high. Conditions that aggravate decay include the use of whole tree chips, high fines fraction that decreases air circulation, pile compaction, high piles, and the storage of hardwoods, which tend to have high starch contents. Loss of terpenes (important if collected at a mill) may be over 50% in the first month.

For these reasons, it is important to rotate chip inventories on a first-in-first-out (FIFO) basis. Mills recovering extractives often use FIFO in combination with pulping some chips directly as they enter the mill to obtain high terpene recoveries. Chip storage is sometimes advantageous to reduce pitch problems during sulfite pulping. Western US kraft mills typically operate with a 3-month supply of chips in storage, whereas mechanical pulp mills are limited to a 1-week supply, as chip darkening leads to inalterable pulp darkening. (Chemical pulping and bleaching of chemical pulps remove most of the dark color.)

There are two principal decay fungi groups, and their observable action is shown in Plate 2.1.

PLATE 2.1 Advanced wood decay by brown rot (left) and white rot fungi (right).

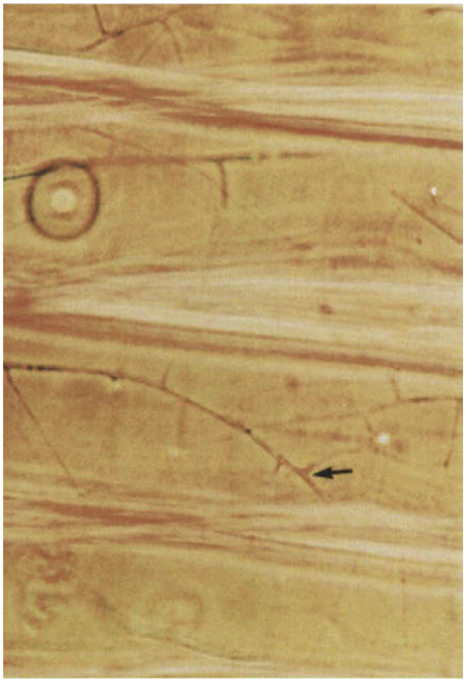


PLATE 2.2 Microscopic view of wood decay fungi (*arrow* points to hyphae).

Actual fungi hyphae are shown in Plate 2.2. Brown rot fungi attack the carbohydrates, leaving a brown chip. Small losses in weight lead to very large decreases in cellulose viscosity and, therefore, pulp strength. White rot fungi attack both the lignin and carbohydrates, leaving a whitish wood. Small losses of wood material do not lead to an appreciable decrease in cellulose viscosity or paper strength; indeed paper strength often increases slightly. Treating wood with white rot fungi or enzymes derived from decay fungi is the basis of the experimental biopulping and some biobleaching methods. *Sap stains*, such as blue stain, darken woods but do not degrade their strength properties.

Fuel Value of Wood

The heating value of wood is about 21 MJ/kg (9000 Btu/lb) for ovendry softwood and 19.8 MJ/kg (8500 Btu/lb) for ovendry hardwood. The higher value for softwood is due to the higher lignin content. (Lignin has a much lower oxygen content than the carbohydrates it displaces.) Actual heating values depend on species, growing conditions, age, etc. The actual fuel value of wet wood or bark is calculated on the basis that 1 kg water takes 2.5 MJ to evaporate (1 lb of water takes 1100 Btu to evaporate). For example, 1 lb of softwood at 50% moisture content is 1/2 lb of wood with 4500 Btu fuel value, but 550 Btu would be needed to evaporate the other 1/2 lb of water. This wet wood would have an effective fuel value of 3950 Btu/lb (wet basis).

2.2 WOOD CHIPS AND SAWDUST

Sawdust

Sawdust is the residue generated by sawteeth when wood is cut into lumber. In the past, it has had some limited use by the pulp and paper industry. It gives a pulp with short fibers that is suitable as part of the furnish for tissue and writing papers. Since the 1970s, saw blades have become thinner with more teeth, which, in many cases, make the sawdust too small to be used as a fiber source for pulp.

Chips

Wood chips are mechanically disintegrated wood, traditionally into pieces 12—25 mm (1/2—1 in.) along the grain, variable in width, and 3—6 mm (1/8—1/4 in.) thick. Uniform chip size is very important in chemical pulping because large chips (particularly overthick chips in kraft cooking) undercook, leaving large amounts of shives, whereas small chips clog the liquor circulation system, use large amounts of chemical, and give a low yield of weak pulp. Bark, dirt, and other materials should always be kept to a minimum (0.5% or less), especially in mechanical pulps where they give a dark pulp that cannot be brightened because lignin must be retained in these pulps.

Short chips will give paper that is slightly weaker due to fiber cutting. Softwood chips less than 12 mm (0.5 in.) long (as this is the axis parallel to fiber orientation) will have reduced average fiber lengths because many of the fibers will be cut. For example, 25-mm-long chips from Douglas fir will have an average fiber length of 3.5 mm; 12-mm long chips will have an average fiber length of 3.0 mm; and 6-mm long chips will have an average fiber length of only 2 mm.

In the western United States, 80% of wood is received as chip waste from primary wood processors and 20% is chipped on site. In the eastern and southern United States, the figures are reversed. (However, in 1947, over 80% of the wood used in the western United States at pulp mills was in the form of roundwood; this decreased to about 40% roundwood by 1960 and 20% by 1980.) Whether wood chips are generated on the mill site or purchased as wood mill residues, quality is extremely important. One key factor in obtaining the highest quality pulp possible with the most efficient use of pulping and bleaching chemicals and the least environmental impact is to have as uniform a chip as possible. This factor cannot be over stressed!

Chip Silos

For the sake of efficiency, after screening, wood chips must be metered into the digesters without constant supervision. One method of accomplishing this is with the use of chip silos that hold 50–300 tons of chips. A representative diagram of a chip silo is shown in Fig. 2.9. Fig. 2.10 shows vertical and horizontal silos for storage of wood chips. The silos may be located below a pile of wood chips and not visible in the woodyard. A large supply of chips in the silo assures a constant wood supply to the digesters. The turntable can meter the chips to the conveyer that then takes the chips to the digester. Controlling the speed of the turntable controls the chip supply.

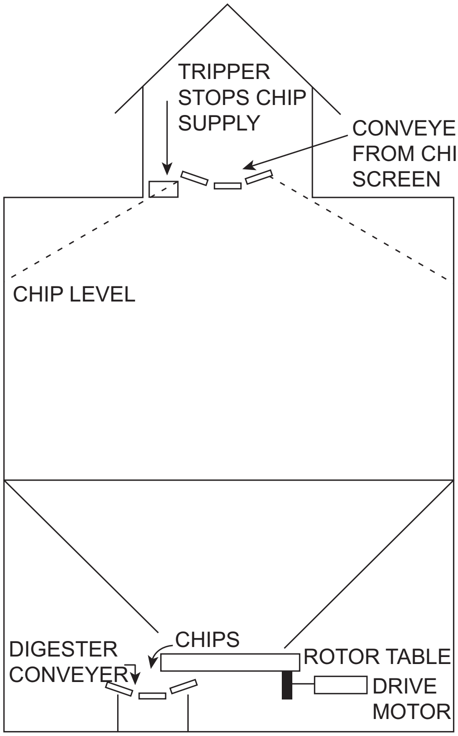


FIGURE 2.9 Chip Silo.

Chip Sources

Whole tree chips are made from the entire stem of the tree, usually in the woods. Whole tree chipping gives more wood chips, but they are contaminated with bark, dirt, twigs, etc.; therefore, they must go through complicated cleaning operations before use. Even so, residual contaminants mean these chips are only useful for coarser grades of paper. Residual chips are made from wood residues generated by solid wood conversion as by sawmills and plywood mills. For example, edgings and cores are chipped. Sawdust is the residue generated by the teeth of a saw. It is chemically pulped in continuous digesters with short residence times, such as the M&D (Messig & Durkee) and Pandia, and is used as a filler to give smoothness to papers. Different saw types generate sawdust of different size distributions; some consist of particles that are too small to give useful pulp.

2.3 WOOD CHIP PREPARATION AND HANDLING AT THE PULP MILL

General Considerations

In many mills, wood chips are made on site from roundwood. The discussion in this book focuses on typical operations at pulp mills producing their own chips or purchasing chips. Many mills rely on purchased chips that are generated by outside facilities such as sawmills, plywood mills, whole tree chips, etc. Note that the people generating such chips use other methods and the ones described here and often do not understand the importance of chip quality (or even what constitutes chip quality) from the point of view of pulp manufactures. For

Vertical Silo

Horizontal Silo

FIGURE 2.10 Silos for storage of wood chips and biomass. *Courtesy of Lippel.*

example, chip suppliers are not apt to use chip thickness screens but oscillating, round-hole screens. The chip buyer for a given mill should work closely with chip suppliers communicating with them as to what the pulp mill requires and how the supplier might best meet these demands. This assumes that the pulp mill is monitoring each supplier for chip quality.

Slasher Deck

The slasher is a deck where saws cut logs into shorter lengths, such as 2.5 m (8 ft), for easier handling. Because slashers require much maintenance, many mills are going to tree length handling of wood although this is much more difficult with hardwoods because of their tendency to have several main trunks.

Plate 2.3 shows a logging operation in Washington State.

PLATE 2.3 A logging operation in Washington State.

Barker

A barker (or debarker) is a device used to remove bark from wood before chipping. Removal of bark is necessary, as it has negligible useful fiber, darkens pulp, requires extra chemical usage, and introduces contaminants such as calcium, silica, and aluminum into the chemical recovery system. Bark adhesion is about 3–5 kg/cm^2 during the growing season and two to three times higher during the dormant season (winter).

One type of barker, the drum barker, is a large, rotating, steel drum 2.5–5.0 m (8–16 ft) in diameter by 8–25 m (30–90 ft) long (12 ft in diameter by 70 ft long is common), mounted with the exit lower than the entrance to promote the flow of logs (Fig. 2.11 and Plate 2.4). The

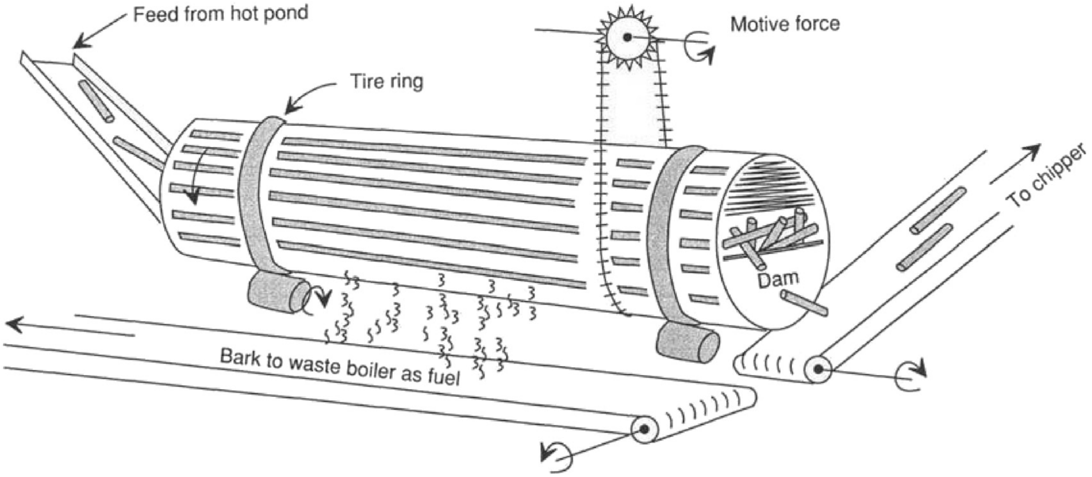


FIGURE 2.11 Schematic diagram of a barking drum. *Redrawn from J. Ainsworth,* Papermaking, *©1957 Thilmany Paper Co., with permission.*

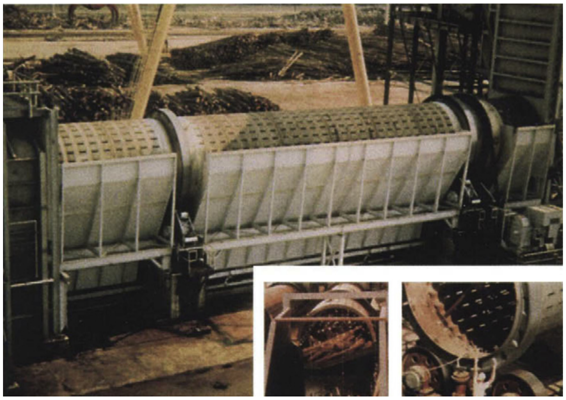


PLATE 2.4 Barking drum 14.5 ft in diameter by 100 ft long. The first insert shows the logs at the dam, and the second insert shows the inside of the drum during construction. *Courtesy of Manitowoc Engineering Co. Ring barker with an insert of a modular, rotary-head option to debark stringy-bark species such as cedar and eucalyptus; Courtesy of Valon Kone Brunette, Ltd.*

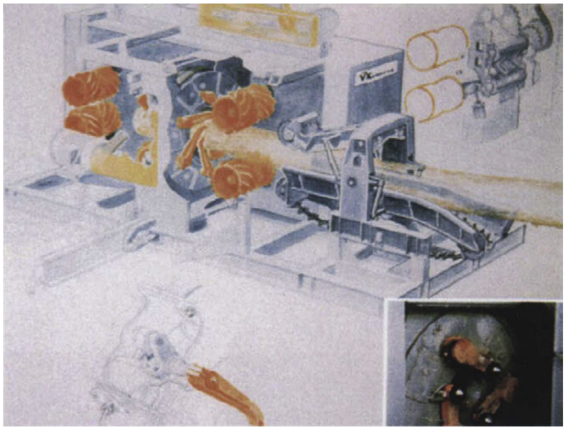


PLATE 2.5 Ring barker with an insert of a modular, rotary-head option to debark stringy-bark species such as cedar and eucalyptus. *Courtesy of Valon Kone Brunette, Ltd.*

drum rotates at about 5 revolutions per minute. A dam at the exit controls the log retention time, which is on the order of 20–30 min. Debarking occurs by mechanical abrasion of the logs against each other. Typically the wood contains 0.5%–1.0% bark after this method although this depends on the type of wood, average log diameters, season of the year, and other factors. Logs that are not adequately debarked may be sent through the drum again. Some disadvantages of the drum barker are the relatively high power requirements, maintenance costs, and bruising of the logs.

The cambial shear barker works with a ring of knives that peel off the bark as the logs are fed individually as shown in Plate 2.5. Feeding the logs individually increases the operating costs because of the required supervision. This method does not work well on frozen logs. The cutterhead or Rosserhead barker works like a planar, where a turning wheel that is toothed or spiked is held against the log and removes the bark by abrasion (see Plate 2.5). It has low capacity because logs are fed individually, requires large amounts of supervision, and has high wood losses. It is used in low-production facilities such as small sawmills. It is suitable for logs that are difficult to debark such as frozen logs.

Hydraulic barkers operate by impinging high-pressure water jets onto the wood. With ring barkers, logs 0.5–1.5 m (1–5 ft) in diameter travel at 1 m/s (3 ft/s), whereas 1500 gallons per minute of water at 1500 psi squirt out of four nozzles in a rotating ring (16 stationary nozzles in older designs) with a velocity of 400 ft/s. As much as 2500 hp is required to drive the water pumps. The water must be very clean for ring barkers as grit and dirt quickly disintegrate the seal.

Single jet units such as the modified Bellingham barker (Fig. 2.12) use a traveling nozzle that moves up and down while the log is moved and rotated using airplane-type controls (joy sticks). Water is supplied by a six-stage impeller pump to produce 1200 gal/min at a nozzle pressure of 1400 psi. Numerous other designs for hydraulic barkers are used as well. The waste water from hydraulic barkers is high in Biological Oxygen Demand (BOD) (a type of pollutant) and color and must be treated before release, a severe drawback. They were once

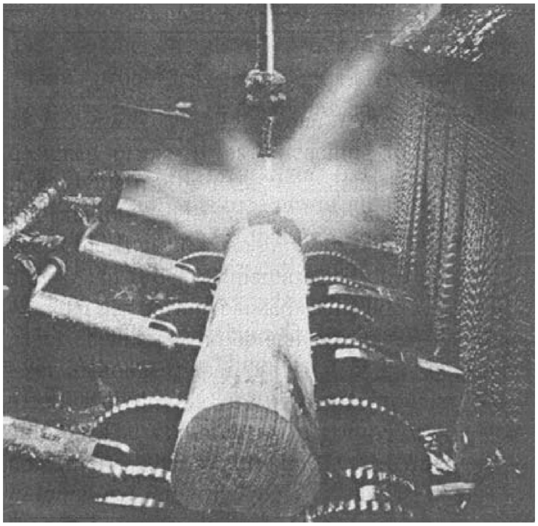


FIGURE 2.12 Bellingham hydraulic barker in action. *From Making Pulp and Paper, ©1967 Crown Zellerbach Corp., with permission.*

common on the West Coast of the United States, as they work well for debarking large logs.

Flail debarkers use a rotating cylinder with numerous chains hanging from it to delimb and debark small diameter material. It is useful for in-the-woods operations for processing precommercial thinnings that would otherwise be unusable. Without debarking, whole tree wood chips are less valuable. Plate 2.6 shows an in-the-woods operation using a flail delimber/debarker. Fig. 2.13 shows flail debarkers with disc chippers from Peterson and Continental Biomass Industries (CBI).

Chippers

Chippers are devices used for mechanically breaking down wood into chips (Fig. 2.14). Chipping takes approximately 7–14 kWh/t (0.4–0.8 HP days/ton). Hardwoods generally are harder to chip and generate fewer fine chips but more large chips than softwoods. The traditional chipper for log lengths of 1.5–3 m (4–10 ft) is the gravity feed (or drop feed) disc chipper, where the logs enter through a spout mounted on the top (or sometimes other) comer of the feed side. Mills that handle tree length wood must use horizontal feed disc chippers that have the feed at the top or the bottom of the feed side. Horizontal chippers use more knives than drop feed chippers to avoid the production of more fine and pin chips. Disc chippers use gravity discharge, which increases the initial capital cost because of the higher elevation required for the chipper, or blowing discharge, which increases the pins and fines content because of the extra chip damage caused by the paddles forcing the chips from the chipper.

PLATE 2.6 Flail barker. *Courtesy of Manitowoc Engineering Co.*

The best chipping of softwood logs leads to 85% accept chips, 4% overthick, 2% overlength chips, 7% pin chips, and 2% fines. A worn blower (for blower discharge units) or excessive anvil gap leads to more pins and fines.

Drum and double cone (V-drum) chippers have very limited use for smaller-sized wood. Because of their design and processing of small residues, the generation of pin chips (15%–25%) and fines (5% or higher) is much higher than chipping softwood logs. Other chippers are designed for specific purposes such as veneer chippers that chip veneer residues from plywood plants and core chippers that chip the core of peeled logs used to make veneer.

Peterson 4810F Chain Flail Debarker and 5900E Disc Chipper

CBI 754 Disc Chipper with CBI 604 Flail debarker

FIGURE 2.13 Flail debarkers. *From Peterson and CBI with kind permission from Peterson Pacific Corp. and Michael Spreadbury (as the photographer) and Continental Biomass industries.*

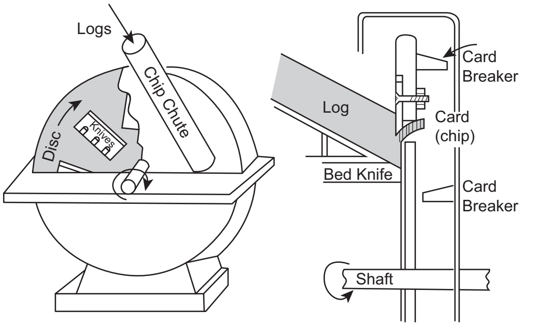


FIGURE 2.14 Drop feed (gravity) wood chipper. *Redrawn from J. Ainsworth,* Papermaking, *1957 Thilmany Paper Co., with permission.*

Chip Size Sorting for Production

Ideally all chips regardless of their source are sorted (screened) at the mill into several fractions according to their size to permit uniform pulping (Fig. 2.15). In the past, most mills classified wood chips by size using oscillating, round-hole screens. During the 1970s, it became apparent that for the kraft cooking process, chip thickness is of primary concern. Since 1980, almost all kraft mills have installed equipment that classifies the chips by thickness (Plate 2.7) to remove the overthick chips. Most mills use additional separations to remove fines. A few mills even separate pin chips going to the process and meter them back into the process. Most sulfite mills and sawmills continue to use chip classification by round-hole screens. The horizontal screening and the rotary classifier (Fig. 2.15) belong to the gravimetric method, which all have the problem that long and thin particles can pass small aperture widths while being in a vertical orientation, and they are thus wrongly allocated if a separation by length is desired. Such disadvantages are overcome by the application of a dynamic online image analysis system (Fig. 2.16). This technique is particularly interesting as it can sort the particle sizes according to more than just one size parameter. However, the image analysis is sensitive toward particle overlappings, resulting in overestimation of particle sizes.

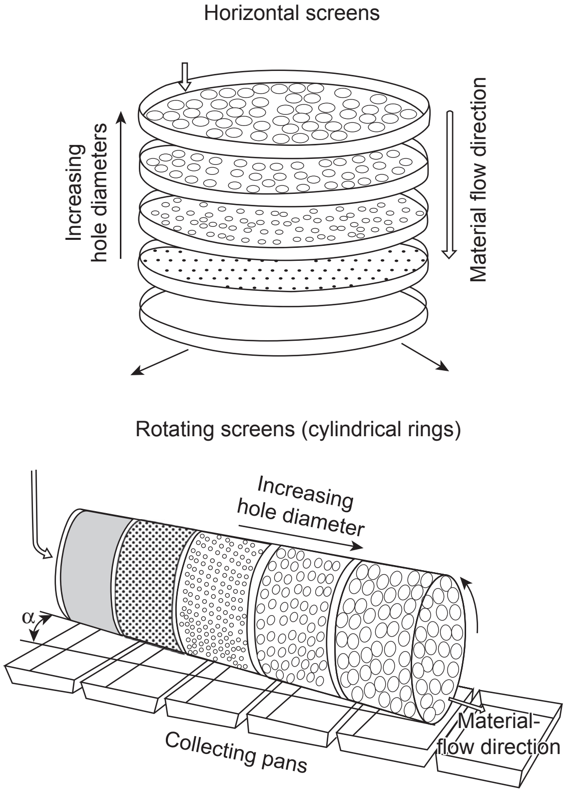


FIGURE 2.15 Horizontal and rotating screens for chip screening. *Hartmann et al. (2006). Reproduced with permission.*

Laboratory Chip Screening

Chip classification is also done in the research and development laboratory (as opposed to production quality control) for experimental protocols and to determine the quality of chips from the various chip vendors although the methods used are not designed for large numbers of samples on a routine basis. Laboratory classification was traditionally based on chip size using round-holed screens and is known as the Williams classification with pans containing 9/8, 7/8, 5/8, 3/8, and 3/16 in. holes.

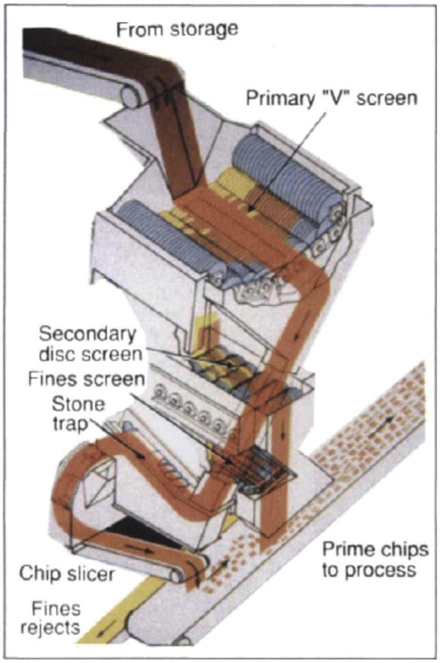


PLATE 2.7 Chip thickness screening system. *Courtesy of Rader Co., Inc.*

This method is now obsolete for most purposes. To more closely duplicate screening at kraft mills, a thickness screen is now included for laboratory screening. The exact definitions of the following chip fractions depend on the nature of the classification scheme. The laboratory screen is shown in Fig. 2.17.

The following definitions are based on typical laboratory screening. Overs are the oversized or overthick fraction of chips and are retained on a 45-mm (1.8 in.)-diameter hole screen and are thicker than 10 mm for conifers or 8 mm for hardwoods. [For sawdust, overs are retained on a 12-mm (1/2 in.)-diameter hole screen.] Accepts are the chip fraction of the ideal size distribution for pulping. These chips pass through an 8- or 10-mm slotted screen and are retained on a screen with holes 7 mm (0.276 in.) or 3/8 in. diameter. Pin chips are the chips that pass through a 7 mm screen but are retained on a 3 mm (0.118 in.) or 3/16 in. hole screen. Fines (unders) are the undersized fraction of chips or sawdust and are collected in the bottom pan.

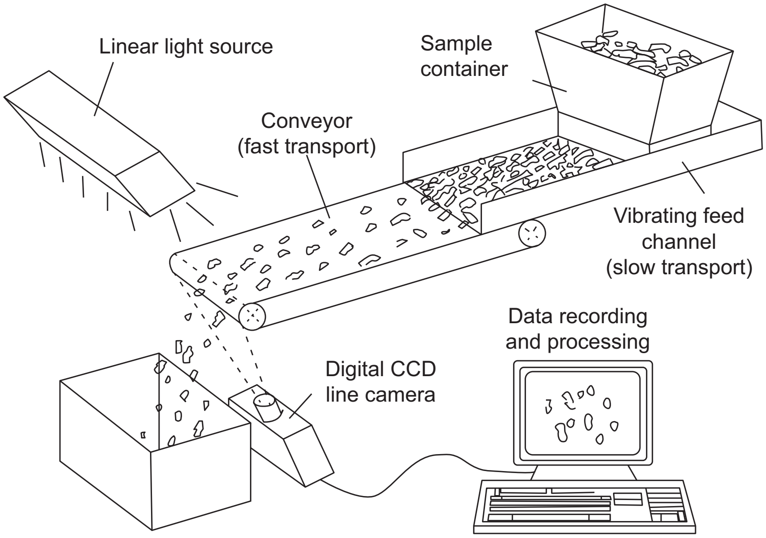


FIGURE 2.16 Image analysis system for wood chip classification. *Hartmann et al. (2006). Reproduced with permission.*

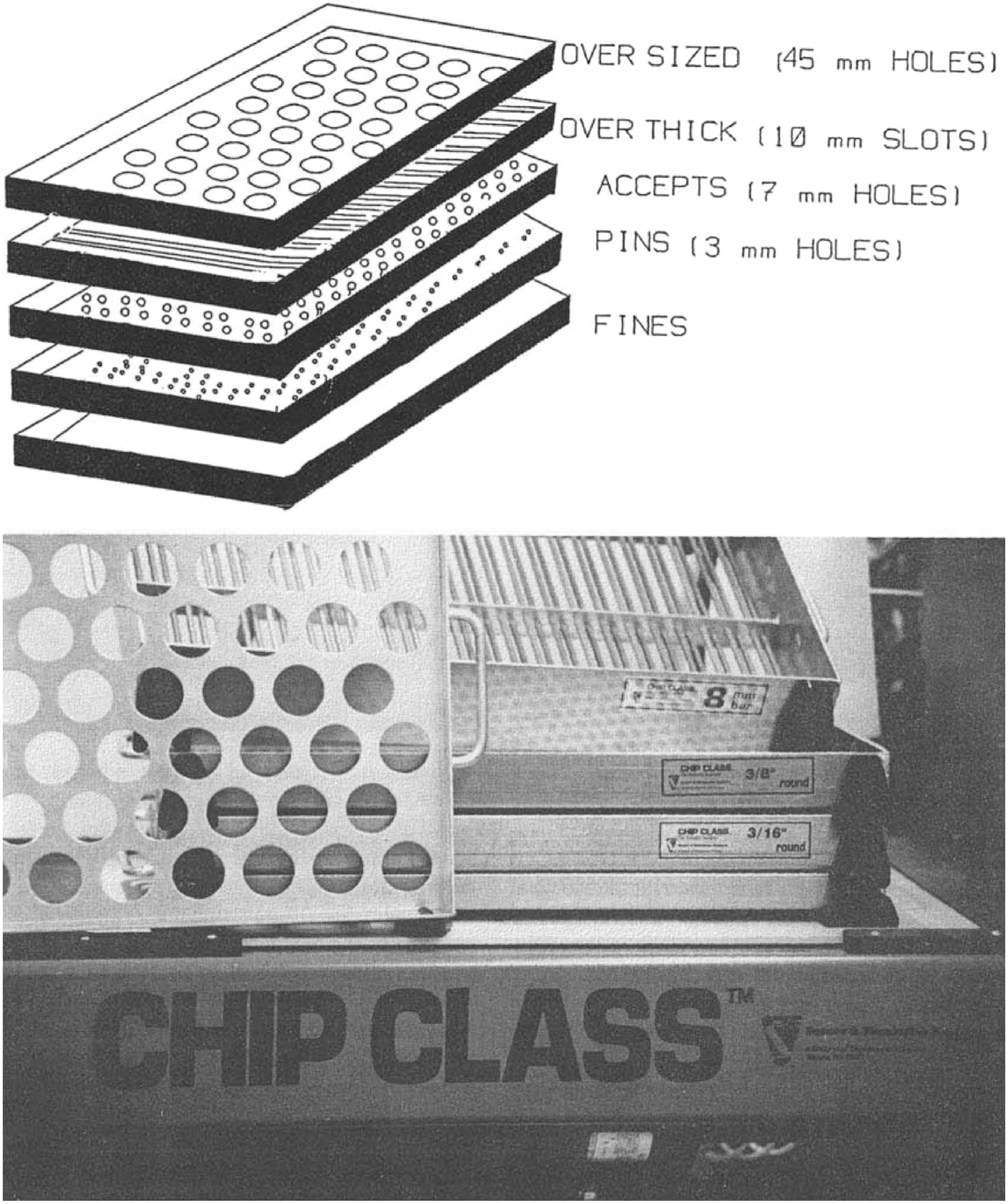


FIGURE 2.17 Laboratory chip size distribution analysis. The top shows the pan configuration; the bottom shows the actual equipment.

The definition of fines will vary with mill specifications, but fines generally consist of material passing through a 3 mm screen.

Wood Chip Quality Control at the Mill

Chip quality control uses devices that are designed to handle numerous samples quickly with a minimum of operator time. It is important to practice wood chip quality control for several reasons. The most basic reason is that the amount of dry wood must be determined for a truck, railcar, or barge load so that the supplier can be paid for the equivalent ovendry wood. An equally important reason to determine chip quality from each load is so that the mill can work with each chip supplier to insure that high-quality chips are supplied in terms of desired species; suitable chip size distribution; and small amounts of dirt, bark, and decayed material.

Like any method to insure quality, a representative sample from each truckload of incoming chips must be obtained. Some mills use continuous samplers to insure the sample represents the entire truckload, but most mills use a simple bucket sampler that is filled from the first 5% of the truckload. Fig. 2.18 shows a continuous sampler and a bucket sampler that grabs a sample from one section of the truck. Plate 2.8 shows a chip truck dumping in an

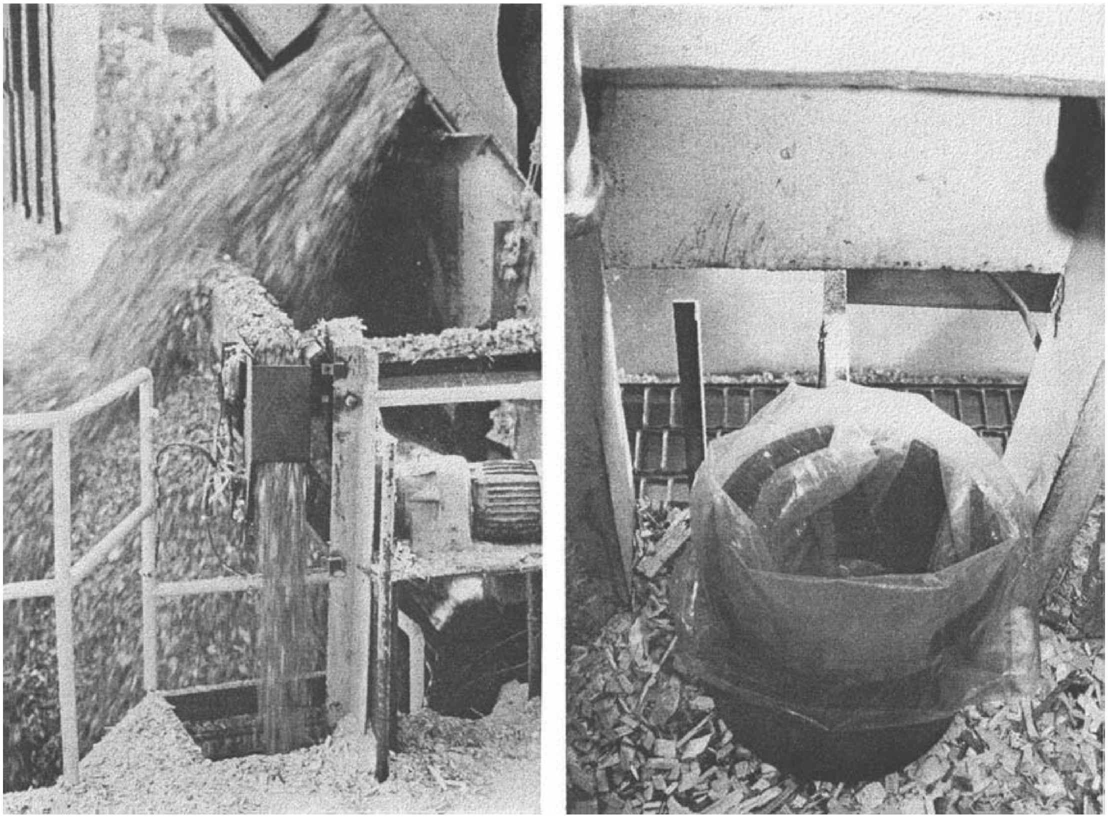


FIGURE 2.18 Continuous sampling during chip truck emptying on the left; on the right a bucket that is filled when it swings out, obtaining a sample that represents only one section of the load.

PLATE 2.8 Chip truck being dumped.

arrangement that also uses a bucket-type sampler. (Stories circulate about unscrupulous suppliers that water down or use inferior chips in the part of the truck that they know will not be sampled.) Many mills may also have a person collect a sample every hour of the chips going to the digester to see how the screening system is working. (Stories also circulate about the person who collects all eight samples for a given shift at one time and submits one sample every hour.)

Ideally, laboratory determinations are made for moisture content; chip size distribution; and bark, rot, and dirt contents. Determinations of wood species, extractives content, chip bulk density, and chip damage are made less often. Chip size distributions are determined in the laboratory using oscillating screen systems, systems with adjustable thicknesses between bars (Fig. 2.19), or other suitable systems. Collection of representative wood chip samples from rail cars or barges can be quite challenging (Fig. 2.20).

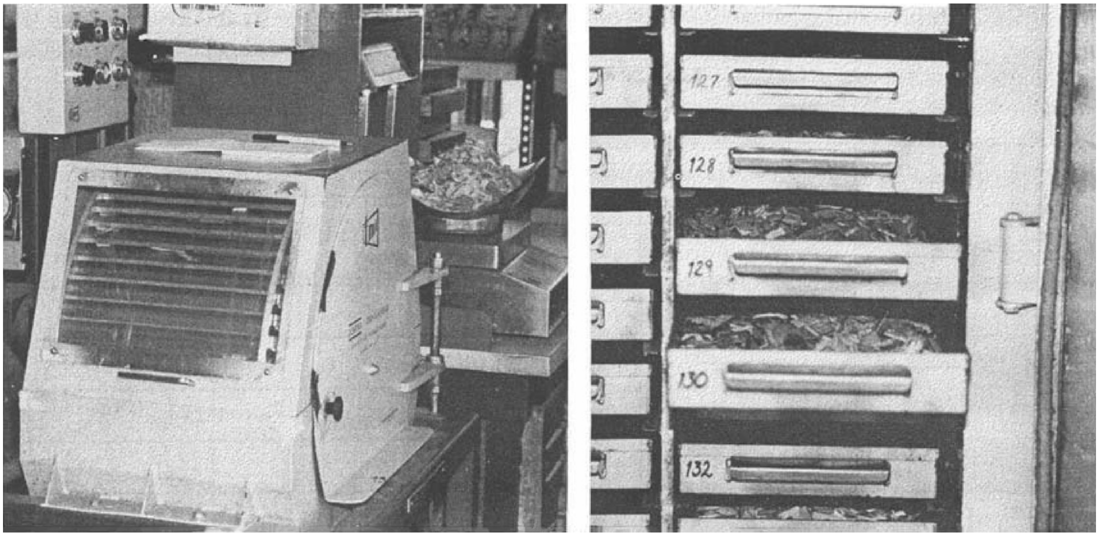


FIGURE 2.19 Chip size classification (left) and moisture content determination (right) in a mill's wood quality control laboratory.

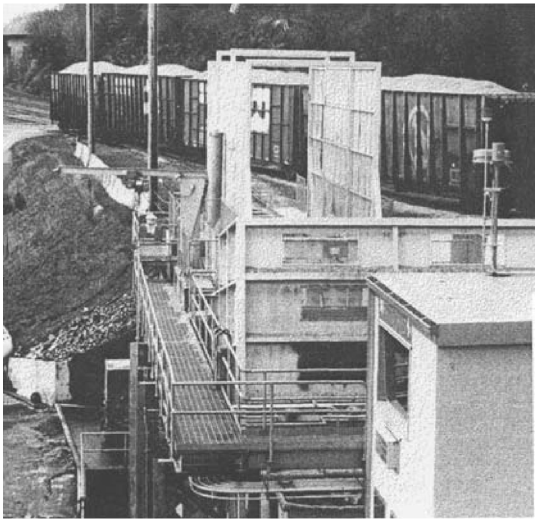


FIGURE 2.20 Rail cars ready to be unloaded. They will be tipped back on the special platform to discharge their contents. Over six cars per hour can be unloaded by this method.

Miscellaneous Analyses

TAPPI Standard T 257 describes the sampling and preparation of wood for analysis whether logs, chips, or sawdust. The basic density and moisture content of pulpwood is determined according to TAPPI Standard T 258. In this test, volume is measured by water displacement and moisture content by the difference in mass before and after drying at 105 ± 3°C. The overall weight-volume of stacked roundwood is determined according to TAPPI Standard T 268. TAPPI Standard T 265 is used to measure the natural (wood-derived) dirt in wood chips. Dirt originates from the outer and inner barks, knots, stains, rot (decay), etc. Color photographs help with identification for the novice. The ash content (i.e., the mineral content including metals and their anions and silicates) of wood and pulp is determined by ignition in a muffle furnace at 575 ± 25°C as described by TAPPI Standard T 211.

TAPPI Standard T 263, with numerous diagrams and photomicrographs, covers identification of wood and fibers from conifers. One should consult the references listed in this method for additional information and high-quality photomicrographs unless experienced in microscopy and, more particularly, wood anatomy.

The amount of hardwood and softwood in wood chips is easily determined with the Maule test, which gives a purple color for hardwoods while leaving softwoods uncolored.

2.4 SOLID WOOD MEASUREMENT

Wood is measured and sold on a variety of bases. The volume of solid wood in stacked roundwood can be determined by *scaling* (a labor-intensive method of sampling volume and log sizes and converting to solid wood volume with tables) or by *water displacement* methods. In practice, it is easier to weigh the wood (using truck scales) and determine the bone-dry weight using moisture contents of the wood. Table 2.2 gives the conversion factors for different units of solid wood and wood chips.

Board Foot

A board foot is a volumetric measurement of solid wood. It is equal to 12 in. × 12 in. ×1 in. or 1/12th ft^3 of solid wood.

Cord

A cord is stacked roundwood occupying a total volume of 4 ft by 8 ft by 4 ft. Typically, a cord of stacked wood contains 80–90 ft^3 of solid wood although this can vary widely and will yield about 500 bd. ft. of lumber or 1.2 BDU of chips. (A face cord is used to sell firewood in some locations; it is 4 ft by 8 ft by the width of the wood pieces.)

TABLE 2.2 Approximate Conversion Factors of Wood of 0.45 Specific Gravity in Various Forms (for 85 ft^3 of Solid Wood per Cord and 2.6 ft^3 of Chips per ft^3 of Solid Wood)

	Convert to ↓ by Multiplication			
Convert From ↓	**Stacked Wood (m^3)**	**Solid Wood (m^3)**	**Bone-Dry Wood (MT)**	**Wood Chips (m^3)**
1000 board ft	3.55	2.3598	1.06	6.1
cord	3.6247	2.41	1.08	6.3
cunit	4.26	2.8318	1.27	7.4
BDU	3.64	2.42	1.0886	6.3
unit	3.28	2.18	0.98	5.6636
ft^3 chips	0.0164	0.0109	0.0049	0.028318

Entries with five significant digits are exact for any wood. Conversion factors for wood varying from these parameters should be calculated for individual situations. Board feet values do not include sawing loses.

Cunit

A cunit is 100 cubic feet of solid wood in stacked roundwood. It is used to determine the wood content of pulp logs.

2.5 WOOD CHIP MEASUREMENT

Bulk Density

The bulk density is the ovendry weight of chips (or sawdust or other wood residue) contained in a given volume of space. The bulk density of the chips depends on the specific gravity of the wood source, the chip geometry, and the chip size distribution. For example, Douglas fir chips from roundwood are typically 192 kg/m^3 (12 Ib/ft^3) (dry wood weights), whereas Douglas fir chips made from veneer are 184 kg/m^3 (11.5 Ib/ft^3). White fir and pine chips are about 168 kg/m^3 (10.5 Ib/ft^3) and those of redwood are about 160 kg/m^3 (10 Ib/ft^3). A rule of thumb is that 1 m^3 of wood yields about 2.6 m^3 of chips (1 ft^3 yields about 2.6 ft^3).

Bone-Dry Unit

A bone-dry unit is the equivalent of 2400 lb of ovendry chips, sawdust, or other wood particles. A BDU of packed Douglas fir chips occupies approximately 200 ft^3.

Unit

A unit is 200 ft^3 of wood chips, sawdust, or other wood particles. A 40-foot open-top chip truck carries about 18 units. One unit of Douglas fir or western hemlock chips is about 0.85 cords of logs or 67 ft^3 of solid wood. One unit of Douglas fir or western hemlock sawdust is about 80 ft^3 of solid wood.

2.6 WOOD CHEMISTRY

The composition of hardwoods and softwoods by the class of compounds is given in Table 2.3. The ultimate (elemental) analysis of wood is given in Table 2.4. Lignin is more highly concentrated in the middle lamella and primary cell wall regions of the wood fiber than any other part of the cell wall. Most of the lignin, however, is actually in the secondary cell wall because the secondary cell wall accounts for most of the mass of the fiber. The concentration of the major components with varying cell wall position is shown in Fig. 2.21.

TABLE 2.3 Typical Compositions of North American Woods (%)

	Hardwoods	Softwoods
Cellulose	40–50	45–50
HEMICELLULOSES		
(Galacto)glucomannans	2–5	20–25
Xylans	15–30	5–10
Lignin	18–25	25–35
Extractives	1–5	3–8
Ash	0.4–0.8	0.2–0.5

TABLE 2.4 The Ultimate Analysis of North American Woods in Percent

Carbon	C	49.0–50.5	%
Oxygen	O	43.5–44.5	%
Hydrogen	H	5.8–6.1	%
Nitrogen	N	0.2–0.5	%

Cellulose

On the molecular level, cellulose is a linear polymer of anhydro-D-glucose connected by β-(1 → 4) linkages as shown in Fig. 2.22. The degree of polymerization (DP), which is the number of units (glucose in this case) that make up the polymer, is above 10,000 in unaltered (so-called "native") wood but less than 1000 in highly bleached kraft pulps.

Physically, cellulose is a white solid material that may exist in crystalline or amorphous states. Cellulose in wood is about 50%–70% crystalline and forms the "back-bone" structure of a wood fiber.

Cotton is about 95% crystalline cellulose. The crystalline form of cellulose is particularly resistant to chemical attack and degradation. Hydrogen bonding between cellulose molecules results in the high strength of cellulose fibers.

Microfibrils are aggregations of cellulose molecules into threadlike structures approximately 3.5 nm in diameter, containing both crystalline and amorphous regions. They occur in the secondary cell wall. They are oriented in different directions in each of the three layers within the secondary cell wall; the fibril angle is measured from the longitudinal axis of the cell.

Hemicellulose(s)

Hemicellulose(s) are actually a class of materials. The plural form should be used to describe

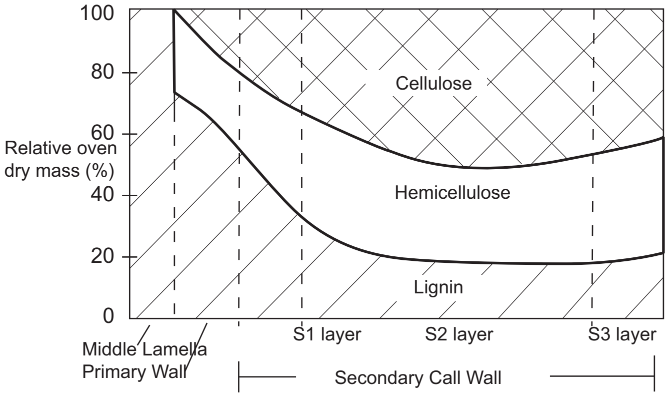


FIGURE 2.21 Typical composition of a conifer fiber across its cell wall. *From Krahmer, R.L. and Van Vliet, A.C., Eds.,* Wood Technology and Utilization, *O.S.U. Bookstores, Corvallis, Oregon 1983.*

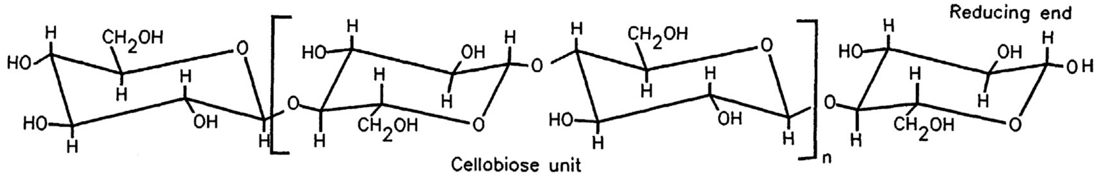


FIGURE 2.22 The primary structure of cellulose.

them generically, but the singular form should be used to describe a particular type such as the hardwood xylan hemicellulose. Physically, hemicelluloses are white solid materials that are rarely crystalline or fibrous in nature; they form some of the "flesh" that helps fill out the fiber. Hemicelluloses increase the strength of paper (especially tensile, burst, and fold) and the pulp yield but are not desired in dissolving pulps. (Dissolving pulps are relatively pure forms of cellulose used to make cellulose-based plastics.) Starch is often added to pulp to increase the strength of paper and probably has a very similar mechanism of effect as the hemicelluloses. Hemicelluloses chemically are a class of polymers of sugars, including the six-carbon sugars mannose, galactose, glucose, and 4-O-methyl-D-glucuronic acid and the five-carbon sugars xylose and arabinose. The structures of these monosaccharides are shown in Fig. 2.23. (Pectin, a related compound, occurs to a small degree in the middle lamella, especially in the pith and young tissue, and consists of polygalacturonic acid.) Hemicelluloses are condensation polymers with a molecule of water removed with every linkage. All of the monosaccharides that make up the hemicelluloses have the D configuration and occur in the six-member pyranoside forms, except arabinose, which has the L configuration and occurs as a five-member furanoside. The number average DP is about 100—200 sugar units per hemicellulose molecule.

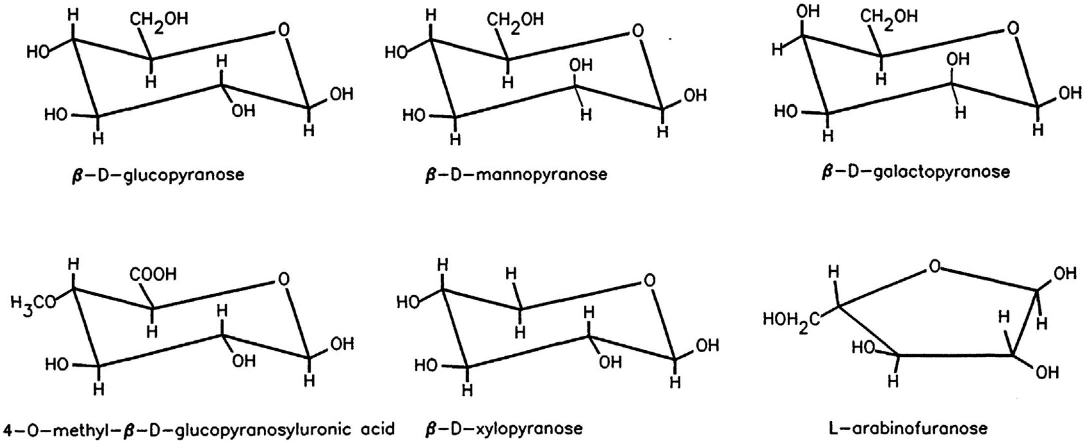
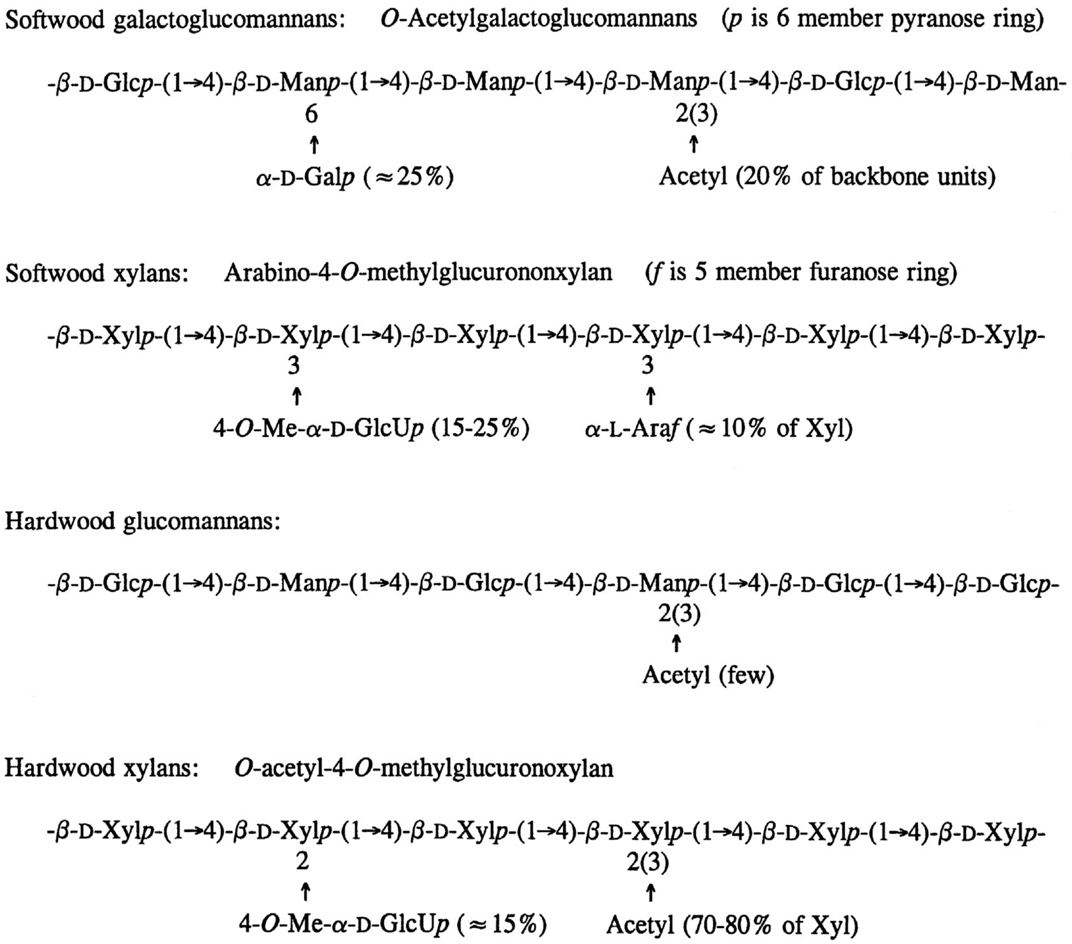


FIGURE 2.23 The principal monosaccharides of wood hemicelluloses.

Hemicelluloses are much more soluble and labile, that is, susceptible to chemical degradation, than is cellulose. They are soluble in 18.5% NaOH (which is the basis of their measurement in Tappi Test Method T203). Low-molecular-weight hemicelluloses become soluble in dilute alkali at elevated temperatures, such as in kraft cooking. Hemicelluloses are essentially linear polymers, except for single-sugar side chains and acetyl substituents. Hemicellulose chemistry is described below; representative hemicellulose structures are shown in Fig. 2.24.

Softwood Hemicelluloses

Galactoglucomannans are polymers of glucose and mannose in the backbone linked by β-(l → 4) bonds with galactose units as side chains connected by α-(1 → 6) bonds. Acetylation is also present. The ratio of glucose:mannose:galactose:acetyl groups is on the order of 3:1:1:1, respectively. Galactoglucomannans make up about 6% of the weight of softwoods. Glucomannans have structures analogous to galactoglucomannans but with about 90% of the



Softwood galactoglucomannans: *O*-Acetylgalactoglucomannans (*p* is 6 member pyranose ring)

$$\text{-}\beta\text{-D-Glc}p\text{-}(1\rightarrow4)\text{-}\beta\text{-D-}\underset{\substack{6\\ \uparrow\\ \alpha\text{-D-Gal}p\ (\approx 25\%)}}{\text{Man}p}\text{-}(1\rightarrow4)\text{-}\beta\text{-D-Man}p\text{-}(1\rightarrow4)\text{-}\beta\text{-D-}\underset{\substack{2(3)\\ \uparrow\\ \text{Acetyl (20\% of backbone units)}}}{\text{Man}p}\text{-}(1\rightarrow4)\text{-}\beta\text{-D-Glc}p\text{-}(1\rightarrow4)\text{-}\beta\text{-D-Man-}$$

Softwood xylans: Arabino-4-*O*-methylglucurononxylan (*f* is 5 member furanose ring)

$$\text{-}\beta\text{-D-Xyl}p\text{-}(1\rightarrow4)\text{-}\beta\text{-D-}\underset{\substack{3\\ \uparrow\\ \text{4-}O\text{-Me-}\alpha\text{-D-GlcU}p\ (15\text{-}25\%)}}{\text{Xyl}p}\text{-}(1\rightarrow4)\text{-}\beta\text{-D-Xyl}p\text{-}(1\rightarrow4)\text{-}\beta\text{-D-}\underset{\substack{3\\ \uparrow\\ \alpha\text{-L-Ara}f\ (\approx 10\%\text{ of Xyl})}}{\text{Xyl}p}\text{-}(1\rightarrow4)\text{-}\beta\text{-D-Xyl}p\text{-}(1\rightarrow4)\text{-}\beta\text{-D-Xyl}p\text{-}$$

Hardwood glucomannans:

$$\text{-}\beta\text{-D-Glc}p\text{-}(1\rightarrow4)\text{-}\beta\text{-D-Man}p\text{-}(1\rightarrow4)\text{-}\beta\text{-D-Glc}p\text{-}(1\rightarrow4)\text{-}\beta\text{-D-}\underset{\substack{2(3)\\ \uparrow\\ \text{Acetyl (few)}}}{\text{Man}p}\text{-}(1\rightarrow4)\text{-}\beta\text{-D-Glc}p\text{-}(1\rightarrow4)\text{-}\beta\text{-D-Glc}p\text{-}$$

Hardwood xylans: *O*-acetyl-4-*O*-methylglucuronoxylan

$$\text{-}\beta\text{-D-Xyl}p\text{-}(1\rightarrow4)\text{-}\beta\text{-D-}\underset{\substack{2\\ \uparrow\\ \text{4-}O\text{-Me-}\alpha\text{-D-GlcU}p\ (\approx 15\%)}}{\text{Xyl}p}\text{-}(1\rightarrow4)\text{-}\beta\text{-D-Xyl}p\text{-}(1\rightarrow4)\text{-}\beta\text{-D-}\underset{\substack{2(3)\\ \uparrow\\ \text{Acetyl (70-80\% of Xyl)}}}{\text{Xyl}p}\text{-}(1\rightarrow4)\text{-}\beta\text{-D-Xyl}p\text{-}(1\rightarrow4)\text{-}\beta\text{-D-Xyl}p\text{-}$$

FIGURE 2.24 Representative structures of the predominant hemicelluloses.

galactose units replaced by mannose units. They make up 10%—15% of the weight of softwoods.

Xylans or arabinoglucuronoxylans are found in all land-based plants and have a backbone of poly-β-(1 → 4)-xylose; corncobs are highly concentrated in xylans. In softwoods, side chains of α-(l → 3)-linked arabinose and (1 → 3)-linked 4-O-methyl glucuronic acid occur. The ratio of xylose to 4-O-methyl glucuronic acid to arabinose is 4—7:1 > 1. These xylans have a DP of 100—120, lack acetyl groups, and make up 5%—10% of their mass.

Arabinogalactans are composed of poly-β-(3-(1 → 3))-galactose with numerous (1 → 6) arabinose and galactose side chains (side chains of DP 2 or less are common) and an overall DP of 200. The ratio of galactose to arabinose is 6:1 in western larch. They occur at about 1% in most softwoods but compose 5%—30% of the weight of larch species. In larch they occur as two types: the first with a DP of 80—100 and the second with a DP of 500—600. Arabinoxylans are water soluble unlike other hemicelluloses, and for this reason they are occasionally classified with the extractives.

Hardwood Hemicelluloses

Glucuronoxylans (xylans) are the principal hemicellulose of hardwoods. Side branches of 4-O-methyl glucuronic acid are linked by α-(l → 2) linkages. The ratio of xylose to 4-O-methyl glucuronic acid is typically 7:1 but varies from 3—20:1. About 70%—80% of the xylose units are acetylated at the C-2 or C-3 positions. These xylans have a DP of 40—200 (typically 180) and make up 15%—30% of hardwoods.

Glucomannans have a backbone of β-(l → 4)-linked glucose and mannose groups in a 1:1 to 2:1 ratio with very small amounts of acetylation and a DP of 40—100. They occur at 2%—5%.

Implications of Hemicellulose Chemistry

The carboxylic acid groups (RCOOH) of 4-O-methyl glucuronic acid residues of xylans contribute to hemicellulose acidity, presumably contribute to hemicellulose solubility under alkaline conditions (by the formation of carboxylate salts), and contribute to the ease of rosin sizing (hardwoods, containing more xylans, are easier to size with alum and rosin than softwoods). The 4-O-methyl glucuronic acid groups tend to be preferentially removed during alkaline pulping either by selective cleavage or, if they are not evenly distributed among the xylans, by selective solubilization.

Acetyl groups are saponified (hydrolyzed to give free acetic acid) very quickly under alkaline conditions. The free acetic acid consumes a significant portion of the alkali used during kraft cooking. Typically softwoods have 1%—2% acetyl groups, whereas hardwoods have 3%—5%.

Lignin

Lignin is a complex polymer consisting of phenylpropane units and has an amorphous, three-dimensional structure. It is found in plants; its molecular weight in wood is very high and not easily measured. Lignin is the adhesive or binder in wood that holds the fibers together. Lignin is highly concentrated in the middle lamella; during chemical pulping its removal allows the fibers to be separated easily. The glass transition temperature (softening temperature) is approximately 130—150°C (265—300°F). Moisture (steam) decreases the glass transition temperature slightly. There are three basic lignin monomers that are found in lignins (Fig. 2.25.) Grasses and straws contain all three lignin monomers, hardwoods contain both coniferyl alcohol (50%—75%) and sinapyl alcohol (25%—50%), and softwoods contain only coniferyl alcohol.

Using coniferyl alcohol as an example, the first step of lignin polymerization in the plant cell wall involves formation of a free radical at the phenolic hydroxyl group (Fig. 2.26). This structure has five resonance structures with the

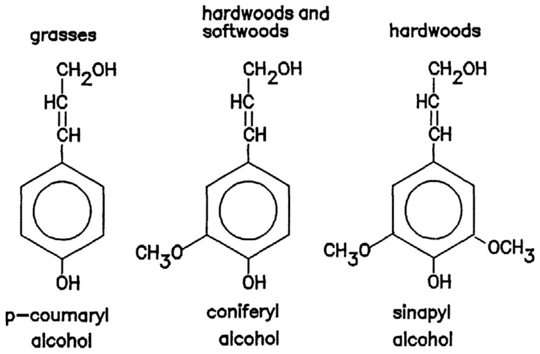


FIGURE 2.25 Lignin precursors for plants. Softwoods have coniferyl alcohol, whereas hardwoods have coniferyl and sinapyl alcohols.

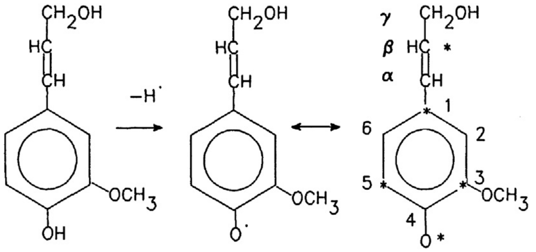


FIGURE 2.26 Formation of free radicals from coniferyl alcohol. *Positions where the free radical occurs in resonance structures.

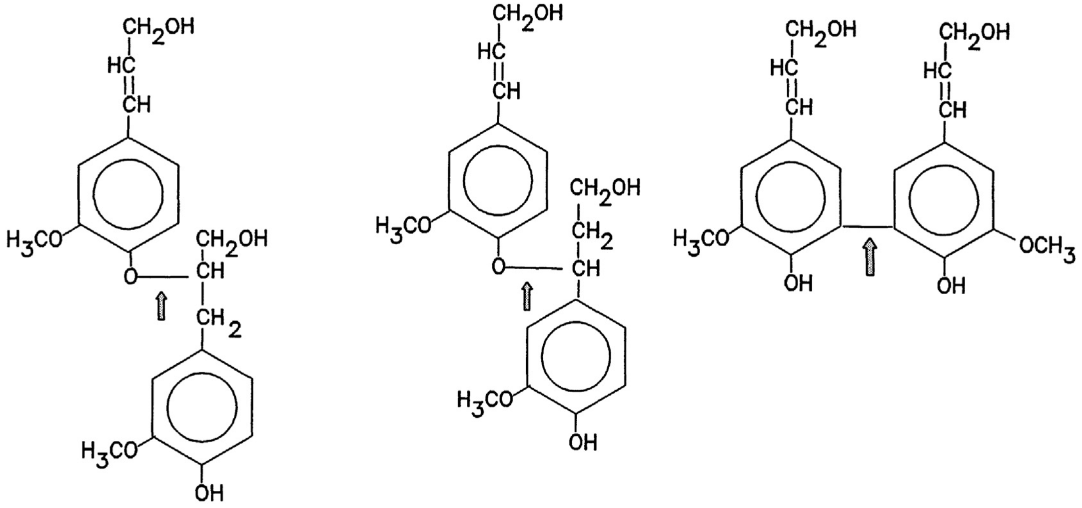
free radical occurring at various atoms as shown on the right of Fig. 2.26. Carbon atoms C-1 and C-3 in softwoods and C-1, C-3, and C-5 in hardwoods do not form linkages due to steric hindrance (crowding). Carbon atoms of the propane unit are labeled from the aromatic ring outward as α, β, and γ, respectively. Carbon atoms of the aromatic ring are labeled from the propane group toward the methoxy group from 1 to 6, respectively. Some commonly occurring lignin linkages are also shown in Fig. 2.27. A "representative" lignin molecule is shown in Fig. 2.28.

Extractives

Extractives are compounds of diverse nature with low to moderately high molecular weights, which by definition are soluble (extracted) in organic solvents or water. They impart color, odor, taste, and, occasionally, decay resistance to wood. There are hundreds of compounds in the extractives of a single sample of wood. The composition of extractives varies widely from species to species and from heartwood to sapwood. Heartwood has many high-molecular-weight polyphenols and other aromatic compounds not found in sapwood, and these give the heartwood of many species (such as cedar and redwood) their dark color and resistance to decay. Some classes of extractives (Figs. 2.29—2.31) important to the pulp and paper industry are described with representative compounds.

Terpenes are a broad class of compounds appearing in relatively high quantities in the softwoods, where they collect in the resin ducts of those species with resin ducts. Species such as pines have large amounts of terpenes. Mills pulping highly resinous species with the kraft process collect the terpenes and sell them. Hardwoods have very small amounts of the terpenes.

Terpenes are made from phosphated isoprene units (Fig. 2.29) in the living wood cells. It is usually very easy to identify the individual isoprene building blocks of a terpene. Isoprene has the empirical formula of C_5H_8, monoterpenes have the empirical formula of $C_{10}H_{16}$, sesquiterpenes are $C_{15}H_{24}$, and the resin acids are oxygenated diterpenes and have the empirical formula of $C_{20}H_{32}O_2$. Higher terpenes are also found. Oxygenated terpenes with alcohol and ketone groups become prevalent with exposure to air, as in the case of pine stumps. Turpentine consists of the volatile oils, especially the monoterpenes such as α- or β-pinene; these are also used in household pine oil cleaners that act as mild disinfectants and have a pleasant aroma. (According to the Merck Index, α-pinene from North American woods is usually the dextrorotary type, whereas that of European woods is of the levorotatory type.) Because turpentine consists of volatile compounds, it is



4-*O*-β-aryl ether linkage **4-*O*-α-aryl ether linkage** **C-C linkage**

FIGURE 2.27 Example linkages between lignin monomers.

recovered from the vent gases given off while heating the digester. Resin acids such as abietic and pimaric acids, whose structures are shown in Fig. 2.30, are used in rosin size and are obtained in the tall oil fraction.

The triglycerides and their component fatty acids are another important class of extractives. Triglycerides are esters of glycerol (a trifunctional alcohol) and three fatty acids. Most fatty acids exist as triglycerides in the wood; however, triglycerides are saponified during kraft cooking to liberate the free fatty acids. (Saponification is the breaking of an ester bond by alkali-catalyzed hydrolysis to liberate the alcohol and free carboxylic acid. Saponification of triglycerides is how soap is made; this is how the reaction got its name. Sodium-based soaps are liquids; potassium-based soaps are solids.)

The principal components are the C-18 fatty acids with varying amounts of unsaturation; that is, the presence of carbon–carbon double bonds, whose structures are shown in Fig. 2.31. [Polyunsaturated fats, a term used to describe "healthy" food fats, are fatty acids (or triglycerides containing fatty acids) with two or three carbon–carbon double bonds such as linoleic or linolenic acids.] Stearic acid is the saturated (with no double bonds) C-18 fatty acid. Other fatty acids, mostly with even numbers of carbon atoms, may be present as well depending on the species of wood.

Just as animal triglycerides (fats) contain small amounts of cholesterols, plant fats contain small amounts of sterols that are very similar to the cholesterols' structures. One example is β-sitosterol. Fatty acids and resin acids constitute the tall oil fraction recovered during black liquor evaporation by skimming the surface. The resin acids are separated by fractional distillation. Phenolic compounds are more common in heartwood than in sapwood and are major constituents in the bark of many wood species. In a few species these compounds can interfere with bisulfite pulping; for example, dihydroquercetin (Fig. 2.30) interferes with sulfite pulping of Douglas fir.

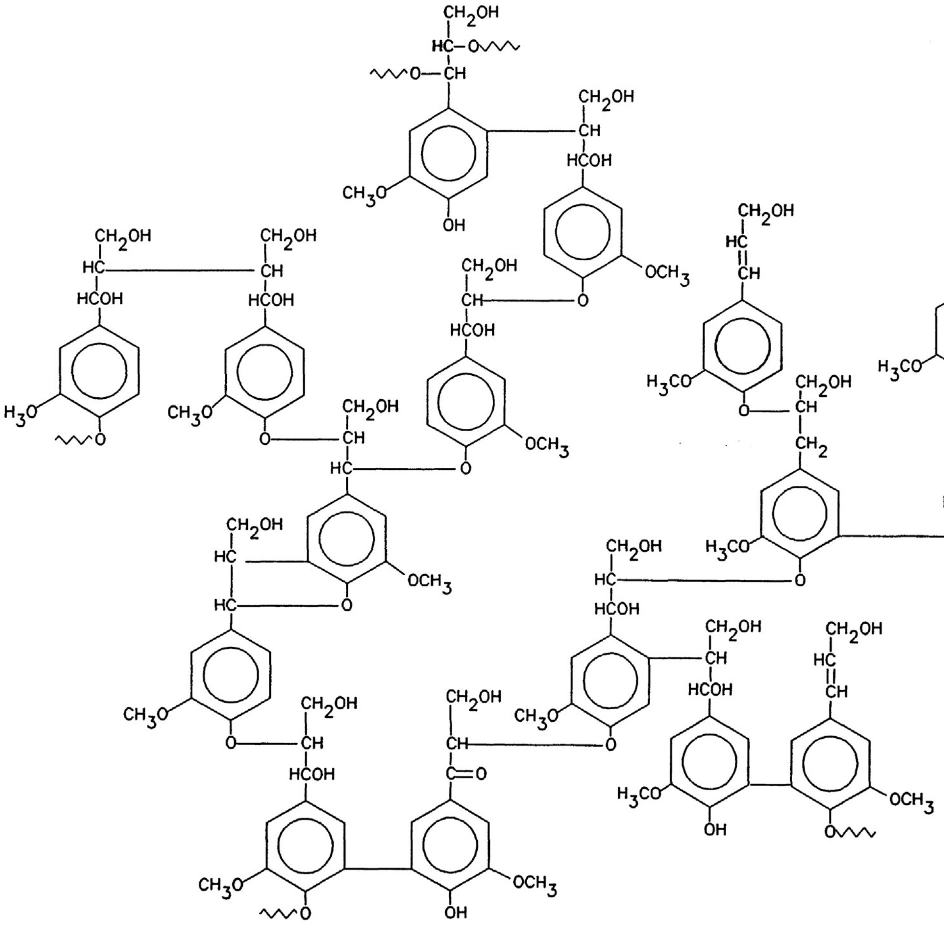
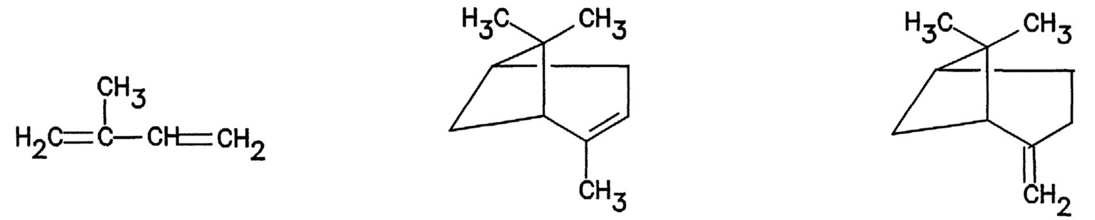
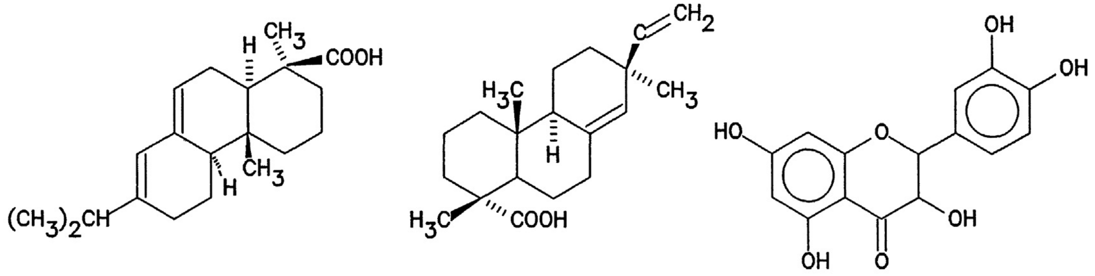


FIGURE 2.28 A hypothetical depiction of a portion of a softwood lignin molecule.



Isoprene **α-Pinene, bp 155-156°C** **β-Pinene, bp 165-166°C**

FIGURE 2.29 Examples of monoterpenes each made from two isoprene units.



Abietic acid, mp 172-175°C Pimaric acid, mp 219-220°C Taxifolin

FIGURE 2.30 Two resin acids (diterpenes) and taxifolin (dihydroquercetin).

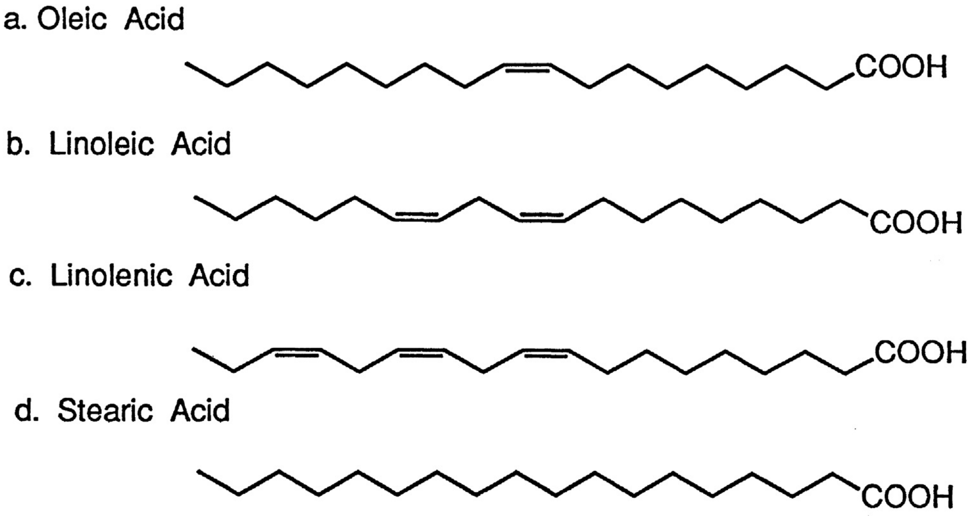


FIGURE 2.31 Examples of fatty acids with 18 carbon atoms in wood.

These compounds contain C_6 aromatic rings with varying amounts of hydroxyl groups. Some classes of these compounds are the flavonoids, which have a $C_6C_3C_6$ structure; the tannins, which are water soluble; polyflavonoids and other polyphenol compounds, which are used to convert animal hides into leather; and the lignans, which have two phenylpropane units ($C_6C_3{-}C_3C_6$) connected between the β-carbon atoms.

Ash

Ash consists of the metallic ions of sodium, potassium, calcium and the corresponding anions of carbonate, phosphate, silicate, sulfate, chloride, etc. remaining after the controlled combustion of wood. Wood ash is sufficiently alkaline so that when added to triglycerides it can be used to make soap; this was practiced by many cultures for centuries using animal fats.

Holocellulose

Holocellulose is a term for the entire carbohydrate fraction of wood, i.e., cellulose plus hemicelluloses.

Alpha Cellulose

Alpha cellulose is a fraction of wood or pulp isolated by a caustic extraction procedure. Although generally it is considered to be "pure" cellulose, actually it is about 96%–98% cellulose.

Cellulose Polymers and Derivatives

Cellulose polymers (Fig. 2.32) are made from dissolving pulp. They include cellulose xanthate (a bright orange–colored solution formed by reaction of alkali cellulose with carbon disulfide, which is an intermediate product that on acidification forms regenerated cellulose such as cellophane, rayon, and meat casings), cellulose acetate (a plastic used in films, eyeglass frames, cigarette filters, etc.), cellulose nitrate (smokeless powder that replaces gunpowder in certain applications), carboxymethyl cellulose (a water-soluble thickener and dispersant), and methyl cellulose (a thickener and plastic).

Chemical Analysis of Wood

Wood is usually ground to 40 mesh (0.6 mm) before chemical analysis. Various chemical analyses of wood are covered in the TAPPI Standards. T 246 describes preparation of wood for chemical analysis, including extraction with neutral solvents, such as ethanol and benzene, to remove the wood extractives. (If one is doing wood extractions, it is highly recommended using toluene in place of benzene; benzene is harmful and toxic. The difference in results will be negligible!)

After acid hydrolysis of the cellulose and hemicellulose, the monosaccharides can be measured by chromatography. T 250 is an archaic method of monosaccharide analysis by paper chromatography. T 249 uses gas chromatography to separate and measure the monosaccharides, but much faster and better methods have been developed. Pentosans in wood and pulp are measured by T 223; the pentoses are converted to furfural that is measured colorimetrically. The solubility of wood or pulp with 1%

Esterification:	Nitration:	$ROH + HNO_3/H_2SO_4 \rightarrow RONO_2 + H_2O$
	Acetylation:	$ROH + Ac_2O/HAc/H_2SO_4 \rightarrow ROCOCH_3 + H_2O$
Etherification:	Methylation:	$2\,ROH + (CH_3)_2SO_4/NaOH \rightarrow 2\,ROCH_3 + H_2SO_4$
	Carboxymethylation:	$ROH + ClCH_2COOH/NaOH \rightarrow ROCH_2COO^- Na^+$
Xanthation:	Formation:	$ROH + CS_2 + NaOH \rightarrow ROCSS^- Na^+ + H_2O$
	Regeneration:	$ROCSS^- Na^+ + H^+ \rightarrow ROH + CS_2 + Na^+$

FIGURE 2.32 Commercial cellulose-based polymers.

sodium hydroxide, T 212, is a measure of hemicellulose and cellulose degraded by decay, oxygen, chemicals, etc.

2.7 WOOD AND FIBER PHYSICS

Equilibrium Moisture Content

Because wood and paper are hygroscopic materials, when fully dried they adsorb water vapor from the atmosphere. The equilibrium moisture content of wood or wood pulp depends on the temperature and relative humidity of the atmosphere surrounding the specimen. Relative humidity is the partial pressure of water vapor divided by the maximum water vapor pressure of saturation at the same temperature.

Fiber Saturation Point

The fiber saturation point (FSP) represents the moisture content of a lignocellulosic material such that additionally adsorbed water is not chemically absorbed to the wood. This occurs at about 30% MC_{OD} (at room temperature) in wood. For example, wood taken at room temperature and 99% relative humidity will have a moisture content approaching 30%. At lower humidities the equilibrium moisture content will be lower. Chemically adsorbed water requires additional energy to remove it from wood beyond the water's heat of vaporization.

Shrinkage

Wood shrinks and swells as a function of moisture content. Above the FSP there is no change in wood dimensions according to moisture content, but as wood dries below the FSP, it shrinks. Because the microfibrils are almost parallel to the longitudinal axis of the fiber in the thick S2 cell wall layer and because water molecules do not increase the length of microfibrils but are added between them, there is very little shrinkage in the longitudinal direction but about 4% shrinkage in the radial direction and 6% in the tangential direction. The difference in shrinkage between the radial and tangential directions occurs due to orientation of microfibrils around the cell wall pits and other factors.

Uneven grain orientation may cause severe warping or fracturing of lumber and furniture due to tremendous stresses that develop from uneven shrinkage as the wood dries.

Fiber Strength

Fiber strength is the strength of an individual fiber. Using small test devices, the strength of individual fibers can be measured. Paper strength can be viewed as a trade off between the strength of individual fibers and the strength of interfiber bonding (the strength of the bonds between fibers that hold them together). In unrefined pulp, the "weak link" in the paper strength is fiber—fiber bonding. In pulp, which is overly refined, the weak link often becomes the strength of the individual fibers. Thus, with increased refining, the properties influenced by interfiber bonding (tensile and burst) increase and by fiber strength (tear) decrease.

The situation becomes more complicated if we consider the microfibril angle of the S2 cell wall layer. Fig 2.33, after the work of Page et al. (1972), shows that the tensile strength of individual fibers in the longitudinal direction depends principally on the S2 fibril angle (in the absence of fiber defects, etc.) and that the tensile strength decreases rapidly with increasing fibril angle. This work also showed that the fibril angle of latewood tends to be lower than that of earlywood in spruce, and the latewood fibers were stronger than the earlywood fibers, which has been reported in the literature with other species as well. (Black spruce also tends to have a lower fibril angle than white spruce; this indicates that the average fibril angle of wood species is as

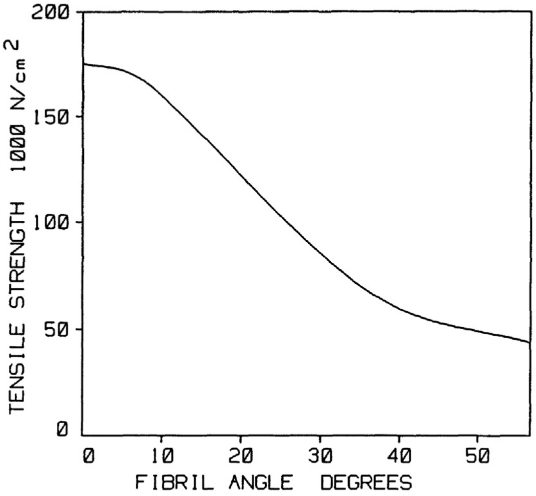


FIGURE 2.33 Fiber strength versus S2 fibril angle (60% yield, kraft spruce fibers). *After Page, et al (1972).*

important as the average fiber length.) The authors concluded that "fibres of the same fibril angle have similar strength, independent of species." The maximum fiber tensile strength of 17,000 N/cm^2 corresponds to a breaking length of over 100 km or about 10 times stronger than paper!

Fiber Bonding in Paper, Hydrogen Bonding

In paper, fibers are held together by hydrogen bonding of the hydroxyl groups of cellulose and hemicelluloses. The carboxylic acid groups of hemicelluloses also play an important role. Water interferes with hydrogen bonding between fibers; thus, paper loses much of its strength when wet. Hemicelluloses increase the strength of paper, whereas lignin on the surface of fibers, which is not able to form hydrogen bonds, decreases the strength of paper. Using water in the formation of paper greatly increases its strength, as capillary action of water pulls the fibers together and may partially solubilize the carbohydrates so hydrogen bonding can occur. There are no methods available for dry formation of paper with appreciable strength although such a process could make papermaking much more economical.

Hydrogen bonding holds lignocellulosic fibers together in paper. The strength of R—OH—R—OH hydrogen bonding is 3—4 kcal/mol. This is relatively weak compared with covalent bonds, which are on the order of 100 kcal/mol. However, the large number of potential hydrogen bonds along the length of the holocellulose molecules means that paper can be quite strong. Modification of hydroxyl groups by acetylation, methylation, etc. prevents hydrogen bonding and decreases the strength of paper dramatically. Also, paper made from a slurry in a solvent of low polarity is weak as the formation of hydrogen bonds is hindered. Factors that increase the fiber surface area (or the area of fiber-to-fiber contact) increase interfiber bonding. Refining tends to allow the interfiber bonding to increase by fibrillation (increasing the surface area) and hydration of fibers (making them more flexible to mold around each other better), but the strength of the individual fibers decreases. More information on fiber physics is found in Chapter 21, Vol. 1.

2.8 PROPERTIES OF SELECTED WOOD SPECIES

This section presents wood properties of selected wood species. Much of the information presented here is from the reports of the US Department of Agriculture Forest Product Laboratory (USDA-FPL) in Madison, Wisconsin. These reports are very useful to demonstrate wood properties and variability in individual species of wood. Remember that there is considerable variation in wood properties and, therefore, reported wood properties! Tables 2.5 and 2.6 show the average fiber lengths, basic densities, basic specific gravities (ovendry weight divided

TABLE 2.5 Basic Pulping Properties of the US Softwoods

Species	Scientific Name	Average Fiber Length (mm)	Density Ib/ft^3	Specific Gravity	Pub Yield (%)[a]	
					Kraft	Sulfite
Bald cypress	*Taxodium distichum*	6.00	26	0.42	48	46
CEDAR						
Atlantic white	*Chamaecyparis thyoides*	2.10	19	0.30	45	
Eastern red cedar	*Juniperus virginiana*	2.80	27	0.43	45	
Incense	*Libocedrus decurrens*	2.00	22	0.35	45	40
Port Orford	*Chamaecyparis lawsoniana*	2.60	25	0.40	45	45
Western red cedar	*Thuja plicata*	3.80	19	0.30	40	43
Douglas fir, coastal	*Pseudotsuga menziesii*	4.50	28	0.45	48	48
FIR						
Balsam	*Abies balsamea*	3.50	21	0.34	50	47
California red	*Abies magnifica*	3.25	23	0.37	48	48
Grand	*Abies grandis*	5.00	23	0.37	48	49
Noble	*Abies procera*	4.00	22	0.35	47	48
Pacific silver	*Abies amabilis*	3.55	22	0.35	49	49
Subalpine	*Abies lasiocarpa*	3.15	21	0.34	48	48
White	*Abies concolor*	3.50	22	0.35	48	48
HEMLOCK						
Carolina	*Tsuga caroliniana*	3.10	30	0.48	45	48
Eastern	*Tsuga canadensis*	3.50	24	0.38	45	44
Mountain	*Tsuga mertensiana*	3.70	26	0.42	45	
Western	*Tsuga heterophylla*	4.00	24	0.38	47	46
LARCH						
Tamarack	*Larix laricina*	3.50	31	0.50	48	42
Western	*Larix occidentalis*	5.00	32	0.51	48	42

TABLE 2.5 Basic Pulping Properties of the US Softwoods—cont'd

Species	Scientific Name	Average Fiber Length (mm)	Density lb/ft^3	Specific Gravity	Pub Yield (%)[a] Kraft	Pub Yield (%)[a] Sulfite
PINE						
Jack	*Pinus banksiana*	3.50	25	0.40	48	45
Loblolly	*Pinus taeda*	4.00	29	0.46	48	45
Lodgepole	*Pinus contorta*	3.50	24	0.38	48	45
Longleaf	*Pinus palustris*	4.00	34	0.54	48	45
Monterey	*Pinus radiata*	2.60	29	0.46	48	45
Ponderosa	*Pinus ponderosa*	3.60	45	0.72	48	45
Red	*Pinus resinosa*	3.70	26	0.42	48	45
Shortleaf	*Pinus echinata*	4.00	29	0.46	48	45
Slash	*Pinus elliottii*	4.00	35	0.56	48	45
Sugar	*Pinus lambertiana*	4.10	22	0.35	48	45
Virginia	*Pinus virginiana*	2.80	28	0.45	48	43
White, eastern	*Pinus strobus*	3.70	21	0.34	48	
White, western	*Pinus monticola*	4.40	23	0.37	48	45
Redwood	*Sequois sempervirens*	7.00	24	0.38	38	
SPRUCE						
Black	*Picea mariana*	3.50	24	0.38	50	48
Blue	*Picea pungens*	2.80	23	0.37	43	48
Engelmann	*Picea engelmannii*	3.00	20	0.33	47	48
Red	*Picea rubens*	3.70	24	0.38	50	48
Sitka	*Picea sitchensis*	5.50	23	0.37	47	48
White	*Picea glauca*	3.50	23	0.37	50	48

[a] *Screened yield for nonbleachable kraft (for bleachable subtract 2%—3%) and bleachable sulfite.*
From USDA FPL-031 (1923, 1964).

by green volume), and chemical pulp yields for softwoods and hardwoods, respectively. The data are from "Pulp yields for various processes and wood species," USDA For. Ser., FPL-031 (Feb., 1964), which is a slight revision of "Density, fiber length, and yields of pulp for various species of wood." Tech. Note No. 191 (1923).

Tables 2.7 and 2.8 show chemical compositions, basic specific gravities, and selected solubilities for softwoods and hardwoods, respectively. The data are from the USDA-FPL.

TABLE 2.6 Basic Pulping Properties of the US Hardwoods

Species	Scientific Name	Average Fiber Length (mm)	Density (lb/ft^3)	Basic Specific Gravity	Pulp Yield (%)[a]	
					Kraft	Sulfite
Ailanthus	*Ailanthus, altissima*	1.20	23	0.37		
Alder, red	*Alnus, rubra*	1.20	25	0.40	50	
Ash, green	*Fraxinus pennsylvanica*	1.05	33	0.53	44	
Ash, white	*Fraxinus americana*	1.20	34	0.54		47
Basswood, American	*Tilia americana*	1.20	20	0.32		
Beech, American	*Fagus grandifolia*	1.20	35	0.56	49	44
Birch, paper	*Betula papyrifera*	1.20	30	0.48	50	46
Birch, yellow	*Betula alleghaniensis*	1.50	34	0.54	53	45
Buckeye, Ohio	*Aesculus glabra*	0.90	21	0.34		47
Butternut	*Juglans cinerea*	1.20	22	0.35		47
Chestnut, American	*Castanea dentata*	1.00	25	0.40		42
Cucumber tree	*Magnolia acuminata*	1.30	27	0.43		45
Elm, American	*Ulmus americana*	1.50	29	0.46	46	
Elm, rock	*Ulmus thomasii*	1.30	36	0.58		47
Elm, slippery	*Ulmus rubra*	1.70	30	0.48		47
Hickory, mockernut	*Carya tomentosa*	1.40	40	0.64	48	40
Hickory, shagbark	*Carya ovata*	1.35	40	0.64		
Mangrove	*Rhizophora mangle*	1.40	55	0.88		
Maple, red	*Acer rubrum*	1.00	31	0.50	43	45
Maple, silver	*Acer saccharinum*	1.75	28	0.45		
Maple, sugar	*Acer saccharum*	1.10	35	0.56	43	45
Oak, blackjack	*Quercus marilandica*	1.00	40	0.64	42	41
Oak, chestnut	*Quercus prinus*	1.35	36	0.58	45	
Oak, northern red	*Quercus rubra*	1.40	35	0.56	46	45
Oak, overcup	*Quercus lyrata*	1.35	36	0.58	46	
Oak, post	*Quercus stellata*	1.50	37	0.59		45
POPLAR						
Aspen, quaking	*Populus tremuloides*	1.20	22	0.35	54	52
Aspen, bigtooth	*Populus grandidentata*	1.20	22		50	
Balsam	*Populus balsamifera*	1.00	19	0.30	50	49

TABLE 2.6 Basic Pulping Properties of the US Hardwoods—cont'd

Species	Scientific Name	Average Fiber Length (mm)	Density (lb/ft^3)	Basic Specific Gravity	Pulp Yield (%)[a]	
					Kraft	Sulfite
Cottonwood, eastern	*Populus deltoides*	1.30	23	0.37	52	52
Cottonwood, swamp	*Populus heterophylla*	1.30	24	0.38	47	47
Sugarberry	*Celtis laevigata*	1.10	29	0.46	46	44
Sweetgum	*Liquidambar styraciflua*	1.60	29	0.46	50	46
Sycamore, American	*Platanus occidentalis*	1.70	29	0.46		47
Tupelo, black	*Nyssa sylvatica* var. *sylvatlea*	1.70	29	0.46	48	48
Tupelo, swamp	*Nyssa sylvatica* var. *biflora*	1.70	34	0.54	48	46
Tupelo, water	*Nyssa aquatica*	1.60	29	0.46		47
Willow, black	*Salix nigra*	1.00	24	0.38	52	52
Yellow-poplar	*Liriodendron tulipifera*	1.80	24	0.38	47	47

[a] *Screened yield of nonbleachable kraft (for bleachable subtract 2%–3%) and bleachable sulfite.*
From USDA FPL-031 (1923, 1964).

TABLE 2.7 Chemical Composition of Softwoods

Species, Location, Average Diameter	Sample Average Age Years	Basic Specific Gravity	Chemical Composition (%)				Solubility	
			Holocellulose	Alpha Cellulose	Lignin	Total Pentosans	Hot, 1% NaOH	EtOH–Benzene
CEDAR								
Western red, residue, west US, 24.5″	205	0.306	48.7	38.0	31.8	9.0	21.0	14.1
Douglas fir, Oregon, old growth, residues		0.439	67.0	50.4	27.2	6.8	15.1	4.5
Oakridge, Ore, second growth, residues		–	69.9	52.6	28.0	4.9	9.7	–
Wyoming, US, 7.8″	182	0.417	65.7	46.9	27.2	6.5	15.8	5.2
FIR								
Balsam, Michigan, US, 6.5″	48	0.330		42.2	28.5	10.8	11.1	3.5
Pacific silver, residue, west US, 19.6″	169	0.385	60.7	43.2	30.5	9.2	10.8	2.6
Suhalpine, Montana, US, 6.4″	44	0.304	67.1	44.2	29.6	8.9	11.5	2.2
White, California, US		0.363	65.5	49.1	27.8	5.5	12.7	2.1

(Continued)

TABLE 2.7 Chemical Composition of Softwoods—cont'd

Species, Location, Average Diameter	Sample Average Age Years	Basic Specific Gravity	Chemical Composition (%) Holocellulose	Alpha Cellulose	Lignin	Total Pentosans	Solubility Hot, 1% NaOH	EtOH—Benzene
HEMLOCK								
Eastern		0.38	68	43	32	10	13	
Western Washington, US			66.5	50.0	29.9	8.8	18.1	5.2
LARCH								
Tamarack, Wisconsin, US, 4.7″	43	0.491	60.4	43.3	25.8	8.6	18.2	3.6
Western Washington, US, 5.4″	53	0.514	66.5	50.0	26.6	7.8	13.4	1.4
PINE								
Jack, Wisconsin, US		0.43	67.0	47.0	27.0	9.1	13.5	3.5
Loblolly, Arkansas, US		0.45		48.7	27.7	8.9	12.0	2.7
Lodgepole, Montana, US								
Sound, 5.1″, little decay	25	0.373	68.8	44.3	26.7	10.3	12.8	3.0
Sound, 7.4″, little decay	135	0.415	71.6	47.3	25.9	10.9	11.6	2.8
Insect-killed, 8.9″, some decay	109	0.400	65.1	44.1	26.5	9.2	14.9	4.2
Down 9.2, sig. decay	112	0.429	67.9	45.2	27.9	10.0	12.9	3.1
Ponderosa, 4.9″, 1.9% heartwood	39	0.40	67.7	45.0	25.1	10.2	13.4	5.6
Red		0.43			24	11		
Shortleaf, Arkansas, US, 6.0″	27	0.49	69.3	48.5	27.6	8.9	12.2	3.3
Slash, thinnings, Louis., US, 3.9″	10	0.484	64.7	47.2	28.5	9.1	11.5	3.2
White, eastern Maine, US, 8.6″	38	0.336	66.3	43.9	26.1	6.6	15.9	5.9
White, western Idaho, US			73.8	50.4	25.4	7.8	11.3	2.9
Redwood, California, US, old growth		0.358	55.1	42.6	33.4	7.2	18.8	9.9
″ ″second growth		0.344	60.5	45.7	33.1	7.2	13.9	0.4
SPRUCE								
Black, Michigan, US, 6.5″	49	0.392		43.1	26.8	11.4	11.4	1.8
Engelmann, Colorado, 13.6″	169	0.333	67.3	45.2	28.2	7.4	11.6	1.7
Red		0.38	73	43	27	12		
White		0.38	73	44	27	11	12	

TABLE 2.8 Chemical Composition of Hardwoods

			Chemical Composition (%)				**Solubility**	
Species, Location, Average Diameter	**Sample Average Age Years**	**Basic Specific Gravity**	**Holocellulose**	**Alpha Cellulose**	**Lignin**	**Total Pentosans**	**Hot, 1% NaOH**	**EtOH—Benzene**
Alder, red, Washington, US, 7.8″	21	0.385	70.5	44.0	24.1	19.2	17.3	1.9
Ash, green, Arkansas, US, 10.2″	46	0.519		41.0	25.3	16.3	18.4	5.5
Ash, white		0.56						
Birch, paper, New York, US		0.49	78.0	46.9	20.5	21.8		
Birch, yellow		0.55						
Elm, American, Arkansas, US, 13.7″	56	0.470		46.9	24.3	18.1	16.7	2.6
EUCALYPTUS								
E. saligna, Brazil, 5″, fibers 0.87 mm		0.546	72.3	49.7	25.3	14.7	13.3	1.7
E. kertoniana,″, 4.5″, fibers 0.93 mm		0.513	74.3	50.3	28.1	15.0	13.6	1.5
E. robusta, Puerto Rico		0.490	66.6	47.7	27.5	16.2	12.2	2.1
Hickory, mockernut, North Carolina, US, 7.2″	65	0.676	69.8	45.0	18.9	16.4	18.5	5.1
Hickory, shagbark, North Carolina, US, 4.4″	29	0.703	71.3	48.4	21.4	18.0	17.6	3.4
Maple, red, Michigan, US		0.45	77.6	48.6	20.6	18.3	15.9	3.0
Maple, sugar, Michigan, US				49.2	21.5	18.6	16.7	
Oak, blackjack, Arkansas, US, 5.6″	48	0.635		43.9	26.3	20.1	15.0	3.5
Oak, northern red, Michigan, US, 5.9″	36	0.582	69.1	46.0	23.9	21.5	21.7	5.2
Oak, white, Virginia, US, 5.4″	41	0.616	62.6	46.1	27.7	18.4	19.8	3.0
Michigan, 7.3″	69	0.613	72.2	47.5	25.3	21.3	19.0	2.7

(*Continued*)

TABLE 2.8 Chemical Composition of Hardwoods—cont'd

			Chemical Composition (%)				**Solubility**	
Species, Location, Average Diameter	**Sample Average Age Years**	**Basic Specific Gravity**	**Holocellulose**	**Alpha Cellulose**	**Lignin**	**Total Pentosans**	**Hot, 1% NaOH**	**EtOH—Benzene**
POPLAR								
Aspen, quaking, Wisconsin, US		0.35	78.5	48.8	19.3	18.8	18.7	2.9
Cottonwood, eastern		0.37		46	24	19	15	
Sugarberry, Arkansas, US, 9.9″	47	0.489		40.2	20.8	21.6	22.7	3.1
Tan oak, California, US, 113″	99	0.601	70.4	45.2	19.0	18.3	18.9	2.0
Tupelo, black, Mississippi, US, 6.3″		0.513	71.7	48.1	26.2	14.5	12.8	2.3
Willow, black, Arkansas, US, 15.5″	28	0.377		46.6	21.9	18.8	17.4	2.2
Yellow-poplar		0.40		45	20	19	17	

References for Tables 2.7 and 2.8.

PP-110, Physical characteristics and chemical analysis of certain domestic hardwoods received at the Forest Products Laboratory for Pulping from October 1, 1948, to November. 1957. PP-112, Physical characteristics and chemical analysis of certain domestic pine woods received at the Forest Products Laboratory for Pulping from October 1, 1948, to September 4, 1956. PP-114, Physical characteristics and chemical analysis of certain softwoods (other than pine) received at the Forest Products Laboratory from October 1, 1948, to August 7, 1947.

Details of some wood samples (with four-digit FPL shipment numbers) were obtained from reports. Occasionally, missing numbers have been filled in from other FPL reports that were used to verify the plausibility of numbers, when available. Softwoods: Douglas fir residues, old growth ship 2655 and second growth ship 2467, Rep. no. 1912 (Rev. July, 1956). Lodgepole pine, ship. 2414—2417, 2434, Rep. no. R1792 (June, 1951). Ponderosa pine sample was 20% w/w, 21% v/v, bark as received. Rep. no. R1909 (Oct., 1951) Pacific silver fir sawmill residues, ship. 2128, heartwood was 16.1″ diameter, Rep. no R1641 (Feb., 1947). Western redcedar sawmill residues, ship. 2132, heartwood was 22.7″ diameter, Rep. no. R1641 (Feb., 1947). Eastern hemlock, red pine, red spruce, and white spruce, Rep no. 1675 (Rev. Nov., 1955).

Hardwoods: red alder, ship 3050, Rep. no. 1912 (Revised, July, 1956). Black willow, American elm, sugarberry, green ash, and blackjack oak, ship. 1549, 1550, 1545, and 1508, respectively, Rep. no. R-1491 (Feb. 1944). American beech, eastern cottonwood, and yellow— poplar, Rep. no. 1675 (Rev. Nov. 1955). Eucalyptus, Rep, no. 2126 (Sept., 1958).

2.9 NONWOOD AND RECYCLED FIBER CONSIDERATIONS

Recycled or Secondary Fiber

Recycled fiber is a fiber whose source is paper or paperboard arising outside of the mill. It is distinguished from broke, which is off-specification paper produced and reused within the mill. Recycled fiber is obtained from recycled paper.

It is very important to have "pure" sources of paper from which to make recycled fiber. Newspapers should not be contaminated with magazines, brown paper, and boxes. Office papers should not be contaminated with newsprint or brown papers. For example, mixed waste paper is worth about $10—20/ton, whereas clean paper clippings from an envelope factory are worth over $250/ton.

The US paper recovery rate increased by 1.4% points in 2015 to a record high 66.8%. The previous high point of 66.4% was recorded in 2011. AF&PA member companies have set a goal to increase the US paper recovery rate to more than 70% by 2020. Globally, about 55% of paper is recovered, and some countries have significantly higher recovery rates, such as Europe (71%), Japan (70%).

The product with the largest recovery by amount and percent in the United States is old corrugated containers (OCC). Over 50% of OCC is recovered in the United States. One reason is that large amounts of OCC are generated at specific sites, such as grocery stores and other retail outlets. Newspapers and other postconsumer wastes are much more expensive to collect and tend to be highly contaminated with unusable papers and trash. Still, 33% of newsprint is recovered, but only one-third of this ends up in new newsprint, with the rest used in chipboard or exported. Several states, however, are in the process of enacting legislation that demands large amounts of recycled fiber (10%—50%) in new newsprint. The recovery and reuse of newsprint will change rapidly over the next several years. On the order, 25% of the US recovered fiber is exported, and the remaining 75% is reused domestically.

Use of Recycled Paper

Generally, freight costs limit the distance that waste paper may be transported. About 80% of all waste paper comes from one of three sources: corrugated boxes, newspapers, or office papers. Only about 10% of waste paper is deinked to be used in printing or tissue papers; mostly it is used in paperboards and roofing materials where color is not important. However, the percentage of deinked paper is expected to increase considerably over the next few years.

Reuse of discarded paper involves extensive systems for removal of foreign materials. This involves skimmers to remove floating items, removal of heavy items at the bottom of a repulper, and the removal of stringy items such as rope, wet strength papers, etc. The so-called nonattrition pulping method works like a giant blender to separate the fibers. Coarse screening is then used for further cleaning before the use of fine screens. These processes are discussed in detail in Chapter 10.

Nonwood Plant Fibers

About 10% of the fiber used to make paper each year worldwide is from nonwood plant fibers, including cotton, straws, canes, grasses, and hemp. Nonvegetable fibers such as polyethylene and glass fibers are also used. Fig. 2.34 shows electron micrographs of "paper" made from four nonwood fibers. In the United States, paper contains only about 2% of nonwood fibers on average. Globally, however, the use of nonwood fiber is increasing faster than wood fiber. Nonwood fiber sources were used for hundreds of years before wood was used as a fiber source for papermaking. Many factors influence the suitability of raw materials for use in paper. These include the ease of pulping and yield of usable pulp; the availability and dependability of supply; the cost of collection and transportation of the fiber source; the fiber morphology, composition, and strength, including the fiber length, diameter, wall thickness, and fibril angle (primarily the thick S2 layer); the presence of contaminants (silica, dirt, etc.); and the seasonability of the supply (storage to prevent decay is costly.)

Nonwood sources of plant fibers include straws such as wheat, rye, rice, and barley; grasses such as bamboo, esparto, and papyrus; canes and reeds such as bagasse (sugar cane), corn stalks, and kenaf; bast (rope material) such as flax (linen), hemp, jute, ramie, and

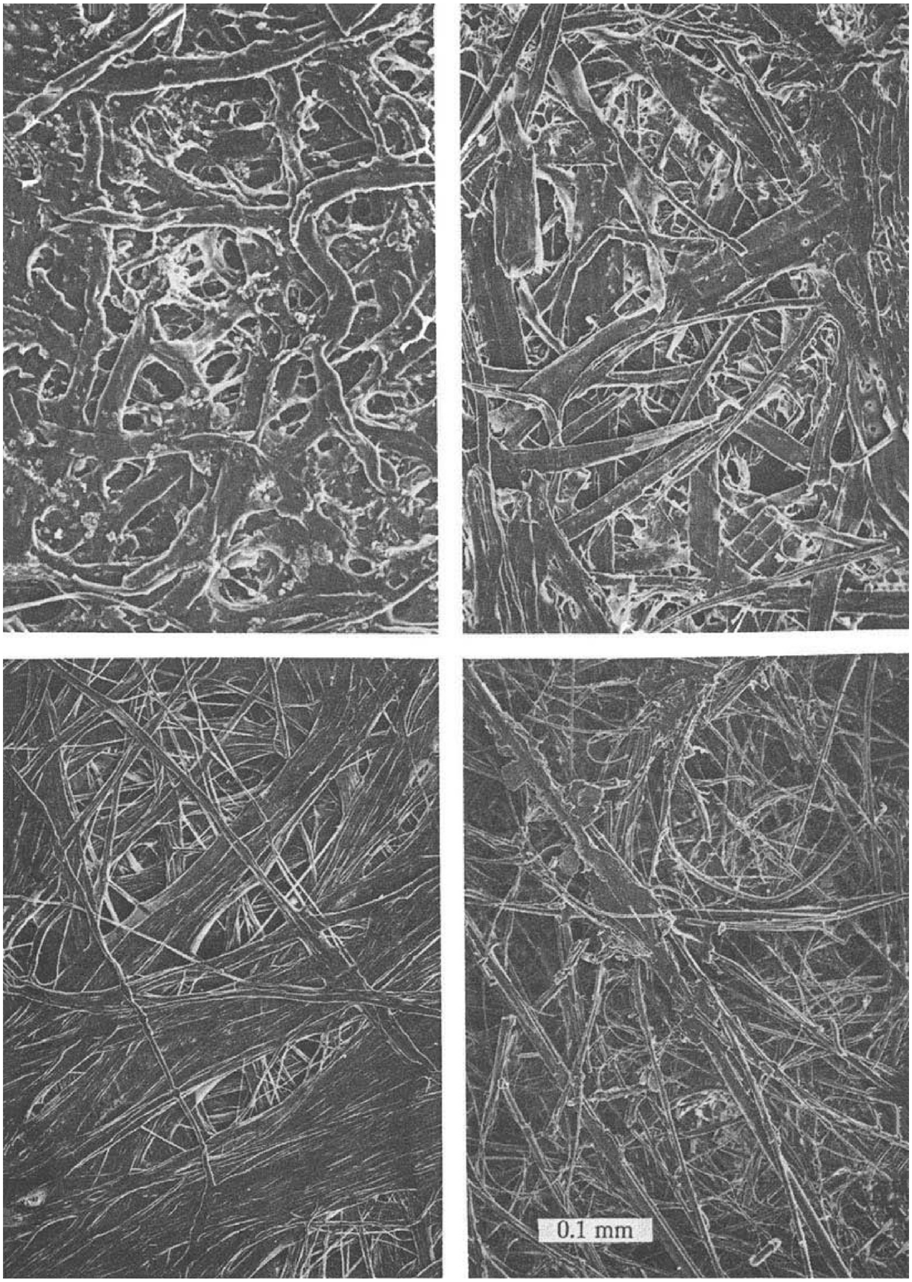


FIGURE 2.34 Cotton paper (top left); kenaf newsprint press run [top right, see *Tappi J*. 70(11):81–83(1987)]; polyethylene nonwoven material (bottom left); and glass fiber battery separator.

mulberry; and seed hairs such as cotton. Tappi Standard T 259 describes the identification of nonwood plant materials that are used or have the potential to be used in the paper industry. Many photomicrographs and detailed information make this a particularly useful resource on nonwood fibers.

In the United States, wood has replaced other fiber sources for a wide variety of reasons (that will be discussed and are later summarized in Table 2.9 for straw). For example, in the United States, all corrugating medium was made from straw before the 1930s. Around this time the chestnut blight made a lot of hardwood available, which was effectively pulped by the new NSSC process to make corrugating board. By the end of the 1950s, most of the straw-using mills had closed or switched to hardwoods. Now almost all corrugating medium in the United States is made with hardwoods and/or recycled fiber.

In contrast to this, Europe's largest corrugating medium mill uses pulp from wheat, rye, oat, and barley grain straws, along with secondary fiber. The mill is owned by Saica and operates in Zaragoza, Spain. Plate 2.9 shows some aspects of the process. The mill boasts a production of 1200 t/day of medium containing 25% or 50% straw pulp, with the higher grade containing the larger amount of straw pulp. The balance of the fiber is from recycled paper. The mill is state of the art with high-speed paper machines using extended nip presses. The mill recovers some of the organic material as fuel by anaerobic fermentation, whereas the sodium is not recovered. Straw pulping technology has sold several of these systems. At present, Saica are leaders in the manufacturing of paper for corrugating with a production capacity of 2.4 million tons per year.

TABLE 2.9 The Advantages and Disadvantages of Straw as a Fiber Source

Advantages	Disadvantages
By-product from agriculture	Transportation and storage problems
Often cheaper than wood	Straws are bulky and contain silica
Large annual crop of 1–10 tons per acre per year	Short harvest time of 1–2 months; thus heavy drain on capital
Needs little refining	Degrades very quickly—high losses
Makes excellent filler, good printing and smoothness	Low freeness (drainage) rates and thus low production rates

Most nonwood fiber is pulped in continuous digesters at temperatures around 130–160°C (265–320°F) for 10–30 min. The Pandia digester, which is a horizontal tube digester with screw feed, is a commonly used digester. However, in Denmark, Frederica Cellulose uses wheat and rye grain straw in batch digesters to make bleached straw market pulp. The mill did not have any liquor recovery or treatment before 1985 but is now the only mill in the world using direct alkali recovery (DARS) to regenerate the sodium hydroxide from the spent cooking liquor. The DARS process is used because the mill is so small that a recovery boiler and limekiln would be uneconomical.

Natural cotton (from the seed pods) is a very pure form of cellulose. In its native form, cotton fibers are too long to make good paper because poor formation (evenness of fiber distribution) in the paper would be the result. Also, cotton suitable for textiles is too expensive for use in paper. Rag (cotton remnants of the textiles industry) cotton has relatively short fibers and is much less expensive. Cotton linters (seed hair) have shorter fibers. Cotton rag fibers are typically 10–45 mm long, whereas cotton linters are 1–2 mm long; both are 0.02–0.04 mm in diameter. Because cotton is almost pure cellulose, it has little hemicellulose and leads to low strength papers. Consequently, cotton fibers are mixed with wood pulp to make a suitably strong paper. Fig. 2.34 shows paper made from cotton fibers.

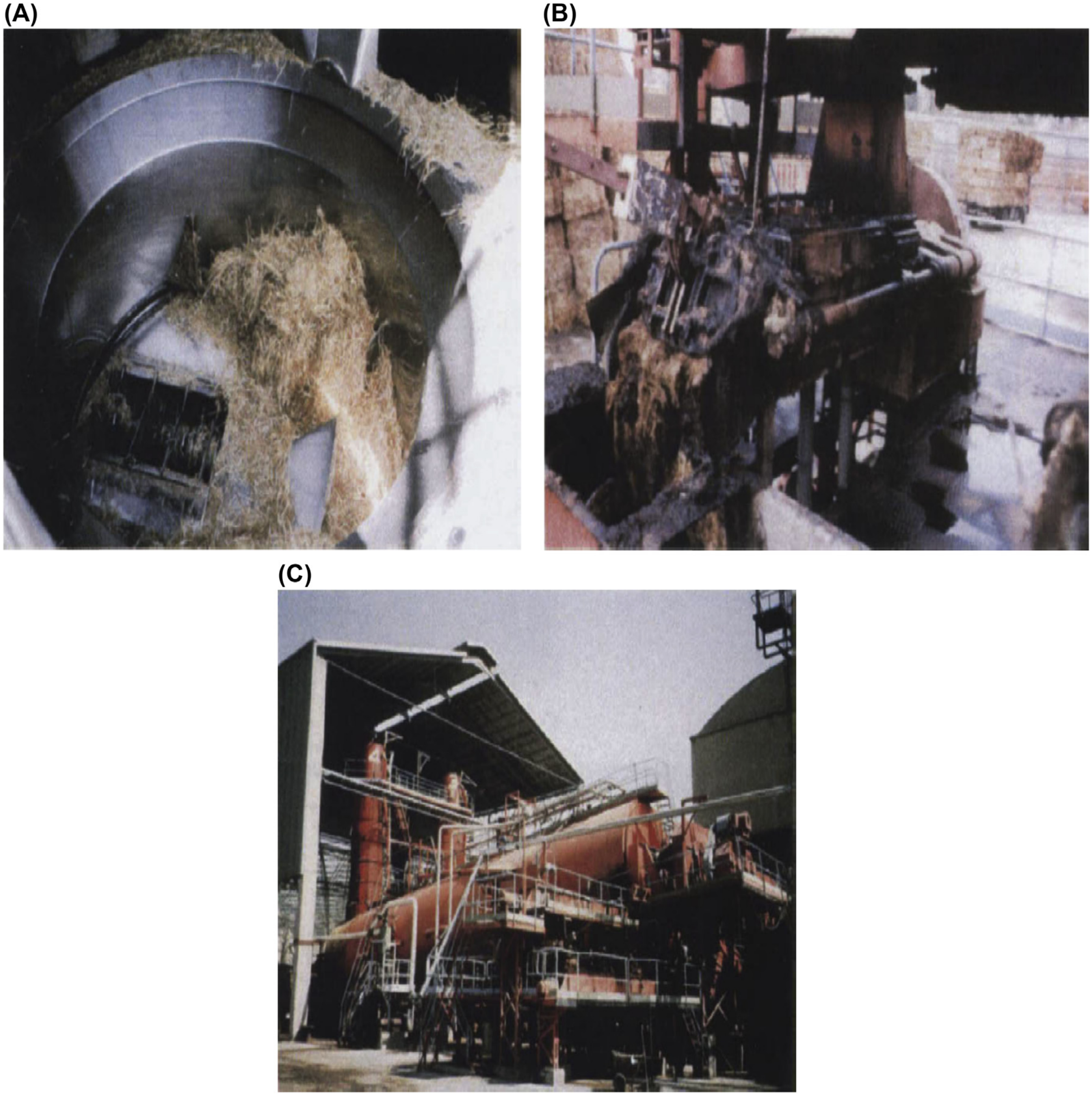


PLATE 2.9 Straw pulping for brown paper. (A) The straw is chopped in a hammermill, (B) pulped at 100°C, and (C) the pulping liquor is pressed from the pulp. *Courtesy of Straw Pulping Technology.*

Bast Fibers

Hemp (used in ropes), jute, and ramie grow in subtropical areas, such as in the Philippines, and have long (20 mm), very strong fibers. These materials have specific applications in cigarette papers, tea bags, sack paper, and saturating papers. Linen (flax) is similar to hemp, but the fibers are shorter (2–5 mm by 0.02 mm diameter). These materials are usually processed by kraft or soda processes.

Straw

Straws, the stalks of grain crops obtained after threshing, may be processed into pulp. Straws from most edible grains are suitable. The most important types pulped are wheat, rice, rye, and barley with yields typically about 35% for bleached grades to 65% for high yield pulps suited for corrugating media or linerboard. Straw is low in lignin and is especially suited for fine papers. Because straw pulps have low drainage rates, it takes more water and large washers to wash them.

The soda process is the most common pulping method for straw; anthraquinone is sometimes used with soda or kraft pulping of straw. Straw fiber lengths are typically 0.5–2.5 mm with diameters of 0.01–0.2 mm. Straw hemicellulose is mostly xylans. All of these factors make straw pulp similar to hardwood pulp. The advantages and disadvantages of straw are summarized in Table 2.9.

There is huge potential for more straw pulping capacity in North America for a range of grades of pulp for packaging, fine paper, and clothing. In addition to meeting market demand, straw pulp capacity brings a host of economical and environmental benefits.

Chemical recovery of straw pulping liquors is complex and has not been practiced until environmental pressures in the 1980s forced some mills to begin this practice. Because large amounts of water are required to wash pulps, much energy is needed to concentrate the dilute liquor from the brown stock washers. However, about one-half of the liquor can be pressed out of the pulp and subjected to chemical recovery to avoid high evaporation costs. (Many mills that pulp wood by semichemical processes do this as well.) Many straws, especially rice straw, have large amounts of silica that are removed during alkaline pulping. The silica interferes with the chemical recovery process. There are about 10 countries that pulp significant amounts of rice despite its high silica content. New techniques for desilicanization of black liquor now allow chemical recovery.

Grasses

Grasses are pulped by the soda process and, like straw, are low in lignin. Grasses have long (up to 3 mm), thin (0.01–0.02 mm) fibers suitable for fine, high-quality papers with good strength and opacity. Esparto grass grows in southern Europe and northern Africa. Pulp from bamboo (grown in India, China, and other Asian countries) is used in fine papers and the resulting paper is stronger than paper of straw pulp. Because of its high silica content, it is pulped using the kraft process. Bamboo pulp is somewhat similar to softwood sulfite pulp.

Canes and Reeds

Bagasse (sugar cane residue) is pulped by the kraft or soda process. It must be depithed because the inner pith cells are useless for papermaking and decrease the pulp freeness considerably. It is used in fine papers. Improvements in processing bagasse have made it more popular around the world as a fiber source for pulp. Because bagasse is often used as a fuel at sugar processing plants, the plant must replace the bagasse with another fuel if it is to make it available for pulping. Kenaf has been investigated in the United States by the USDA. It is a member of the hibiscus group of plants and is being investigated for use in newsprint. Fig. 2.34 shows a sample of newsprint made from kenaf from an actual press run.

Glass and Polymers

Nonwovens are fiber mats made using synthetic fibers. They can be formed much like paper into a cloth material instead of using a weaving process, hence the term nonwoven. Paper receives some competition from nonwovens in products such as tote bags, envelopes, and computer diskette sleeves. The long fibers give these products very high tear strengths. Glass fibers (often with chemical additives) are used in products such as battery separators, glass fiber filter mats, and as reinforcement in a large variety of composite materials. Fig. 2.34 shows mats constructed with polyethylene and glass fibers.

2.10 ANNOTATED BIBLIOGRAPHY

Wood

Wood Procurement

Slinn, R.J., The impact of industry restructuring on fiber procurement, *J. Forestry* (2)17–20(1989).
"The past and present roles of the pulp and paper sector in wood procurement."

Wood Handling

Lamarche, F.E., Preparation of pulpwood, in *Pulp and Paper Manufacture*, Vol. 1, second ed., MacDonald, R.G., Ed., McGraw-Hill, New York, 1969, pp 73–147.
This is a thorough look at handling roundwood and wood chips at the mill, especially in regard to the equipment. It includes pulpwood measurement, log storage and handling, debarking, chipping, and chip quality and handling. Chip screening by *thickness* is not mentioned as the article predates the widespread understanding of the importance of chip thickness screening for kraft pulping. It is well illustrated.

Piggott, H.R. and R.A. Thompson, Drum barking: key factors for design and performance, *Tappi* J. 70(8):37–41(1987).

Wood Physics and Transport Properties

Woods, such as redwood that has a high level of water-soluble extractives, have a low apparent value for the FSP; it is believed that these extractives use some of the sites that water normally uses. Perhaps, this effect is observed in paper with certain water-soluble materials (such as polymers). On the other hand, hemicellulose has a high FSP, so starch might increase the FSP of paper. Pulps generally have a slightly lower FSP than the woods from which they were derived.

Cellulose molecules have an index of refraction of 1.599 in the axial direction and 1.532 in the transverse direction. The dielectric constant is 5.7 and the breakdown voltage is 500 kV/cm.

Dunlop, F., U. S. Dept. Ag. Bull. 110 (1912).
The specific heat of wood as 0.266 at 0°C and 0.382 at 100°C for wood with 0% moisture. A correction for specific heat at 0% moisture, c_o, is calculated from the fractional moisture content of wood, m, and the specific heat due to wood–water bound energy, *A*, as follows:

$$\text{Specific heat} = \mathrm{A} + (m + c_o)/(1 + m).$$

where at 0.10 water content A varies from 0.02 at 85°F to 0.04 at 140°F and at 0.30 water content A varies from 0.04 to 0.09 for 85–140°F.

Huang, CL., Revealing the fibril angle in wood sections by ultrasonic treatment. *Wood and Fiber Sci*. 27(1):49–54(1995).

James, W.L, Y.-H.Yen, and R.J. King, A microwave method for measuring moisture content, density, and grain angle of wood, USDA, For. Ser. Res. Note FPL-0250 (1985), 9 p.

The attenuation, phase shift, and depolarization of a polarized 4.81 GHz wave transmitted through a wood specimen can provide estimates of the moisture content, density, and grain angle of the specimen.

Jimenez, G, W.T. McKean, and R.R. Gustafson, Using a kraft pulping model to improve pulp uniformity, *Tappi J*. 73(7) 173—176(1990).

This article covers diffusion of solutions at high pH (12—14), such as in kraft pulping, where swelling of wood increases the diffusion in the radial and tangential directions to that approaching the longitudinal direction.

Siau, J.F., *Transport Processes in Wood*, Springer—Verlag, New York, 1984. 245 p.

This is not written for pulp and paper specifically but for those who need information on the wood—moisture relationship, transport of fluids in wood (of use in pulping), capillary and water potential, thermal conductivity, and moisture movement under steady-state or unsteady-state conditions; this is a good starting point.

Stamm, A.J., *Wood and Cellulose Science*, Ronald Press Co., New York, 1964. 549 p.

This book might be entitled "The Physical Chemistry of Wood." It covers microscopy; X-ray structure; solution properties of lignin, cellulose, and cellulose derivatives; sorption behavior of wood with water vapor and other gases; surface area and accessibility; shrinking and swelling of wood and cellulose in various liquids; mechanical, electrical, and thermal properties of wood; diffusion through wood; wood drying and preservation; adhesion; and fiber bonding. Stamm pioneered many aspects of the physical chemistry of wood.

Steinhagen, H.P., Thermal conductivity properties of wood, green or dry, from −40 degrees to +100°C: a literature review, USDA For. Ser. Rep. general tech. report FPL-9, (1977), 10 p.

This work investigates heat transfer in frozen logs and includes information on the specific heat of wood from 0 to 30% moisture. Values are given in the USDA reference below.

Stone, J.E., The effective capillary cross-sectional area of wood as a function of pH, *Tappi*, 40(7):539—541(1957).

This classic work shows (see page 88) that the diffusion of wood in the radial and tangential directions, while normally about 20% of that of the longitudinal direction, begins to increase significantly above pH 12.5 and increases to 80% of that of the longitudinal direction at pH above 13.5, typical of kraft pulping. This is why kraft chips are screened by thickness, and not size, as the thickness is the limiting factor.

USDA, Agriculture Handbook No. 72, *Wood Handbook*, 1986 gives many properties of wood.

The thermal conductivity (k) of softwood for construction is about 0.75 Btu-in./(ft^2-h-°F) compared with aluminum at 1500, steel at 310, glass at 7, concrete at 6, plaster at 5, and glass wool at 0.25. k in Btu-in./(ft^2-h °F) is perpendicular to the grain (its about 2—2.8 times higher parallel to the grain) as a function of percent moisture content ovendry basis, M, and specific gravity, S, is:

$$k \approx S(1.39 + 0.028M) + 0.165 \quad M < 30\%$$
$$k \approx S(1.39 + 0.038M) + 0.165 \quad M < 30\%.$$

The coefficient of thermal expansion of ovendry wood parallel to the grain (α) is 0.0000017—0.0000025 per F over the temperature range of −60 to 130°F. For ovendry wood of specific gravity 0.1 to 0.8:

$$\alpha_1 = [(\text{sp.gr}) \times 18 + 5.5] \times 10^{-6} \text{ per °F}$$
$$\alpha_1 = [(\text{sp.gr}) \times 18 + 10.2] \times 10^{-6} \text{ per °F}$$

The electrical resistivity of wood varies from 10^{14} to 10^{16} Ωm when ovendried to 10^3—10^4 at the fiber saturation point. Wood is about twice as conductive in the longitudinal direction as in the other two directions.

Wahren, D. (Bonano, E.J., Ed.), *Paper Technology, Part 1: Fundamentals*, Institute of Paper Chemistry, Appleton, Wisconsin, 1980. pp. 60–96.

The wood–water relationship, especially in regard to drying paper, capillary action, and other forces that hold paper together during pressing and drying, and principles of drying are well covered from the pulp and paper point of view.

Wenzl, H.F.J., *The Chemical Technology of Wood*, Academic Press, New York, 1970, pp. 410–416. The permeability of wood to gases and liquids is discussed, especially in regard to sulfite pulping.

Roundwood Properties

Sapwood Thickness

Lassen, L.E. and E.A. Okkonen, Sapwood thickness of Douglas-fir and five other western softwoods, USDA For. Ser. Res. Pap. FPL 124 (Oct. 1969).

The sapwood thickness was measured on increment cores at breast height (4.5 ft above the ground) on the title species. Sapwood thickness, such as any wood property, is highly variable and depends on many factors. Generally, fast-growing trees have a wider band of sapwood than slow-growing trees. Sapwood thickness decreases with increasing trunk height in some species. Table 2.10 summarizes the results of this work but does not indicate the high variability encountered.

TABLE 2.10 Average Sapwood Thickness (in.) at 4.5 ft Versus Species and Tree Diameter

	Tree Diameter Inside Bark (in.)					
Species	**5**	**10**	**15**	**20**	**25**	**30**
Coast Douglas fir	0.75	1.5	1.8	1.9	2.0	2.1
Interior Douglas fir	0.55	1.2	1.4	1.5	1.6	1.7
Ponderosa pine	2.0	3.0	4.5	5.0	5.0	5.0
Lodgepole pine	1.3	1.9	2.2	2.5	3.0	3.5
Engelmann spruce	0.9	1.4	1.7	2.0	2.0	2.1
Western red cedar	0.7	0.8	0.9	1.0	1.1	1.1
Western larch	0.7	0.7	0.7			

Wood Density

The US Forest Products Laboratory has numerous studies on wood density of trees. For example, report FPL 176–177 (rev. 1975) is a survey of wood density and structural properties of the southern pines. At least several hundred samples from each species were taken. From these samples, regression equations have been developed to predict the average specific gravity of trees based on the results of increment cores.

Wood Chemistry

General Wood Chemistry

Browning, B.L., Ed., *The Chemistry of Wood*, R.E. Krieger Pub. Co., Huntington, New York, 1975, 689 p.

Although first published in 1963 by Interscience, the addendums of each chapter of the later edition add little. This volume is particularly useful for detailed chemical compositions of hemicellulose, lignin, bark, and extractives. The chemical and physical properties of fibers, cellulose, and cellulose derivatives are well covered.

Browning, B.L., *Methods of Wood Chemistry*, Interscience, New York, 1967.

This is an excellent resource for laboratory procedures of wood chemistry. It is required reading for workers in this area. Volume I, 384 p.; Volume II, 384 p.

Hon, D.N.S. and N. Shiraishi, Ed., *Wood and Cellulosic Chemistry*, Marcel Dekker, Inc., New York, 1991, 1020 p.
This is an extensive look at many aspects of wood chemistry. The work is divided into three sections of approximately equal length: (1) Structure and Chemistry, (2) Degradation, and (3) Modification and Utilization. The areas of fiber chemistry and morphology and the chemical structure of wood components are particularly useful.

Wenzl, H.F.J., *The Chemical Technology of Wood* (translated from the German by Brauns, F.E. and Brauns, D.A.) Academic Press, New York, 1970, 692 p.
This is a fairly practical volume on wood chemistry, including world distributions of forests, anatomical and physical properties of wood, wood chemistry, and chemical wood processing including pulping, acid hydrolysis, and pyrolysis. There are about 150 pages, each on sulfite and alkaline pulping chemistry. Each chapter contains 150—500 references covering the time period of 1945—1967 and many from the 19th century.

Lignin Chemistry

Adler, E., Lignin chemistry—past, present and future. *Wood Sci. Technol.* 11: 169—218(1977).
The article summary is "some pertinent results and views from the earlier history of lignin chemistry, pointing to the importance of the arylpropane skeleton, are outlined. Later development, beginning with the dehydrogenation theory and experimental studies on the dehydrogenation polymerization of p-hydroxycinnamyl alcohols, is then reviewed. Finally, degradative work resulting in a detailed picture of lignin structure is discussed."

Sarkanen, K.V. and C. H. Ludwig, *Lignins: Occurrence, Formation, Structure and Reactions,* Wiley—Interscience, New York, 1971, 916 p.
This is a useful work on lignin chemistry.

Carbohydrate Analysis

Bieraiann, CJ. and G.D. McGinnis, Eds., *Analysis of Carbohydrates by GLC and MS*, CRC Press, Boca Raton, Florida, 1988, 292 p.
This book covers hydrolysis of wood, pulp, and other polysaccharides and analysis of carbohydrates by gas—liquid chromatography and mass spectrometry.

Mineral Composition of Wood and Wood Ash

The composition of wood ash is relevant to impurities that might build up in pulping systems with increasing closure (such as Al, Si, and Ca in the kraft chemical recovery system) and as a potential feedstock. Bark is considered to have a 10-fold amount of minerals such as Ca, Si, and Al compared with wood.

Bailey, J.H.E. and D.W. Reeve, Spatial distribution of trace elements in black spruce by imaging microprobe secondary ion mass spectrometry, *J Pulp Paper Sci* 20(3): J83-J86(1994).

Campbell, A.G., Recycling and disposing of wood ash, *Tappi J.* 73(9): 141—146(1990).
In preference to being put in landfills, wood ash may be used as a mineral source for agriculture or even as a source of potash and calcium. The macroelemental and microelemental analyses of six wood ashes are included. The macro elements are Ca (7.4%—33.1%), K (1.7%—4.2%), Al (1.59%—3.2%), Fe (0.33%—2.10%), Mg (0.7%—2.2%), P (0.3%—1.4%), Mn (0.3%—1.3%), and Na (0.2%—0.5%). The composition in wood ash depends on the ashing procedure as some elements are relatively volatile.

Guyette, R.P., Cutter, B.E., and G.S. Henderson, Inorganic concentrations in the wood of western redcedar grown on different sites. *Wood and Fiber Sci* 24(2): 133—140(1992).

This includes the analysis of 30 elements in wood. The mean and standard deviation in ppm for several elements in sapwood are Ca, 1347 (167); Fe, 2.27 (1.19); K, 478 (135); Mg, 103 (27.6); Mn, 25.7 (28.6); Na, 16 (13.2); P, 71 (19,5); Si, 23.9 (28.9). These results with those of Campbell would indicate that most iron in wood ash comes from the processing equipment or additives.

Okada, N., et al. Trace elements in the stem of trees, V, *Mokuzai Gakkaishi* 39(10): 1111−1118(1993); ibid. VI 39(10): 1119−1127(1993).

These papers give radial distributions in Japanese softwoods and hardwoods, respectively. In softwoods, alkali metal (group I) concentrations are generally higher in heartwood than sapwood, but the opposite is true for Mn and CI. Alkaline earth (group II) concentrations did not change abruptly except for Mg. In hardwoods, the elements were generally of higher concentration in the sapwood than in the heartwood. Concentrations of metals are typically Ca, 500−2000 ppm; K, 500−2000; Mg, 50−400 ppm; CI, highly variable by species from 10 to 1000 ppm; Mn, highly variable by species, 0.5−500 ppm; Al, 10−100 ppm.

Chipping

Robinson, M.E., Optimizing chip quality through understanding and controlling chipper design characteristics and other variables, *Proceedings, 1989 TAPPI Pulping Conference,* pp 325−338.

Here the importance of proper chipper maintenance is stressed. Some of the conclusions are as follows: using knives to chip more than 500−1000 tons (dry basis) of chips with dirt or gritty bark in the wood will result in poor chips because of nicks in the knives; dry wood produces more oversized and overthick chips than green wood; high chipping velocity; postchipping damage to chips because of harsh handling, and frozen wood produces larger amounts of fines, especially in softwoods; shortwood chips better in gravity feed machines than in horizontal chippers; because chip thickness is directly proportional to chip length, chip length can be used as a means of controlling chip thickness; reductions in the pins fraction can be gained by removing the card breakers or slowing the chipper speed.

Hartler, N. Chipper design and operation for optimum chip quality, *Tappi j.*, 69(10): 62−66(1986; *Proceedings, 1985 TAPPI Pulping Conference,* pp 263−271.

Hartler is a respected expert on wood chip quality. A target cutting speed of 20−25 m/s for the knives is typical. A decrease in the spout angle results in a lower fines content in the wood chips but has the disadvantages of increased damage to chips, decreased chip bulk density, and a decrease in the maximum diameter of wood that can be processed.

Twaddle, A.A. and W.F. Watson, Survey of disk chippers in the southeastern USA, and their effects of chip quality. *Proceedings, 1990 Tappi Pulping Conference,* pp 77−86. *Also m Tappi J.* 75(10): 135−140(1992).

The authors found from their survey of 101 chippers that about 40% of the chippers were either the 112 in.-15 knife (powered with 800−2500 hp) or 116 in.-12 knife (powered with 1250−3000 hp but most with 2500 hp) combinations. Chippers typically ran at 300−450 rpm with almost 40% at 360 rpm. 43% of the chippers were manufactured by Carthage. 15% used disposable knives. About 50% ran with middisc operating speeds below 25 m/s. 62% of the chippers used passive, gravity *bottom discharge,* whereas 37% used *blowing discharge,* induced by vanes mounted on the back of the disc. Four correlation equations for pins and fines generation for hardwoods and softwoods each were developed from the parameters of discharge type, chipper rpm, and chip setup length.

(They defined pins as less than 2 mm thick and retained on a 5-mm round hole pan and fines as less than 2 mm thick passing through a 5-mm round hole pan, which was the classification used at 70% of the yards measuring fines.) The regression equations can be used to compare the performance of one's chipper with the average although there can be large variations expected for various species of wood. The equations are as follows with r^2 of 0.27 for softwoods and 0.39 for hardwoods:

Softwood pins (subtract 1.58% for bottom discharge units):

$\% = 6.34 + (0.0092 \times \text{rpm}) + (-0.26 \times \text{chip setup length in mm})$

Softwood fines (subtract 1.16% for bottom discharge units):

$\% = 3.02 + (0.0062 \times \text{rpm}) + (-0.15 \times \text{chip setup length in mm})$

Hardwood pins (subtract 0.65% for bottom discharge units):

$\% = 3.64 + (0.0062 \times \text{rpm}) + (-0.17\times \text{chip setup length in mm})$

Hardwood fines (subtract 1.17% for bottom discharge units):

$\% = -0.28 + (0.0081 \times \text{rpm})$

These equations show that an increase in speed of 50 rpm will lead to about 0.3%–0.4% increase in fines and pins each. Analysis of chippers using softwoods and bottom discharge units showed that there was about a 50% increase in fines content (1%–1.5%), as new knives aged to midlife but no decrease from midlife knives to old knives. Keep in mind that other factors besides the chip size distribution, such as chip bruising and geometry, are important in the pulping and papermaking properties of wood chips.

Chip Quality, Uniformity, and Testing

Hatton, J.V. *Chip Quality Monograph, Pulp and Paper Series,* No. 5, Joint Textbook Committee of the Paper Ind., 1979, 323 p.

This work is the classic on the topic of wood chip quality. Before Hatton's research in the 1970s on wood chip thickness screening for kraft mills, screening of wood chips was done with round-hole screens. The importance of uniform chip thickness and quality in kraft pulping cannot be overstressed. Even under ideal cooking conditions, for a cook at a Kappa number of 20, some of the fibers from pin chips will have a kappa as low as 10, and other fibers from overthick chips will have a kappa as high as 50, with the concomitant problems of each.

Christie, D., Chip screening for pulping uniformity, *Tappi J.* 70(4): 113–117(1987).

This article summarizes the importance of *chip thickness screening* in kraft pulping.

Luxardo, J. and S. Javid, New technology for chip thickness and fines screening. *Pulp Paper Can.* 93(3):39–46 (T56-T63) (1992).

A similar paper appears as Smith, D.E. and S.R. Javid, Trends in chip thickness screening, *Tappi J.* 73(10): 185–190(1990). This work also appears in at least three conference proceedings.

Nelson, S.L. and P. Bafile, Quinnesec woodyard focuses on chip thickness control at the chipper, *Tappi J.* 72(3):95–106(1989).

Thimons, T., Chip-thickness screening with an oscillating bar screen, *Tappi J,* 74(11): 183–185 (1991) (ibid., Chip thickness screening without rotating wear surfaces, *1991 TAPPI Pulping Conf. Proc,* pp 553–555.)

Chip thickness screens have saved mills millions of dollars. Most thickness screens use rotating metal discs that have high wear and must be properly maintained for good performance. A new system has been developed that uses longitudinal distribution bars attached to two eccentric shafts with bars alternating as to which shaft they are connected. The system looks remarkably simple and effective. Overthick removal is very high, whereas accept carryover is very low. The method is called Dynagage Bar Screen and is shown in Fig. 2.35.

Hartmann H, Böhm T, Daugbjerg Jensen P, Temmerman M, Rabier F, Golser M (2006).

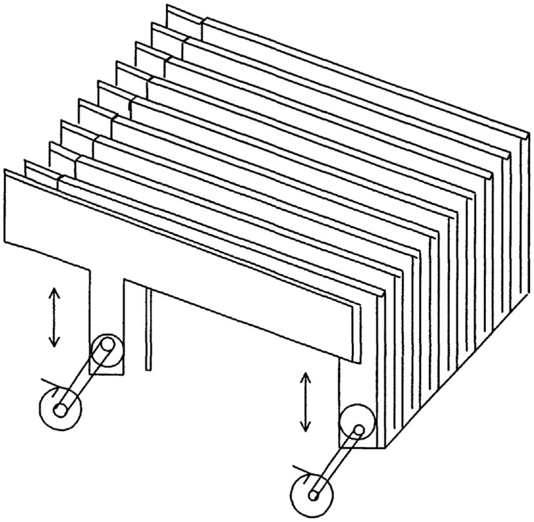


FIGURE 2.35 Diagram of Dynagage bar screen with bars anchored on left hand side in lower position.

Methods for size classification of wood chips, Biomass and Bioenergy, 30, 944–953. Methods for size classification of wood chips are presented in this paper. Five different horizontal and three rotary screening devices were studied using five different screen hole diameters. These systems were compared with a commercially available continuously measuring image analysis equipment.

Berlyn, R.W. and R.B. Simpson, Upgrading wood chips: the Paprifer process, *Tappi/.* 71(3):99–106(1988). A wide variety of chips, including whole-tree chips, chips from partially decayed trees, and logging residues, are claimed to be improved by the Paprifer process.

Marrs, G., Measuring chip moisture and its variations, *Tappi J.* 72(7):45–54(1989). Chip moisture meters, even though they have inherent imprecision, may give the best available estimates of chip moisture during processing.

Chip Pile

Fuller, W.S., Chip pile storage—a review of practices to avoid deterioration and economic losses, *Tappi J.* 68(8):48–52(1985). This article is a concise summary of wood chip 2 pile management with 24 references.

Fiber Physics

Page, D.H., F. El-Hosseiny, K. Winkler, and R. Bain, The mechanical properties of single wood-pulp fibres. Part I: A new Approach, *Pulp Paper Mag, Can,* 73(8):72–77(1972).

Nonwood Fibers

Clark, T.F, Annual crop fibers and the bamboos, in *Pulp and Paper Manufacture,* Vol. 2, second ed., MacDonald, R.G., Ed., McGraw-Hill, New York, 1969, pp 1–74. Processing of a variety of nonwood fibers is considered. It seems likely that the United States will start using nonwood fibers in brown papers or newsprint within the next two decades.

Atchison, J.E., World capacities for nonwood plant fiber pulping increasing faster than wood pulping capacities, *Tappi Proceedings, 1988 Pulping Conference,* pp 25–45. This is a good summary about who is pulping what around the world.

EXERCISES

Wood

1. True or false? Bark in the wood chip supply is unimportant as it has good fiber for making paper. Why?
2. Circle the correct choice in each set of parentheses. (White *or* Brown) rot in wood chips affects the ultimate paper strength properties the most for a given weight loss. (Hardwood *or* Softwood) pulp is used to make strong paper, whereas (hardwood *or* softwood) pulp is used to make smoother paper. (Hardwoods *or* Softwoods) have more lignin. Short storage time of wood chips is most important for (mechanical *or* kraft) pulping.

3. List two changes that take place in chips during storage in a chip pile.
4. Wood chip quality is very important in the final properties of paper. List five parameters for chip quality and their effect(s) on the final paper property.
5. What chip size fractions cause the most problems in kraft pulping, and what are the problems they cause?

Fraction	Problem
___________	______________
___________	______________

6. Approximately % of the production cost of pulp is due to the cost of wood chips.

Wood Chemistry

7. What are the three major components of wood?
8. Circle the correct choice in each set of parentheses. (Cellulose *or* Hemicelluloses) provide (s) individual wood fibers with most of their strength. (Cellulose *or* Hemicelluloses) is/are appreciably soluble in alkaline solutions at elevated temperatures.
9. What material holds the fibers together in wood?
10. How does softwood lignin differ from hardwood lignin?
11. What is turpentine? From what woods is it obtained?
12. Name three commercial materials made from dissolving pulp (cellulose). What are their uses?
13. Describe the process of making carboxymethyl cellulose and show the principal chemical reaction.

Wood and Fiber Physics

14. In the absence of fiber defects, what factor determines the longitudinal tensile strength of individual fibers? For a similar reason, wood fibers do not shrink nearly as much in their longitudinal direction as in their radial or tangential directions. Why is this so? See Fig. 2.36 to help see why this is so.
15. Wood and paper are hygroscopic materials. What does this mean?
16. What holds fibers together in paper?

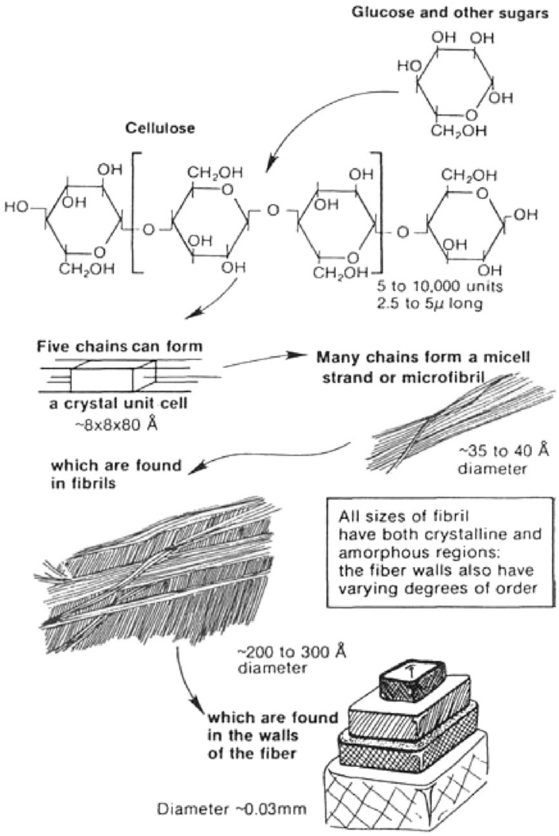


FIGURE 2.36 Relative sizes of fibers and fibrils. 1982, 1991 James E. Kline. *Reprinted from Paper and Paperboard with permission.*

Nonwood and Recycled Fiber

17. Is most recycled fiber deinked? Discuss.

18. What is (considered to be) the maximum percentage of fiber recovery that can be sustained. Why is this so? At what levels do the United States, Japan, and W. Germany recycle?

19. The value of mixed paper waste is on the order of $.........../ton. The value of high-quality trimmings from an envelope factory is on the order of $------/ton. What concept do these facts demonstrate?

20. Trees have replaced all other plants as a fiber source for paper around the world. Discuss this statement.

CHAPTER 3

Wood and Fiber—Growth and Anatomy

3.1 INTRODUCTION

This chapter presents an overview of the anatomy of the wood of temperate softwoods and hardwoods. The growth characteristics of tropical species are somewhat different, especially in regard to growth rings, and a few examples are included as examples of this vast resource. Most tropical woods are hardwoods, but a few softwoods are commercially important. Detailed anatomies of softwoods, hardwoods, and some nonwood fiber sources are each considered in their own separate chapters. An overview of the growth of wood is considered in this chapter to give some context to wood anatomy. The anatomy of various woods is important for several reasons. For example, the characteristics of papermaking fibers depend much upon their anatomy. The pulping characteristics of various fiber sources are dependent upon their species and growing conditions. One should review the fundamental concepts presented in Chapter 2, Vol.1 if the terminology is unclear in this chapter; Chapter 2 also has tables of wood properties and chemical compositions.

Flat or plain sawnwood has a tangential surface as the widest surface. Quartersawn boards have a radial surface as the widest surface. Letters are often used to indicate which plane of the wood to observe to see a particular feature including *x* for cross-sectional, *r* for radial, and *t* for tangential surfaces. Some features are observed in individual fibers. Traditionally, wood has been used locally in manufacturing processes even if the final products have been transported some distance. More and more, however, wood is being bought and sold on the international market as local supplies dwindle in many locations. Because of this trend, much information on global supply and properties of many internationally important woods is included in this chapter. As wood becomes a more valuable material, its properties become even more important. Wood quality and the manipulation of wood quality are becoming increasingly important.

Woody Plants

There are over 500 species of softwood and over 12,000 species of hardwoods (dicotyledons, plants containing seeds with two leaves that are woody) worldwide. In the United States there are about 30 softwood and 50 hardwood species of commercial importance. This number is increasing as wood becomes in higher demand. For example, some *Populus* species were not used commercially until it was realized that they had good papermaking qualities. Even red gum, *Liquidambar styraciflua*, was considered to be a weed tree before 1900 until methods were developed to properly kiln-dry it. About two-thirds of the commercial species used for lumber have appreciable use in pulp and paper, but

Biermann's Handbook of Pulp and Paper: Raw Material and Pulp Making
https://doi.org/10.1016/B978-0-12-814240-0.00003-3

others are also considered in this chapter as common commercial species which may enter the pulp mill.

All woody plants are perennial, i.e., live for a number of years. They have stems consisting of xylem and phloem tissues that conduct water and nutrients. The xylem is lignified and constitutes the wood. Their stems live and thicken by growing outward from the cambium each year. Although most paper have more softwood fiber than hardwood fiber, the anatomy and number of hardwoods often make them more difficult to identify than softwood. Woody plants can also be classified as trees, shrubs, or liana (climbing vines). *Dendrology* is the study of woody plants. Some herbaceous (nonwoody) plants (such as cereal straws and bagasse) are important sources of fiber for paper products in various countries.

Global Wood Production Data

Tables 3.1 and 3.2 show production of roundwood and sawnwood in 2015 in different regions of the world. Figs. 3.1 and 3.2 show the composition of US forests. Most of the commercial hardwoods of the United States grow east of the Great Plains and overall account for less than 20% of the total timber resource. Most of the commercial softwood resource is west of the Great Plains with high concentrations in western Oregon and Washington (Douglas fir) and in the South Atlantic and Southern States (southern pines).

TABLE 3.1 Production of Roundwood (2015)

	Industrial Roundwood			
	Production	**Imports 1000 cum**	**Exports**	**ANC**
World	1,847,719	123,422	122,408	1,848,733
United States	368,572	1196	11,498	358,270
China	167,203	45,174	56	212,321
Russian Federation	190,507	13	19,437	171,083
Canada	151,358	4614	6063	149,909
Brazil	136,277	21	111	136,188

From Forest products statistics.

TABLE 3.2 Production of Sawnwood (2015)

	Sawnwood			
	Production	**Imports 1000 cum**	**Exports**	**ANC**
World	452,255	130,829	134,450	448,634
China	74,344	27,545	287	101,603
United States	76,904	24,497	6299	95,102
Germany	21,466	4971	7179	19,258
Canada	47,114	1280	30,795	17,599
Japan	9569	5997	60	15,506

From Forest products statistics.

Botanical Classification of Wood

All living organisms are classified according to their similarities. Because of the hundreds of thousands of organisms, methodical titles must be given to assure that one is talking about the same thing as one's colleagues who are working around the world. Common names may vary from one region to another. Often misleading names are assigned to wood from various species to help market them; there are distinctions made between a tree and its wood. The botanical system of nomenclature is complicated and uses scientific (Latin) names. This system has been under development for hundreds of years and undergoes changes with time so that each name should have an author name with it in the most technical and formal literature. This practice has not been followed in this work as commercial species are well known. The most obvious division is that of the kingdoms: plants and animals. Additional divisions are made as

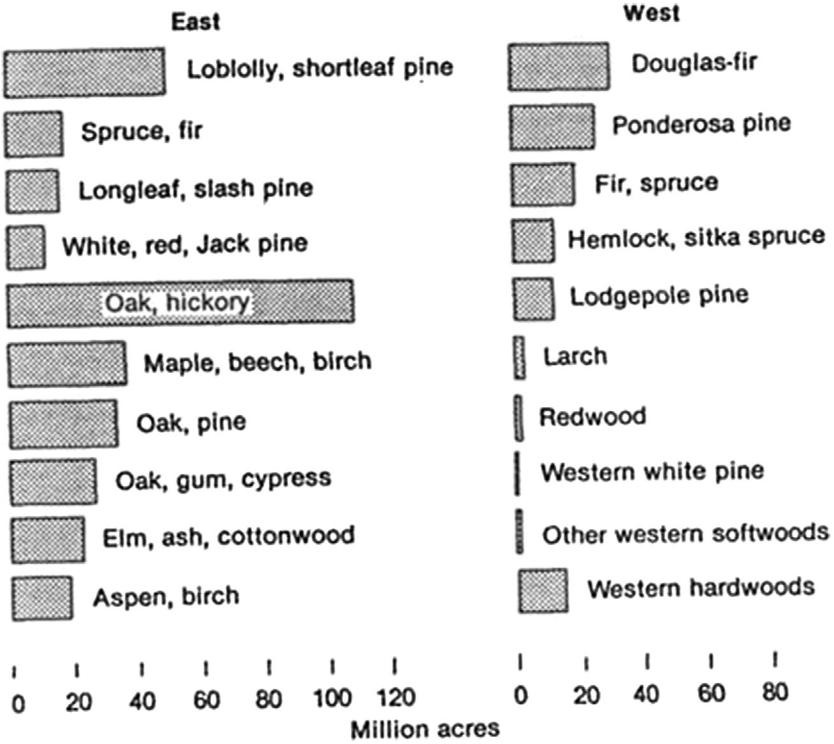


FIGURE 3.1 US commercial timberland by area. *From USDA For. Res. Rep. No. 23 (1982).*

follows: phylum, class, order, family, genus, and species. (The genus and higher levels always begin with a capital letter; the species always begins with a lowercase letter. Each type of plant has a unique combination of genus and species, but the species *rubra*, for example, might be a red oak, *Quercus rubra*, or red alder, *Alnus rubra*.) These have subgroupings such as subphyla; however, a given species of plant or animal may not have classifications at each of these levels. For example, all seed plants (members of the phylum Spermatophyta) are divided into two subphyla: Gymnospermae (gymnosperms, those with naked seeds) and Angiospermae (angiosperms, those with seeds enclosed within the ovary of the flower). The Gymnospermae are not a group with many members so it is divided next into orders. The commercial timber species are all in the order Coniferales, the wood from which are the softwoods. From here they are divided into families, genera, and species. Fig. 3.3 demonstrates the classification of one hardwood and softwood. Softwoods are divided into seven botanical families. Four of these each contain commercial species important in the United States. Table 3.3 shows the genera in each of these families that contain commercial species.

Angiospermae are arranged into two groups: commonly referred to as *monocots* (*monocotyledons*) and *dicots* (*dicotyledons*). Monocotyledoneae have one leaf in the seed and include mostly herbaceous plants such as grasses and corn. A few woody plants such as bamboo, palm, and other "nonwood" fiber sources used in pulp and paper are members of this class.

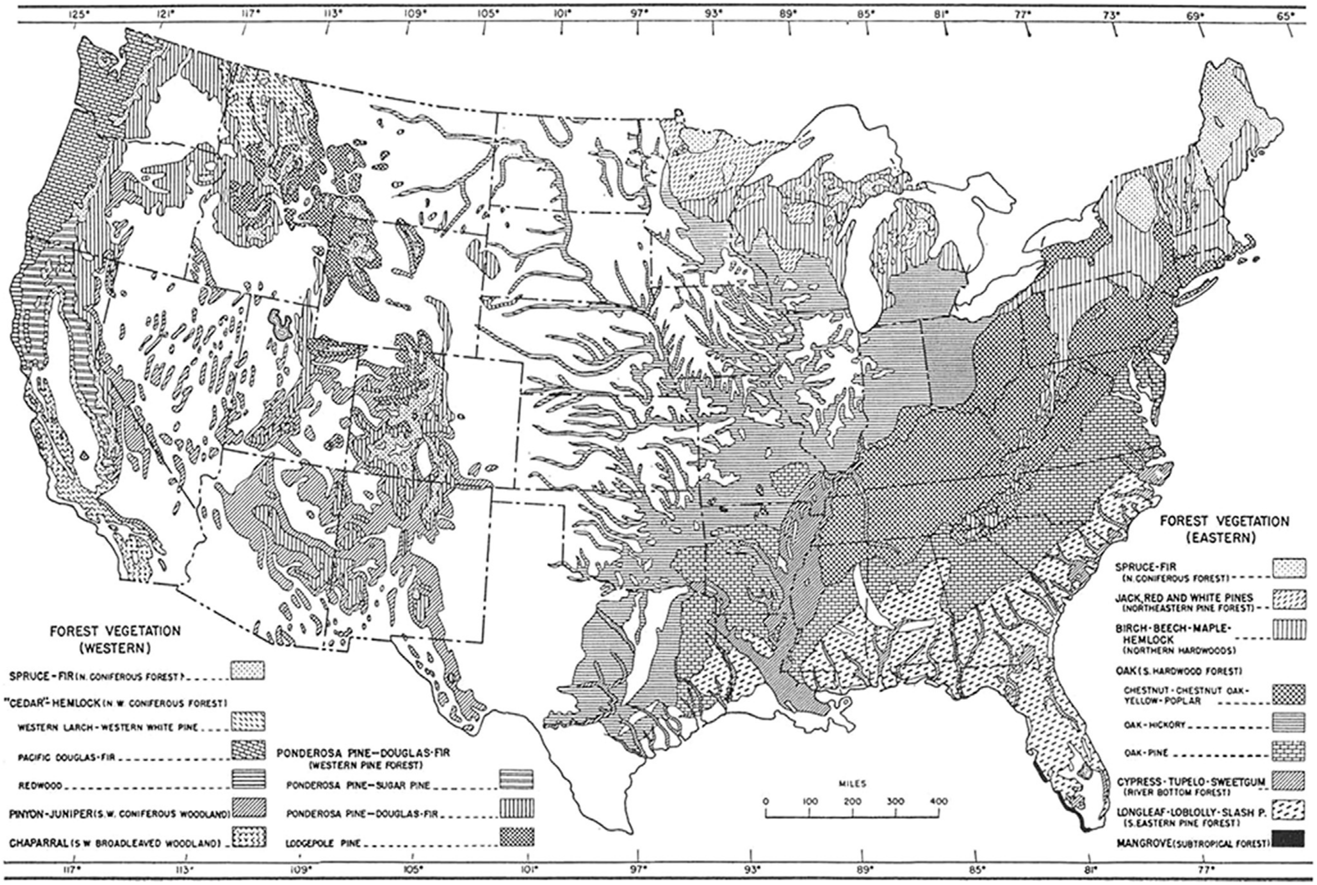
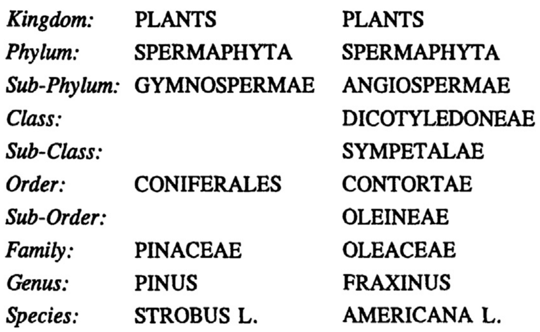


FIGURE 3.2 US forest vegetation. *Reprinted from USDA Handbook No. 72 (1955), p. 10.*



Kingdom:	PLANTS	PLANTS
Phylum:	SPERMAPHYTA	SPERMAPHYTA
Sub-Phylum:	GYMNOSPERMAE	ANGIOSPERMAE
Class:		DICOTYLEDONEAE
Sub-Class:		SYMPETALAE
Order:	CONIFERALES	CONTORTAE
Sub-Order:		OLEINEAE
Family:	PINACEAE	OLEACEAE
Genus:	PINUS	FRAXINUS
Species:	STROBUS L.	AMERICANA L.

FIGURE 3.3 The full classification of a softwood and a hardwood.

Dicotyledoneae have two leaves in the seed and include peanuts, string beans, and many other plants, including the hardwoods. The numerous Dicotyledoneae are further divided into subclasses, orders, suborders, families, and some subfamilies. The anatomy of monocot and dicot stems will be considered in Chapter 10, Volume 1) along with pulping on nonwood fibers.

Hardwoods are divided into scores and scores of families. A relatively few contain all of the species used for papermaking in the United States. Table 3.4 shows the genera for some of

TABLE 3.3 Genera of Softwood Families With Commercial Species in North America

Family	Genus	Common Name	Notes (Northern or Southern Hemisphere)
Pinaceae	*Pinus*	Pine	N.
	Pseudotsuga	Douglas fir	North America, Eastern Asia
	Picea	Spruce	N.; temperate
	Abies	Firs, true, silver	N.; temperate
	Larix	Larch	N.
	Tsuga	Hemlock	N.; Eastern Asia
	Cedrus[a]	True cedars	North Africa, Asia Minor
Cupressaceae	*Chamaecyparis*	False cypress	North America; East Asia
	Juniperus	Juniper, pencil cedar	N.
	Libocedrus	Incense cedar	North America
	Thuja	Cedar	North America; Eastern Asia
	Cupressus	True cypresses	N.
	Widdringtonia[a]		South and East Africa
	Fitzroya[a]		Also *Callitris*[a], *Tetraclinis*[a]
Taxodiaceae	*Taxodium*	Swamp cypresses	
	Sequoia	Sequoia, redwood	Western North America
	Cryptomeria[a]		Eastern Asia
Taxaceae	*Taxus*	Yew	N.; temperate
OTHER GENERA OF GLOBAL IMPORTANCE (ARE NOT NATIVE TO NORTH AMERICA)			
Podocarpaceae	*Dacrydium*		S.; temperate, esp. New Zealand
	Podocarpus	Podocarp	S.; esp New Zealand
Araucariaceae	*Araucaria*		S.; not Africa; also *Phyllocladus*
	Agathis	Kauris	S.; Southeast Asia, Australasia

[a] *Not native to North America, but an important genus globally.*

TABLE 3.4 Genera of Hardwood Families With Commercial Species in North America (Jane, 1956)

Order	Family	Genus	Common Name or Example	Notes (Northern or Southern Hemisphere, etc.)
SUBCLASS ARCHICHLAMYDEAE				
Salicales	Salicaceae	*Populus*	Cottonwood, aspen	N.; temperate
		Salix	Willow	N.; temperate
Juglandales	Juglandaceae	*Carya*	Hickory, pecan	N. Amer.; Asia
		Juglans	Walnut, butternut	N.
Fagales	Betulaceae	*Alnus*	Alder	N. mostly
		Betula	Birch	N.
		Carpinus	Hornbeam	N.
		Ostrya	Hop hornbeam	N.
	Fagaceae	*Castanea*	Chestnut	N.; temperate
		Castanopsis	Chinkapin	N. Amer.
		Fagus	Beech	N.; temperate
		Lithocarpus	Tan oak	N. Amer.
		Quercus	True oak	N.
		Nothofagus[a]	Beech	S. Amer; Austral
Urticales	Ulmaceae	*Celtis*	Hackberry	N.; South Africa
		Ulmus	Elm	N.;
		Phyllostylon[a]		Tropical Amer.
Moraceae	Moraceae	*Maclura*	Osage orange	N.
		Morus	Mulberry	N.
		Chlorophora[a], *Artocarpus*[a], *Antiaris*[a], *Brosimum*[a], *Piratinera*[a]		
Ranales	Magnoliaceae	*Liriodendron*	Yellow-poplar	N. Amer; China
		Magnolia	Magnolia	N. Amer; Asia
	Lauraceae	*Sassafras*	Sassafras	
		Umbellularia	Myrtle	
		Phoebe[a], *Ocotea*[a], *Eusideroxylon*[a], *Beilschmiedia*[a], *Endiandra*[a]		

TABLE 3.4 Genera of Hardwood Families With Commercial Species in North America (Jane, 1956)—cont'd

Order	Family	Genus	Common Name or Example	Notes (Northern or Southern Hemisphere, etc.)
	Cercidiphyllaceae[a]	*Cercidiphyllum*	*C. japonicum*	Japan, China
	Annonaceae[a]	*Oxandra*	*O. lanceolata*	Tropical Amer.
	Myristicaceae[a]	*Virola, Pycnanthus*		Trop. Amer, Africa
	Monimiaceae[a]	*Laurales, Persea*		Chile, N. Zealand
Rosales	Hamamelidaceae	*Liquidambar*	Sweet gum	N.
	Platanaceae	*Platanus*	Sycamore	N.; temperate
	Rosaceae	*Prunus, Malus*	Cherry, apple	N.; temperate
	Leguminosae[b]			
	Mimosoideae[a]	*Acacia, Xylia, Piptadenia, Cylicodiscus, Erythrophleum*		
	Caesalpinioideae[a]	*Mora, Copaifera, Peltogyne, Intsia, Berlinia, Daniellia,* etc.		
	Papilionatae	*Gleditsia*	Honey locust	N.
		Robinia	Black locust	North America
		Laburnum[a], *Byra*[a], *Dalbergia, Pterocarpus, Andira,* etc.		
Sapindales	Aquifoliaceae	*Ilex*	Holly	
	Aceraceae	*Acer*	Maple	N.; temperate
	Hippocastanaceae	*Aesculus*	Buckeye	N.temperate; S.
	Rhamnaceae	*Rhamnus, Maesopsis*[a]		
	Buxaceae[a]	*Buxus*	Box	Eurasia, C. Amer.
	Anacardiaceae[a]	*Dracontomelon, Campnosperma, Astronium, Schinopsis*		
	Celastraceae[a]	*Euonymus, Goupia*		
	Sapindaceae[a]	*Harpullia*	*H. pendula*	
Malvales	Tiliaceae	*Tilia*	Basswood	N.; temperate
		Pentace[a], *Cistanthera*[a]		
	Gonystylaceae[a]	*Gonystylus*	(Melawis, ramin)	Malaya
	Triplochitonaceae[a]	*Triplochiton*	(Obeche, wawa, ayous)	West Africa

(*Continued*)

TABLE 3.4 Genera of Hardwood Families With Commercial Species in North America (Jane, 1956)—cont'd

Order	Family	Genus	Common Name or Example	Notes (Northern or Southern Hemisphere, etc.)
	Bombacaceae[a]	*Bombax, Ceiba, Ochroma*		Tropical species
	Sterculiaceae[a]	*Sterculia, Tarrietia*		Mostly tropical
Myrtiflorae	Nyssaceae	*Nyssa*	Tupelo	N. Amer, Asia
	Myrtaceae	*Eucalyptus*		Common
		Eugenia[a], *Syncarpia*[a], *Tristania*[a]		
	Lythraceae[a]	*Lagerstroemia*		Tropical
	Lecythidaceae[a]	*Cariniana*		Tropical America
	Rhizophoraceae[a]	*Bruguiera, Carallia,*	*Anisophyllea*	the mangroves
	Combretaceae[a]	*Terminalia, Anogeissus*		Tropical
Umbelliferae	Cornaceae	*Cornus*	Dogwood	N.; temperate
	Araliaceae[a]	*Acanthopanax*		Asia
SUBCLASS SYMPETALAE				
Ericales	Ericaceae	*Arbutus*	Madrone	North America
		Erica		
Ebenales	Sapotaceae	*Palaquium, Achras, Mimusops*		
	Ebenaceae	*Diospyros*	Persimmon	United States, Africa
		Oxydendrum	Sourwood	
Contortae	Oleaceae	*Fraxinus*	Ash	N.
		Olea[a]	Olive	Warm climates
	Apocynaceae[a]	*Gonioma, Alstonia, Dyera, Aspidosperma*		
Tubiflorae	Bignoniaceae	*Catalpa*	Catalpa	America, East Asia
		Tabebuia[a], *Paratecoma*[a]		Tropical America
	Scrophulariaceae	*Paulownia*		East Asia, now U.S.
	Boraginaceae[a]	*Cordia*		Tropical America
	Verbenaceae[a]	*Tectona, Gmelina*	Teak, gray teak	Asia, Australia

[a] *Not native (or minimal) to North America, but of importance, globally.*

[b] *An extremely complicated family of thousands in three subfamilies.*

the major families of the United States with commercial species, and Table 3.5 lists several genera with commercial species of global importance. Common names of woods that do not really belong to suggested genera are hyphenated or spelled as one word. Douglas fir is not a true fir, tan oak is not a true oak, and Parana pine is not a true pine.

TABLE 3.5 Genera of Hardwood Families With Commercial Species Globally (Jane, 1956)

Order	Family	Genus	Common Name (or Example)	Notes (Northern or Southern Hemisphere, etc.)
SUBCLASS ARCHICHLAMYDEAE				
Verticillatae	Casuarinaceae	*Casuarina*	She or Forest oak	Australia, Polynesia
Proteales	Proteaceae	*Grevillea, Knightia, Cardwellia*		Australia
Santalales	Santalaceae	*Santalum*	Sandalwood	Indomalaya
Geraniales	Erythroxylaceae	*Erythroxylum E. mannii*		West Africa
	Zygophyllaceae	*Guaiacum, Bulnesia*		
	Rutaceae	*Fagara, Flindersia, Chloroxylon, Amyris*		
	Simarubaceae	*Ailanthus*	Tree of heaven	Asia
	Burseraceae	*Canarium, Aucoumea*		Trop. Asia Africa
	Meliaceae	*Cedrela, Khaya, Carapa, Guarea, Lovoa, Sandoricum,* etc.		
	Vochysiaceae	*Vochysia, Qualea*		Tropic America
	Euphorbiaceae	*Aextoxicon, Croton, Hura, Ricinodendron*		Most tropical
Parietales	Ochnaceae	*Lophira*		Tropical Africa
	Theaceae	*Tetramerista*		Malaya
	Guttiferae	*Cratoxylon, Mesua, Calophyllum, Symphonia*		
	Dipterocarpaceae	*Dipterocarpus, Hopea, Shorea, Pentacme*, etc.		Eastern Tropics
	Flacourtiaceae	*Scottellia, Gossypiospermum*		
SUBCLASS SYMPETALAE				
Primulales	Myrsinaceae	*Rapanea*		Africa, Asia
Rubiales	Rubiaceae	*Calycophyllum, Adina, Mitragyna, Gardenia, Canthium*		

Plant Growth Tissues

The growth tissues of plants are meristems; they have rapidly dividing cells that enlarge (grow) to provide the bulk of the plant. Examples of several meristematic tissues will be considered here: the root tip (radical), the terminal bud (apical meristem), and the *cambium*. The first two provide growth with an increase in length; the latter provides growth in diameter and is of the most interest to wood scientists. A perfunctory discussion is given here.

Primary growth results in plant elongation at the root and bud apical meristems. Fig. 3.4 shows a root tip from onion. (Onion was selected because it shows many features unusually well.) The root shows the division of the cell nucleus; individual chromosomes can be seen. Fig. 3.5 shows a shoot apex (bud) for maple (hardwood) and pine (softwood). Growth originates from the tiny mass of close-packed cells known as the apical meristem. As the apical meristem grows upward, the center cells remain parenchymatous. The epidermis is formed from the outermost cells, and the cortex is adjacent to the epidermis. The vascular tissue forms between the cortex and pith and consists of the xylem (which will expand and grow into wood) and phloem (bast, which will grow into the inner bark). The primary vascular tissue exists in small bundles. In monocots these bundles are scattered in the stem, whereas in dicots the bundles are all about the same distance from the center and form a ring of bundles. The morphology of the vascular tissue of various categories of these plants is detailed in Chapter 10, Volume 1. The scattering of the xylem remains in those monocots that undergo secondary growth. The vascular cambium (Plate 3.1) of dicots and coniferous species will form between the xylem and phloem and result in *secondary growth*; it increases the diameter of the stem but not the length and is called a *lateral meristem*. The cambium has two types of cells: *fusiform initials*, which are vertically elongated and divide into the longitudinal cells, and *ray*

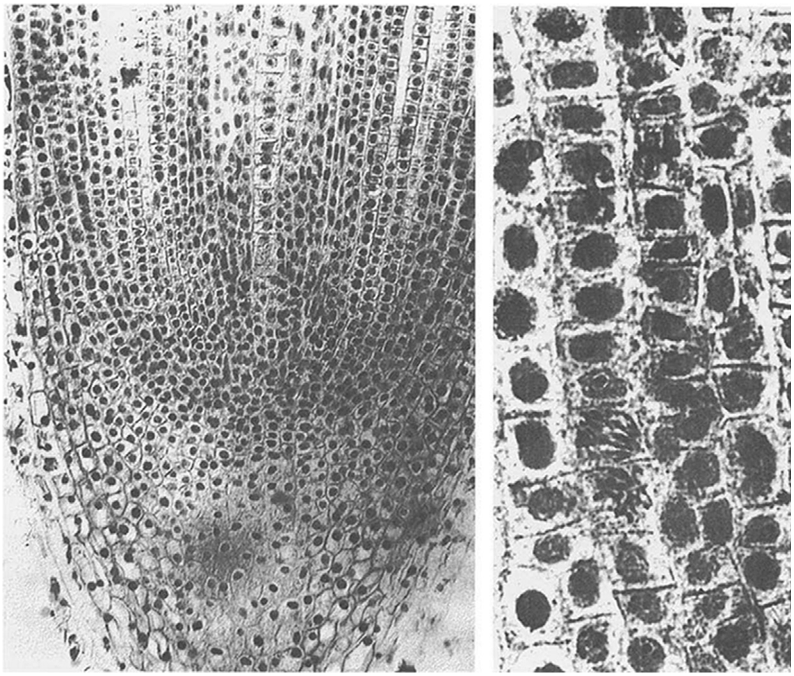


FIGURE 3.4 Onion root tip magnified 150× and 600×. The individual chromosomes can be seen in cells undergoing division.

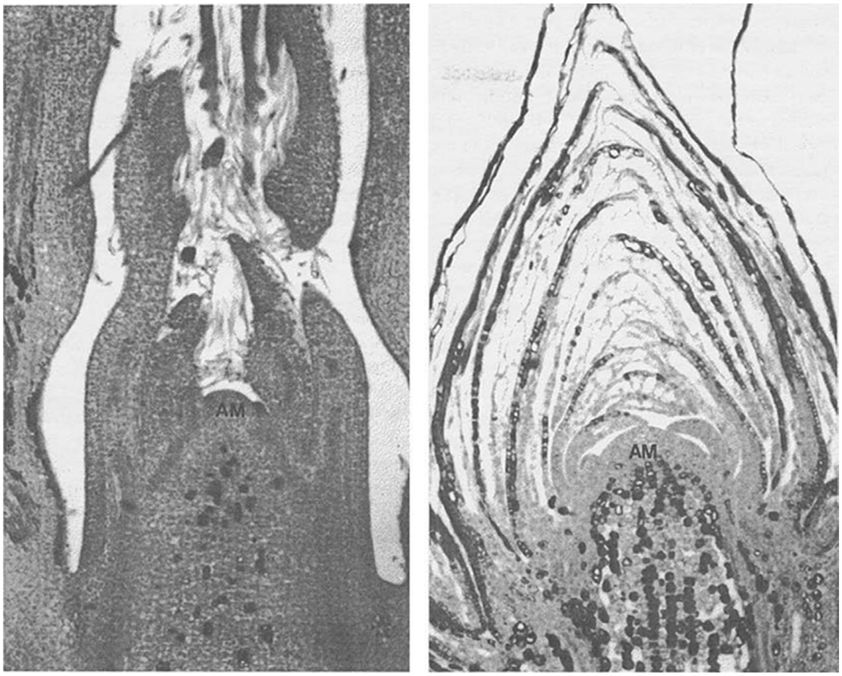


FIGURE 3.5 Shoot apices with apical meristems (marked AM) of maple (left) and pine (*SSx*).

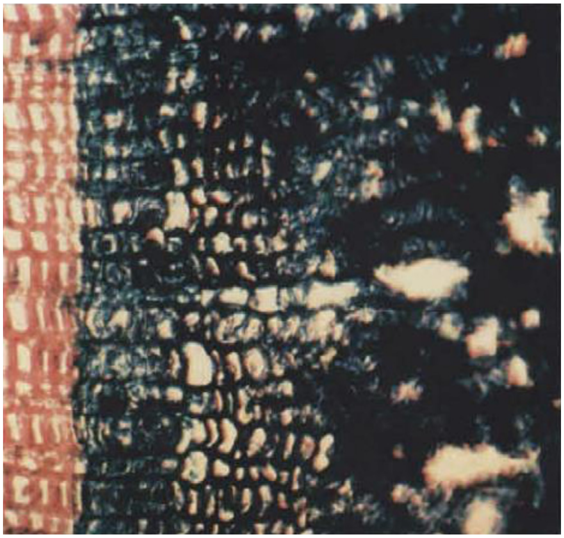


PLATE 3.1 Vascular cambium of a softwood with the xylem stained red and the phloem stained green.

initials, which are more cubical in shape and divide into the ray cells. These cells divide by forming tangential walls (periclinal division) and give rise to daughter cells. One of the daughter cells, called the mother cell, retains the ability to divide. The daughter cells differentiate into the xylem (if interior to the mother cell) or phloem (if exterior to the mother cell). Some hardwoods have cell division in the radial direction (anticlinal) for an increase in diameter. Softwoods and other hardwoods have a diagonal division, and differential growth forms two side-by-side cells for an increase in diameter.

Parenchyma cells of the xylem will usually live until heartwood formation; the prosenchyma cells of the xylem differentiate into their final form within a few days or weeks and die. The anatomy of the xylem (wood) will be considered in detail.

Phloem

Phloem typically grows at only one-sixth to one-tenth of the rate of xylem. Phloem consists of sieve tubes, companion cells, parenchyma, and bast fibers (*sclerenchyma*). Bast fibers are formed directly from cambial initials of modified parenchyma. The latter are called *sclereids* and may have highly branched, unusual shapes. Companion cells are so named because each sieve tube has at least one companion cell associated with it. Bast fibers are lignified and do not easily crush. The walls of sieve tubes and companion cells do not become lignified. The sieve tubes usually function for 1 year and then die and collapse. The collapse provides some additional space for new growing tissue to the interior. Tangential growth in the bark is sometimes provided by flaring of the rays.

Bark

Initially a twig is protected from the environment (against desiccation and mechanical injury) by the thin epidermis. When the cambium becomes active, the increase in diameter will cause the epidermis to rupture. By this time, however, the *periderm* (also called *rhytidome* or outer bark) has begun to form. It consists of the *phellogen* or cork cambium, the tissue outward of the phellogen that is called the *phellem* and is composed of cork cells with much suberin, and the tissue inner to the phellogen that is called the *phelloderm* and is composed of a thin layer of thin-walled tissue. Thick-walled fibers (sclerenchyma) may also be present in the periderm. Sclerenchyma cells from the bark are called *stone cells* by the pulp and paper industry, but the botanical use of the term stone cells is much more limited. The periderm is eventually cut off as dead phloem underneath is shed. Secondary periderms form in arcs from phloem parenchyma cells to continue the growth of the outer bark. This accounts for the layered nature of bark and the deep fissures that may form. Detailed bark anatomy is considered by Chang (1954).

Rays

Most cells of wood are oriented vertically to conduct nutrients and water up and down the bole. Some cells provide conduction from the pith outward to the bark. They vary in height from a few cells in some species to several inches in the oaks; in the oaks they cause the *ray flecks* or silver grain observed on the radial surfaces. The rays of softwoods generally account for less than 5% of the volume of the wood. The rays serve to store food and transport it horizontally in the stem.

General Types of Cells in Wood

(The term cell is correctly used for living cells only, but its use to previously living cells of wood is in common practice.) There are two broad categories of cells in mature wood: *prosenchyma and parenchyma*. They may each be oriented longitudinally and, in the case of ray cells, horizontally. The term prosenchyma is not used commonly in the pulp and paper literature, but it includes fibers (tracheids of softwoods and hardwoods), libriform fibers, and vessel elements. The latter two occur in hardwoods only. Prosenchymas are dead in the mature xylem. Parenchyma cells are rectangular with an aspect (length to width ratio) of about 2—4 compared with 50—100 that is typical of elongated fibers. They are small, thin-walled cells and function in the wood by storage, secretion, and wound healing. They may occur longitudinally or radially, with the latter outnumbering the former in most species. They may store calcium oxalate as crystals, tannins, starch, fats, or proteins. Parenchyma cells are often living in sapwood. Calcium oxalate crystals are observed in some true firs, Sitka spruce, incense cedar, and black walnut. Rhomboidal

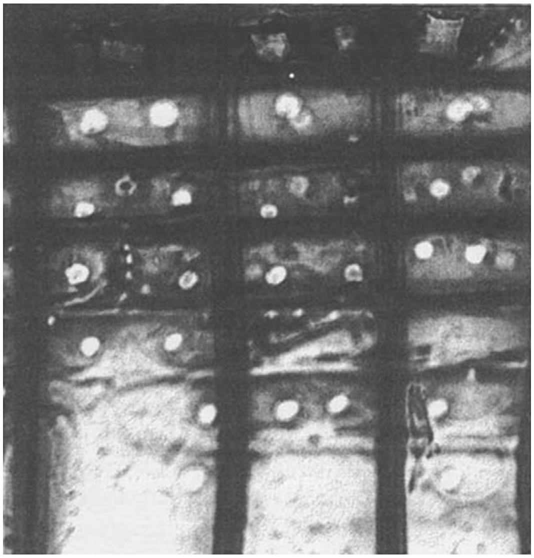


FIGURE 3.6 Crystals (top) of the marginal ray cells of *Abies concolor*.

and rectangular crystals are found in marginal parenchyma cells of some *Abies* (Fig. 3.6). Specific crystal types occur in certain tropical species (Brown and Panshin, 1940, p. 214).

Softwood Cell Types

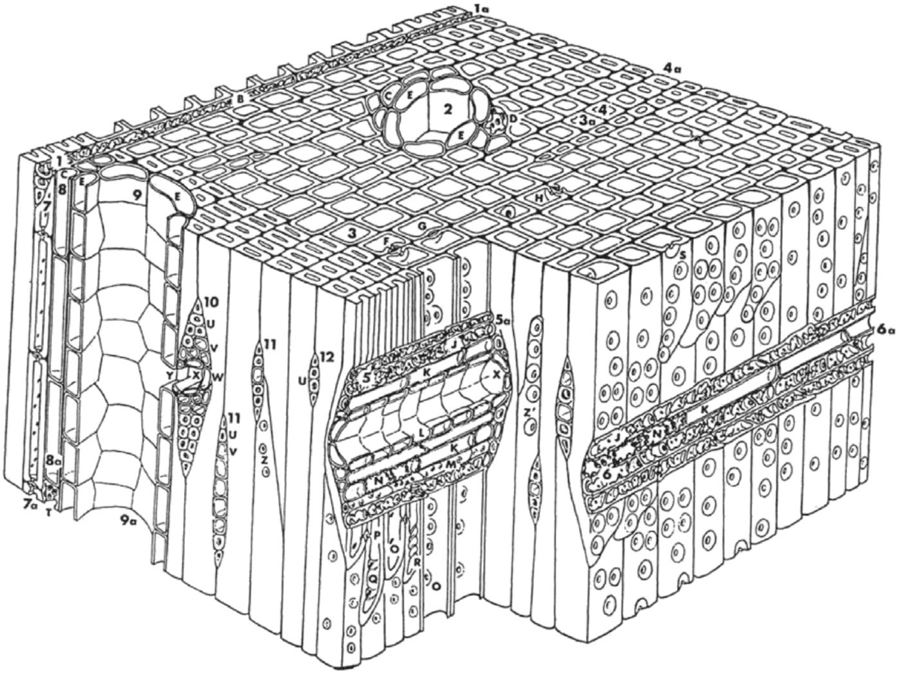
The volume of parenchyma cells in softwoods is typically 5% in spruce and pine to 10% in larch and fir; however, their mass is only 1–2.5% of the total mass. They may occur as strand or epithelial (around resin canals) cells in the longitudinal or horizontal (as part of the rays) directions. Likewise, tracheids may be longitudinal or horizontal. All softwoods have at least longitudinal tracheids and ray parenchyma. The nonparenchyma cells of softwoods are all tracheids and fibers. Fig. 3.7 shows the structure of a representative softwood.

Hardwood Cell Types

The amount of parenchyma cells in hardwoods is much higher and more variable with a volume percentage of 10–35% and mass percentage of 5% or more. They may occur as strand, fusiform, or epithelial cells (such as those found in longitudinal gum canals in injured sweet gum) if they are oriented longitudinally (named axial) and as ray (*upright ox procumbent*) or epithelial parenchyma if oriented horizontally (Some of these parenchyma types are rare in US species.). Fusiform parenchyma occurs as marginal parenchyma of red maple. Fibers include *vessel elements* and fiber cells. The fiber cells include the ubiquitous *libriform fibers*. The other fiber cells include *fiber tracheids, vasicentric tracheids* found in the genus *Fraxinus* and the family Fagaceae, and *vascular tracheids* found in the Ulmaceae family of elms and hackberry. Fig. 3.8 shows the structure of a representative hardwood.

The cell composition of hardwoods and other properties such as fiber length are very important due to their higher complexity compared with softwoods. The high amount of parenchyma cells in many species is detrimental to papermaking. Table 3.6 gives some values for US southern hardwoods growing on softwood sites. This table also shows that average fiber length is quite variable among species, position in the tree, and other factors. Because of their small size, they do not contribute to paper strength, but they contribute appreciably to low freeness in pulp.

The vessel element content of hardwoods is about 10% in birches, 40% in oaks, and over 55% in red gum by volume. In the latter two cases, the volume is empty space. The length of vessel amount by mass is much smaller as most of the elements range from 0.1 to 2 mm (but 0.5–1 mm is common) depending on the species; some values are given in Table 3.6. Libriform fibers have small, simple pits. Fiber tracheids have bordered pits smaller in size than the intervessel pits. Tracheids have numerous pits of about the same size as the intervessel pits. All of these fiber types will be discussed in more detail in the appropriate chapters.



Key: **Cross section:** 1-1a, ray; B, dentate ray tracheid; 2, resin canal; C, thin-walled longitudinal parenchyma; D, thick-walled longitudinal parenchyma; E, epithelial cells; F, radial bordered pit pair cut through torus and pit apertures; G, pit pair cut below apertures; H, tangential pit pair; 4-4a, latewood.

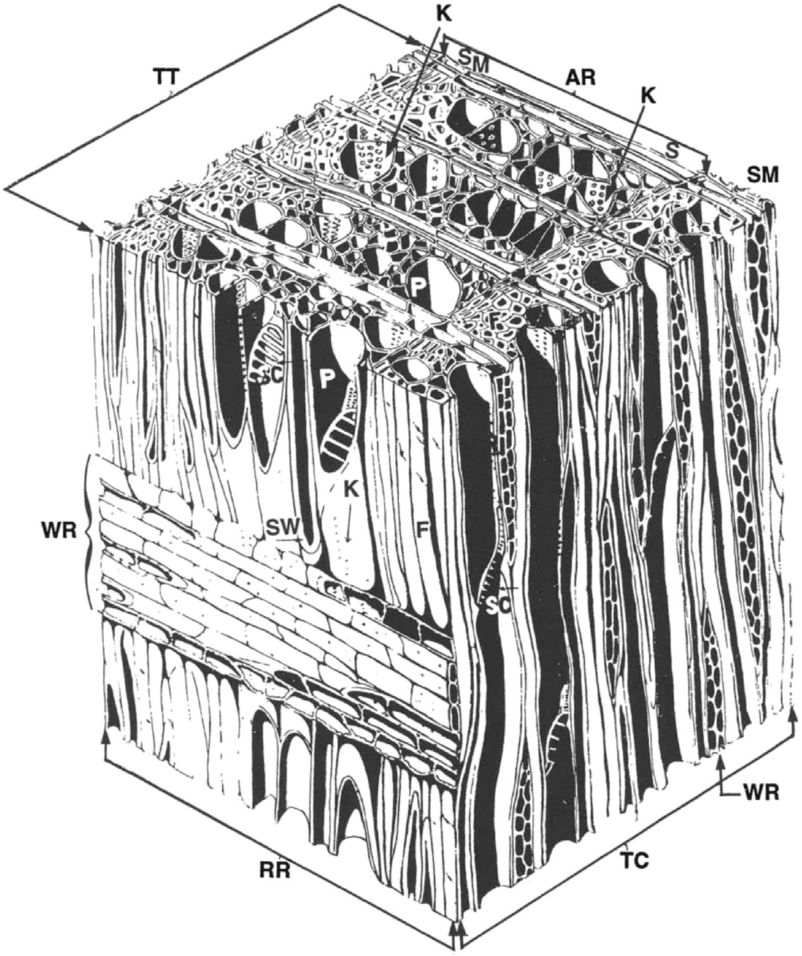
Radial view: 5-5a, sectioned fusiform ray; J, dentate ray tracheid; K, thin-walled ray parenchyma; L, epithelial cells; M, unsectioned ray tracheid; N, thick-walled parenchyma; O, latewood radial pit (inner aperture); O', earlywood radial pit (inner aperture); P, tangential bordered pit; Q, callitroid-like thickenings; R, spiral thickenings; S, radial bordered pits (middle lamella removed); 6-6a, sectioned uniseriate, heterocellular ray.

Tangential view: 7-7a, strand tracheids; 8-8a, longitudinal parenchyma (thin walled); T, thick-walled parenchyma; 9-9a, longitudinal resin canal; 10, fusiform ray; U, ray tracheids; V, ray parenchyma; W, horizontal epithelial cells; X, horizontal resin canal; Y, opening between horizontal and vertical resin canals; 11, uniseriate, heterocellular rays; 12, uniseriate, homocellular ray; Z, small tangential pits in latewood; Z', large tangential pits in earlywood. Reprinted from Howard and Manwiller (1969).

FIGURE 3.7 The three-dimensional structure of southern pine, a softwood.

Cell Pits

Pits are openings in the fiber wall that allow conduction of materials between cells. A pit of one cell is almost always associated with a pit of a second wall so the term *pit pair* is often used. There are three types of pit pairs as shown in Fig. 3.9. Each half of a pit pair may be simple (with a uniform hole, as in parenchyma cells) or bordered (with a thickening in the wall around it, as in most tracheids and vessels). Two simple pits form a simple pit pair, one simple pit with a bordered pit form a half-bordered pit pair, and two bordered pits form a full bordered pit (Fig. 3.9). The pits of hardwoods lack the thickening in the middle, the *torus* (*tori* is the plural form), and are much more variable than those of softwoods.



Key: Surfaces are given as TT for the cross section, RR for the radial surface, and TC for the tangential surface. Structures include WR for wood ray and AR for annual growth ring with S for earlywood and SM for latewood. P is a vessel with SC for sclariform plate. F denotes libriform fiber. K is cell pit. Approx. 125×. Reprinted from USDA For. Ser. Tech. Note No. 210, 1952.

FIGURE 3.8 The three-dimensional structure of yellow poplar, a hardwood.

Miscellaneous Considerations

The wood first laid down in an annual growth ring of temperate woods is called the earlywood. It is especially suited for conduction. The remainder of the growth ring, the latewood, is especially suited for strength. These purposes will become clearer as the anatomy of wood is considered.

3.2 SAMPLE PREPARATION FOR IDENTIFICATION OR MICROSCOPY

Preparation of Wood Samples

Details on sample preparation and microscopy of a wide variety of plant tissues are found in any of the several classic microtechnique books such as Johansen (1940) or Sass (1940).

TABLE 3.6 Proportions of Cells in 6 in. Diameter Hardwoods Growing on Southern Pine Sites[a]

	% Composition by Volume of Stems				Mean Cell Length, Millimeter			
					Fibers			
Species	**Vessels**	**Fiber**	**Rays**	**Lognitude Parenchyma**	**Stem**	**Branch**	**Vessel[b] Elements**	**Mean Tree Age (Years)**
Ash, green	14.5	57.3	14.2	14.0	1.16	0.84	0.26	37
Ash, white	14.5	57.0	14.0	14.4	1.22	0.87	0.29	40
Elm, American	31.1	42.2	12.0	14.8	1.30	0.99	0.22	40
Elm, winged	28.2	40.0	15.5	16.2	1.25	0.93		47
Hackberry	20.1	50.9	13.6	15.4	1.12	0.86	0.26	28
Hickory, true. *Carya*	14.7	53.2	18.1	14.0	1.29	0.98	0.44	54
Maple, red	23.2	50.6	12.8	13.4	0.83	0.66	0.42	40
Oak, black	14.7	37.1	20.8	27.4	1.30	0.98	0.43	39
Oak, northern red	15.3	41.3	19.0	24.5	1.27	0.90	0.42	40
Oak, white	14.7	41.2	20.7	23.5	1.22	0.88	0.40	41
Sweet bay (Magnolia)	30.1	50.3	15.2	4.4	1.24	0.97		39
Sweet gum	46.2	37.6	14.0	2.1	1.54	1.20	1.32	29
Tupelo, black	38.4	39.8	17.2	4.6	1.76	1.40	1.33	59
Yellow poplar	43.3	42.6	11.4	2.7	1.39[c]	0.97	0.89	27
Average, stemwood	20.5	44.4	17.0	18.1	1.27			
Average, branchwood	19.7	45.6	15.9	18.8		0.96		

[a] *From Koch (1985). Averages of woods of 10 trees.*

[b] *From Panshin and de Zeeuw as listed in Koch (1985).*

[c] *Other works show values on the order of 1.7—1.8 mm in mature wood.*

Details on the preparation of wood samples are given in many of the wood anatomy resources listed later. If you are serious about wood identification with a hand lens and knife, see Hoadley, 1990; this is an excellent and reasonably priced resource.

For routine analysis of large numbers of wood samples in a mill, where often only a few species must be distinguished, freehand cutting with a very sharp knife or single-edged razor blade may be suitable. A 10× hand lens may provide the necessary resolution of the transverse section (and others, if necessary) for identification. Moistening the freshly cut surface often helps see detail. In most cases, one will probably want to use a single-edged razor blade to prepare samples for examination under the microscope. Double-edged platinum chrome blades will give very good results (for safety, the edge not being used can be wrapped in cardboard and taped); also, they may be cut in half lengthwise with two pairs of pliers and mounted in a pencil-type hobby knife holder with split collet. The preparation of wood and fiber samples for microscopy is in many regards easier than for other plant tissues as wood is relatively inert

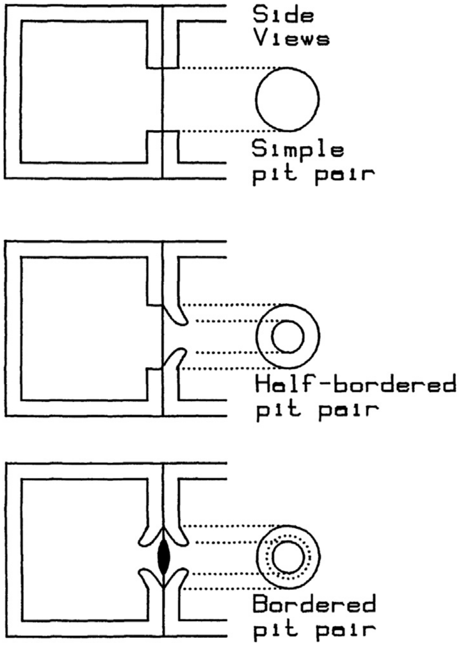


FIGURE 3.9 The three types of pits: simple, half bordered, and bordered.

and strong. It is, however, difficult to cut on the microtome. Wood sections for high-quality photomicrographs (i.e., those presented in this chapter) are prepared on a microtome to give sections about 10–25 μm thick. The magnification of a microscope is about 35–600×, although an oil immersion lens brings this to 1000×. This corresponds to a resolution of about 0.3 μm for routine work. Dissection microscopes have a range in magnification from about 5× to 50×. For high-quality sectioning (photomicroscopy), small cubes (about 1 cm per side) are prepared. Soft species of wood (white pine, aspen, and spruce) are merely boiled until they sink before cutting. Other species are softened with 2–4% KOH in refluxing ethanol for 1 hour or longer, followed by washing. Acetic acid/hydrogen peroxide or any of a multitude of reported methods has also been used. Tropical species with high levels of $\mathrm{SiO2}$ (several percent) may require treatment with HF (special precautions must be used with this material) to remove it as $\mathrm{SiF4}$. Fig. 3.10 shows the standard arrangement of wood sections on a microscope slide. An alternate arrangement is to have the cross and radial sections on top and the tangential section beneath the radial section.

Wood and fiber samples are often stained with safranin O (0.5–1% in water or 50% ethanol), a red stain selective for cellulose. Fast green is used with safranin on many other botanical samples as a counterstain (for example, to show phloem tissue).

Analysis of Wood Chips

Many mills purchase wood chips from a wide variety of suppliers. Often they wish to confirm the identity of the wood species occurring from a supplier. A random sample should be obtained that represents the population of interest. In the laboratory, highly skilled anatomists can identify about one wood chip each minute (60/hr). About 50 or 100 chips might be identified from the representative sample depending on the requirements of the study. As the chips have already darkened, microscopic examination is usually required for confidence in the species determination.

It may be difficult to determine the orientation of the wood chip, but snapping it in half usually presents a fresh radial surface. Decay in wood chip piles occurs faster with hardwoods than with softwoods. Hardwoods have more parenchyma (that initially heat the pile by respiration of food), and the heartwood of species used

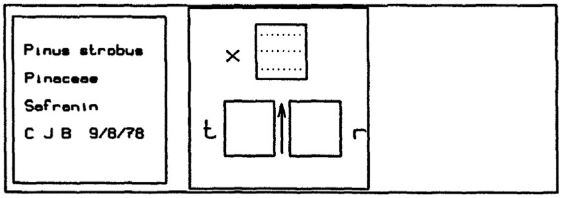


FIGURE 3.10 One arrangement of wood samples on a slide (t is the longitudinal direction).

in pulping is generally not as decay resistant as that of the softwoods. Hemlocks, lodgepole pine, and most spruces have only moderate decay resistance in the heartwood. True firs are the only US softwoods with minimal decay resistance in the heartwood.

Macerations

Wood samples are macerated to study the liberated fibers, such as for fiber length studies. Maceration is a highly selective pulping operation. Wood is first cut into pieces about 2 mm square by 25 mm in the longitudinal direction. Air is removed by soaking (perhaps with vacuum) or boiling in water.

The most gentle maceration technique is the use of sodium chlorite acidified with acetic acid [Spearin and Isenberg, *Science*, 105(2721):214 (1947)]. Caution: impurities can make sodium chlorite explosive. In one method, 35 mL of water is used with 0.6 g sodium chlorite and 5 drops of glacial acetic acid for 1 h at 90°C in a hood. Alternately 2 g of sodium chlorite with 12 drops of acetic acid can be used for 3 h at 85 °C in a hood. The method of Franklin is also gentle. Wood pieces are treated with a solution consisting of equal parts of glacial acetic acid and 6% hydrogen peroxide at 60°C for 48 h. Wilson [(*Pulp Paper Mag, Can*. 55(7): 127–129(1954)] has reviewed maceration techniques. After the chemical treatment, the wood chips are washed in gently flowing water overnight so the fibers do not separate. The pieces are then teased apart and stained as appropriate. Temporary slides are made with Karo. Permanent slides are made by dehydration using an ethanol series of 15%–30%–50%–70%–85%–95%–absabs—50% abs + 50% xylene–xylene.

Preparation of Paper Samples

A small sample of paper can be boiled in 1% NaOH to hydrolyze the sizing and help disperse the fibers. The sample is then washed and agitated to disperse the fibers.

Mounting of Sections and Macerated Fibers

Mounting media have an index of refraction similar to that of the glass microscope slide. Corn syrup (Karo) is useful for temporary slides; it is often diluted with water (about 80:20 syrup: water) to give a good working solution where bubbles do not interfere. Tappi T 263 suggests the use of 50:50 solution of glycerin and 95% ethanol with heating to the boiling point (after the cover glass is applied) to drive off air. These do not require dehydration of the sample. (Dehydration involves replacing water with ethanol and ethanol with xylene so that nonpolar materials can be used.) Canadian balsam (from the pitch pockets of the bark of the balsam fir) is the traditional mounting medium for permanent slides. Synthetic resins are also available. A coverslip can be held in place with two clothespins when waiting for the mounting medium to dry when making permanent slides.

The Use of Keys

Dichotomous keys involve a series of separations of possible wood species based on identifying characteristics. Each selection is a choice of two possibilities (such as the presence or absence of a feature). A key in using hand lens identification is included to demonstrate their use. For example, a wood that has vessels must be a hardwood, so all softwood species are eliminated. If it is ring-porous, then many of the hardwood species are eliminated. Identification of additional features eventually results in its species determination. An alternate to the key is the use of end-punched cards where each number corresponds to (the presence or absence of) a single feature (hardwoods: Brazier and Franklin, 1961; softwoods: Phillips, 1948).

A hole away from the edge is used if the feature is absent, and a notch (where the hole is enlarged to include the edge) is used if the feature is present. By using a wire in a location corresponding to a given observed feature in the unknown, appropriate cards can be made to fall from the deck. The use of a second feature narrows the determination to a smaller group. Eventually the correct species is determined. The observation of a few key features (such as spiral thickening in tracheids) allows the correct determination very quickly. This system has been computerized for faster use (North Carolina State University). The use of keys for softwoods and hardwoods is considered in their respective chapters.

3.3 WOOD VARIATION

Reaction wood consists of compression wood in softwoods and tension wood in hardwoods. A variety of grain distortions are also considered in this section.

Compression Wood

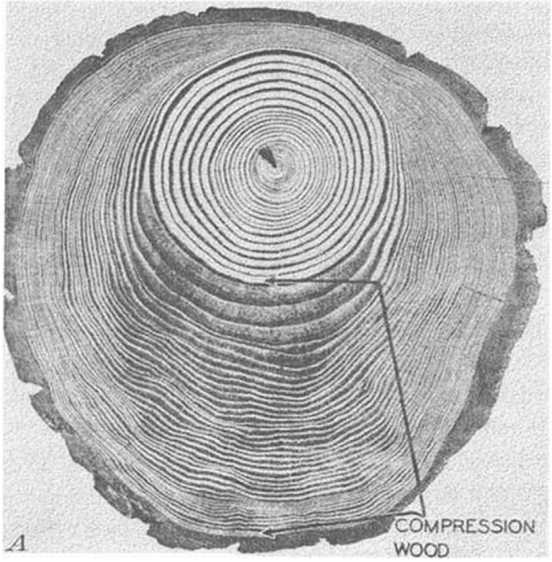


FIGURE 3.11 Cross section of southern pine log with conspicuous compression wood. *From PiUow and Luxford (1937).*

Pillow and Luxford (1937) summarize compression wood as an abnormal type of wood occurring as a rule on the lower side of nonvertical trunks and branches among all coniferous species of trees. An increase in the amount of deviation of trunks from a vertical position or in the rate of diameter increment of individual trees increases the formation of compression wood. Compression wood is identified by markedly eccentric annual growth rings (Fig. 3.11). In the wide portion of the growth ring there is a higher than normal level of latewood that has a more gradual transition from the earlywood to latewood than in normal wood. Under a microscope, the latewood tracheids of compression wood appear to be nearly circular in cross section, whereas those of normal wood are more or less rectangular (Fig. 3.12). The fibrils of the secondary cell walls in compression wood make a higher angle in relation to the longest axis of the cells than do the fibrils of normal wood, and these walls contain microscopic checks. The spiral thickenings that normally occur in Douglas fir and a few other coniferous species are fewer in number and less distinct in compression wood than in normal wood and may be confined to earlywood fibers in pronounced compression wood. The length of tracheids in compression wood is generally 20–30% less than that in normal wood. The fibril angle of the secondary cell wall layer of softwood tracheids is typically about 20–24 degrees in earlywood and below 10 degrees in latewood; in pronounced compression wood, the angles are about 35–38 degrees and 24–30 degrees, respectively. The lignin content of compression wood is about 5% higher and the cellulose content is about 8% lower than normal wood in spruce and redwood. The density of pronounced

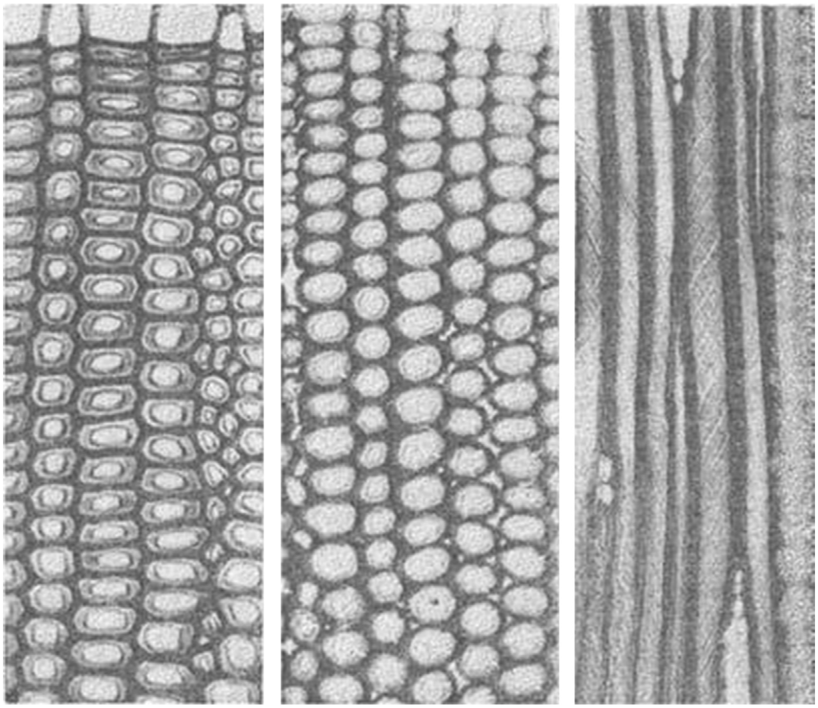


FIGURE 3.12 Normal wood of Douglas fir with rectangular cells (left) and compression wood with rounded cells (center), and checks in fibers with low S-2 fibril orientation (right) (200×).

compression wood is 15%–40% greater than normal wood. The longitudinal shrinkage of compression wood from green to ovendry condition varies from 0.3% to 2.5%, whereas normal wood has a shrinkage of 0.1%–0.2%. The transverse shrinkage of compression wood is less than that of normal wood. When adjustments are made for differences in density, compression wood is lower in practically all strength properties as compared with normal wood (although it is quite hard) and is highly correlated to the differences in the slope of fibrils in compression wood. It is brittle and fails in clean pieces without the splintering normal wood has during failure. Compression wood accounts for much bowing and twisting in manufactured lumber. Pulp from compression wood tends to fragment rather than fibrillate and generally leads to very weak pulps with poor bonding potential.

Tension Wood

Tension wood (Perem, 1964) occurs on the underside of branches and leaning stems of angiosperms (hardwoods) and is not easily observed in freshly felled timber. Upon aging (by weathering or exposure to strong UV light) it becomes visible by its light color or higher luster compared with normal wood (Fig. 3.13). Tension wood often occurs without the eccentric growth ring pattern of compression wood. It is less obvious and considered to be much less of a problem than compression wood and, therefore, is not as well studied. Tension wood has much higher longitudinal shrinkage (0.3%–0.7% compared to 0.0%–0.25%) and toughness and lower modulus of rupture than normal wood. It has a strong tendency to give a fuzzy surface on green wood and to cause warping and other

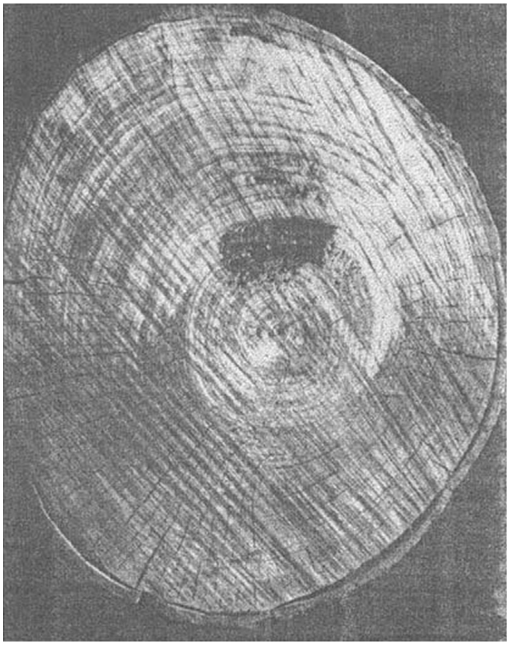


FIGURE 3.13 Tension wood (top) of weathered trembling aspen. *From Perem (1964).*

distortions in lumber products during drying. It may be slightly higher, slightly lower, or of no significantly different specific gravity than normal wood depending on the species. Most species (basswood is an exception) have gelatinous fibers in the tension wood (Fig. 3.14). It is the layer inside the S-2 layer that is gelatinous and this often separates from the rest of the fiber cell wall during sample cutting for microscopy, especially in thin-walled fibers. This layer is almost entirely free of lignin. On average, these fibers are about 5% lower in lignin and correspondingly higher in cellulose than normal fibers. Staining with safranin and fast green shows normal fibers as red and gelatinous fibers as green. The number of vessels is decreased in tension wood. The microfibril angle is lower than in normal wood, but the numerous incipient tension failures in the fiber cell walls give a weak wood or pulp. Elm is an example of a hardwood with much branching (bifurcating trunk). It is bound to have large areas of tension wood because of its normal growth form. Tension wood from the genus *Eucalyptus* is associated with permanent collapse during drying.

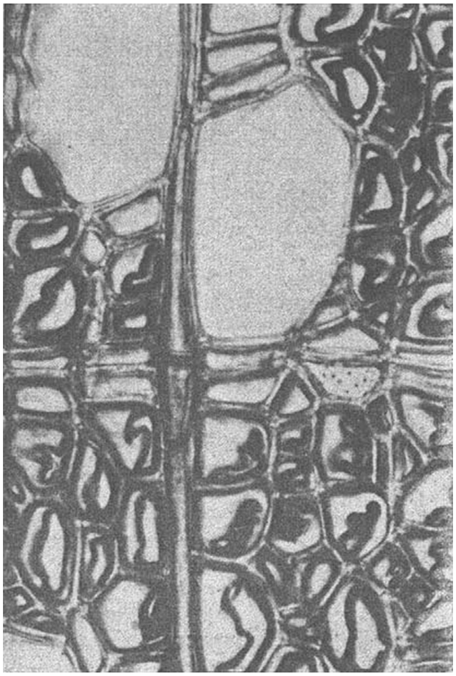


FIGURE 3.14 Fibers with gelatinous layers (separated from the rest of the cell wall) of tension wood from trembling aspen at 500×. *From Perem (1964).*

Pith, Juvenile Wood

The pith and the first 5 to 10 growth rings, corresponding to a core of several inches of wood, have properties that vary greatly from the rest of the wood (Besley in Anon., 1962). The juvenile wood is generally much weaker than normal wood and often shows leaf scars. The wood has lower specific gravity, shorter fibers, and lower cellulose content than normal wood. In loblolly pine, the juvenile wood averages 7 growth rings with a diameter of about 3.5 in. and has a density of about 80% of that of normal wood. Trees (such as southern pine) growing in the open have more knotwood and juvenile wood of lower quality than trees growing under some cover (Paul, 1963).

False Growth Rings

False growth rings are an additional growth region (visible in the cross section of wood) that is produced by a pronounced decrease in the growth rate followed by resumption of growth within a single season. This may be a result of defoliation followed by foliage growth or temporary adverse conditions of temperature or moisture (too much or too little). False growth rings are relatively common in bald cypress.

Interlocking Grain

Interlocking grain occurs in wood when the fibers are inclined in one direction through several growth rings, slowly return to perpendicular in succeeding growth rings, then gradually reverse to become inclined in the opposite direction for several growth rings, and reverse again to repeat the process. Interlocked grain gives a ribbon or stripe figure on radial surfaces.

Spiral Grain

Spiral grain is a type of growth where the fibers take a spiral course around the center of the tree instead of being longitudinal. The spiral may be clockwise or counterclockwise.

3.4 SILVICULTURE AND WOOD QUALITY

Wood is a variable material. Its properties depend on the species, individual genetics, location within a tree, and growing conditions. There are many well-known relationships among the actual properties, such as fiber length and microfibril angle with position within a growth ring or tree, but other relationships vary with species. All of these factors contribute to wood quality. There is much talk about growing "super" trees that meet specific purposes. For example, fast-growing trees with long fibers and low lignin contents are ideal for pulp and paper. However, genetic selection of trees has been largely limited to growth rates and specific gravities of wood. Wood quality is in the domain of the forest scientist, but the wood scientist must work with the forest scientist to define wood quality.

Wood Quality

Wood quality might be defined in a number of ways from the practical to the esoteric. It may be defined as the "suitability for its purpose" or merely "the economic value of the wood." Like wood chip quality, wood quality assumes someone is actually monitoring it; i.e., there is no impetus such as financial reward (or even recovery of investment) for increased wood quality if the wood user is not quantifying it.

Many properties contribute to wood quality, and these depend on the end use of the wood. Specific gravity, cellulose content, number of knots, uniformity, and microfibril angle of the S-2 cell wall layer are several important factors. Specific gravity is, in turn, a function of the percentage of latewood and cell diameters and wall thicknesses. These are functions of the species and growing conditions (see Chapter 2, Volume 1 on fibril angle and Chapter 1, Volume 2 on latewood vs. earlywood). It is no coincidence that the two major US structural woods, Douglas fir and southern yellow pine, have thick, dense latewood. There is some contradiction of the desired properties of wood. For various paper types one might want more or less latewood. There are some common qualities that most wood users agree on, however, including a higher level of uniformity. To a degree, wood quality depends on technology. New processes allow some woods to be used in products where they could not be used previously. Also, as technology changes, the ideal requirements of the wood may change.

Wood Variability Within a Tree

Panshin and de Zeeuw (1980) is a useful, general resource for this topic. Fig. 3.15 shows the variation in fiber length for spruce pine as an example of a softwood. It is well known that the average fiber length in trees increases from the pith outward to a nearly constant average fiber length after about 30–50 years growth from the pith. Also, the fiber length in latewood is appreciably higher than in the earlywood of softwoods. Fig. 3.16 demonstrates the variability of fiber length in a hardwood, southern red oak. The same trend (as in softwoods) in average fiber length is shown. With other factors equal (like growth rate), the specific gravity in a tree is variable, decreasing from the center outward in oak (Paul, 1963); other hardwoods have increasing specific gravity from the pith outward. Softwoods generally have increasing specific gravity from the pith outward to the bark. *Chamaecyparis* and *Thuja* are exceptions where the opposite is true.

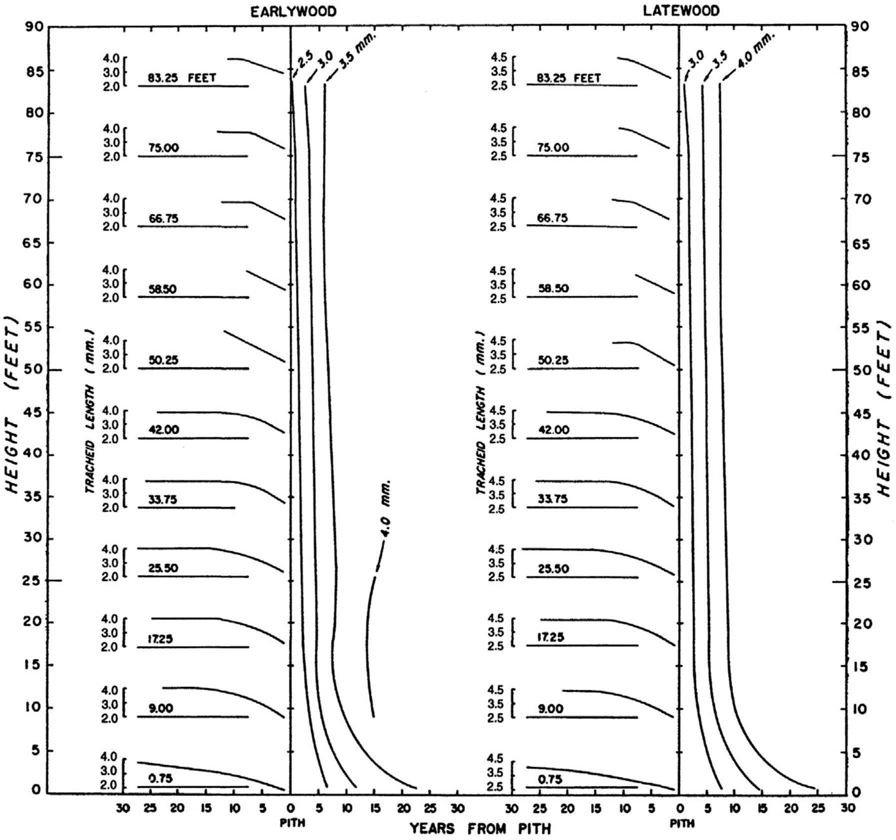


FIGURE 3.15 Fiber length analysis of macerated samples of spruce pine wood. Curves to the right of the pith are tracheid length contour lines. *From Manwiller (1972).*

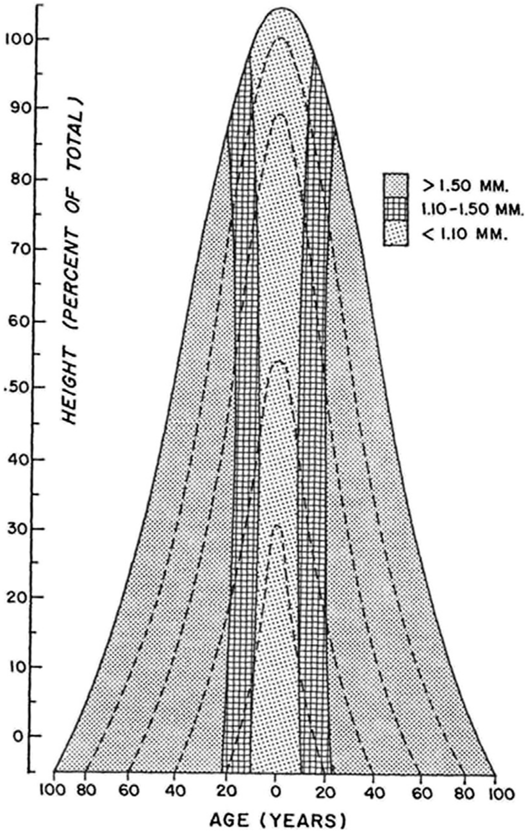


FIGURE 3.16 Variation in fiber length of southern red oak. *Reprinted from Koch (1985).*

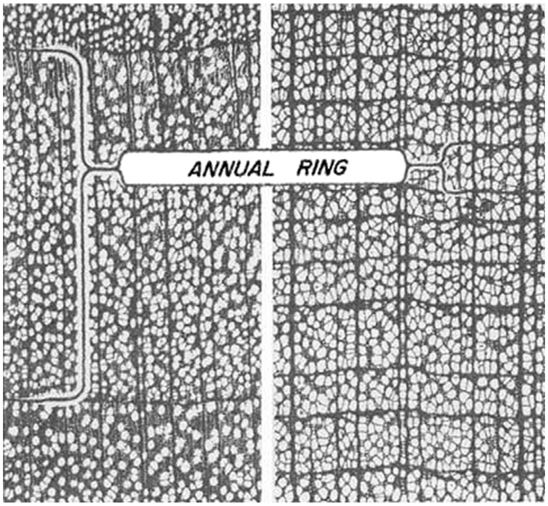


FIGURE 3.17 Fast (left, specific gravity of 0.41) and slow (sp. gr. of 0.31) growing yellow-poplar from a single tree. *Reprinted from Paul (1963).*

Silviculture and Wood Specific Gravity

Latewood is much denser than earlywood in softwoods. As slow-growing softwoods have a higher proportion of latewood, they also have a slightly higher density. However, the percentage of latewood accounts for only about 45%–75% of the variation in wood specific gravity as the specific gravity of both latewood and earlywood is variable. The amount of moisture in the soil and the size of the tree crown are key variables that are inversely related to the percentage of latewood. Other factors such as the age of the growth ring and position within a tree also contribute to the variation. In softwoods, the wood density generally increases from the pith outward and levels off (at the age of 20–50 years) until the tree is very old (100 years old), when it may decrease. Paul (1963) summarized his work of four decades on the application of silviculture to control specific gravity of wood and gave a good review of the topic. Conifers have an ideal growth rate with at least 10 growth rings/in., although 15 is ideal. One worker suggested 12 rings/in. for Douglas fir in Germany. With hardwoods, however, a slow growth rate usually leads to a wood of low density. Fig. 3.17 demonstrates the effect of growth rate on specific gravity of yellow-poplar (diffuse-porous) and Fig. 3.18 for white ash (ring-porous). Contrasted to this, Fig. 3.19 demonstrates where slow growth gives somewhat higher density in softwood. Genetics plays a role in wood quality. Selection of trees for fast growth, high-density wood, and other desirable characteristics improves wood quantity and quality. Tree selection, however, tends to reduce the genetic variability within the species. Large tracts of land are planted with a single species

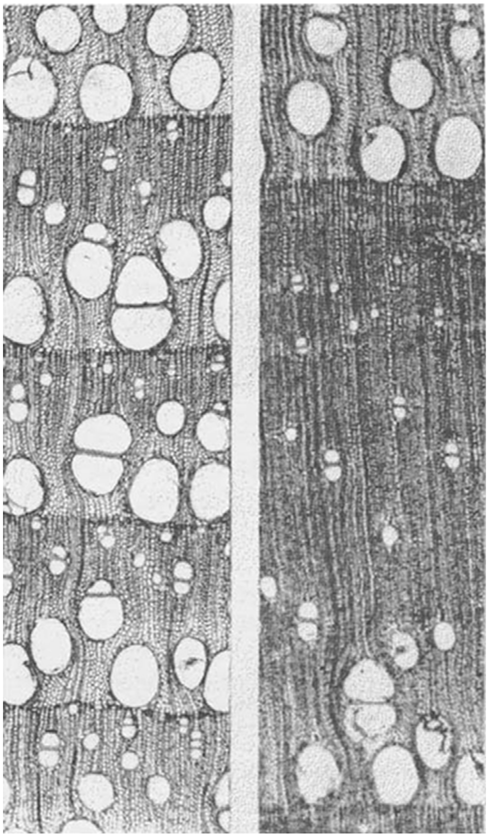


FIGURE 3.18 Slow Geft, (specific gravity of 0.48) and fast (sp. gr. of 0.65) growing white ash from a single tree. *Reprinted from Paul (1963).*

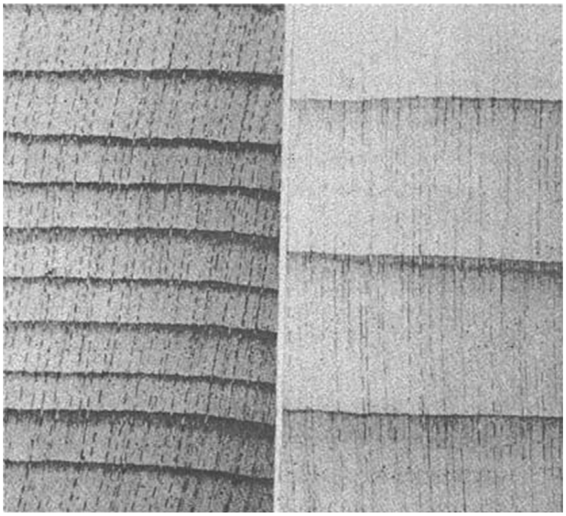


FIGURE 3.19 Old growth (left, 24 rings/in.) and second growth, 12 rings/in. redwood (Paul, 1963).

of the same age in monoculture that is susceptible to massive damage by disease. Many other factors contribute to wood quality. Do the logging operations involve clear cutting of large tracts of land or is the logging limited to thinning and cutting rows? Can the proper selection of fungi from the *Rhizobium* genus in the growth of leguminous plants under various conditions greatly improve their productivity? Should labor-intensive pruning and tree planting be used? How can one predict the economic return, which may not occur for 40 years? Are economic considerations important only for the relatively short term when predictions can be made?

Silviculture and Compression Wood

Proper forestry can minimize compression wood formation in young, second-growth stands under a relatively high degree of management (Pillow and Luxford, 1937). In such even-aged stands, thinnings should be made to remove overtopped trees if they are at an incline, twin trees with two stems from a single stump, and defective or crooked trees. The dominant trees tend to be straighter than suppressed trees, which may grow at an angle trying to obtain light. Other trees should be removed to obtain the proper stocking to give the proper spacing between trees. However, in partially cut stands, wind action and increased vigor may contribute to increased compression wood formation. In partial cuttings made to improve a stand, the formation of compression wood will be decreased if large, irregular openings in the crown canopy are avoided and the action of violent winds thereby reduced.

Wood Use Patterns and Wood Quality

In areas that use residual chips from sawmill operations, one would expect very good wood quality for packaging papers as most of the wood comes from slabs containing wood of the outer growth rings. On the other hand, wood that comes from precommercial thinnings will have a very high percentage of juvenile wood. Usually it costs more to handle small wood than large wood. Questions remain as to the long-term effects of plantation-grown wood of short rotation compared with longer rotations on soil properties.

3.5 ANNOTATED BIBLIOGRAPHY

General Wood Anatomy

Brazier, J.D. and G.L. Franklin, Identification of hardwoods. *Forest Prod, Res, Bull* 46, London, 1961.

Core, H.A., W.A. Cote, and A.C. Day, *Wood Structure and Identification*, 2nd ed., Syracuse University Press, 1979, 138 p. and appendix.
Numerous optical and scanning electron micrographs describe the important features of wood; identification keys are included.

Harrar, E.S. and J.E. Lodewick, Identification and microscopy of woods and wood fibers used in the manufacture of pulp, *The Paper Ind*. February:630–637; ibid., May:103–111; ibid., Aug.:327–335(1934).
A summary of wood and anatomy of fiber for pulp and paper technologists. Coniferous woods are considered in the first article, hardwoods in the second, and fibers in the third.

Hoadley, R.B., *Identifying Wood*, Taunton Press, Newtown, Connecticut, 1990, 223 p.
This book has a high circulation and is of modest cost. It includes many color plates and a long bibliography; it is a practical book on wood identification with a hand lens and includes sources of authentic wood samples, prepared slides, equipment, etc.

Ilic, J., *CSIRO Atlas of Hardwoods*, CSIRO, Australia, 1991.
Text is minimal and photographs are maximal: 69 pages show the cross sections of 1284 species (1.6 by 1.7 in., in color) organized by family and genus at 6.5×; 402 pages show microscopic images of the three (A:, r, *t*) sections (25×), and vessel-ray pitting (l00×).

Jane, F.W., *The Structure of Wood*, A. and C. Black, Ltd., London, 1956, 427 p. (2nd ed., 1970).
This resource has a more detailed discussion of many aspects of wood anatomy than other references. It is global in perspective.

Koehler, A., Guidebook for the identification of woods used for ties and timbers, USD A Forest Service, Misc. RL-1, 1917, 79 p.
31 plates showing 62 cross sections at 15×. Numerous maps are included showing the distribution of many species. The photographs were made by passing light through thin specimens, which gives better detail than photographing the cross sections of large pieces.

Panshin, A.J., and C. de Zeeuw, *Textbook of Wood Technology*, 4th ed., McGraw-Hill Book Company, New York, N.Y., 1980, 722 p.
"Structure, identification, uses, and properties for the commercial woods of the U. S. and Canada" with many micrographs and descriptions by wood species. Keys for identification are included for hardwoods and softwoods. The 4th ed. has minor changes over the 1970 3rd ed. (705 p.) This work goes back before the 1st ed. of 1949 to the 1934 *work Identification of Commercial Timbers of the United States* of H.P. Brown and A.J. Panshin. [*Commercial timbers of the United States* was published in 1940 by the same authors and has key references on wood identification that are omitted in the later editions, which is the origin of much of the material; the quality of photographs in the 1940 ed. with coated paper is higher than the 1980 and 1970 eds. on uncoated paper.]

Phillips, E.W.J., Identification of softwoods by their microscopic structure. *For. Prod. Res. Bull.* 22:1—56(1948), London.

Staining of Wood

Kutscha, N.P. and LB. Sachs, Color tests for differentiating heartwood and sapwood in certain softwood species, USD A FPL Rep. No. 2246, 1962, 13 p. Includes 21 solutions for 23 species.

Parham, R.A., *Tappi* 65(4): 122(1982).

It is very useful to determine the hardwood fraction of chips in chip mixtures using a reaction which specifically stains hardwoods. A very useful, well-known reaction is the Maule reaction. Chips in a plastic mesh (for ease of transfer) are treated at room temperature in a fume hood with 1% KMn04 for 10 min, brief rinse, 6 *N* HCl for 1 min, brief rinse, 10% NH3 for 1 min. The chips are dried in the hood. The weight of the red (hardwood) portion as a percentage of the total is determined.

Plant Microtechnique

Johansen, D.A., *Plant Microtechnique*, McGraw-Hill, New York, 1940, 523 p.

Sass, J.E., *Elements of Botanical Microtechnique*, McGraw-Hill, New York, 1940, 222 p. The 3rd edition of this book appeared in 1958. The book was rewritten by G.P. Berlyn and J.P. Miksche as *Botanical Microtechnique and Cytochemistry* and published by the Iowa State University Press (Ames, Iowa) in 1976.

Fiber and Wood Microscopy

Carpenter, C.H., et al, *Papermaking Fibers*, Tech. Pub, 74, State University College of Forestry, Syracuse, New York, 1963.

This is a photomicrographic atlas of woody and other fibers with 77 plates. Entire isolated fibers of numerous species are featured. It is an update of the 1952 work; the original version of 1932 is the *Atlas of Papermaking Fibers* by C. H. Carpenter with 56 plates.

Graff, J.H., *A Color Atlas for Fiber Identification*, Inst. Paper Chem., Appleton, Wise, 1940, 27 p. 4- V color plates.

Three classes of stains are described; the five color plates are used to compare the results of the tests.

Isenberg, I.H., *Pulp and Paper Microscopy*, 3rd ed., Inst. Paper Chem., Appleton, Wise, 1967, 395 p.

This work is an expansion of Graff (1949) above with much detail, but without color plates. It includes a foundation in optics and microscopy, fiber dimension measurements by microscopy, descriptive fiber morphologies of wood and nonwood plant fibers, animal fibers, and mineral fibers with numerous pictures of actual fibers, and discussions on numerous color stains useful for fiber characterizations. The color stains can often be used directly on paper to characterize its properties. This is a comb-bound notebook.

Parham, R.A. and R.L. Gray, *The Practical Identification of Wood Pulp Fibers*, TAPPI Press 1982, 1990, 212 p.

This comb-bound book has very high quality paper that helps reproduce the photographs. This work is very useful for wood fiber identification. Optical microscopy and SEM photos are included with each species. There are no keys, and the format is much like an atlas, although there is moderate text included. Numerous fibers from each species indicate the variability of the fiber morphology.

Strelis, I. and R.W. Kennedy, *Identification of North American Commercial Pulpwoods and Pulp Fibres*, University of Toronto Press, 1967, 117 p.

This work is especially useful for fiber analysis; photomicrographs of animal, mineral, and wood and nonwoody vegetable fibers are included. Techniques for fiber identification by solubility analysis and staining are included. (Of course, FT-IR analysis of individual fibers as a useful tool for fiber analysis was not commonly available at the time of this work.)

Tappi Standard T 401 om-82, Fiber analysis of paper and paperboard, 14 p., 32 references.

This standard discusses fiber morphology and many staining techniques for quantitative analysis of fiber types.

Tappi Standard T 263 om-82, Identification of wood and fibers from conifers, 13 p., 3 references.

It is a reprint of B.F, Kukachka's article in *Tappi* 43(11):887—896(1960) with some added information; *Araucaria—Agathis* is listed as having spirals (should be pits 2—4 alternate).

Reaction Wood

Perem, E., Tension wood in Canadian hardwoods. Can. Dept. of For. Pub. No. 1057, 1964, 38 p.

Pillow, M.Y and R.F. Luxford, Structure, occurrence, and properties of compression wood, USD A Tech. Bull. No. 546, 1937, 32 p.

Silviculture and Wood Quality

Anon., *Wood Quality, Proceeding of three symposia*, Dept. of Lands and Forests Res. Rep. No. 46, Ontario Research Foundation Rep. No. 601, 1962. Published in *Pulp Paper Mag. Can*, (2nd symp. in Aug., 1960 Woodland's Section, but in the nontechnical pages omitted in many libraries) and *Timber Mag. Can*. (3rd symp., issue unknown).

Kellison, R.C. and R.G. Hitchings, Harvesting more southern pines will require pulp mill changes, *Pulp & Paper* 59(7):53—56 (1985).

This article summarizes problems associated with using young trees as an increasing percentage of raw material.

Paul, B.H., The application of silviculture in controlling the specific gravity of wood, USDA Tech. Bull. No. 1288, 1963, 97 p.

This is a superb reference on the topic; it was first published in 1930 as No. 168.

Bark Anatomy

Chang, Y.-P., *Bark Structure of North American Conifers*, USDA Tech. Bull. No. 1095, 1954, 86 p.

Keys are included to identify the origin of bark samples.

Chang, Y.-P., *Anatomy of Common North American Pulpwood Barks*, Tappi Monograph Series 14, 1954, 249 p.

Pulpwoods

Isenberg, I.H., Ed. (revised by Harder, M.L., and L. Louden), *Pulpwoods of the United States and Canada*, 3rd edition. Institute of Paper Chemistry, Appleton, Wisconsin, 1981.

This two-volume set (Volume 1, conifers; Volume 2, hardwoods) lists tree species, their silvics, wood properties, and general pulping characteristics with references. It includes the commercial species of North America.

Statistical Information on Wood Industry

F. A.O., World Forest Inventory 1963, Rome, 1966.

FAO, Yearbook, Rome, 1992. Forest Products 1990.

U.S. Bureau of the Census, Statistical Abstract of the United States, 111th ed., 1991, Washington, D.C., $28, pp 675—683 for wood products industry.

Forest products statistics.

FAO Yearbook of Forest Products 2015

Miscellaneous

Bamber, R.K. and J. Burley, *The properties of radiata pine*. Commonwealth Agric. Bureaux, England, 1983, 84 p.; large bibliography.

Chattaway, M.M., The development of tyloses and secretion of gum in the heartwood formation, *Aust. J. Sci. Res. B. I'.lll-* 240(1949).

Howard, E.T. and E.G. Manwiller, Anatomical characteristics of southern pine stemwood. *Wood Sci.* 2(2):77–86(1969).

Koch, P., *Utilization of Hardwoods Growing on Southern Pine Sites*, USDA Agric. Handbook No. 605, 1985.

Kukachka, B.F., Properties of imported tropical woods, USDA Eor. Ser. Res. Paper FPL 125, March, 1970, 67 p.

EXERCISES

1. Write a one-page essay discussing some of the major differences between softwood and hardwood anatomy.
2. Would you say compression wood generally has advantages in pulping and papermaking (compared with normal wood)?
3. Describe how softwood of the same species could vary drastically in two different plantations
4. Which are more prevalent globally: hardwoods or softwoods?

CHAPTER

4

Softwood Anatomy

4.1 GROSS ANATOMY OF SOFTWOODS

Introduction

The references for this chapter are found in Chapter 3.

This chapter presents the detailed anatomy of the wood of temperate softwoods. The anatomy of various woods is important for several reasons. The characteristics of papermaking fibers depend much on their anatomy. The pulping characteristics of various fiber sources are dependent on their species and growing conditions. Some species are lumped together as an indistinguishable lumber commodity but may have greatly differing pulping and papermaking characteristics. For example, southern pine is really four different species of pine. For these reasons it is important to be able to verify the species types of wood chips or even pulp mixtures. One may wish to examine the alterations of individual fibers by processes such as refining. Identification of trees in forests allows the use of flora, bark, twigs, and other features; this topic is not discussed here.

The gross description and uses of many of the wood species contain information from the USDA *Wood Handbook* (Ag. Handbook No. 52, 1935, 1955, 1974, 1987) with minor alterations. Some of the hardwoods contain anatomy information from Koch (1985) with minor alterations. Ag. Handbook No. 101 (1956) was of some use, and Koehler (1917) was used extensively. These resources are in the public domain. Some details have been added from the references listed in Chapter 3 (Vol. 1). The wood uses are somewhat dated as plastics, and other materials have replaced some of the uses; nevertheless, the listed uses say much about the wood properties in manufacturing and use. Other photographs and information are from OSU forest product courses courtesy of Drs. R.L. Krahmer and A.T. Van Vliet.

Softwoods are distinguished from hardwoods by the absence of vessels. The characteristic features of softwoods that are visible with a hand lens will be demonstrated. In the next section, microscopic features of softwood will be considered. Then, in the section after that, the anatomy of many individual softwood species is given.

Resin Canals

The most pronounced feature of softwoods is resin canals (shown using microscope in Fig. 4.1) in those species which have them. Resin canals are not formed by cells but are voids surrounded by epithelium cells. (In contrast, hardwood vessels are made up of individual cells.) Tyloses

https://doi.org/10.1016/B978-0-12-814240-0.00004-5

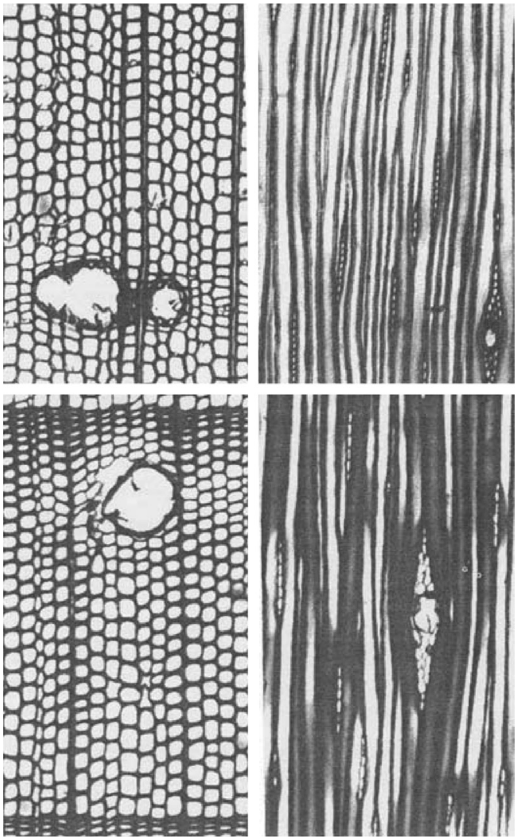


FIGURE 4.1 Longitudinal (top left) and radial (top right) resin canals from *Picea sitchensis* with thick-walled epithelium and from *Pinus strobus* (bottom) with thin-walled epithelium.

may occasionally form in the resin canals of heartwood. The pines, spruces, larches, and Douglas fir genera of Pinaceae contain normal resin canals in the longitudinal and radial directions. The radial canals are part *of fusiform* rays and are smaller than longitudinal resin canals. The resin canals in pines are particularly large and numerous and occur throughout the growth ring. In the other three genera, they are small, less numerous, appear to be missing from some growth rings, and may be grouped in small, tangential rows. Brown and Panshin (1940) give northern white pine longitudinal resin canals as 135–150 μm average diameter but as high as 200 μm; radial canals average 80 μm in diameter. They may be difficult to find in eastern spruce samples (Hoadley, 1990).

The large resin canals of pines appear as short dark lines on the longitudinal surfaces (*r*, *t*) because of the pitch or dirt trapped by the pitch. Epithelium cells, which secrete resin, surround both the longitudinal and ray resin canals. In pines, they are thin walled and easily torn away when freehand sectioning (or even often when microtoming an embedded sample as in Fig. 4.1). In the other three genera, they are thick walled and usually remain intact with freehand sectioning. True firs, hemlocks, and cedars may form *traumatic resin canals* in response to injury in the tree. These small resin canals occur in relatively long rows in the tangential direction when the wood cross section is viewed but do not occur enough to cause difficulty in wood identification. These genera only have traumatic longitudinal resin canals; radial resin canals (fusiform rays) are always absent. North American hardwoods normally lack resin canals but can form traumatic resin canals as well.

Earlywood—Latewood Transition

Another easily observed trait is the transition between the earlywood and latewood. It is characterized as abrupt or gradual (shown through a microscope in Fig. 4.2). For example, in the soft pines it is gradual but in the hard pines it is abrupt. Engelmann spruce has a more abrupt transition than the other domestic spruces.

Color

Sapwood always has a relatively light color from near white to tan or yellow. The heartwood of some species may be light or dark or of distinctive color. Redwood heartwood is a distinctive brown-red color. Junipers have a deep purple-red heartwood. Douglas fir usually has a bright reddish hue. A reference collection for color comparison is very useful.

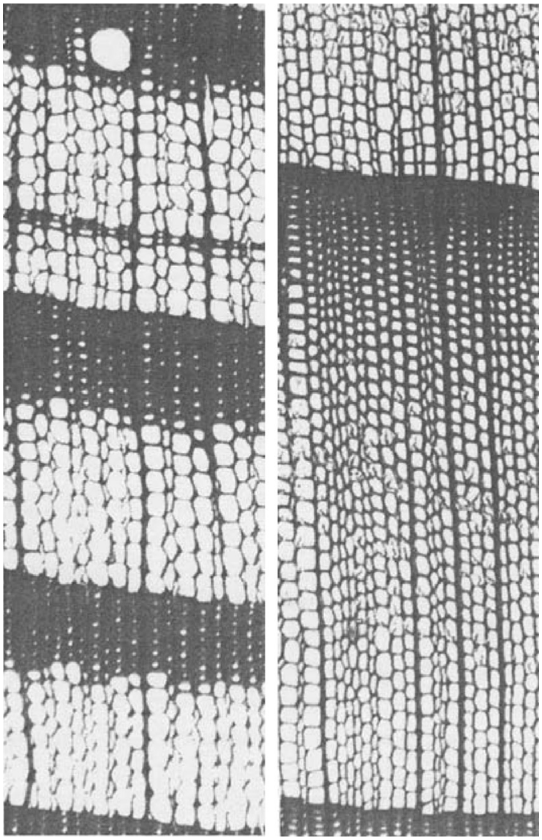


FIGURE 4.2 Abrupt transition between earlywood and latewood of *Larix occidentalis* (left) and gradual transition of *Abies concolor*.

Odor

Odor is particularly useful in green wood of freshly cut surfaces. One must learn odors on known samples of the wood; do not try to recognize them by their descriptions. Kiln-dried wood will not exhibit as strong an odor as green wood. The pine genera all share a characteristic odor. Cedars, *Thuja plicata* and *Libocedrus decurrens*, have aromatic smells that may be accented by moisture and/or mild heat. Douglas fir also has a unique odor.

Dimpled Surfaces

Some species have a dimpled grain [lodgepole (pronounced) and ponderosa pines and Sitka spruce] on the tangential surface (*t*) that is distinctive; this is caused by crystals in the bark that press against the cambium, which deforms it. The growth rings reflect this by being uneven when viewed with magnification.

Greasy Feel, etc. (Hoadley, 1990)

Taxodium species have a greasy or tacky feel, whereas redwood feels dry. Tamarack feels waxy (less greasy than bald cypress). Figure in wood, the appearance of the tangential surface (such as on flat-sawn wood), is not overly relevant to pulp and paper although it can be used in wood identification. Figure is most pronounced on woods with an abrupt latewood transition, such as with Douglas fir and southern pines, or ring-porous hardwoods such as oak and hickory. Special figures also occur by grain deviations such as at the crotch of trunk splits and at burls (outgrowths of the trunk), especially with hardwoods. Spruces are separated from white pines or firs by their glossy (having luster) longitudinal surfaces. The volatile material of Jeffrey pine contains a high percentage of n-heptane, whereas that of ponderosa pine is high in pinenes. For some mixtures of species, machines are being developed to sort logs or boards by, more or less, smelling each one. This technique is similar to that used at airports to detect plastic explosives in luggage. There is some literature on *chemotaxonomy*, taxonomy based on the chemical components of wood and other tissues.

Hand Lens Key for Softwoods

Table 4.1 is a dichotomous hand lens key designed for major US commercial softwoods

TABLE 4.1 Dichotomous Hand Lens Key of Major US Commercial Softwoods

1. Wood with normal resin ducts	2
1. Wood without normal resin canals	8
2. Resin ducts numerous, evenly distributed in outer portion of every ring; generally visible to naked eye, easily seen with hand lens; resinous odor	3
2. Resin ducts sparse, unevenly distributed and sometimes absent in some rings; occasionally appear as too many in a tangential row, barely visible to the naked eye as light or dark flecks	5
3. Transition from earlywood to latewood gradual; wood soft, light, quite even in density; coarse to medium textured *Pinus lambertiana*, *Pinus montícola*	
3. Transition from earlywood to latewood abrupt; wood medium hard to hard	4
4. Wood medium hard; resin canals confined mostly to outer (latewood) portions of growth rings *Pinus ponderosa*, *Pinus contorta*	
4. Wood often heavy and hard to cut; resin ducts distributed throughout center and outer portions of growth rings *Pinus* spp.	
5. Transition from earlywood to latewood gradual	6
5. Transition from earlywood to latewood abrupt	7
6. Wood light pinkish yellow to pale brown, often somewhat lustrous *Picea sitchensis*	
6. Wood yellowish to orange red; characteristic odor *Pseudotsuga menziesii*	
7. Wood yellowish to orange red or deep red, not oily, characteristic odor on fresh cut surface; rings often wavy in slow growth; resin canals often in tangential lines of 2—3 *Pseudotsuga menziesii*	
7. Wood brownish cast, somewhat oily appearance; no characteristic odor; in slow growth, ring contours generally smooth; resin canals in groups of 2—5 but not in tangential lines *Larix occidentalis*	
8. Wood without distinct odor	9
8. Wood with distinct odor	12
9. Wood medium to coarse textured	10
9. Wood fine textured, dense, fairly heavy; heartwood light orange to rose red *Taxus brevifolia*	
10. Wood whitish to pale brown sometimes with purplish tinge; gradual transition from earlywood to latewood; medium textured *Tsuga heterophylla*, *Abies* spp.	

TABLE 4.1 Dichotomous Hand Lens Key of Major US Commercial Softwoods—cont'd

10. Wood red to deep reddish brown or yellowish to dark reddish brown to almost black; coarse textured; abrupt transition	
11. Wood light cherry red to deep reddish brown; light to moderately lightweight; usually uniform rate of growth *Sequoia sempervirens*	
11. Wood variable in color, yellowish to light or dark brown, reddish brown to almost black; wood often greasy or oily; cuts like hard rubber with knife; usually irregular rate of growth and discontinuous growth rings *Taxodium distichum*	
12. Wood with fragrant, "cedar-like" or sweetish odor	13
12. Wood with ill-scented or with rancid odor	17
13. Wood reddish brown to dull brown	14
13. Wood yellowish white to pale yellowish brown	16
14. Wood dull reddish to pinkish brown, often with streaks of included sapwood; fine textured, moderately hard and heavy; characteristic mild spicy odor *Juniperus occidentalis*	
14. Wood reddish brown to dull brown; medium to coarse textured	15
15. Wood sometimes with lavender tinge; frequently with pecky rot; texture within growth rings even, cuts smoothly across growth rings; distinct odor like pencils; and with distinct acrid taste *Libocedrus decurrens*	
15. Texture with growth rings uneven, cuts brashly across growth rings because latewood considerably harder than earlywood; never with pecky rot; sweet "cedar" odor *Thuja plicata*	
16. Wood yellowish white to pale yellowish brown; distinct pungent, gingerlike odor; medium to coarse textured *Chamaecyparis lawsoniana*	
16. Wood bright, clear yellow, darkens on exposure; odor resembles raw potatoes; fine to medium texture *Chamaecyparis nootkatensis*	
17. Wood yellowish white to pale brown; uniform rate of growth *Chamaecyparis lawsoniana*	
17. Wood variable in color, yellowish to light or dark brown, reddish brown to almost black; irregular rate of growth *Taxodium distichum*	

of the western United States. It is presented courtesy of R.L. Krahmer and A.C. Van Vliet. Each number is a step where one must decide between a pair of mutually exclusive choices. The format is typical of many keys used to identify species of wood. Microscopic examination of wood is often needed for conclusive identification of most woods.

4.2 MICROSCOPIC ANATOMY OF SOFTWOODS

Rays

Most softwood rays are uniseriate (1 cell wide) unless they contain resin canals; fusiform rays, when present, constitute about 5% of the rays. A few species (redwood, incense cedar) are biseriate for at least a portion of the ray, but many species can be sporadically biseriate. The height of the ray (number of cells) is a useful tool for softwood identification. Cedars tend to have low rays (Port Orford cedar and eastern red cedar are generally 6 or less high), whereas the true firs and bald cypress tend to have high rays (25 to over 40 high and occasionally almost 1 mm high).

Ray Tracheids

Ray tracheids (Fig. 4.3) are easily found in many species, especially the hard pines. In other species they are found only with great difficulty and should be counted as absent. Ray tracheids are differentiated from ray parenchyma by their small bordered pits in the cross field. In larches and hemlocks they occur at the upper and lower margins and are called *marginal ray tracheids*. In pines they occur marginally and throughout the height of the ray. In coniferous species, rays containing both tracheids and parenchyma are termed heterocellular, whereas rays with only one type of cell are termed homocellular. Alaska yellow cedar is unique in that it has homocellular rays composed of either parenchyma or tracheids and very few heterocellular rays. The low rays of hard pines are often homocellular with tracheids.

Ray tracheids may be *dentate* when toothlike projections on the horizontal walls are present. In the spruces these are small and observed in the latewood. Hard and red pines have dentate ray tracheids, whereas soft pines have nondentate ray tracheids. These are depicted in Fig. 4.3.

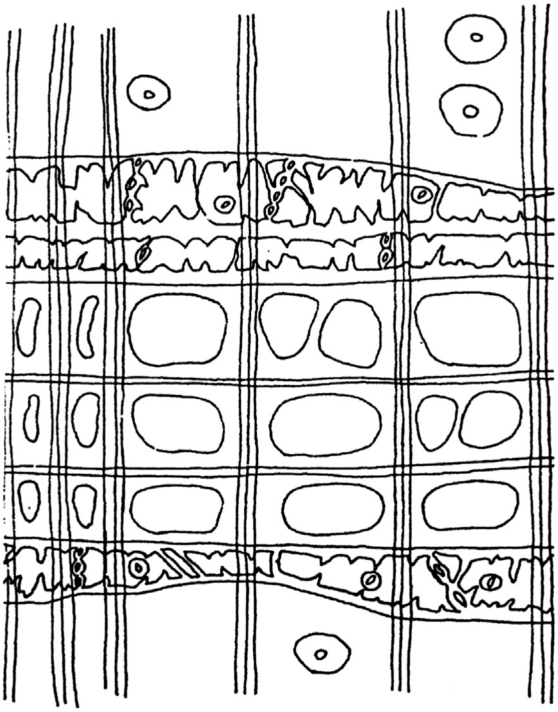


FIGURE 4.3 Sketch of *Pinus resinosa* (*r*) showing two rows of dentate ray tracheids on the upper margin of a wood ray and one on the lower margin. The three layers of ray parenchyma show 1–2 simple cross-field pitting. *From Kukachka (1960).*

Ray parenchyma end walls may be smooth (e.g., *Thuja*) or nodular with beadlike projections (e.g., *Abies*). In some species the corners of the ray parenchyma are observed to have pitlike depressions, called *indentures*, where the vertical and horizontal walls meet. These features are depicted in Fig. 4.4.

Ray Cross-Field Pits

Cross-field pits occur between ray parenchyma and longitudinal tracheids. Phillips (1948) described five types of cross-field pits that are of importance in identification of softwoods. Use cross fields of the first few earlywood tracheids (if possible) of a growth ring, as those of the latewood tracheids vary in

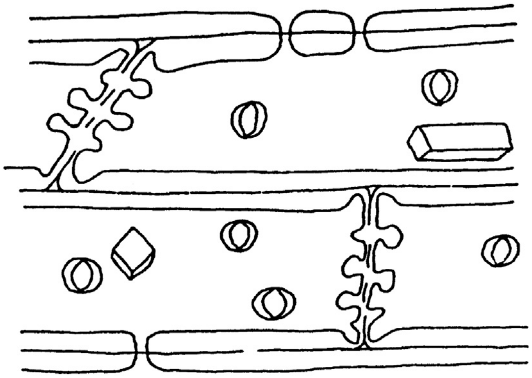


FIGURE 4.4 Sketch of *Abies magnifica* (*r*) showing nodular end walls and indentures. Two crystals also appear. *From Kukachka (1960).*

structure. Fenestriform and pinoid pittings are easy to distinguish; the latter generally occur with dentate ray tracheids although red pine has dentate ray tracheids with fenestriform pitting. Piceoid, cupressoid, and taxodioid (especially the latter two) are difficult to discern because there is overlap between these types. Hoadley, page 26, and Jane, page 95, have excellent diagrams of these. Fig. 4.5 shows diagrams of these pits.

Fenestriform pits are large, borderless, rectangular "window-like" pits with usually 1–2 pits per cross field (Fig. 4.6). Most other types have 2–6 pits per cross field. These distinctive pits are characteristic of the soft (white, scotch, etc.) and red pines. Sugar pine has 2–4 fenestriform pits per cross field.

Pinoid pittings are elliptical to irregular polygons in shape (Fig. 4.7). They vary in size. The borders may or may not be visible around the apertures. When they are visible they are narrow and usually wider on one side than the other. These are characteristic of the hard pines (except

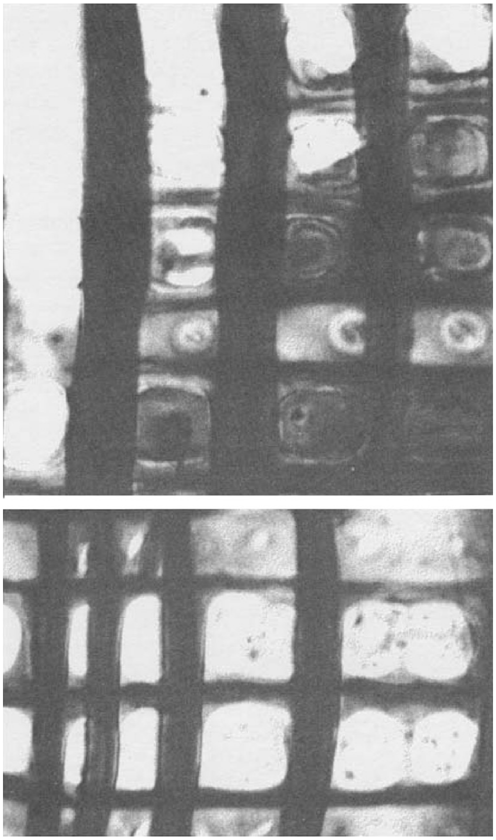


FIGURE 4.6 Fenestriform pitting in *Pinus strobus* (top, with a row of interspersed ray tracheids) and *Pinus monticola* (bottom), approximately 600×.

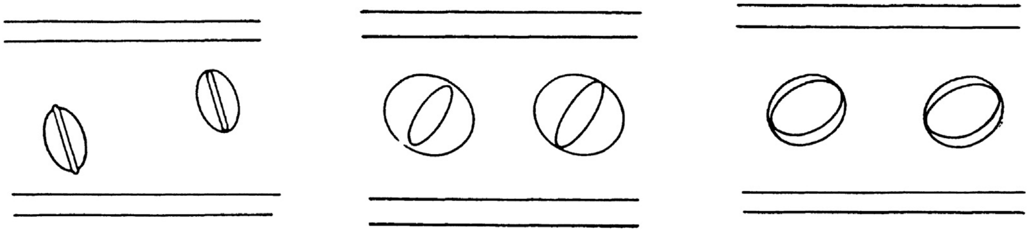


FIGURE 4.5 Cross-field pitting: piceoid (left), cupressoid (center), and taxodioid (right).

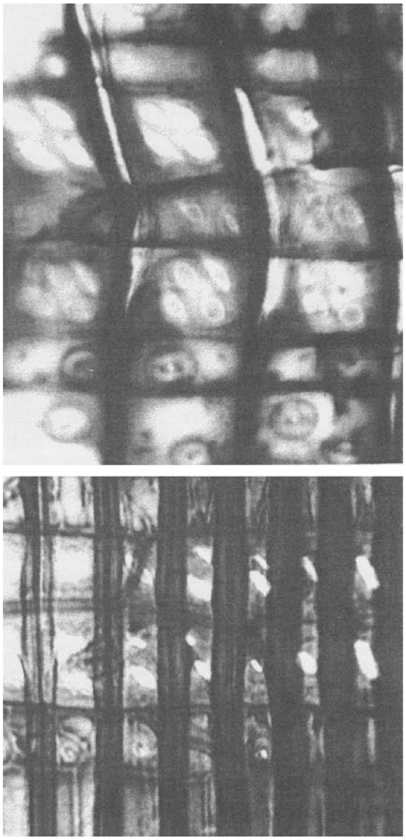


FIGURE 4.7 Pinoid pitting in *Pinus banksiana* (top, with shallowly dentate ray tracheid) and *Pinus ponderosa* (bottom, prominently dentate ray tracheids), approximately 600×.

red pine) and occur in species with dentate ray tracheids.

Piceoid pittings have slit-like apertures that may extend beyond the visible border (Fig. 4.8). The width of the aperture is less than that of the aperture to the border. They occur in spruce, larch, and Douglas fir.

Cupressoid pittings are similar to piceoid, but the apertures are contained within the boundaries of the border, and their width is slightly less than that of the border on either side (Fig. 4.9). They occur in most of the genera of Cupressaceae (except in *Thuja*) and in *Tsuga*.

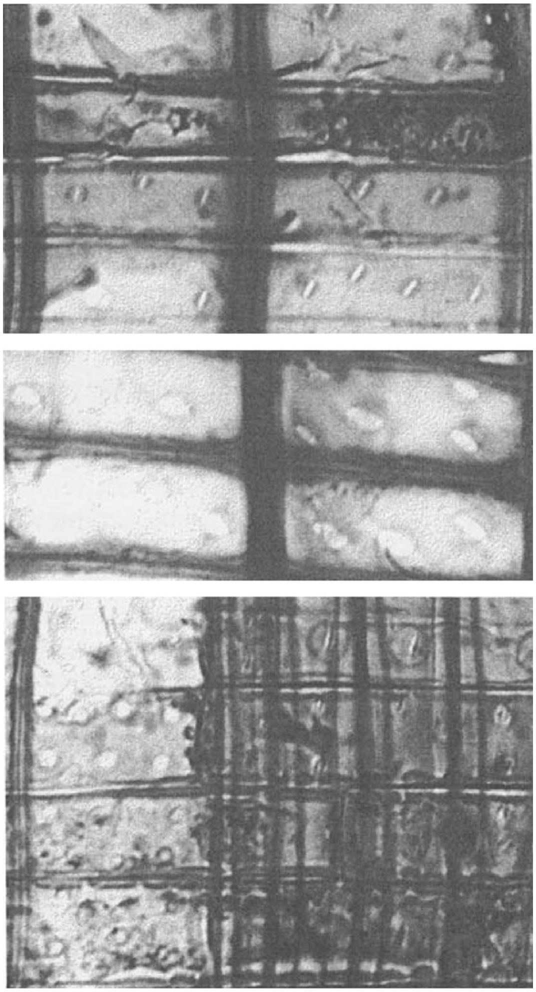


FIGURE 4.8 Piceoid pitting in *Picea sitchensis* (top, note nodular end wall), *Larix occidentalism* (center), and *Pseudotsuga menziesii* (bottom, note indentures), approximately 600×.

Taxodioid pits have a regular elliptical shape with apertures that are larger than those of the previous two types (Fig. 4.10). The aperture is wider than the border on either side of the aperture. They occur in *Sequoia, Taxodium, Thuja*, and *Abies* genera.

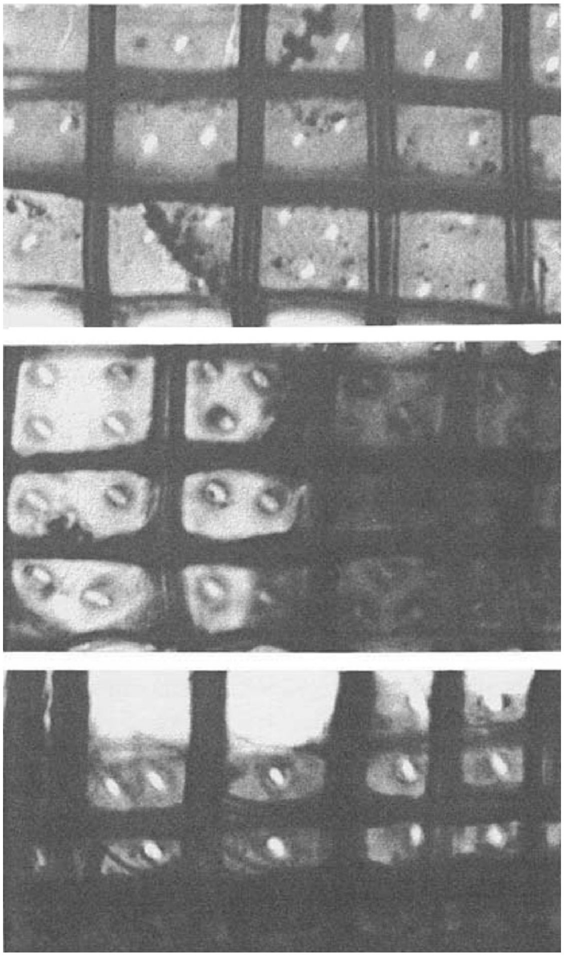


FIGURE 4.9 Cupressoid pitting in *Libocedrus decurrens* (top, see nodular end walls), *Juniperus virginiana* (center), and *Taxus brevifolia* (bottom), approximately 600×.

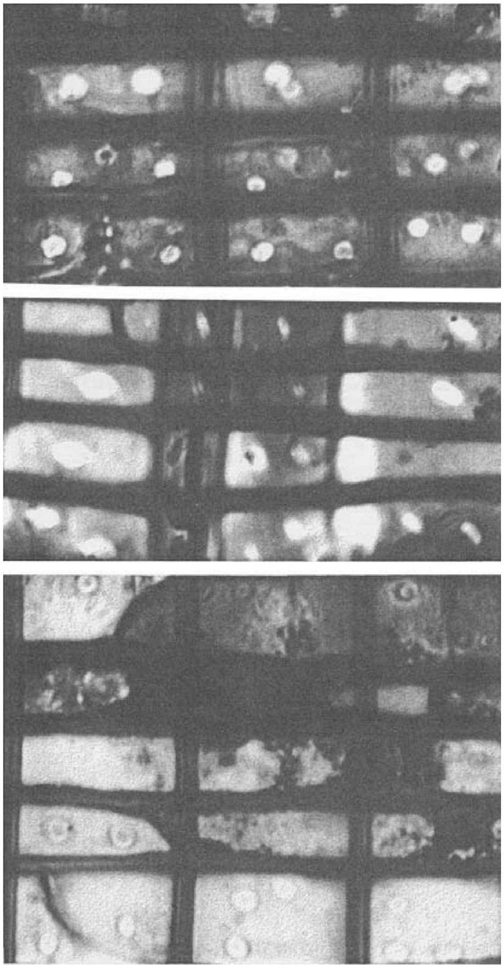


FIGURE 4.10 Taxodioid pitting in *Abies concolor* (top, note crystals in marginal parenchyma), *Sequoia sempervirens* (center), and *Thuja plicada* (bottom), approximately 600×.

Number of Intertracheid Pits Across the Fiber

The intertracheid, bordered pitting of tracheid pits (r) is usually uniseriate (generally only one pit across the width of the tracheid although two may occur where tracheids overlap). Sugar pine may have four consecutive pit pairs in the first few fibers of the earlywood. In some species there are two or more columns of pits that may be alternate or opposite. Opposite multiseriate pitting occurs in *Sequoia* and *Taxodium* (Fig. 4.11). Alternate multiseriate pitting is characteristic of only *Araucaria* and *Agathis* among all conifers. Intertracheid pitting is usually confined to the radial surface although its presence on the tangential surface in the latewood is common. The lack of intertracheid pitting on the radial walls of the latewood of southern pines is used to distinguish them from the soft pines. In

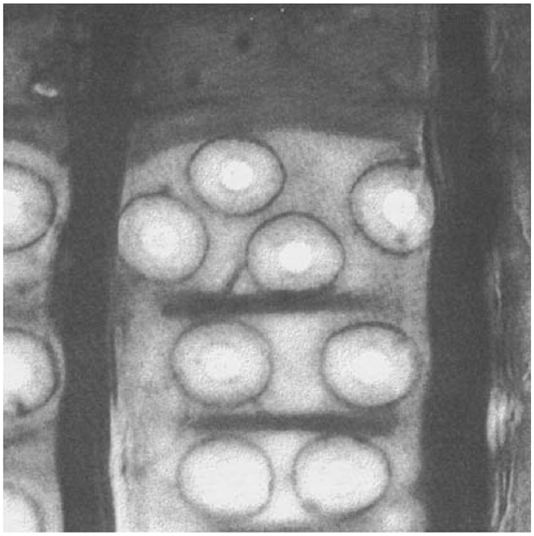


FIGURE 4.11 Opposite, paired border pits of *Taxodium distichum* with crassulae, approximately 600×.

coniferous species, *crassulae*, thickenings in the shape of an arc around the pit, as observed in the radial section, are common.

Spiral Thickening of Tracheids (Fig. 4.12)

Spiral thickening of tracheids occurs in only a few species (Douglas fir, Pacific yew, and the relatively rare *Torreya*), so this is an important characteristic if present. Douglas fir may not have spiral thickening in the latewood tracheids. Spiral thickening occasionally occurs in the latewood tracheids of southern pines (loblolly) and *larix*, but these species may also have seasoning checks. Spiral thickening occurs at a smaller angle to the longitudinal axis (steeper spirals) in fibers with thin lumens as in the latewood. Compression wood leads to seasoning checks parallel to the S2 microfibril angle (Fig. 3.12, Vol. 1). Checks usually form an angle <45 degrees with the longitudinal axis, whereas spiral thickening usually forms an angle >45 degrees.

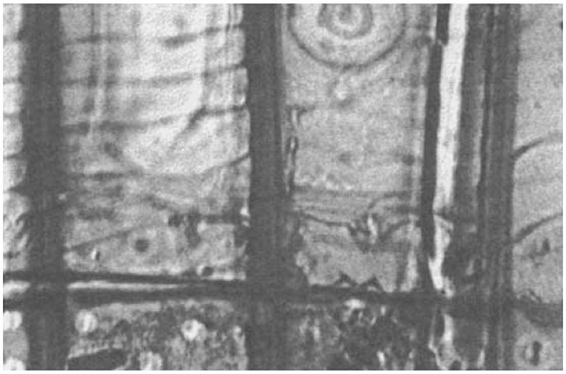


FIGURE 4.12 Spiral thickening in Douglas fir tracheids, approximately 600×.

Tracheid Diameter

Diameters of tracheids can be used to separate some species from each other. Redwood is very coarse, whereas eastern red cedar has a very fine texture; compare Figs. 4.44 and 4.52.

Longitudinal Parenchyma

Strand (axial or vertical) parenchyma is never as abundant in the softwoods as in some of the hardwoods. They are moderately abundant throughout the growth ring in the families Taxodiaceae and Cupressaceae and other genera. These are *diffuse* parenchyma when the strands occur singularly as in redwood (Fig. 4.13) or bald cypress. When strands are grouped, they are *zonate parenchyma*, which may be *banded* (the old term is metatracheal, as in eastern red cedar or incense cedar) or in *clusters* as in the hardwoods. In the coarse-textured species, redwood and bald cypress, they can be barely seen with a hand lens as streaks on the radial and tangential surfaces because of their extractives. Strand parenchyma at the boundaries of the growth rings (*marginal* or *terminal* parenchyma) occurs in *Abies* and *Tsuga*. In the heartwood, these cells are often filled with extractives. Longitudinal parenchyma is lacking in *Pinus* and

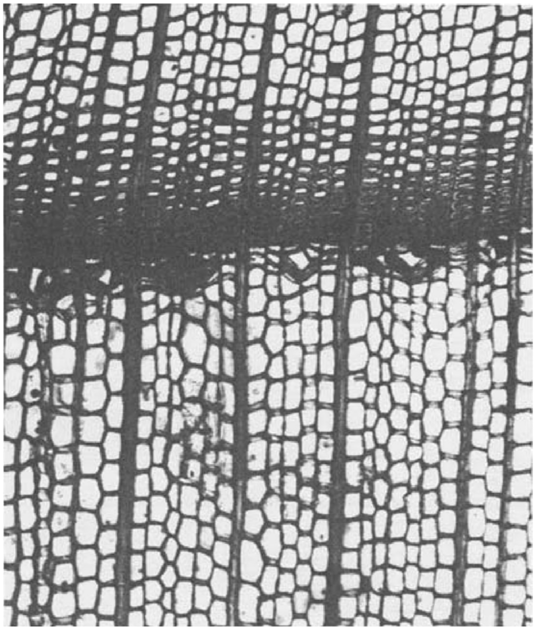


FIGURE 4.13 Diffuse strand parenchyma of *Sequoia sempervirens* shows up as dark squares because of the pitch contents. Resin crystals are also present at the margin of the growth ring.

Taxus. They occur in the root wood of *Picea* but not in the wood above ground. The end walls of longitudinal parenchyma of softwoods are usually *nodular*, but they are inconspicuous in redwood and absent (smooth walls) in southern pines and Atlantic white cedar and help identify these species.

Intercellular Spaces

Eastern red cedar has intercellular spaces between the tracheids where they meet at the corners. This feature must not be confused with compression wood where the same effect is noted. The pronounced roundness and spiral checks of compression wood cells help distinguish this from normal intercellular spaces of eastern red cedar.

4.3 ANATOMY OF SOFTWOOD SPECIES

Table 4.2 helps separate softwoods by genera. Table 4.3 gives a summary of softwood features useful in their identification. Table 4.4 gives properties of tracheids. The *uses* section includes the properties related to the uses of wood. The mechanical properties are of relevance to wood chipping. The *color* section includes the

TABLE 4.2 Separation of Softwoods Into Genera by Microscopic Features

1. Axial resin canals normally present	2
1. Axial resin canals absent, unless traumatic type in tangential rows or groups	5
2. Epithelial cells of resin canals are thin walled; ray tracheitis present *Pinus*	
2. Epithelial cells of resin canals are thick walled	3
3. Tracheids with helical thickenings, especially in earlywood; ray tracheids present *Pseudotsuga*	
3. Tracheids rarely with helical thickenings	4
4. Abrupt transition between earlywood and latewood; ray tracheid walls of latewood rarely with minute denticulations *Larix*	
4. Gradual transition between earlywood and latewood; ray tracheids of latewood with minute denticulations *Picea*	
5. Axial parenchyma present and conspicuous; end walls of ray cells not conspicuously pitted *Sequoia*	
5. Axial parenchyma absent or sparse	6
6. End walls of ray parenchyma conspicuously pitted, i.e., nodular end walls *Abies*	
6. End walls of ray parenchyma are not conspicuously pitted *Thuja*	

TABLE 4.3 Anatomical Characteristics of Coniferous Woods Useful in Their Identification

Common name	Baldcypress	Cedar, (not true)	Incense-	Alaska-	Atlantic white-	Port-Orford-	Eastern redcedar	Western redcedar	Northern whitecedar	Douglas-fir, coastal	Fir	Balsam	California red	Grand	Noble	Pacific silver	Subalpine	White	Hemlock	Eastern	Western	Larch	Tamarack	Western		
Scientific name	*Taxodium distichum*		*Libocedrus decurrens*	*Chamaecyparis nootkatensis*	*Chamaecyparis thyoides*	*Chamaecyparis lawsoniana*	*Juniperus virginiana*	*Thuja plicata*	*Thuja occidentalis*	*Pseudotsuga menziesii*		*Abies balsamea*	*A. magnifica*	*A. grandis*	*A. procera*	*A. amabilis*	*A. lasiocarpa*	*A. concolor*		*Tsuga canadensis*	*T. heterophylla*		*Larix laricina*	*L. occidentalis*		
Page no.	000		000	000	000	000	000	000	000	000		000	000	000	000	000	000	000		000	000		000	000		
Use this for alignment	1	2	3	4	5	6	7	8	9	0	1	2	3	4	5	6	7	8	9	0	1	2	3	4	5	6
Resin canals																										
Present										X													X	X		
Epithelium thin-walled																										
Latewood transition abrupt	X							X	X	X										X			X	X		
Tracheids																										
Helical thickening (s in LW only)										X													s	s		
Bordered pits 2-4 opposite	X																			X			X	X		
Bordered pits 2-4 alternate																										
Rays																										
Homocellular of tracheids present			X																							
Tracheids present				X						X										X	X		X	X		
Tracheids dentate																										
Indenture				V	V	V	X	X	X	X		X	X	X	X	X	X	X		X	X		X	X		
Parenchyma end walls nodular	s		X	V			X			X		X	X	X	X	X	X	X		X	X		X	X		
Marginal parenchyma with crystals													X	X	X			X								
Cross—field pitting:																										
Fenestriform																										
Pinoid																										
Piceoid										X										X	X		X	X		
Cupressoid	V		X	X	X	X	X													V	V					
Taxodioid	X							X	X			X	X	X	X	X	X	X								
Longitudinal parenchyma																										
Present	X		X	X	X	X		X	X	X		X	X	X	X	X	X	X		X	X					
End walls smooth					X																					
End walls nodular	X		X	X		X	X	X	X	X		X	X	X	X	X	X	X		X	X		V			
Miscellaneous																										
Dimpled tangential surface																										
Heartwood distinct	X		X		X		X	X	X	X													X	X		
Greasy feel	X																									
Odor	X		X	X	X	X	X	X	X	X							X									
Use this for alignment	1	2	3	4	5	6	7	8	9	0	1	2	3	4	5	6	7	8	9	0	1	2	3	4	5	6

TABLE 4.3 Anatomical Characteristics of Coniferous Woods Useful in Their Identification—cont'd

Common name	Pine, soft or white	Jack	Lodgepole	Monterey	Red	Sugar	White, northern	White, western	Pine, hard or yellow	Ponderosa	Southern U.S.	Loblolly etc.	Redwood	Spruce	White, etc.	Sitka	Yew, Pacific	Other non U.S.,	Alerce	Almaciga (sakar)	Klinki pine	Parana pine				
Scientific name		*Pinus banksiana*	*P. contorta*	*P. radiata*	*P. resinosa*	*P. lambertiana*	*P. strobus*	*P. monticola*		*P. ponderosa*		*P. spp*	*Sequoia sempervirens*		*P. spp*	*P. sitchensis*	*Taxus brevifolia*		*Fitzroya cupressoides*	*Agathis philippinesis*	*Araucaria klinkii*	*A. angustifolia*				
Page No.		000	000	000	000	000	000	000		000		000	000		000	000	000		000	000	000	000				
Use this for alignment	1	2	3	4	5	6	7	8	9	0	1	2	3	4	5	6	7	8	9	0	1	2	3	4	5	6
Resin canals																										
Present		X	X	X	X	X	X	X		X		X			X	X										
Epithelium thin-walled		X	X	X	X	X	X	X		X		X														
Latewood transition abrupt					X					X		X	X						X							
Tracheids																										
Helical thickening (s in LW only)												s					X									
Bordered pits 2-4 opposite													X			X										
Bordered pits 2-4 alternate																				X	X	X				
Rays																										
Homocellular of tracheids present										X		X														
Tracheids present		X	X	X	X	X	X	X		X		X			X	X										
Tracheids dentate				X	X					X		X														
Indenture															X	X	V		X							
Parenchyma end walls nodular						X	V	X							X	X			X							
Marginal parenchyma with crystals																										
Cross—field pitting																										
Fenestriform					X	X	X	X																		
Pinoid		X	X	X						X		X														
Piceoid															X	X										
Cupressoid																	X		X	X	X	X				
Taxodioid													X													
Longitudinal parenchyma																										
Present													X													
End walls smooth																	X									
End walls nodular																			X							
Miscellaneous																										
Dimpled tangential surface			x									x				x										
Heartwood distinct		X	X	X	X	X	X	X		X		X	X				X		X							
Greasy feel																										
Identifying odor													X													
Use this for alignment	1	2	3	4	5	6	7	8	9	0	1	2	3	4	5	6	7	8	9	0	1	2	3	4	5	6

Key: X indicates characteristic is pronounced; x indicates characteristic is present but not pronounced (when used with X, it is the less likely of the two choices); V indicates variable according to sample or sources disagree; s indicates sporadic and may not be of diagnostic value.

TABLE 4.4 Properties of Softwood Tracheids

Common Name	Scientific Name	Diameter, µm[a]		Length[b,c] (mm)	L/D_{ave}	Coarseness[c] (mg/100 m)
		Maximum	Average			
Bald cypress	*Taxodium distichum*	70	52	6.0, 6.2	117	
Cedar, true: incense	*Libocedrus decurrens*	50	38	2.0, 3.6	53–95	
CEDAR, OTHERS						
Alaska cedar	*Chamaecyparis nootkatensis*	40	30			
Atlantic white cedar	*Chamaecyparis thyoides*	40	30	2.1, 2.1	70	
Port Orford cedar	*Chamaecyparis lawsoniana*	50	40	2.6	65	
Eastern red cedar	*Juniperus virginiana*	35	25	2.8, 2.8	112	
Western red cedar	*Thuja plicata*	45	35	3.8, 3.5	105	15.4
Northern white cedar	*Thuja occidentalis*	35	25	–, 2.2	88	
Douglas fir, coastal	*Pseudotsuga menziesii*	55	40	4.5, 3.9	105	26–31
FIR						
Balsam	*Abies balsamea*	50	35	3.5, 3.5	100	
California red	*Abies magnifica*	60	40	3.3	83	
Grand	*Abies grandis*	60	40	5.0	125	
Noble	*Abies procera*	60	40	4.0	100	
Pacific silver	*Abies amabilis*	60	45	3.6, 3.4	78	
Subalpine	*Abies lasiocarpa*	45	38	3.2, 3.0	82	
White	*Abies concolor*	60	40	3.5, 3.4	86	24.0
HEMLOCK						
Eastern	*Tsuga canadensis*	45	34	3.5, 3.0	96	
Western	*Tsuga heterophylla*	50	35	4.0, 4.2	120	29.0
LARCH						
Tamarack	*Larix laricina*	45	32	3.5, 3.6	111	
Western	*Larix occidentalis*	60	44	5.0, 5.0	114	32.5
PINE, SOFT OR WHITE						
Jack	*Pinus banksiana*			–, 3.5		18.0
Lodgepole	*Pinus contorta*	55	40	3.5, 3.1	83	23.0
Monterey	*Pinus radiata*					
Red	*Pinus resinosa*	45	35	3.7, 3.4	101	21.4

TABLE 4.4 Properties of Softwood Tracheids—cont'd

Common Name	Scientific Name	Diameter, Maximum	μm[a] Average	Length[b,c] (mm)	L/D_{ave}	Coarseness[c] (mg/100 m)
Sugar	*Pinus lambertiana*	65	45	4.1, 5.9	90–130	
White, northern	*Pinus strobus*	45	30	3.7, 3.0	100–123	19.8
White, western	*Pinus montícola*	60	40	4.4, 2.9	73–110	24.0
PINE, HARD OR YELLOW						
Ponderosa	*Pinus ponderosa*	60	40	3.6, 3.6	90	26.0
Southern US, loblolly	*Pinus taeda*	60	40	4.0, 3.6	90–100	23.5
Redwood	*Sequoia sempervirens*	80	58	7.0, 7.0	121	26.8
SPRUCE						
White, etc.	*Picea* spp.	35	28	3.5, 3.3	122	
Sitka	*Picea sitchensis*	55	40	5.5, 5.6	139	
Yew, Pacific	*Taxus brevifolia*	25	18			
OTHER NON–UNITED STATES						
Alerce	*Fitzroya cupressoides*					
Almaciga (sakar)	*Agathis philippinensis*					
Klinki pine	*Araucaria klinkii*					
Parana pine	*Araucaria angustifolia*					

[a] *Brown and Panshin (1940) p. 112; Panshin and de Zeeuw (1980) p. 133; and Hoadley (1990) p. 17.*

[b] *USDA FPL-031 (1923, 1964).*

[c] *Isenberg (1981) p. 212.*

overall appearance. Many sapwoods are stained with blue stain, a type of fungi, that changes the color.

Macroscopic features can be seen with the unaided eye or with a magnification 10 times lens. The terms pores and vessels are used synonymously. The presence of tyloses often tends to make the vessels difficult to see on the cross section with the unaided eye, so the appearance and the actual sizes of vessels are not the same. Parenchyma descriptions in this section refer to longitudinal parenchyma. Most of the macroscopic cross sections are courtesy of R.L. Krahmer and A.C. Van Vliet; they are all the same magnification, about 15–20 times. Although the taste of some woods is mentioned, it is not a good idea to apply this for routine sample identification of large numbers of samples. Softwoods are conveniently classified by their taxonomy in the order presented in Table 4.3. Most softwoods do not have longitudinal parenchyma observable with the unaided eye or even a lens. Softwoods with normal resin canals will have two ray sizes, the fusiform rays that may be visible with the unaided eye and the normal rays that may or may not be visible.

Pinaceae

Pinus

Pines are easily divided into two groups: the soft pines and the hard, yellow, or pitch pines

Soft pines have 5 needles per bundle; hard pines are 2 or 3 needled. Soft pines have a gradual transition to latewood, whereas hard pines have an abrupt transition. Slow-growth ponderosa pine may appear like white pine because of its narrow latewood. The lack of intertracheid pitting on the radial walls of the latewood of southern pines is used to distinguish them from the soft pines. Hard and red pines have dentate ray tracheids, whereas soft pines have nondentate ray tracheids. The resin canals of *Pinus lambertina* and *Pinus ponderosa* are large, whereas those of *Pinus contorta* and *Pinus resinosa* are small for pine resin canals.

Southern Pines (Figs. 4.14 and 4.15)

There are a number of species included in the group marketed as southern pine lumber. The most important, and their growth ranges, include: (1) longleaf pine (*Pinus palustris*), which grows from eastern North Carolina southward to Florida and westward to eastern Texas; (2) shortleaf pine (*Pinus echinata*), which grows from southeastern New York and New Jersey southward to northern Florida and westward to eastern Texas and Oklahoma; (3) loblolly pine (*Pinus taeda*), which grows from Maryland southward through the Atlantic Coastal Plain and Piedmont Plateau to Florida and westward to eastern Texas; (4) slash pine (*Pinus elliotii*), which grows in Florida and the southern parts of South Carolina, Georgia, Alabama, Mississippi, and Louisiana east of the Mississippi River. Grading standards classify lumber from any one or any mixture of two or more of these species as southern pine and lumber that is produced from longleaf and slash pine species, if longleaf pine conforms to the growth ring and latewood requirements. The lumber that is classified as longleaf in domestic trade is also known as pitch pine in the export trade. Three southern pines, pitch, pond, and Virginia pine, are designated in published grading rules as "minor species," to distinguish them from the four principal species. Southern pine lumber comes mainly from the Southern and South Atlantic States: from North Carolina to Arkansas and Louisiana.

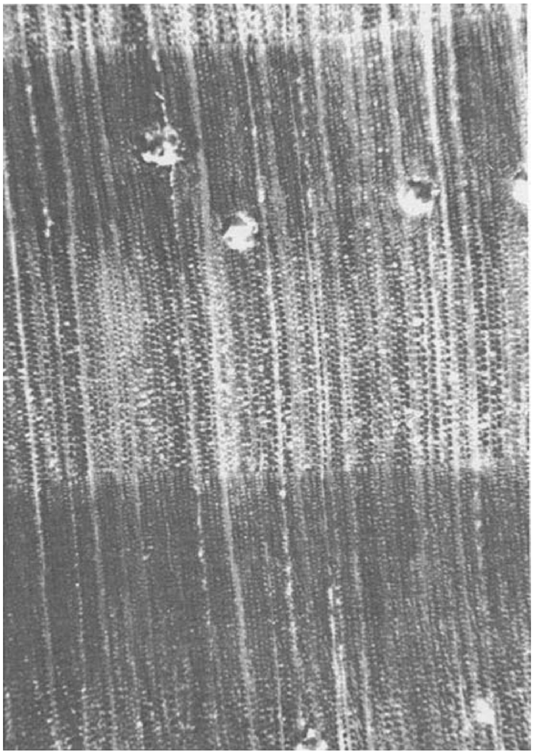


FIGURE 4.14 Southern pine, *Pinus* spp.

Uses. Longleaf and slash pines are classified as heavy, strong, stiff, hard, and moderately high in shock resistance. Shortleaf and loblolly pines are usually somewhat lighter in weight than longleaf. All the southern pines have moderately large shrinkage but are stable when properly seasoned. The pith has been used to distinguish longleaf, shortleaf, and loblolly pines (Koehler, 1917). To obtain heavy, strong wood of the southern pines for structural purposes, a density rule has been written that specifies certain visual characteristics for structural timbers.

Dense southern pine is used extensively in construction of factories, warehouses, bridges, trestles, and docks in the form of stringers, beams, posts, joists, piles, and plywood. Lumber of lower density and strength finds many uses

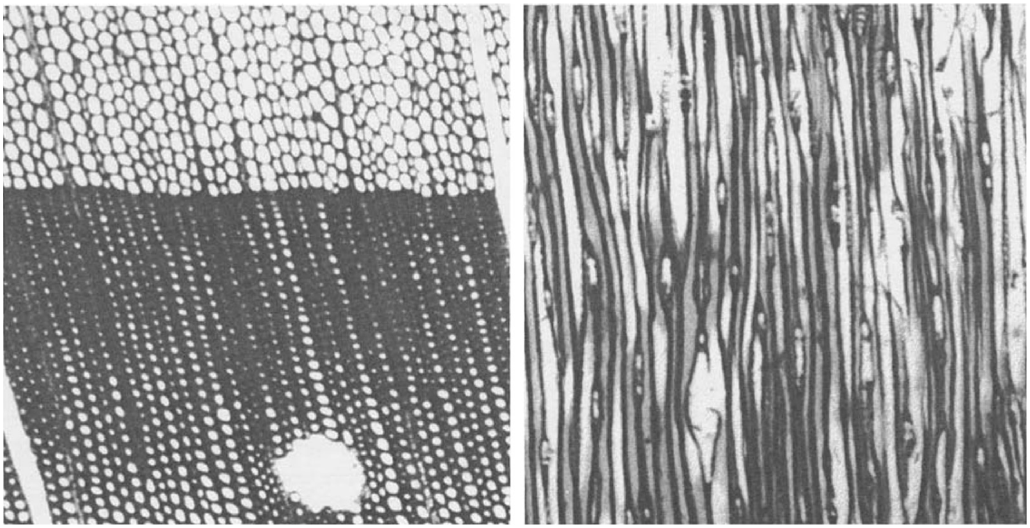


FIGURE 4.15 Loblolly pine (*Pinus taeda*) (50×).

for building material, such as interior finish, sheathing, subflooring, and joists, and for boxes, pallets, and crates. Southern pine is also used for tight and slack cooperage. When used for railroad ties, piles, poles, and mine timbers, it is usually treated with preservatives.

The southern pines are widely used in pulp and paper products. They compete with Douglas fir for most linerboard and packaging papers where high strength is required. Like Douglas fir, they form coarse papers.

Color. The wood of the various southern pines is quite similar in appearance. The sapwood is yellowish white and is usually wide in second-growth stands. The heartwood is reddish or orangish brown and begins to form when the tree is about 20 years old. In old, slow-growth trees, sapwood may be only 1—2 in. wide.

Macroscopic Structure

The wood has an abrupt latewood transition with a variable width latewood. Resin canals are scattered throughout the growth ring and are small for pine; the openings are rarely visible without a lens (visible to the unaided eye sometimes in longleaf pine). Nonfusiform rays are fine and distinct with a lens.

Pitch, Pond, and Virginia Pines

These three species are the "minor" southern pines in the southern pine grading rules; see the previous entry for their structures. Pitch pine (*Pinus rigida*) grows from Maine along the mountains to eastern Tennessee and northern Georgia. The heartwood is brownish red and resinous; the sapwood is thick and light yellow. The wood of pitch pine is medium heavy to heavy, medium strong, medium stiff, medium hard, and medium high in shock resistance. Its shrinkage is medium small to medium large. It is used for lumber, fuel, and pulpwood. Pond pine (*Pinus serotina*) grows in the coast region from New Jersey to Florida. It occurs in small groups or singly, mixed with other pines on low flats. The wood is heavy, coarse grained, and resinous with dark, orange-colored heartwood and thick, pale yellow sapwood. Shrinkage is moderately large. The wood is moderately strong, stiff, medium hard, and medium high in shock resistance. It is used for construction, railway ties, posts, and poles.

Virginia pine (*Pinus virginiana*), known also as Jersey pine and scrub pine, grows from New Jersey and Virginia throughout the Appalachian region to Georgia and the Ohio Valley. The heartwood is orange and the sapwood nearly white and relatively thick. The wood is rated moderately in weight, strength, hardness, and stiffness. It has moderately large shrinkage and high shock resistance. It is used for lumber, railroad ties, mine props, pulpwood, and fuel.

Jack Pine (Fig. 4.16)

Jack pine (*Pinus banksiana*), sometimes known as scrub pine, gray pine, or black pine in the United States, grows naturally in the Lake States and in a few scattered areas in New England and northern New York. In lumber, jack pine is not separated from the other pines with which it grows, including red pine and eastern white pine.

Uses. It is moderately light in weight, moderately low in bending strength and compressive strength, moderately low in shock resistance, and low in stiffness. It also has moderately small shrinkage. Lumber from jack pine is generally knotty. Jack pine is used for pulpwood, box lumber, pallets, and fuel. Less important uses include railroad tie, mine timber, slack cooperage, poles, and posts.

Color. The sapwood of jack pine is nearly white; the heartwood is light brown to orange. The sapwood may make up 50% or more of the volume of a tree. The wood has a rather coarse texture and is somewhat resinous.

Lodgepole Pine (Figs. 4.17 and 4.18)

Lodgepole pine (*P. contorta*), also known as knotty pine, black pine, spruce pine, and jack pine, grows in the Rocky Mountain and Pacific coast regions as far northward as Alaska.

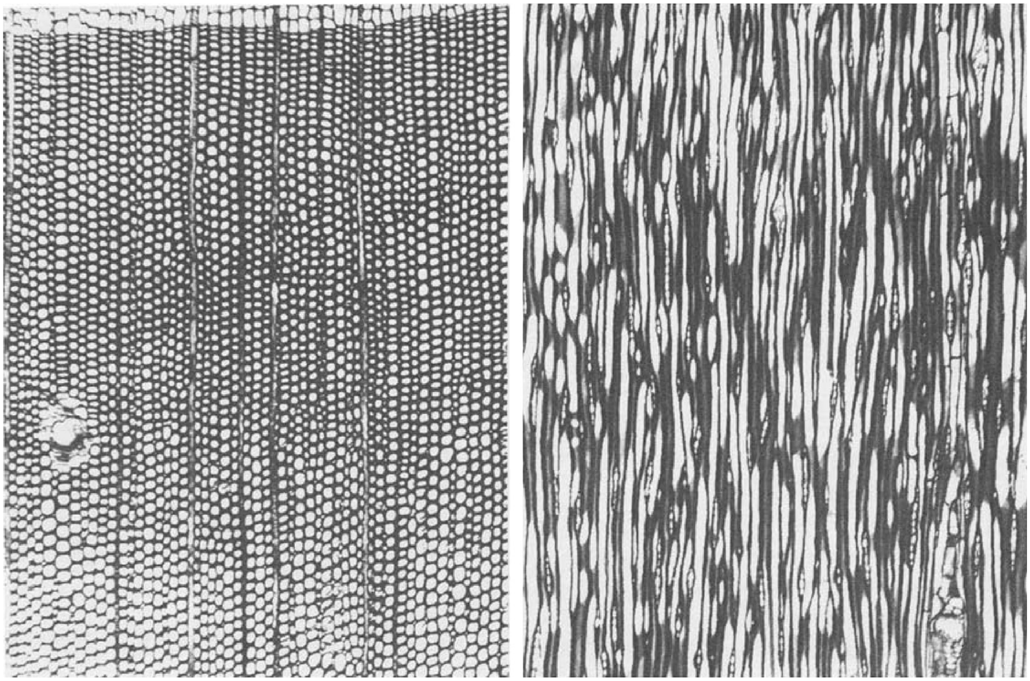


FIGURE 4.16 Jack pine (*Pinus banksiana*) (50×).

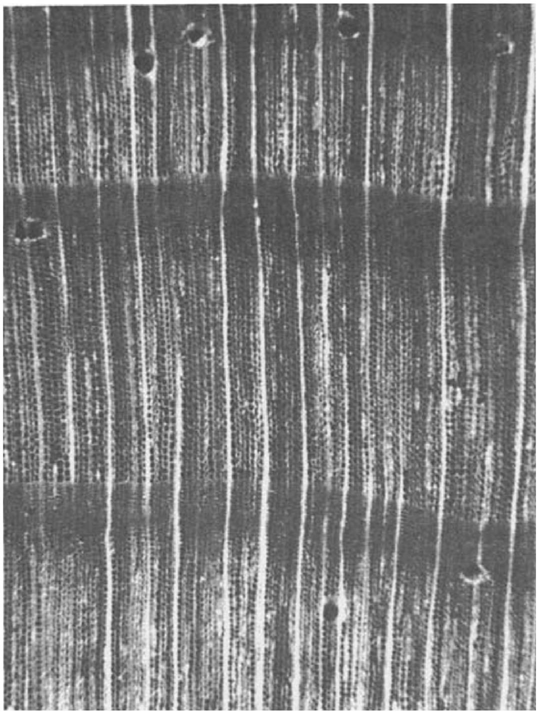


FIGURE 4.17 *Pinus contorta.*

Harvesting occurs largely from the central Rocky Mountain States; other producing regions are Idaho, Montana, Oregon, and Washington.

Uses. The wood is generally straight-grained with narrow growth rings (20–30/in.). The wood is moderately light in weight, is fairly easy to work, and has moderately large shrinkage. Lodgepole pine rates as moderately low in strength, moderately soft, moderately stiff, and moderately low in shock resistance. It is used for lumber, mine timbers, railroad ties, and poles. Less important uses include posts and fuel. Other uses include for framing, siding, finish, and flooring.

Color. The heartwood of lodgepole pine varies from light yellow to light yellow brown and is only slightly darker than the sapwood; often it is not clearly defined from the sapwood. The sapwood is yellow or nearly white, usually 1 in. wide but sometimes over 2 in. wide.

Macroscopic features. The wood has a fairly abrupt transition to the narrow latewood. The resin ducts are small and numerous. They are not distinctly visible without a lens although the

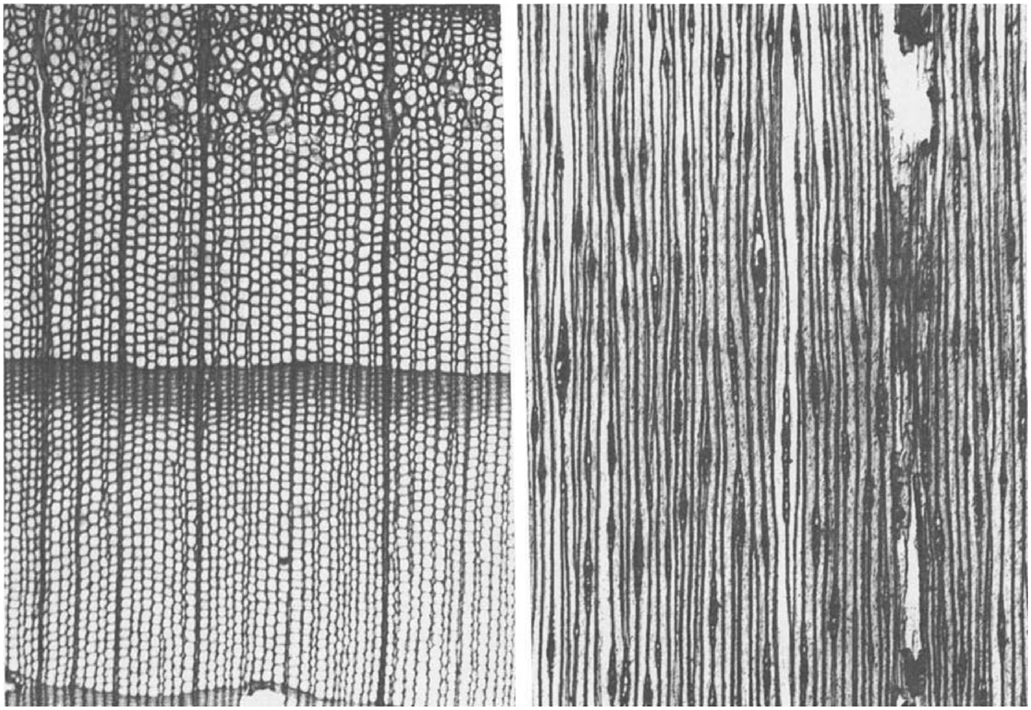


FIGURE 4.18 Lodgepole pine (*Pinus contorta*) (50×).

sap is sometimes visible. The rays are very fine, except for the fusiform rays, which are quite distinct under a lens. The tangential surface is slightly dimpled. The wood has a distinct resinous odor that is stronger than that of most pines.

Similar woods. Ponderosa pine resembles lodgepole pine, but it has darker and more distinct heartwood, wider sapwood, larger growth rings, and larger resin ducts and rarely has the pronounced dimpled surface (*t*) of lodgepole pine.

Ponderosa Pine (Figs. 4.19 and 4.20)

Ponderosa pine (*P. ponderosa*) is also known as western soft pine, western pine, California white pine, bull pine, and black jack pine. Jeffrey pine (*Pinus jeffreyi*), which grows in close association with ponderosa pine in California and Oregon, is usually marketed with ponderosa pine and sold under that name. Major producing areas are in Oregon, Washington, and California; moderate amounts come from Idaho and Montana; and small amounts come from Wyoming and the Black Hills of South Dakota.

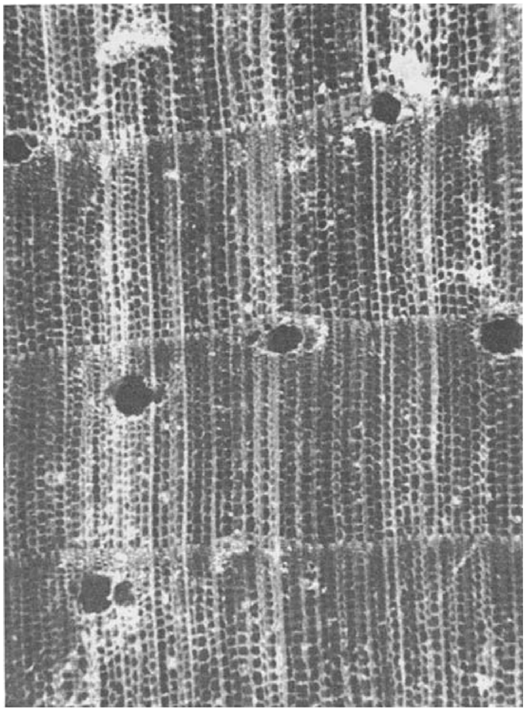


FIGURE 4.19 *Pinus ponderosa.*

Uses. The wood of the outer portions of ponderosa pine of sawtimber size is generally moderately light in weight, moderately low in strength, moderately soft, moderately stiff, and moderately low in shock resistance. It is generally straight-grained, has moderately small shrinkage, is quite uniform in texture, and has little tendency to warp and twist. Ponderosa pine is used mainly for lumber, particleboard, and pulp chips and to a lesser extent for piles, poles, posts, mine timbers, veneer, and ties. The clear wood goes into sash, doors, blinds, moldings, paneling, mantels, trim, and built-in cases and cabinets. Knotty pine is also used in paneling. Lower grade lumber is used for boxes and crates.

Color. Ponderosa pine belongs to the yellow pine group. Much of the wood, however, is somewhat similar to the white pines in appearance and properties. The heartwood is light reddish or orangish brown and clearly defined from the sapwood. The wide sapwood (2.5–4 in.) is nearly white to pale yellow.

Macroscopic structure. The transition to latewood is abrupt as in the southern pines, but the latewood bands are narrow although variable. The tangential surface is often dimpled as in lodgepole pine, but in the latter they are small and more abundant. The numerous resin canals are larger than those of lodgepole pine. The heartwood of lodgepole pine is lighter in color than that of ponderosa pine.

Microscopic features. Ponderosa pine may be distinguished from Jack pine because the dentations of the ray tracheids are more pronounced than those of Jack pine.

Red Pine

Red pine (*P. resinosa*) is frequently called Norway pine. It is occasionally known as hard pine and pitch pine. This species grows in the New

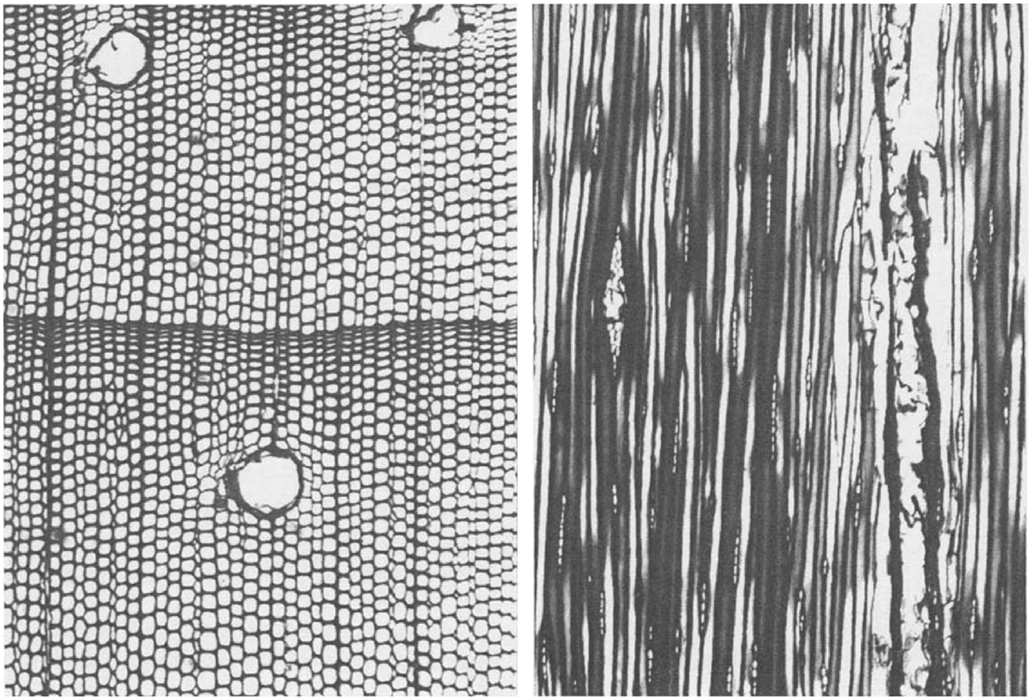


FIGURE 4.20 Ponderosa pine (*Pinus ponderosa*) (50×).

England States, New York, Pennsylvania, and the Lake States. In the past, lumber from red pine has been marketed with white pine without distinction as to species.

Uses. Red pine is moderately heavy, moderately strong and stiff, moderately soft, and moderately high in shock resistance. The wood is the lightest of the hard pines east of the Mississippi River. It is generally straight-grained, not as uniform in texture as eastern white pine, and somewhat resinous. The wood has moderately large shrinkage but is not difficult to dry and stays in place well when seasoned.

Red pine is used principally for lumber and to a lesser extent for piles, poles, cabin logs, posts, pulpwood, and fuel. The wood is used for many of the purposes for which eastern white pine is used. It goes mostly into building construction; siding; flooring; sash; doors; blinds; general millwork; and boxes, pallets, and crates.

Color. The heartwood of red pine varies from pale red to reddish brown. The sapwood is nearly white with a yellowish tinge and is generally from 2 to 4 in. wide. The wood resembles the lighter weight wood of southern pine. Latewood is distinct in the growth rings.

Macroscopic structure. The wood has a somewhat abrupt transition to latewood. The resin ducts tend to be concentrated in the outer half of growth rings with openings that are not visible without a lens. Nonfusiform rays are fine. The annual rings are fairly wide.

Similar woods. Red pine resembles the southern pines; it is quickly separated by its fenestriform pitting in the cross fields.

Spruce Pine

Spruce pine (*Pinus glabra*), also known as cedar pine, poor pine, Walter pine, and bottom white pine, grows on low moist lands of the coastal regions of southeastern South Carolina, Georgia, Alabama, Mississippi, Louisiana, and northern and northwestern Florida. The heartwood is light brown, and the wide sapwood zone is nearly white.

Uses. Spruce pine wood is lower in most strength values than the major southern pines. It compares favorably with white fir in bending properties, in crushing strength perpendicular and parallel to the grain, and in hardness. It is similar to the denser species such as coast Douglas fir and loblolly pine in shear parallel to the grain. The principal uses of spruce pine were locally for lumber and for pulpwood and fuelwood. The lumber, which is classified as one of the minor southern pine species, reportedly was used for sash, doors, and interior finish because of its lower specific gravity and less marked distinction between earlywood and latewood. It has qualified for use in plywood.

Sugar Pine (Fig. 4.21)

Sugar pine (*Pinus lambertiana*) is sometimes called California sugar pine. Most of the sugar pine lumber is produced in California and the remainder in southwestern Oregon.

Uses. The wood is straight-grained, fairly uniform in texture, and easy to work with tools. It has very small shrinkage, is readily seasoned without warping or checking, and stays in place well. This species is light in weight, moderately low in strength, moderately soft, low in shock resistance, and low in stiffness. Sugar pine is used almost entirely for lumber products. The largest amounts are used in crates, sash, doors, frames, blinds, general millwork, building construction, and foundry patterns. Like eastern white pine, sugar pine is suitable for use in nearly every part of a house because of the ease with which it can be cut, its ability to stay in place, and its good nailing properties.

Color. The heartwood of sugar pine is buff or light brown, sometimes tinged with red; it is lighter than that of *Pinus strobus* or *Pinus monticola*. The sapwood is creamy white.

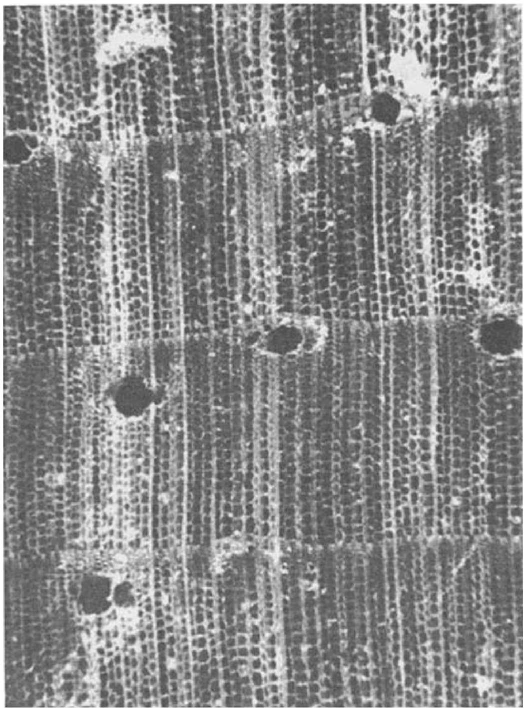


FIGURE 4.21 *Pinus lambertiana*.

Macrostructure. Resin canals are abundant and commonly stain the longitudinal surfaces. Transition from earlywood to latewood is gradual, and the growth rings are not prominent on flat-sawn surfaces. The wood is coarse textured.

Microscopic structure. The intertracheid pitting may be biseriate for four or more consecutive pit pairs in the first part of the earlywood.

Eastern White Pine (Fig. 4.22)

Eastern white pine (*P. strobus*) grows from Maine to northern Georgia and in the Lake States. It is also known as white pine, northern white pine, Weymouth pine, and soft pine. About 50% of the lumber is produced in the New England States, about 30% in the Lake States, and most of the remainder in the Middle Atlantic and South Atlantic States.

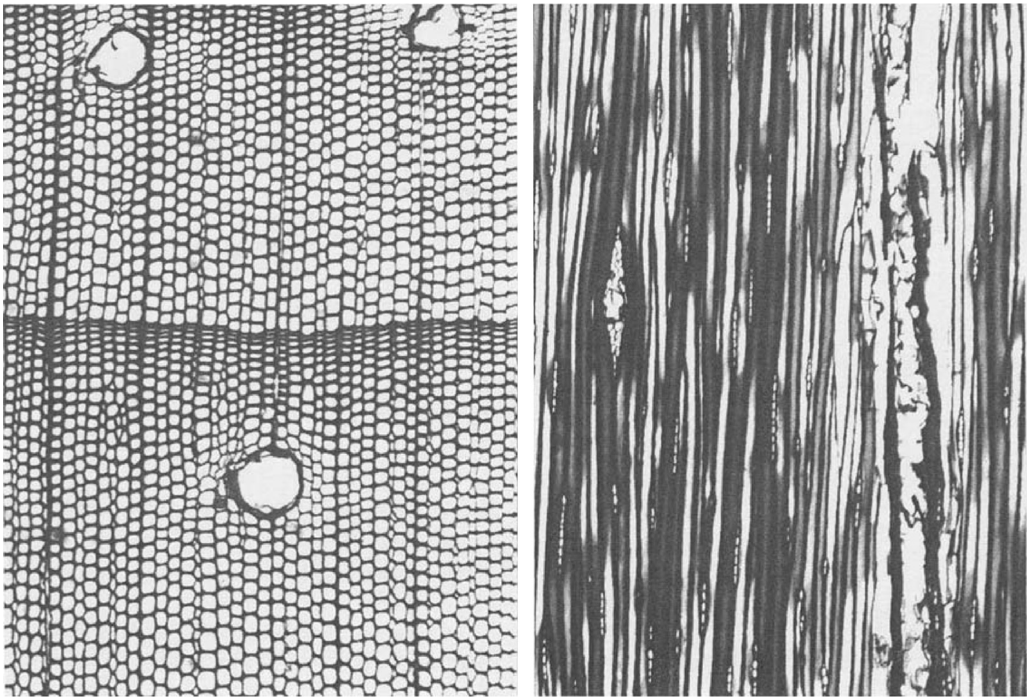


FIGURE 4.22 Eastern white pine (*Pinus strobus*) (50×).

Uses. It is easily kiln dried, has small shrinkage, and ranks high in stability. The wood has comparatively uniform texture and is straight-grained. It is also easy to work and can be readily glued. It is light in weight, moderately soft, moderately low in strength, and low in resistance to shock. Almost all eastern white pine is converted into lumber; a large proportion, which is mostly second-growth knotty lumber of the lower grades, goes into container and packaging applications. High-grade lumber goes into pattern forecastings. Other uses are sash, door, furniture, trim, knotty paneling, finish, caskets and burial boxes, shade and map rollers, toys, and dairy and poultry supplies.

Color. The heartwood of eastern white pine is light brown, often with a reddish tinge. It turns considerably darker on exposure.

Macrostructure. The wood has a gradual transition to latewood. The latewood is narrow and darker than the earlywood.

Western White Pine (Figs. 4.23 and 4.24)

Western white pine (*P. monticola*) is also known as Idaho white pine or white pine. About four-fifths of the cut comes from Idaho with the remainder mostly from Washington; small amounts are cut in Montana and Oregon.

Uses. The wood is straight-grained, easy to work, easily kiln dried, and stable after seasoning. This species is moderately light in weight, moderately low in strength, moderately soft, moderately stiff, moderately low in shock resistance, and has moderately large shrinkage. Practically all western white pine is sawed into lumber and used for building construction, matches, boxes,

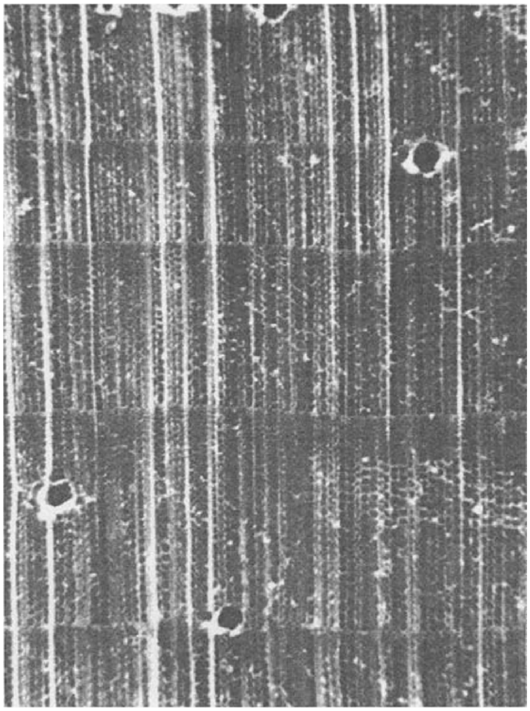


FIGURE 4.23 *Pinus monticola.*

patterns, and millwork products, such as sash, frames, doors, and blinds. In construction, boards of the lower grades are used for sheathing, knotty paneling, subflooring, and roof strips. High-grade material is made into siding of various kinds, exterior and interior trim, and finish. It has practically the same uses as eastern white pine and sugar pine.

Color. Heartwood of western white pine is cream colored to light reddish brown and darkens on exposure. The sapwood is yellowish white and generally from 1 to 2 (occasionally 3) in. wide.

Macroscopic features. The openings of the resin canals are plainly visible with a lens and sometimes without a lens. The canals are abundant throughout the growth ring. The rays are mostly fine although the fusiform rays are more pronounced. The annual rings are distinct and moderately wide. The wood has gradual transition to the narrow latewood.

Similar woods. It is separated from sugar pine by the larger resin canals in sugar pine and

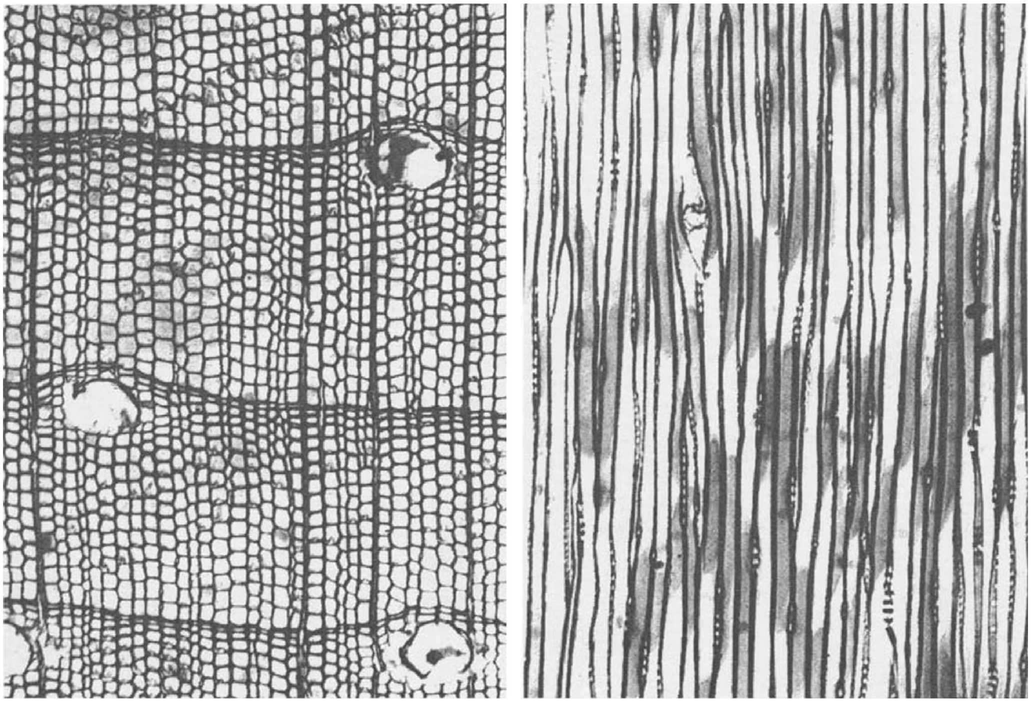


FIGURE 4.24 Western white pine (*Pinus monticola*) (50×).

microscopic features. It is difficult to separate from *P. strobus*. Limber pine is very similar, but it is usually heavier.

Scotch Pine

Scotch pine (*Pinus sylvestris*) is native to Europe and Asia but now grows in southeastern Canada and northeastern United States. A British term for construction lumber from this species (or softwoods, in general) is *deal*.

Pseudotsuga

Douglas Fir (Figs. 4.25 and 4.26)

Douglas fir (*Pseudotsuga menziesii* var. *glauca*) is also known locally as red fir, Douglas spruce, and yellow fir. (The older literature refers to it as *Pseudotsuga taxifola*.) There are two varieties: the coastal and the mountain types. The range of Douglas fir extends from the Rocky Mountains to the Pacific coast and from Mexico to central British Columbia. The Douglas fir production comes from Oregon, Washington, California, and the Rocky Mountain States.

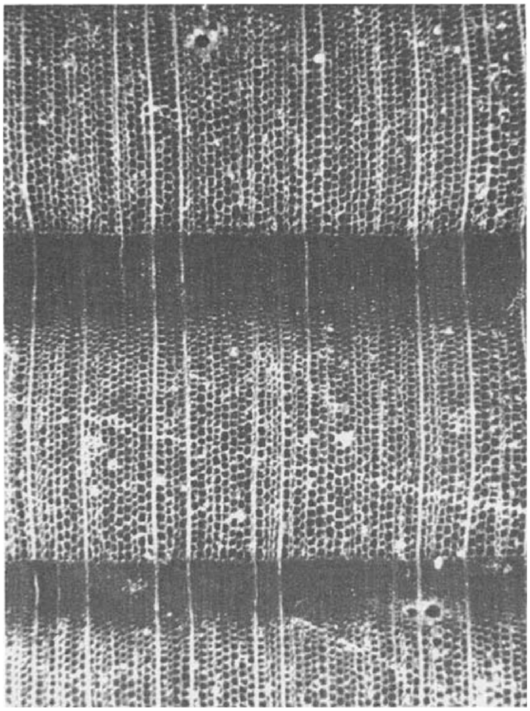


FIGURE 4.25 *Pseudotsuga menziesii.*

Uses. The wood of Douglas fir varies widely in weight and strength. When structural lumber of high strength is required, selection can be improved by applying the density rule, which has latewood percentage and growth rate criteria. Douglas fir is used mostly for building and construction purposes in the form of lumber, timbers, piling, and plywood. Considerable quantities go into railroad ties, cooperage stock, mine timbers, poles, and fencing. Douglas fir lumber is used in the manufacture of various products, including sash, doors, general millwork, railroad—car construction, boxes, pallets, and crates. Small amounts are used for flooring, furniture, ship and boat construction, wood pipe, and tanks. Douglas fir is widely used in pulp and paper products, especially in linerboard and sack papers, where it competes with southern pine, where high strength is required. It forms coarse papers, and obtaining good formation is difficult.

Color. Sapwood of Douglas fir is narrow in old-growth trees but may be as much as 3 inches wide in second-growth trees of commercial size. Young trees of moderate to rapid growth have reddish heartwood and are called red fir. Very narrow-ringed wood of old trees may be yellowish brown and is known on the market as yellow fir.

Macroscopic structure. The resin canals may form tangential rows of 2—20 (traumatic resin canals would have much longer tangential rows). The resin canals are much smaller than those of the pines, and Douglas fir normally has a distinctive odor. The bark of Douglas fir has layers that distinguish it from other species with which it may be confused.

Microscopic structure. Spiral thickening (yew has this but no resin canals) in the tracheids is a characteristic feature of Douglas fir. Marginal longitudinal parenchyma is sometimes observed.

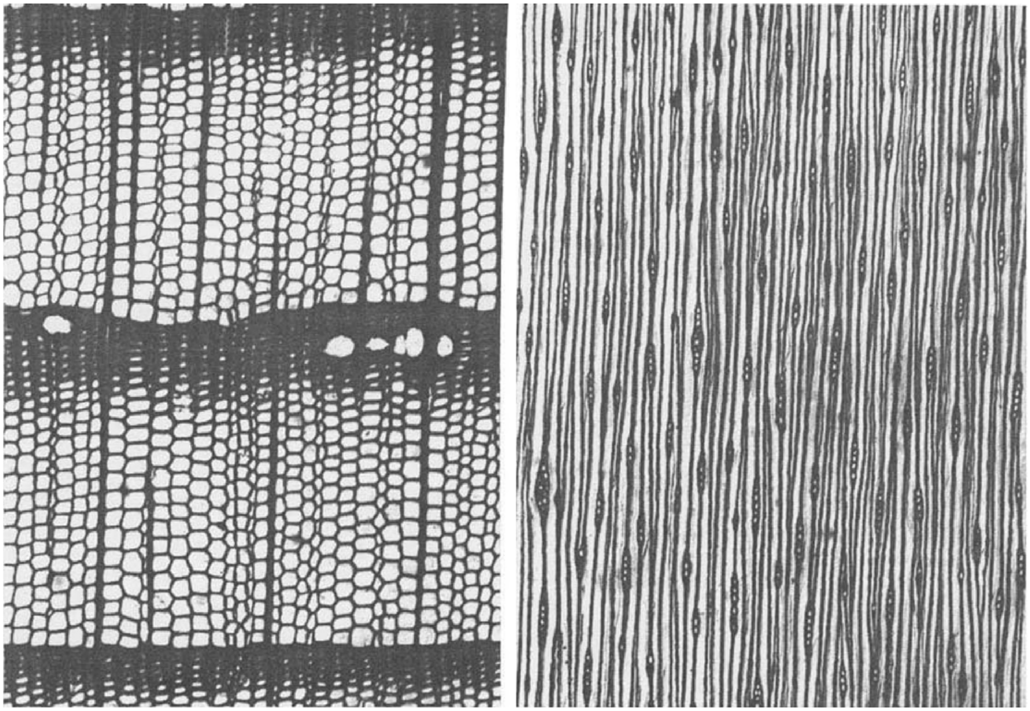


FIGURE 4.26 Douglas fir (*Pseudotsuga menziesii*) (50×).

Picea

With the exception of Sitka spruce, woods of spruces are not readily assigned to individual species without additional information because their anatomies are very similar. Engelmann spruce, however, tends to have an abrupt transition to latewood because it grows at high elevation in the Rocky Mountains.

Eastern Spruce

The term "eastern spruce" includes three species: red (*Picea rubens*), white (*Picea glauca*), and black (*Picea mariana*) (Fig. 4.27). White spruce and black spruce mainly grow in the Lake States and New England, and red spruce in New England and the Appalachian Mountains. All three species have about the same properties, and in commerce, no distinction is made between them.

Uses. The wood dries easily, is stable after drying, is moderately light in weight and easily worked, has moderate shrinkage, and is moderately strong, stiff, tough, and hard. The largest use of eastern spruce is for pulpwood. It is also used for framing material, general millwork, boxes and crates, ladder rails, scaffold planks, and piano sounding boards. Eastern spruce is sold with balsam fir as spruce fir, but the latter lacks resin canals. Balsam fir is heavier than eastern spruce when wet because of its higher moisture content but is lighter when dry.

Color. The wood is light in color, and there is little difference between the heartwood and sapwood colors. The high luster of eastern spruce is used to help distinguish it from northern white pine.

Macroscopic structure. The transition to the very narrow latewood is gradual. The resin canals are small and appear as white dots [in the cross

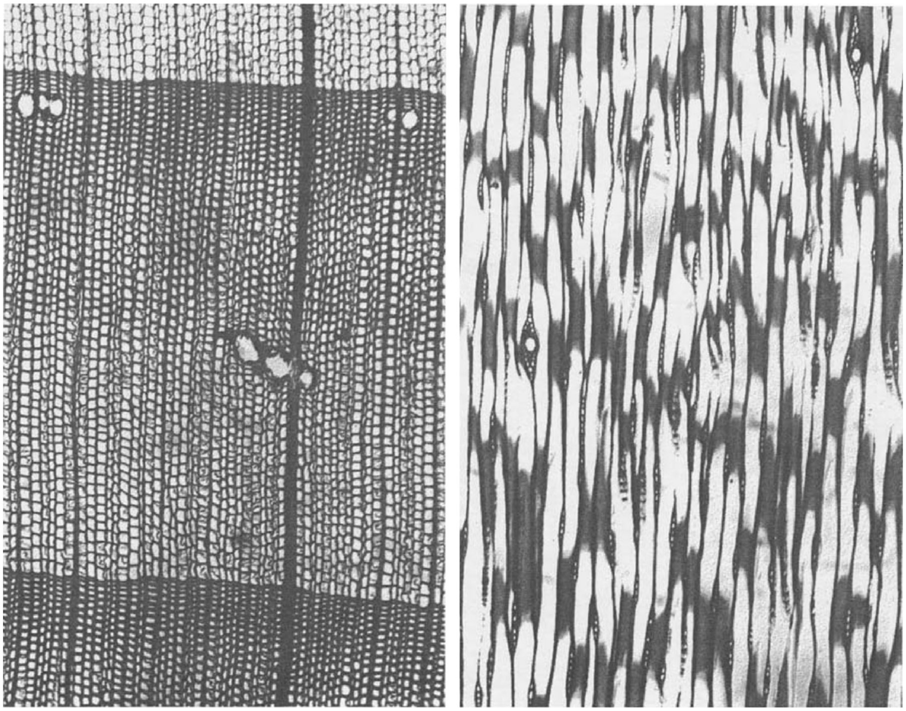


FIGURE 4.27 Black spruce (*Picea mariana*) (50×).

section (*x*)]. The rays are visible with a lens on wet surfaces (*x*). Fusiform rays occur randomly and are widely spaced.

Sitka Spruce (Figs. 4.28 and 4.29)

Sitka spruce (*Picea sitchensis*) is a tree of large size growing along the Pacific coast from California to Alaska. Local names include yellow spruce, tideland spruce, western spruce, and silver spruce. About two-third of Sitka spruce lumber comes from Washington and one-third from Oregon.

Uses. It is moderately light in weight, moderately low in bending and compressive strength, moderately stiff, moderately soft, and moderately low in resistance to shock. It has moderately small shrinkage. On the basis of weight, it rates high in strength properties and can be obtained in clear, straight-grained pieces.

Sitka spruce is used principally for lumber, pulpwood, and cooperage. It ranks high as a pulpwood because of its long, strong fibers and ease of pulping. Boxes and crates account for a considerable amount of the remanufactured lumber. Other important uses are furniture, planning mill products, sash, doors, blinds, millwork, and boats. Sitka spruce has been by far the most important wood for aircraft construction. Other specialty uses are ladder rails and sounding boards for pianos.

Color. The heartwood of Sitka spruce is a light brown with a pinkish or purple cast and is darker than that of eastern spruce. The sapwood is creamy white and shades gradually into the heartwood; it may be 3–6 in. wide or even wider in young trees. The wood has a comparatively fine, uniform texture, generally straight grain, and no distinct taste or odor.

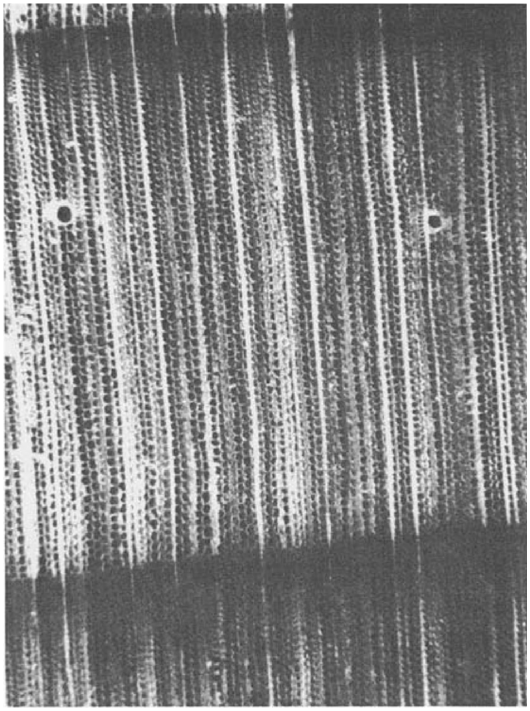


FIGURE 4.28 *Picea sitchensis*.

Macrostructure. The dimpled grain, if present, is darker and pinkish in heartwood, and its somewhat larger resin canals help identify it. It may be mistaken for soft pine.

Microstructure. This species is separated from other spruce by the occurrence of biseriate pitting in longitudinal tracheids. Its ray cells may contain darker (brownish) deposits than other species and crystals.

Engelmann Spruce (Fig. 4.30)

Engelmann spruce (*Picea engelmannii*) grows at high elevations in the Rocky Mountain region of the United States. It is known by other names, such as white spruce, mountain spruce, Arizona spruce, silver spruce, and balsam. About 60% of the lumber comes from the southern Rocky Mountain States, with most of the remainder from the northern Rocky Mountain States and Oregon.

Uses. The wood has medium to fine texture. It is generally straight-grained. Engelmann spruce is rated as light in weight. It is low in strength

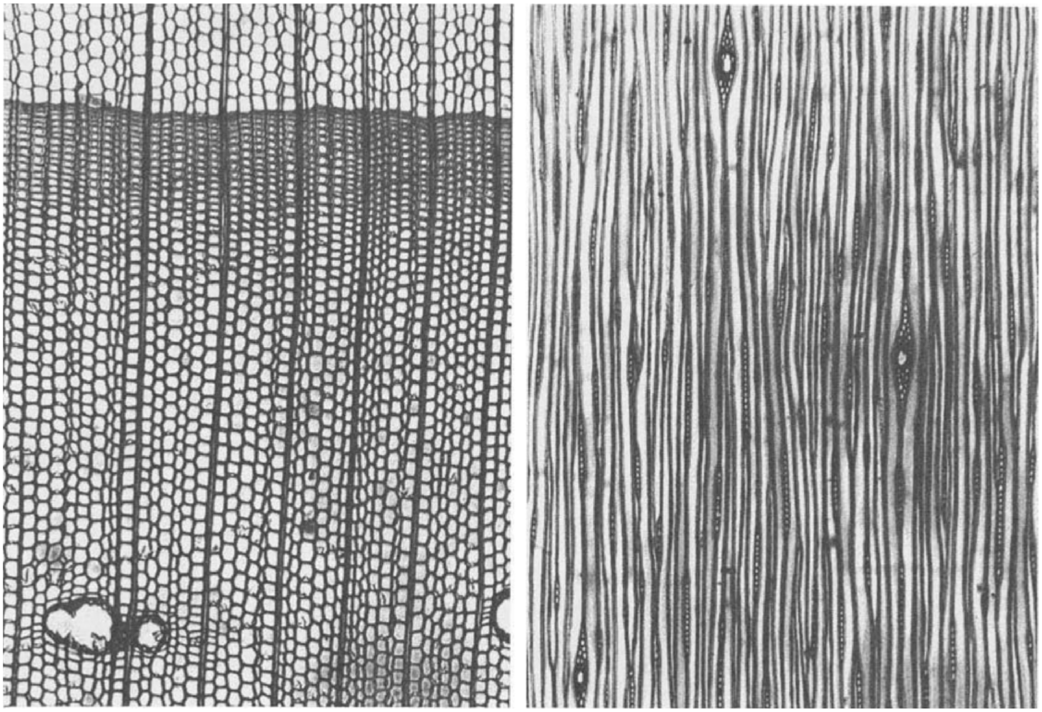


FIGURE 4.29 Sitka spruce (*Picea sitchensis*) (50×).

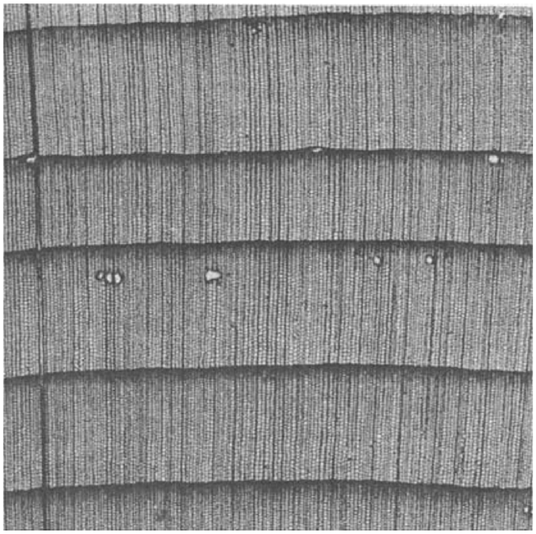


FIGURE 4.30 *Picea engelmannii* (Koehler, 1917), 15×.

as a beam or post. It is limber, soft, low in shock resistance and has moderately small shrinkage. The lumber typically contains numerous small knots. Engelmann spruce is used for lumber, mine timbers, railroad ties, and poles. It is used also in building construction in the form of dimension stock, flooring, sheathing, and studding. It has excellent properties for pulp and papermaking.

Color. The heartwood of Engelmann spruce is nearly white with a slight tinge of red. The sapwood is 3/4 to 2 in. wide and is often difficult to distinguish from heartwood, except for its high moisture content in green timbers.

Macroscopic features. The transition from earlywood to latewood is somewhat more abrupt than in other spruces. Resin canals are present, comparatively few, and are often difficult to find. They often appear as white dots in the latewood. The rays are very fine; the fusiform rays occur sporadically and are widely spaced.

Similar woods. Engelmann spruce is easily confused with the white (true) firs and lodgepole pine, which have almost white heartwoods. The true firs lack resin canals. Engelmann spruce lacks the dimpled surface of lodgepole pine.

Norway Spruce

Norway spruce (*Picea abies*) is native to Europe. It has been planted in the northeast United States.

Abies

Uses. The white firs are very useful in pulp products and produces strong, high-quality paper.

Color. The wood of the true firs (*Abies*) is creamy white to pale brown. The heartwood and sapwood are usually indistinguishable. The similarity of wood structure in the true firs makes it impossible to distinguish the species by an examination of the wood alone. Firs tend to be intolerant (of shade, when growing) and are, therefore, often fast growing with wide growth rings having especially gradual transition to latewood.

Microscopic Structure. Resin canals and ray tracheids are absent, end walls of ray parenchyma are nodular, and cross-field pits are nodular. *Abies lasiocarpa* may be foul smelling with knots that are a distinct yellow color. Crystals may be found in all species but especially in *Abies magnifica* and *Abies concolor*. In the eastern species and *Abies lasiocarpa*, the ray parenchyma contents are yellow to clear, whereas those of the other species are reddish brown. Generally the true firs have taller rays than the hemlocks.

Hoadley (1990) describes the use of Ehrlich's reagent (4 parts p-dimethyl amino benzaldehyde dissolved in 92 parts ethanol made acidic by adding 8 parts concentrated HCl) to distinguish subalpine fir (which turns purple) from Pacific silver fir (which remains clear or pale green).

Eastern Species (Figs. 4.31 and 4.32)

Balsam fir (*Abies balsamea*) grows principally in New England, New York, Pennsylvania, and the Lake States; it is the only eastern *Abies* of commercial importance. Eraser fir (*Abies fraseri*) has limited distribution in the Appalachian Mountains of Virginia, North Carolina, and

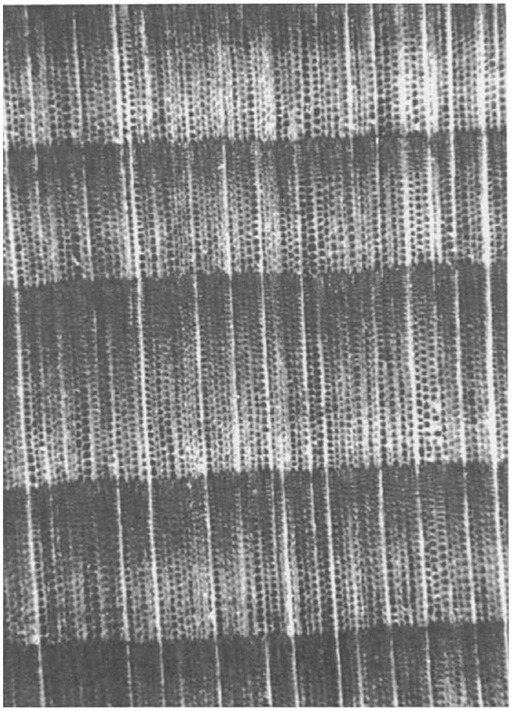


FIGURE 4.31 *Abies* spp.

Tennessee; this species sometimes has resinous tracheids (near parenchyma) in the heartwood that are filled with reddish brown to black amorphous deposits. Balsam fir is light in weight when dry, low in bending and compressive strength, moderately limber, soft, and low in resistance to shock. The eastern firs are used mainly for pulpwood although some lumber is produced from them, especially in New England and the Lake States. Balsam fir latewood often has a light purple cast to it. See Eastern Spruce section for additional information.

Western Species (*Fig. 4.33*)

Six commercial species make up the western true firs: subalpine fir (*Abies lasiocarpa*), California red fir (*A. magnifica*), grand fir (*Abies grandis*), noble fir (*Abies procera*), Pacific silver fir (*Abies amabilis*), and white fir (*Abies concolor*).

The western firs are light in weight, but, with the exception of subalpine fir, have somewhat higher strength properties than balsam fir. Wood shrinkage is small to moderately large.

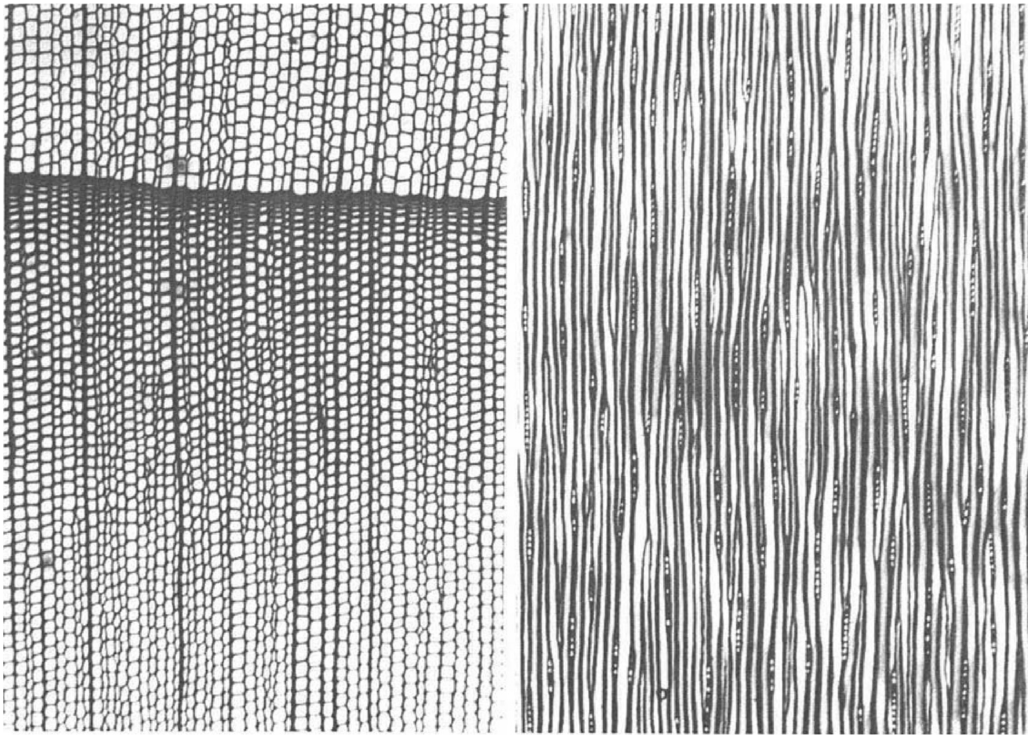


FIGURE 4.32 Balsam fir (*Abies balsamea*) (50×).

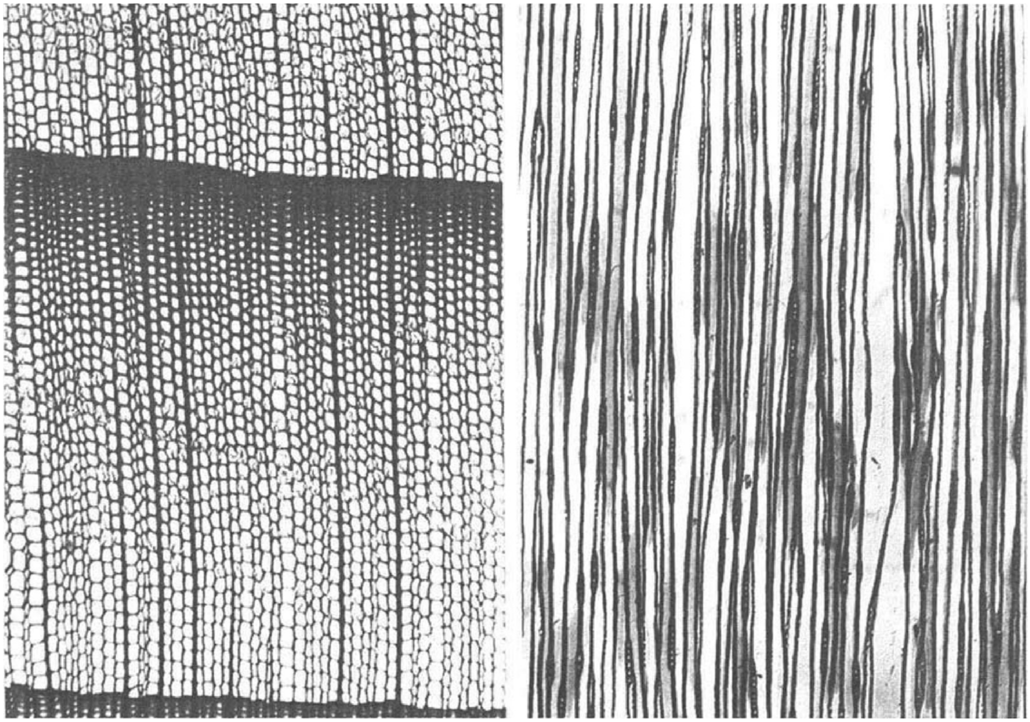


FIGURE 4.33 White fir (*Abies concolor*) (50×).

The sapwood is not distinguishable from the heartwood in some of these species.

The western true firs are largely cut for lumber in Washington, Oregon, California, western Montana, and northern Idaho and marketed as white fir throughout the United States. Lumber of the western true firs goes into building construction, boxes and crates, and general millwork. In house construction, the lumber is used for framing, subflooring, and sheathing. Some western true fir lumber goes into boxes and crates. High-grade lumber from noble fir is used mainly for interior finish, moldings, siding, and sash and door stock. The best material is used for aircraft construction and ladder rails.

Macroscopic structure. Resin canals are normally absent, but occasionally traumatic resin canals are present in the outer latewood in tangential rows extending 1/8 in. or more. *Abies grandis* sometimes has resinous tracheids (near parenchyma) in the heartwood that are filled with reddish brown to black amorphous deposits.

Similar woods. Western hemlock is very similar, but microscopic features can be used to distinguish these two woods. Western fir has taxodioid cross-field pits and lacks ray tracheids.

Larix

Larix species have resin canals with thick-walled epithelium cells. There is an abrupt transition from earlywood to latewood. The bordered pitting of vertical tracheids is often biseriate. Eastern larch has lighter color heartwood (more yellow than brown), a lower degree of biseriate bordered pitting, and a finer texture than western larch.

Western Larch (Figs. 4.34 and 4.35)

Western larch (*Larix occidentalis*) grows in western Montana, northern Idaho, northeastern Oregon, and the eastern slope of the Cascade Mountains in Washington. About two-third of the lumber of this species is produced in Idaho and Montana and one-third in Oregon and Washington.

Uses. The wood is stiff, moderately strong and hard, moderately high in shock resistance, and moderately heavy. It has moderately large shrinkage. The wood is usually straight-grained, splits easily, and is subject to ring shake. Knots are common but small and tight. Western larch is used mainly in building construction for rough dimension, small timbers, planks and boards, and for railroad tie and mine timbers. It is used also for piles, poles, and posts. Some high-grade material is manufactured into interior finish, flooring, sash, and doors.

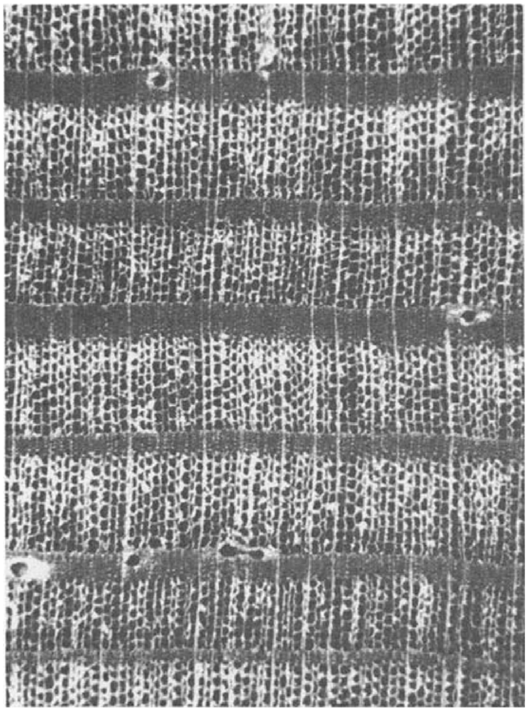


FIGURE 4.34 *Larix occidentalis*.

Color. The heartwood of western larch is yellowish brown and the sapwood is yellowish white. The sapwood is generally 0.5–0.75 in. and not more than 1 in. thick.

Macrostructure. The wood has a very abrupt transition to the narrow, conspicuous latewood. The resin canals occur sporadically and may be in tangential groups.

Microstructure. Marginal parenchyma is occasionally present.

Eastern Larch, Tamarack (Fig. 4.36)

Tamarack (*Larix laricina*) is a small- to medium-sized tree with a straight, round slightly tapered trunk. In the United States, it grows from Maine to Minnesota, with the bulk of the stands in the Lake States. It was formerly used in considerable quantity for lumber, but in recent years, production for that purpose has been small. The heartwood of tamarack is yellowish brown to russet brown. The sapwood is whitish, generally less than an inch wide. The wood is coarse in texture, without odor or taste, and the transition from earlywood to latewood is abrupt. The wood is intermediate in weight and in most mechanical properties. Tamarack is used principally for pulpwood, lumber, railroad ties, mine timbers, fuel, fence posts, and poles. Lumber goes into framing material, tank construction, boxes, and pallets.

European Larch

European larch (*Larix decidua*), native to Europe, is planted in Canada and northeast United States.

Tsuga

The presence of ray tracheids is useful in distinguishing the hemlocks, especially western hemlock, from the true firs (*Abies*). The growth rate of hemlock (especially eastern hemlock) can vary greatly even in a relatively small sample. A smooth cut is difficult to make on the end grain of eastern hemlock (using a knife)

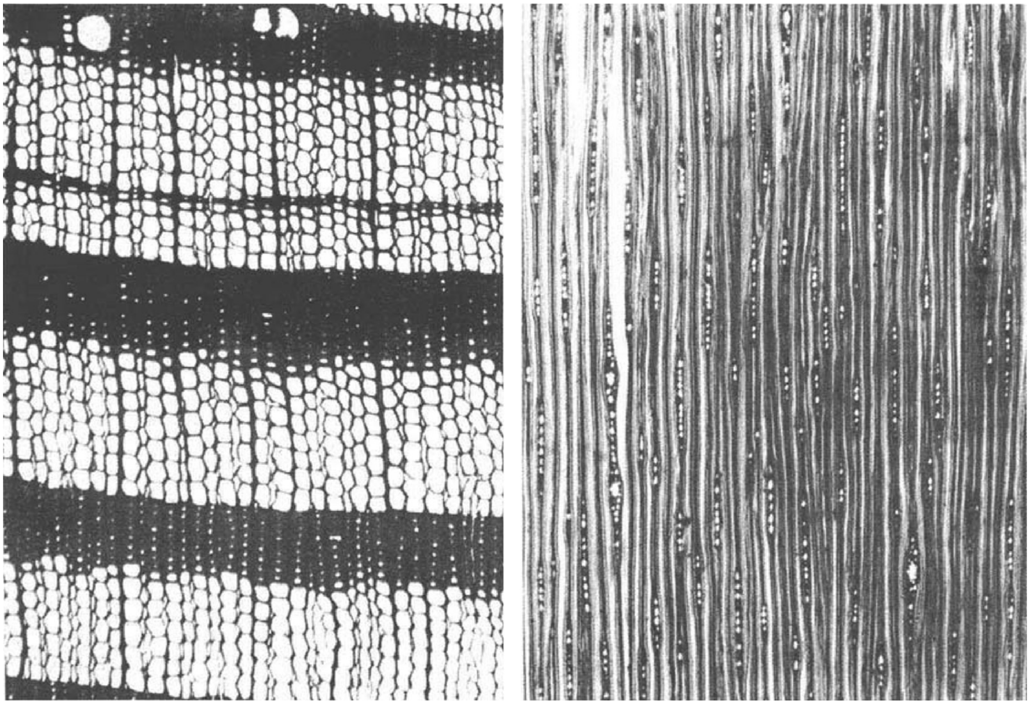


FIGURE 4.35 Western larch (*Larix occidentalis*) (50×).

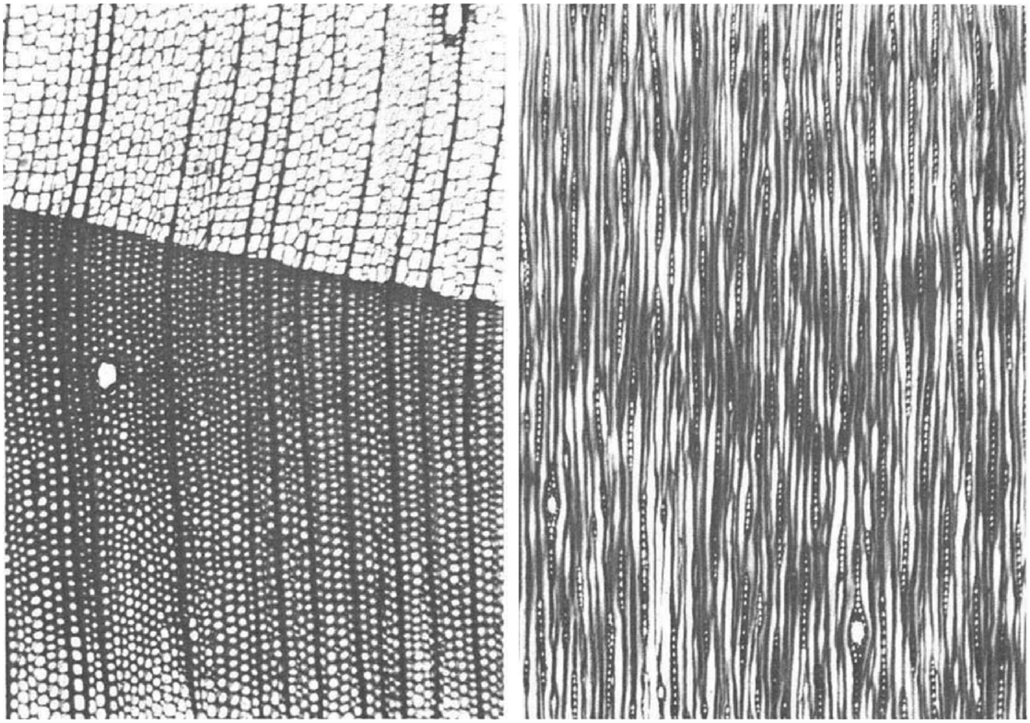


FIGURE 4.36 Tamarack, eastern larch (*Larix laricina*) (50×).

but is easily made on western hemlock. Western hemlock wood may have traumatic resin canals, is less splintery, and is usually free of cup shake.

Eastern Hemlock

Eastern hemlock (*Tsuga canadensis*) grows from New England to northern Alabama and Georgia and in the Lake States. Other names are Canadian hemlock and hemlock spruce. The production of hemlock lumber is divided fairly evenly between the New England States, the Middle Atlantic States, and the Lake States.

Uses. The wood is moderately light in weight, moderately hard, moderately low in strength, moderately limber, and moderately low in shock resistance. It is used principally for lumber and pulpwood. The lumber is used largely in building construction for framing, sheathing, subflooring, and roof boards and in the manufacture of boxes, pallets, and crates.

Color. The heartwood of eastern hemlock is pale brown with a reddish hue. The sapwood is not distinctly separated from the heartwood but may be lighter in color. The wood is coarse and uneven in texture (old trees tend to have considerable shake).

Similar woods. Spruce is lighter in color, weighs less, does not tend to splinter, and has resin canals. Most of the firs are of light color, especially in the earlywood, and do not tend to splinter. Noble fir should be distinguished with a microscope.

Western Hemlock (Figs. 4.37 and 4.38)

Western hemlock (*Tsuga heterophylla*) (also called west coast hemlock, hemlock spruce, western hemlock spruce, western hemlock fir, Prince Albert fir, gray fir, silver fir, and Alaska pine) grows along the Pacific coast of Oregon and Washington and in the northern Rocky Mountains, north to Canada and Alaska. Mountain hemlock, *Tsuga mertensiana,* inhabits mountainous country from central California to Alaska; it is treated as a separate species in assigning lumber properties.

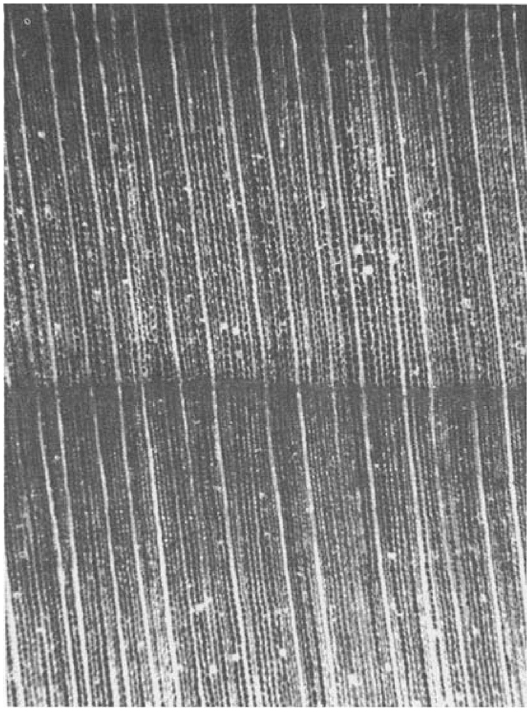


FIGURE 4.37 *Tsuga heterophylla.*

Uses. Western hemlock is moderately light in weight and moderate in strength. It is moderate in its hardness, stiffness, and shock resistance. It has moderately large shrinkage, about the same as Douglas fir. Green hemlock lumber contains considerably more water than Douglas fir and requires longer kiln-drying time. Western hemlock is used mainly for pulpwood, lumber, and plywood. The lumber goes largely into building material, such as sheathing, siding, subflooring, joists, studding, planking, and rafters. Major quantities are used in the manufacture of pallets, crates, and flooring, and smaller amounts for furniture and ladders.

Color. The heartwood and sapwood of western hemlock are almost white with a purplish tinge. The sapwood, which is sometimes lighter in color, is generally not more than 1 inch thick. The wood contains small, sound, black knots that are usually tight and stay in place. Dark

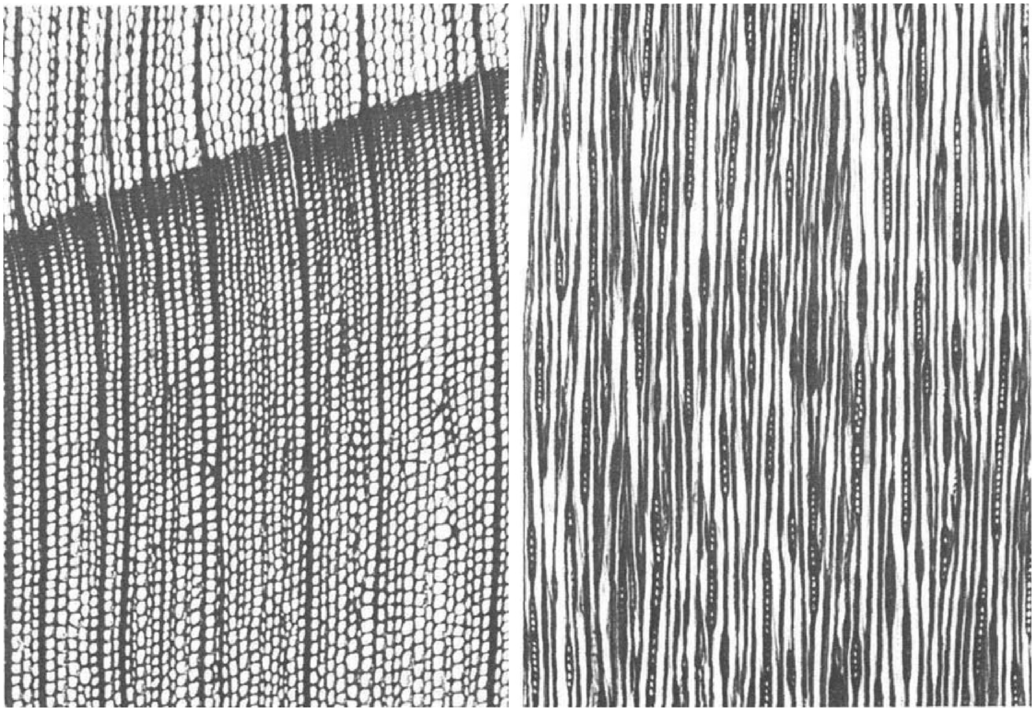


FIGURE 4.38 Western hemlock (*Tsuga heterophylla*) (50×).

streaks are often found in the lumber and caused by hemlock bark maggots that as a rule do not reduce strength.

Cupressaceae

Chamaecyparis (False Cypresses)

ALASKA CEDAR (FIG. 4.39)

Alaska cedar (*Chamaecyparis nootkatensis*) grows in the Pacific coast region from southeastern Alaska to southern Oregon.

Uses. The wood is fine textured and generally straight-grained. It is moderately heavy, moderately strong and stiff, moderately hard, and moderately high in resistance to shock. Alaska cedar shrinks little in drying, is stable in use after seasoning, and the heartwood is very resistant to decay. The wood has a mild, unpleasant, characteristic odor that resembles that of raw potatoes. Alaska cedar is used for interior finish, furniture, small boats, cabinetwork, and novelties.

Color. The heartwood of Alaska cedar is bright, clear yellow; it tends to darken somewhat with exposure to air. The sapwood is narrow, white to yellowish, and hardly distinguishable from the heartwood. The growth rings tend to be very narrow and inconspicuous.

Microscopic structure. The ray tracheids may be large. Some rays have no parenchyma. Ray and longitudinal parenchyma end walls are nodular with indentures.

PORT ORFORD CEDAR (FIGS. 4.40 AND 4.41)

Port Orford cedar (*Chamaecyparis lawsoniana*) (also called Lawson cypress, Oregon cedar, and white cedar) grows along the Pacific coast from Coos Bay, Oregon, southward to California. It does not extend more than 40 miles inland.

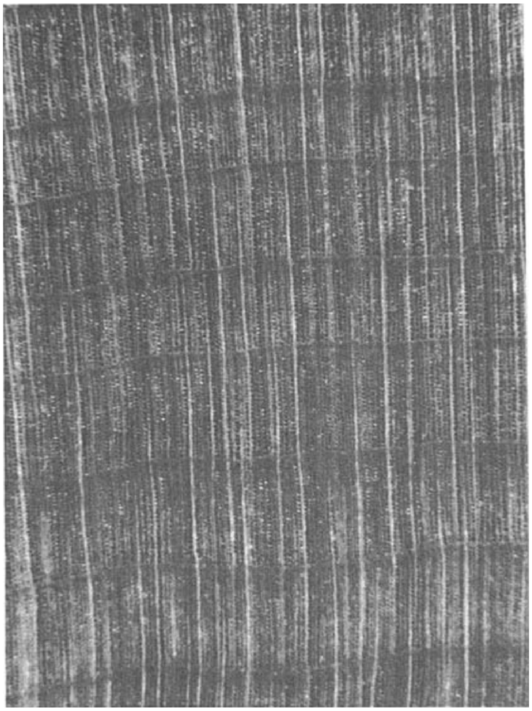


FIGURE 4.39 *Chamaecyparis nootkatensis.*

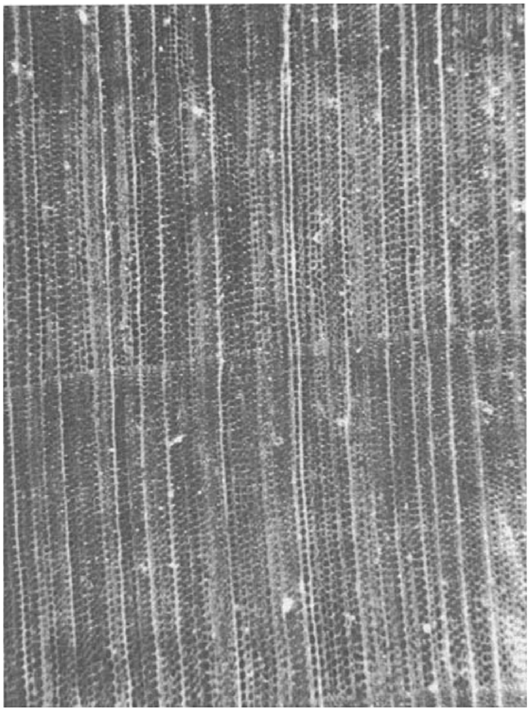


FIGURE 4.40 *Chamaecyparis lawsoniana.*

Uses. It is moderately light in weight, stiff, moderately strong and hard, and moderately resistant to shock. Port Orford cedar heartwood is highly resistant to decay. The wood shrinks moderately, has little tendency to warp, and is stable after seasoning. Some high-grade Port Orford cedar was used in the manufacture of battery separators. Other uses are venetian blind slats, mothproof boxes, archery supplies, sash and door construction, stadium seats, flooring, interior finish, furniture, and boatbuilding.

Color. The heartwood of Port Orford cedar is light yellow to pale brown in color and has a strong, pungent odor. The sapwood is narrow (1—3 in.) and hard to distinguish from the heartwood. The wood has a fine, even texture, generally straight-grained, and a pleasant spicy (gingerlike) odor and a bitter, spicy taste. Parenchyma is usually visible (wetting helps) with a lens as reddish lines or zones.

Microscopic structure. Ray tracheids are lacking, ray parenchymas have smooth end walls, and the transverse walls of the vertical parenchyma are nodular.

ATLANTIC WHITE CEDAR

This species is strictly a swamp tree and is very similar in properties and uses to northern red cedar; both grow in the eastern United States (*Chamaecyparis thyoides*) (also known as juniper, southern white cedar, swamp cedar, and boat cedar); it grows near the Atlantic coast from Maine to northern Florida and westward along the gulf coast to Louisiana. Commercial production centers in North Carolina and along the Gulf Coast. White cedar lumber is used principally where a high degree of durability is needed, as in tanks and boats, and for woodenware.

Color. The heartwood is light brown with a reddish cast that is sharply demarcated from

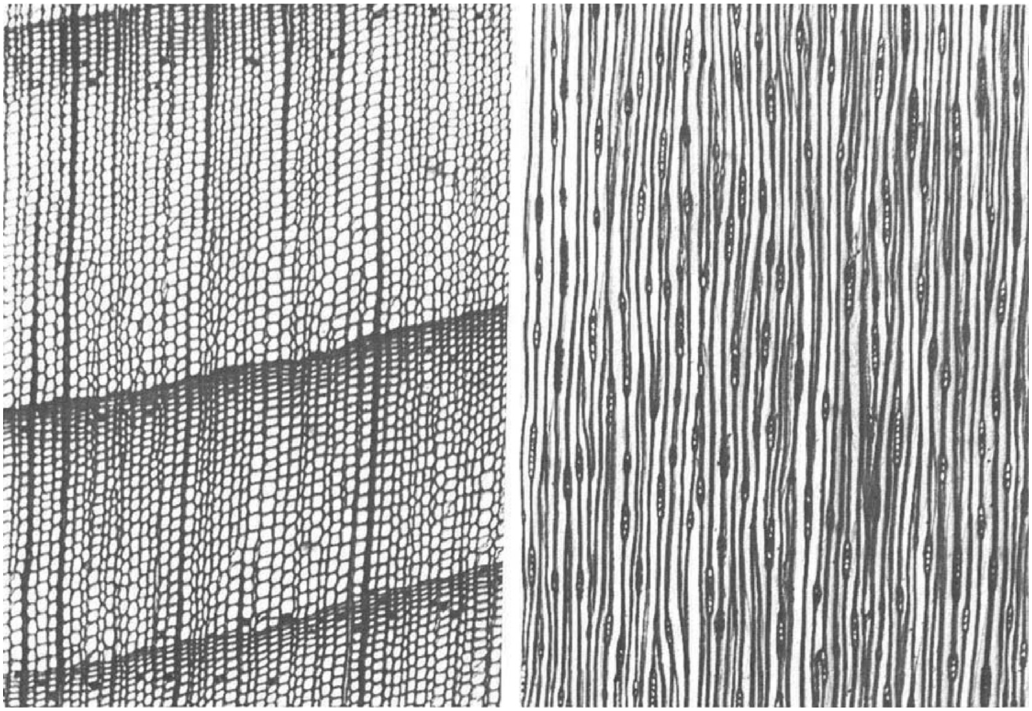


FIGURE 4.41 Port Orford cedar (*Chamaecyparis lawsoniana*) (50×).

the sapwood. It is aromatic and has a similar odor to that of northern white cedar.

Microscopic structure. Ray tracheids are lacking, ray parenchymas have smooth end walls, and the transverse walls of the vertical parenchyma are smooth.

Juniperus

The heartwood of trees of this genus are all aromatic with a pencil or cedar chest smell. Eastern and southern species have deep red heartwood; the western species are more brownish in color. Western juniper is *Juniperus occidentalis* (Figs. 4.42 and 4.43).

Microscopic features. This genus is characterized by large amounts of vertical parenchyma with dark-colored contents, nodular end walls, and indenture. Intercellular spaces occur between vertical tracheids.

Eastern Red Cedar (Fig. 4.44)

Eastern red cedar (*Juniperus virginiana*) grows throughout the eastern half of the United States, except in Maine, Florida, and a narrow strip along the gulf coast, and at the higher elevations in the Appalachian Mountain Range. Commercial production is principally in the southern Appalachian and Cumberland Mountain regions. Another species, southern red cedar (*Juniperus silicicola*), grows over a limited area in the South Atlantic and Gulf Coastal Plains.

Uses. The wood is moderately heavy, moderately low in strength, hard, and high in shock resistance but low in stiffness. It has very small shrinkage and stays in place well after seasoning.

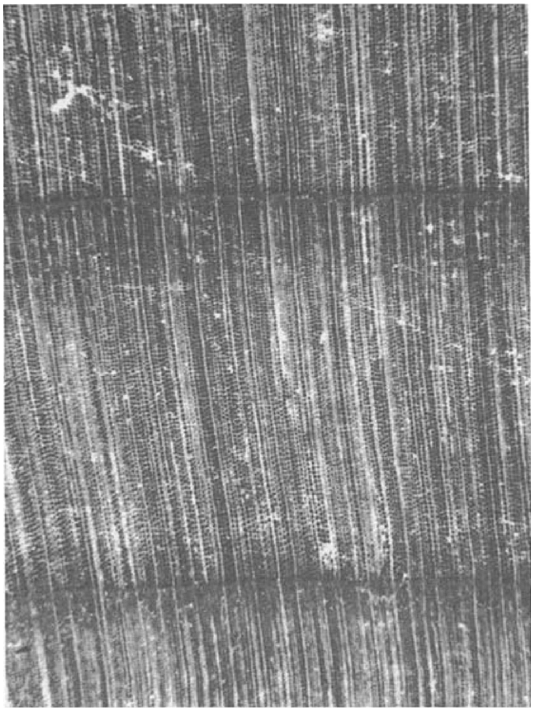


FIGURE 4.42 *Juniperus occidentalis.*

The texture is fine and uniform. Grain is usually straight, except where deflected by knots, which are numerous. Eastern red cedar heartwood is very resistant to decay. The greatest quantity of eastern red cedar is used for fence posts. Lumber is manufactured into chests, wardrobes, and closet lining. Other uses are flooring, novelties, pencils, and small boats. Southern red cedar is used for the same purposes.

Color. The heartwood of red cedar is bright to dull red, and the thin sapwood is nearly white.

Macroscopic structure. The longitudinal parenchyma is visible as several dark lines, particularly in the sapwood.

Libocedrus

Many species in this family are similar in appearance. Heartwood color and odor help to distinguish them.

Incense Cedar (Figs. 4.45 and 4.46)

Incense cedar (*L. decurrens*) grows in California and southwestern Oregon and a little in

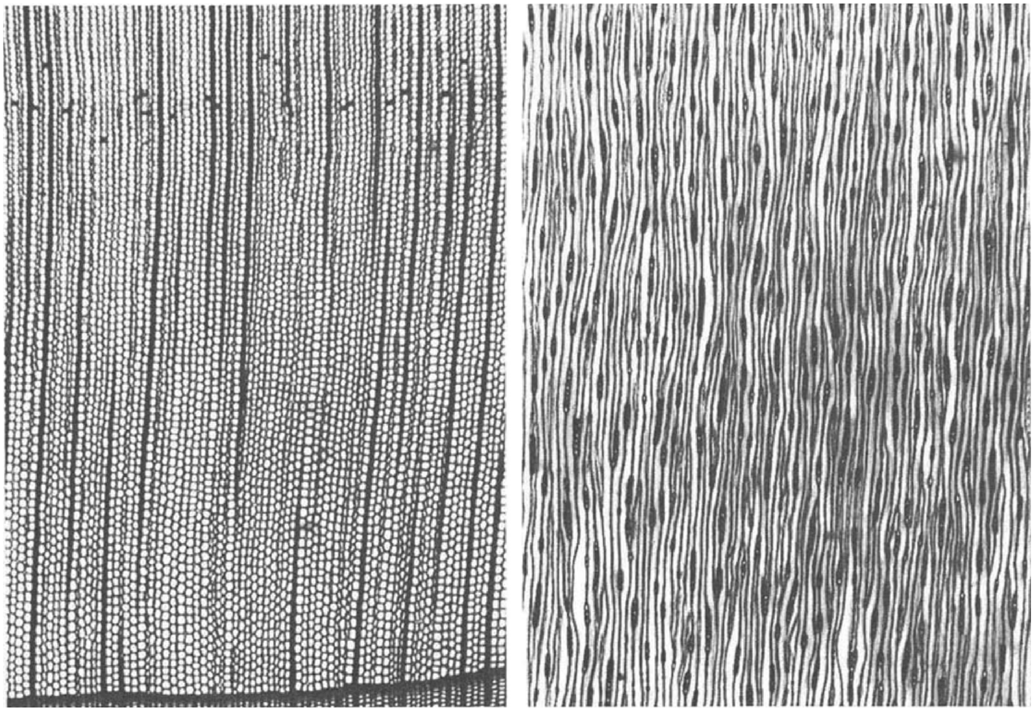


FIGURE 4.43 Western juniper (*Juniperus occidentalis*) (50×).

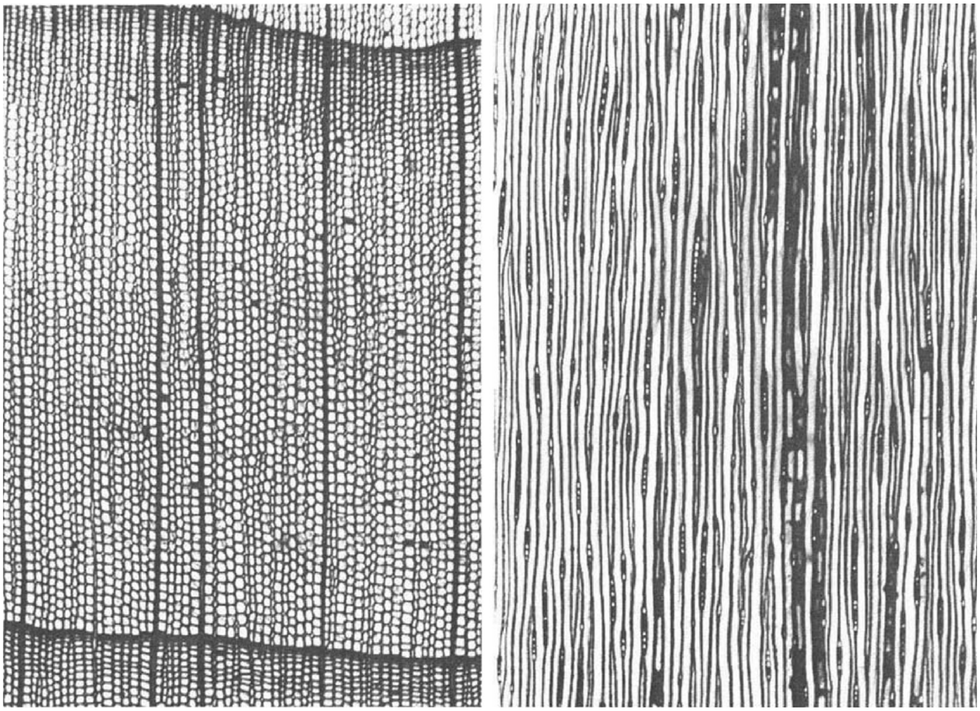


FIGURE 4.44 Eastern red cedar (*Juniperus virginiana*) (50×).

Nevada. Most incense cedar lumber comes from the northern half of California and the remainder from southern Oregon.

Uses. Incense cedar is light in weight, moderately low in strength, soft, low in shock resistance, and low in stiffness. It has small shrinkage and is easy to season with little checking or warping. Incense cedar is used for lumber and fence posts. Nearly all the high-grade lumber is used for pencils and venetian blinds. Some is used for chests and toys. Much of the incense cedar lumber is more or less pecky; that is, it contains pockets or areas of disintegrated wood caused by advanced states of localized decay in the living tree. Peck development is arrested once the lumber is seasoned. This lumber is used locally for rough construction where cheapness and decay resistance are important. Because of its resistance to decay, incense cedar is well suited for fence posts. Other products are railroad ties, poles, and split shingles.

Color. The sapwood of incense cedar is white or cream colored, and the heartwood is light brown, often tinged with red or pale purple. The wood has a fine, uniform texture, a spicy odor, and acrid taste.

Macroscopic features. The transition from earlywood to latewood is more or less abrupt, and the growth rings are prominent on flat-sawn surfaces. Incense cedar is similar to western red cedar, but the latter lacks the acrid taste. Longitudinal parenchyma is visible in the latewood as dark reddish lines or zones.

Microscopic structure. Incense cedar lacks indentures in the ray parenchyma, which distinguishes it from other species with nodular ray cell end walls on transverse surfaces of longitudinal parenchyma.

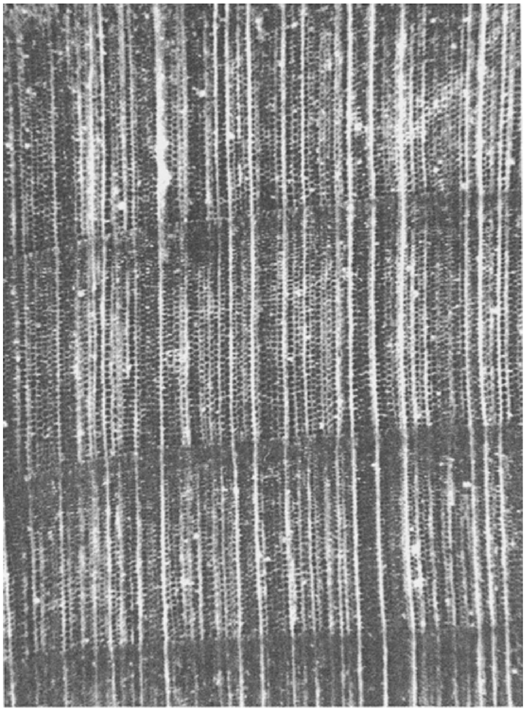


FIGURE 4.45 *Libocedrus decurrens.*

Thuja

Western Red Cedar (Figs. 4.47 and 4.48)

Western red cedar (*T. plicata*) grows in the Pacific Northwest and along the Pacific coast to Alaska. Western red cedar is also called canoe cedar, giant arborvitae, shinglewood, and Pacific red cedar. Western red cedar lumber is produced principally in Washington, followed by Oregon, Idaho, and Montana.

The wood is generally straight-grained and has a uniform but rather coarse texture and very small shrinkage. It is light in weight, moderately soft, low in strength when used as a beam or post, and low in shock resistance. It has a higher density in the pith that decreases outward. It has a sweet odor that some say is like chocolate. Western red cedar is used principally for shingles, lumber, poles, posts, and piles. The lumber is used for exterior siding, interior finish, greenhouse construction, shipbuilding and boatbuilding, boxes and crates, sash, doors, and millwork.

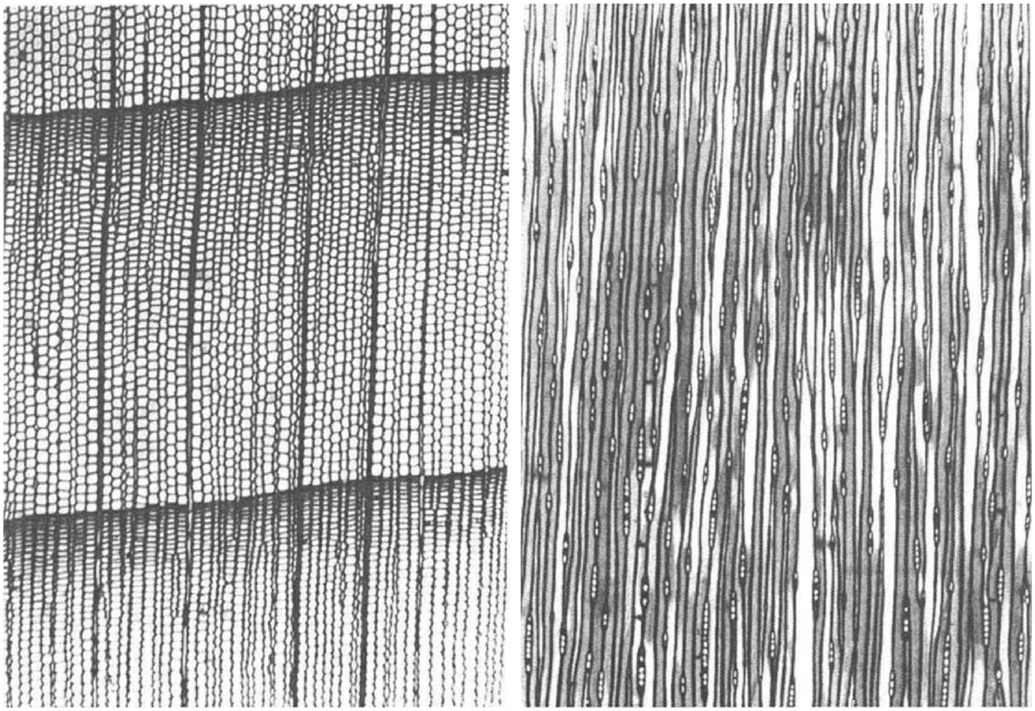


FIGURE 4.46 Incense cedar (*Libocedrus decurrens*) (50×).

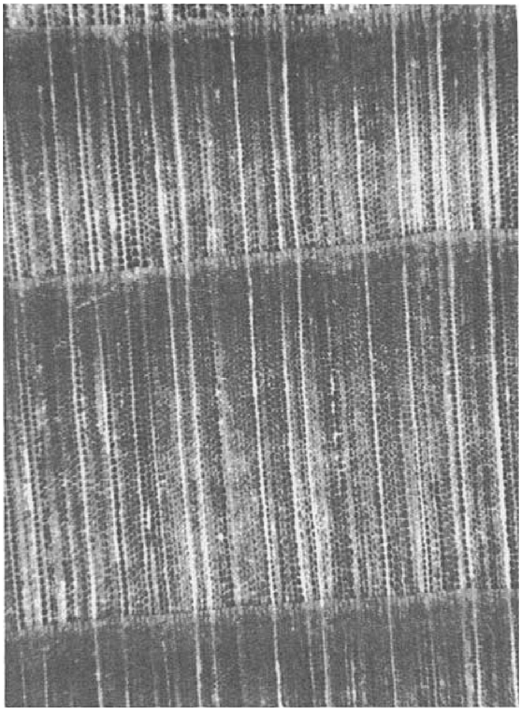


FIGURE 4.47 *Thuja plicata*.

Color. The heartwood of western red cedar is reddish or pinkish brown to dull brown and very resistant to decay. The sapwood is nearly white and narrow, often 1/4—1 in. wide.

Similar woods. Western red cedar closely resembles northern white cedar but the latter is of slower growth and has a plain light brown color usually without a reddish tinge. Dark grades resemble redwood, but redwood lacks the characteristic odor and taste.

Northern White Cedar

This species is very similar in properties and uses to Atlantic white cedar; both grow in the eastern United States. The two species are used for similar purposes, mostly for poles, ties, lumber, posts, and decorative fencing. Northern white cedar (*Thuja occidentalis*) is also known as arborvitae, or simply cedar. It grows from Maine along the Appalachian Mountain Range and westward through the northern part of the Lake States. Production of northern white cedar lumber is probably greatest in Maine and the lake States.

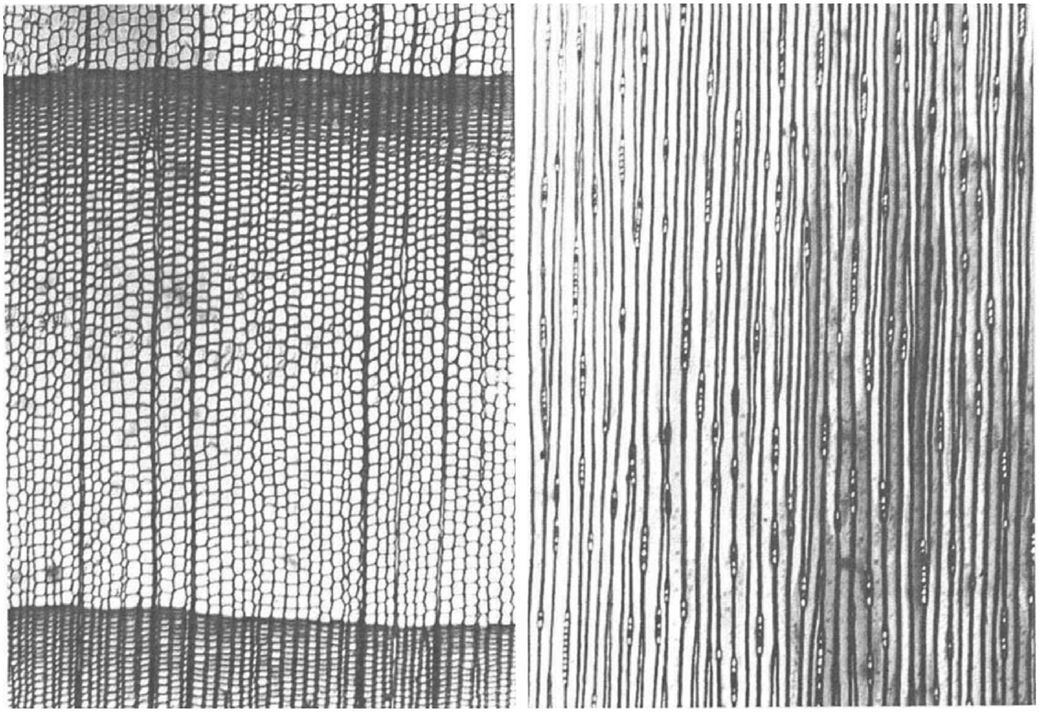


FIGURE 4.48 Western red cedar (*Thuja plicata*) (50×).

Uses. The wood is light in weight, rather soft and low in strength, and low in shock resistance. It shrinks little in drying. It is easily worked and holds paint well; the heartwood is highly resistant to decay.

Color. The heartwood of white cedar is light brown, and the sapwood is white or nearly so. The sapwood is usually thin, not over 1 in. except in very fast growth.

Similar woods. *Chamaecyparis thyoides* is similar but has a more pinkish hue, a spicy odor, and, as a rule, wider growth rings. Western red cedar generally has wider growth rings and a reddish hue. Bald cypress has a more dingy color and a rancid odor that is much different from that of cedar.

Cupressus

Arizona Cypress

Arizona cypress (*Cupressus arizonica*) grows in the southwest United States. The heartwood merges into the sapwood, and both are yellowish in color. Many of the microscopic features resemble those of *Juniperus*, although the parenchyma end walls are not as obviously nodular and the rays are not as high.

Taxodiaceae

Taxodium

BALD CYPRESS (FIGS. 4.49 AND 4.50)

Bald cypress (*Taxodium distichum*) is commonly known as cypress, southern cypress, red cypress, yellow cypress, and white cypress. Commercially, the terms tidewater red cypress, gulf cypress, red cypress (coast type), and yellow cypress (inland type) are often used. About one-half of the cypress lumber comes from the southern states and one-fourth from the South Atlantic States although the supply has decreased.

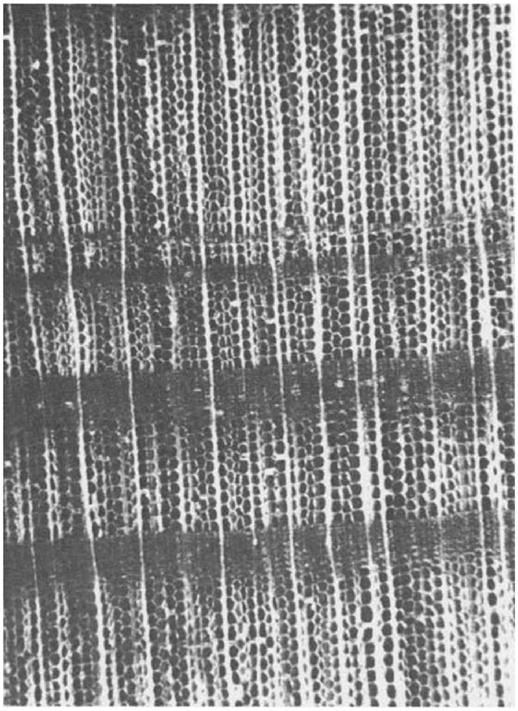


FIGURE 4.49 *Taxodium distichum.*

Uses. The wood is moderately heavy, moderately strong, and moderately hard. The heartwood of old-growth timber is one of our most decay-resistant woods. Shrinkage is moderately small: greater than that of cedar and less than that of southern pine. Often the wood of certain cypress trees contains pockets or localized areas that have been attacked by a fungus. Such wood is known as pecky cypress. The decay caused by this fungus is arrested when the wood is cut into lumber and dried. Pecky cypress is durable and useful where water tightness is unnecessary and appearance is not important or a novel effect is desired. Cypress has been used principally for building construction, especially where resistance to decay is required. It was used for beams, posts, and other members in docks, warehouses, factories, bridges, and heavy construction.

Color. The sapwood of bald cypress is narrow (1−2 in., gradually merging into heartwood) and nearly white. The color of the heartwood varies widely, ranging from light yellowish brown to dark brownish red, brown, or chocolate. The wood is dull, lacking sheen or luster.

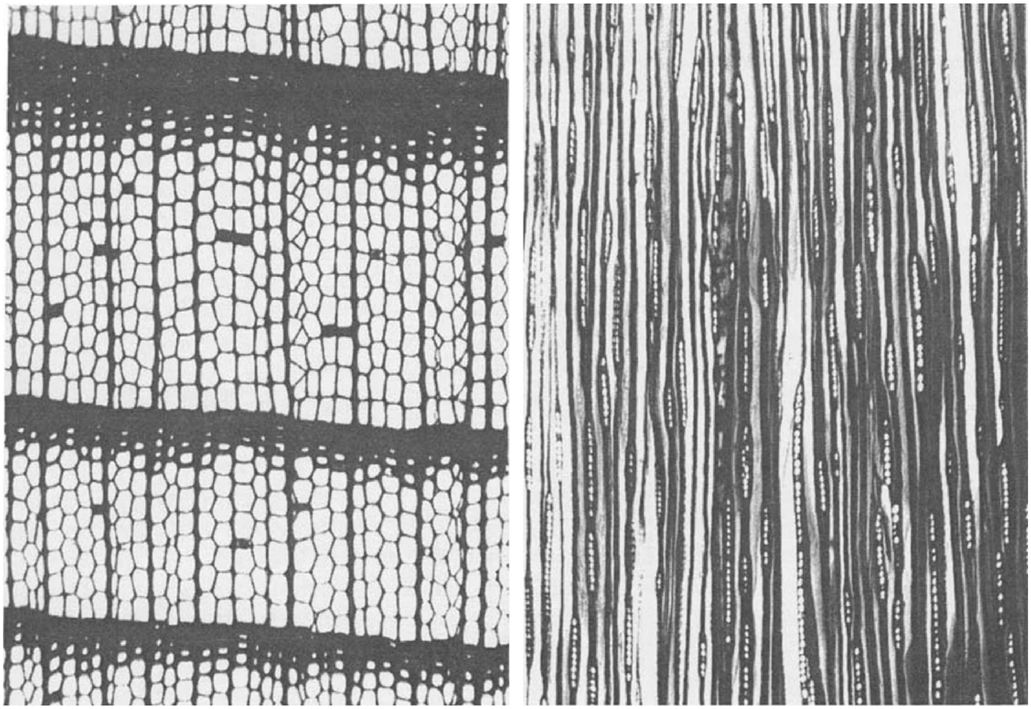


FIGURE 4.50 Bald cypress (*Taxodium distichum*) (50×).

Macroscopic features. The darker heartwood has a more or less rancid odor; the longitudinal surfaces feel distinctly greasy or waxy. The wood lacks resin canals and has an abrupt transition from earlywood to latewood. The growth rings are distinct and irregular in outline and width. The longitudinal parenchyma is often visible with a lens on longitudinal surfaces as strands.

Similar woods. Cypress has a high degree of variability. It resembles the cedars, but the odor is entirely different. Some species of *Cupressus* spp. of the western United States are called cypress but are much different from bald cypress.

Sequoia

***Redwood* (*Figs. 4.51 and 4.52*)**

Redwood (*Sequoia sempervirens*) is a very large tree growing on the coast of northern California. Another sequoia, giant sequoia (*Sequoia gigantea*), grows in a limited area in the Sierra Nevada of California but is used in very limited quantities. Other names for redwood are coast redwood, California redwood, and sequoia. Production of redwood lumber is limited to California, but a nationwide market exists.

Uses. Typical old-growth redwood is moderately light in weight, moderately strong and stiff, and moderately hard. The wood is easy to work, generally straight-grained, and shrinks and swells comparatively little. The heartwood has high decay resistance. Redwood lumber is used for building. It is remanufactured extensively into siding, sash, doors, blinds, finish, casket stock, and containers. Because of its durability, it is useful for cooling towers, tanks, silos, wood-stave pipe, and outdoor furniture. It is used in agriculture for buildings and equipment.

Its use as timbers and large dimension in bridges and trestles is relatively minor. The wood splits readily, and the manufacture of split products (posts and fence material) is an important business in the redwood area. Some redwood decorative veneer is used.

Color. The unique color of redwood heartwood varies from a light cherry to a dark mahogany and distinguishes it from bald cypress. The narrow sapwood (1—3 in.) is almost white.

Macroscopic features. The wood is without normal resin canals and has no distinctive odor, taste, or feel. The wood is coarse textured. The transition to the narrow, dark latewood is abrupt. Western red cedar heartwood may approach redwood in color, but the odor of the former is distinct. The longitudinal parenchyma is visible on longitudinal surfaces with a lens as strands.

Microscopic features. Biseriate or triseriate pitting of tracheids, ray cell smooth end walls, and taxodioid pitting on the cross fields are present.

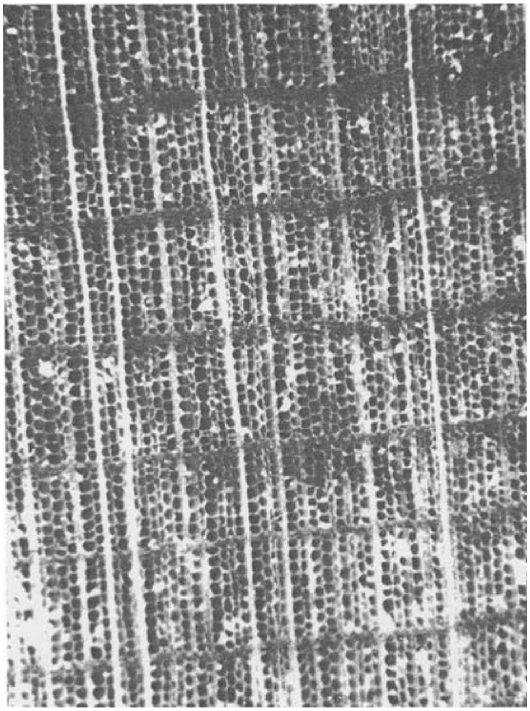


FIGURE 4.51 *Sequoia sempervirens*.

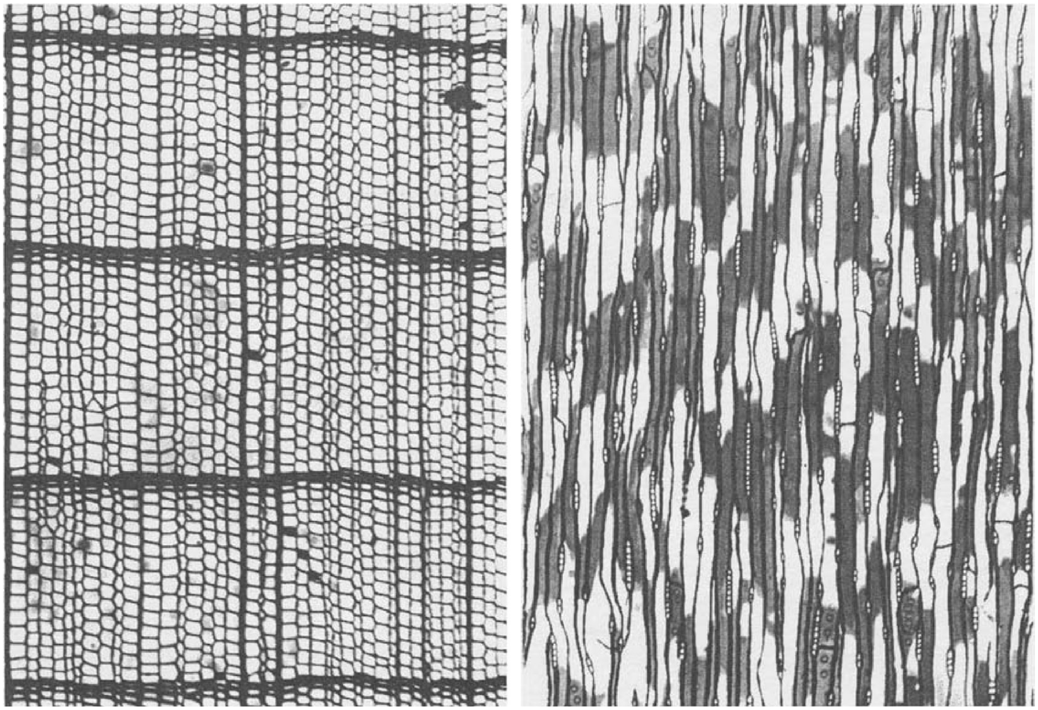


FIGURE 4.52 Coast redwood (*Sequoia sempervirens*) (50×).

Taxaceae

Taxus

YEW (FIGS. 4.53 AND 4.54)

Taxus is a genus of yew family of minor wood importance in the United States. Florida yew (*Taxus floridana*) is rare and confined to a few counties in northwestern Florida. Pacific yew (*Taxus brevifolia*) is native to the United States. A compound called taxol, which is extracted from the bark and needles, has been used in the last few years to treat certain types of cancer. Taxol will be synthesized in the laboratory, and the yew tree will not be harvested for this drug in the future. Pacific yew grows from southeast Alaska to northern California.

Microscopic features. The spiral thickening of yew tracheids and the lack of resin canals are shared with the rare *Torreya,* but yew has cross-field pits that are 8–10 μm, larger than those of *Torreya* (6 μm). The spiral thickenings of *Torreya* are less numerous and steep than those of yew. Information on non–North American species is available in Kukachka (1970).

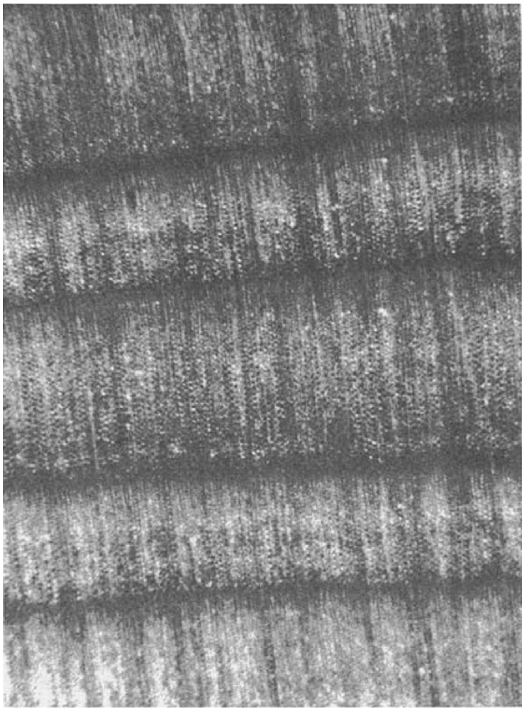


FIGURE 4.53 *Taxus brevifolia.*

Pinaceae

Pinus

RADIATA PINE

Radiata or Monterey pine (*Pinus radiata*) is native to a small area of California but is planted extensively in the southern hemisphere, mainly in Chile, New Zealand, Australia, and South Africa. Plantation-grown trees may reach a height of 80–90 feet in 20 years. The species is not commercially significant in its native United States in part because of its large number of knots. Plantation-grown heartwood is variable in color among trees and is light brown to pinkish brown. It is distinct from the paler creamy sapwood in older trees (more than 40 years old). Growth rings are mostly wide and distinct. False growth rings may be common. Texture is moderately even and fine, and the grain is usually straight. Plantation-grown radiata pine averages about 30 Ib/ft^3 at 12% MCQD (specific gravity of 0.48). The strength is comparable to red pine (*P. resinosa*) although there may be considerable variation because of location and growth rates. The sapwood is prone to attack by stain fungi and vulnerable to boring insects. Radiata pine can be used for the same purposes as other pines of the United States. Bamber and Burley (1983) review the properties of this species. It had been introduced to Australia in the 1850s. In 1979, there were 430,000 ha in Australia, 800,000 in New Zealand, and 600,000 in Chile. It is mostly three needled, with markedly dentate walls in the ray tracheids and 1–4 pinoid cross-field pits of small size. The uniseriate rays have marginal tracheids. The fusiform rays may be 3–5 seriate and 15–20 cells high. The earlywood longitudinal tracheids average 3.0 mm long, 0.045 mm in diameter, and 0.003 mm in thickness. The latewood longitudinal tracheids average 3.5 mm

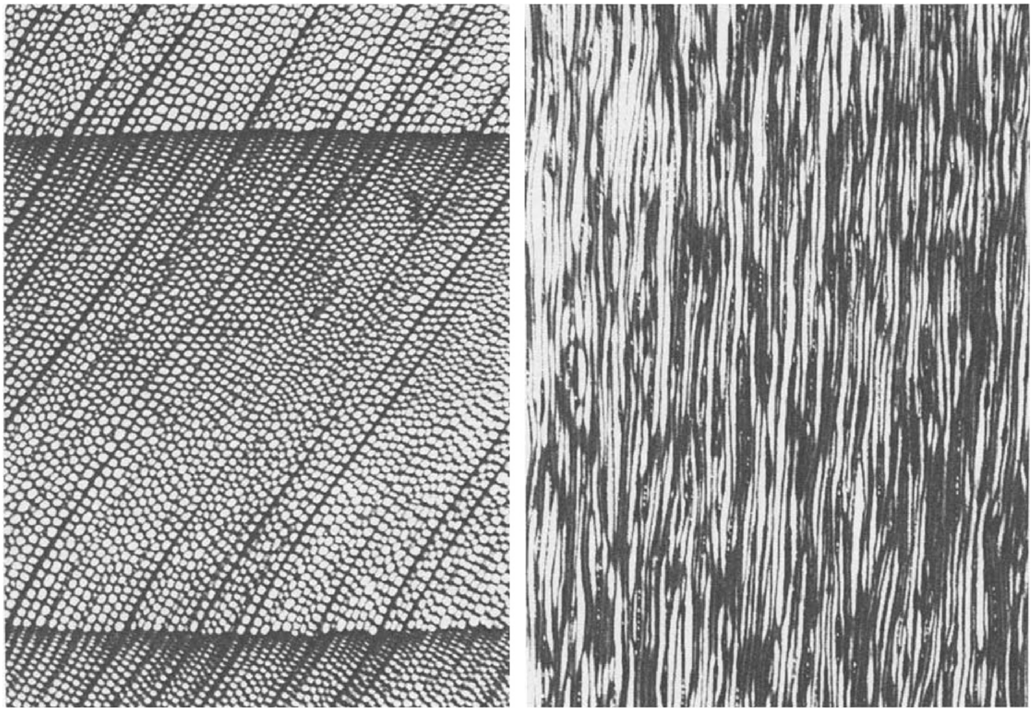


FIGURE 4.54 Pacific yew (*Taxus brevifolia*) (50×).

long, 0.013 mm in diameter, and 0.005 mm in thickness. The cellulose content in mature wood is over 50%, and the lignin content is about 26%.

CARIBBEAN PINE

Caribbean pine (*Pinus caribaea*) occurs along the Caribbean side of Central America from Belize to northeastern Nicaragua. It is also native to the Bahamas and Cuba. It is also called slash pine and British Honduras pitch pine. This tree of the low elevations is widely introduced as a plantation species throughout the world tropics. The heartwood is golden brown to red brown and distinct from the sapwood, which is 1–2 inches in thickness and a light yellow. The softwood species has a strong resinous odor and a greasy feel. The weight varies considerably and may vary from 24 to 51 Ib/ft3 at 12% MCQD although the higher density is much more common. Caribbean pine may be appreciably heavier than slash pine (*Pinus elliotti*), but the mechanical properties of these two species are rather similar. The durability and resistance to insect attack vary with resin content, but generally the heartwood is rated moderately durable. The sapwood is highly permeable. Caribbean pine is used for the same purposes as the southern pines of the United States.

SCOTS PINE

Scots pine (*Pinus sylvestris*), also called red deal, yellow deal, or redwood, grows in Europe.

Picea

Norway Spruce

Norway spruce (*Picea abies*) is also called white deal or whitewood and grows in Europe.

Larix

European Larch

European larch (*Larix decidua*) is also called common larch and grows in Europe.

Cupressaceae

Cupressus

BENTHAM CYPRESS

Bentham cypress (*Cupressus lusitanica*) grows in Mexico and Guatemala. The heartwood is distinct from the sapwood and light reddish brown. The wood is aromatic. The end walls of the ray parenchyma are not nodular, and the indenture is lacking or not obvious.

Fitzroya

Alerce

Alerce (*Fitzroya cupressoides*) is native to southern Chile. The heartwood is reddish brown and sharply defined from the narrow and very light-colored sapwood. The density is 26 Ib/ft^3. Alerce is much like redwood in most regards and used as redwood, but redwood rays are two or three times taller. Alerce has indenture and nodular end walls in ray cells. The rays are mostly under 12 cells high.

Araucariaceae

All three of the species listed in this section lack growth rings and have vertical tracheids with 2—4 bordered pits across their widths in alternate arrangement that are distinctive for this family.

Agathis

Almaciga (Sakar)

Almaciga or sakar (*Agathis philippinensis*) is from the Philippine Islands. *Agathis* lacks the leaf scars that cause the pin knots. Klinki pine lacks the reddish streaks.

Araucaria

A unique characteristic of *Araucaria* and *Agathis* among all other conifers is the 2—4 seriate, alternate intertracheid pitting. Resinous tracheids (near parenchyma) occur in the heartwood of *Agathis* and *Araucaria* of Araucariaceae. They are filled with reddish brown to black amorphous deposits.

Parana Pine

Parana pine (*Araucaria angustifolia*) is not a true pine. It is a softwood that comes from southeastern Brazil and adjacent areas of Paraguay and Argentina. It is available in large clear boards of uniform texture. The small pinhead knots that appear on flat-sawn surfaces (caused by leaf scars) and the light brown or reddish brown heartwood, which is frequently streaked with red, provide desirable figured effects for matching in paneling and interior finishes. The growth rings are fairly distinct and more nearly like those of white pine (*P. strobus*) rather than those of the yellow pines. The wood has relatively straight grain; takes paint well; glues easily; and is free from resin ducts, pitch pockets, and streaks. The sapwood is yellowish and not always distinct from the heartwood, which is a very light brown and frequently shows bright streaks of red. The strength is similar to that of other US softwoods of similar density (loblolly and shortleaf pine), except for its deficiency in compression strength across the grain. Splitting and warping of the kiln-dried wood is due to the presence of compression wood. The principal uses include framing lumber, interior trim, furniture, case goods, and veneer.

Klinki Pine

Klinki pine of hoop pine (*Araucaria klinkii*) is from Australia, New Guinea, New Caledonia, and Norfolk Island. It typically grows to 150 ft with a trunk diameter of 3 ft. The heartwood is light yellowish brown, not sharply demarcated from the straw-colored sapwood. The basic specific gravity is 0.42.

Podocarpaceae

Podocarpus

PODOCARP

A variety of podocarp species (*P.* spp) have limited the use as pulpwood. Common names include podo, yellow wood, and manio. The anatomy of the species varies greatly. Some have resin canals, others do not. The cross-field pitting can be of almost any type, except pinoid. *Podocarpus amarus* grows in New Zealand, South Africa, and Chile and looks somewhat like eastern white pine.

CHAPTER

5

Hardwood Anatomy

5.1 GROSS ANATOMY OF HARDWOODS

Introduction

The references for this chapter are found in Chapter 3 (Vol. 1).

Hardwoods are identified by the presence of vessels (pores), although a few (commercially unimportant) species lack them. *Vessels* are the long tubes (which may extend the length of the tree) for conduction of water made up of individual *vessel elements* (or members) attached end to end. Vessels may be barely visible with a lens in some species and quite obvious in others.

Vessel size distribution (seen in cross section, *x*) *Ring-porous* woods (oaks, ash, elm, hickory, hackberry) have large-diameter vessels in the earlywood that soon decrease in diameter toward the latewood. *Semi-ring-porous* woods have a gradual decrease in vessel diameter through the width of the growth ring, with the earlywood vessels of moderately larger diameter than the latewood. *Diffuse-porous* woods have vessels that do not change much in diameter throughout the growth ring (maple, yellow poplar, sweet gum). Obviously the distinction is somewhat arbitrary, but Fig. 5.1 shows representative samples. The diameter of vessels increases with increasing growth ring width and distance from the pith. Tropical woods tend to be diffuse porous.

The vessel diameters can be very small, below 30 μm; small, 30—100 μm; medium, 100—300 μm; and large, greater than 300 μm. *Vessel position arrangement, grouping* (Fig. 5.2)

In some species, the vessels are isolated and independent of each other (*solitary* as in some maples). The vessels of other species (maple, cottonwood, and alder) form radial rows or multiples of 2—4 or more (*pore multiples*). Some species form radial chains with numerous pores (*pore chains* as in holly). Vessels may also form oblique (diagonal) lines, while still independent of each other. *Ulmiform* latewood vessels occur in wavy, concentric, tangential (parallel to the growth ring) bands in the latewood. Vessels may also cluster (*nested* vessels as in Kentucky coffee tree and black locust), and these clusters may have a characteristic arrangement.

Tyloses

The vessel elements of some species become occluded with tyloses originating from outgrowths of adjacent (often ray, but sometimes longitudinal) parenchyma (Fig. 5.1). This is common during heartwood formation, except in red maple and red oaks. White oaks have large amounts of tyloses, which greatly decreases their permeability. A classic work (Chattaway, 1932)

Biermann's Handbook of Pulp and Paper: Raw Material and Pulp Making
https://doi.org/10.1016/B978-0-12-814240-0.00005-7

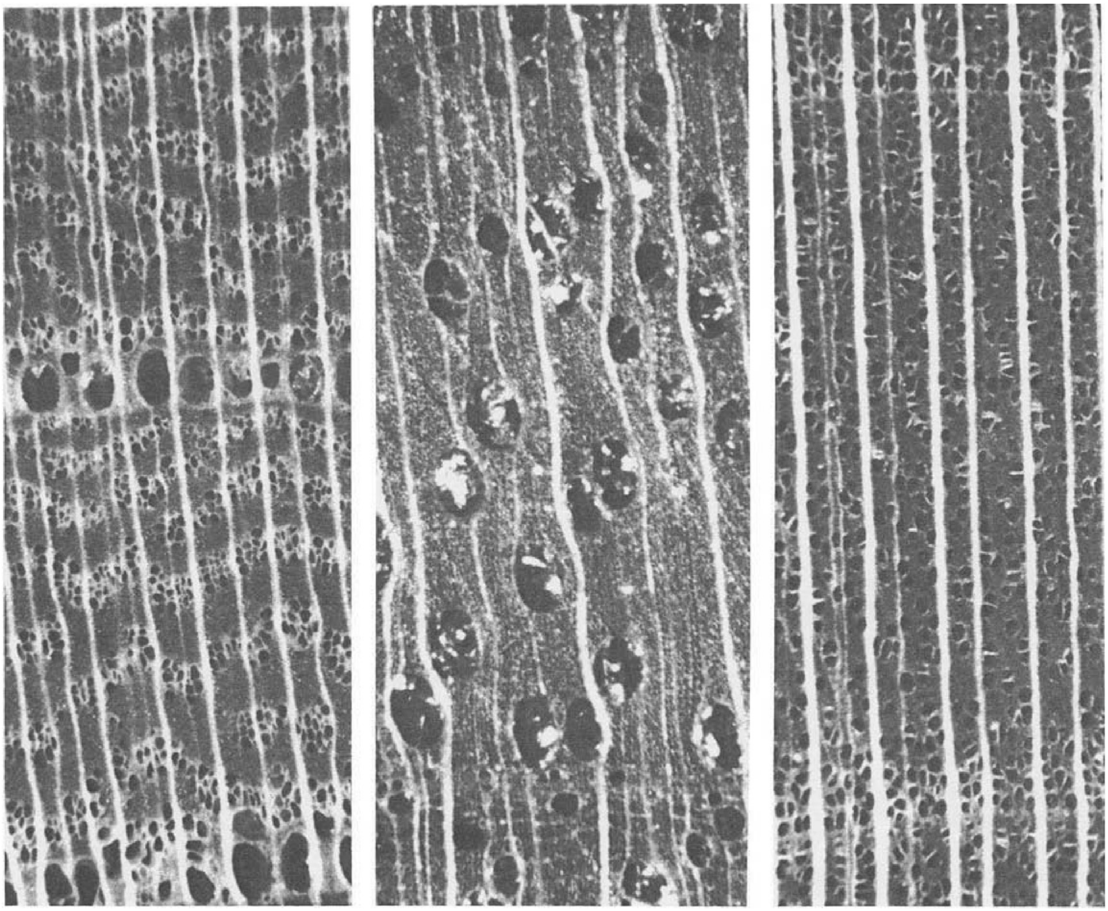


FIGURE 5.1 Ring-porous (*Ulmus americana*), semi-ring-porous (*Juglans nigra*), and diffuse-porous (*Prunus serotina*) woods. Tyloses fill many of the vessels of the first two examples.

hypothesizes that if pits between vessel and adjacent parenchyma are 8–10 μm or larger, tyloses are able to form; otherwise occlusion may be by gum formation as in black cherry or maple.

Parenchyma Cell Arrangement (×)

Parenchyma cells are arranged longitudinally (*axial*) or radially (*ray*). Axial parenchyma may be rare or absent but are generally present. The longitudinal arrangement has been described by Jane (1956, p. 115) based on work by Kribs in 1950. Parenchyma cells are often visible as white bands in hardwoods. *Marginal* (boundary) parenchyma is found in bands near the boundary of the growth ring Plate 5.1A. They may be *terminal* if occurring in the latewood or *initial* if occurring in the earlywood. *Epithelial* parenchyma surrounds longitudinal gum canals in traumatic gum canals (for example, in wounded sweet gum).

Apotracheal parenchyma is arranged independently of the vessels. They may be *diffuse* or *banded* (forming groups of 2–4 or more cells

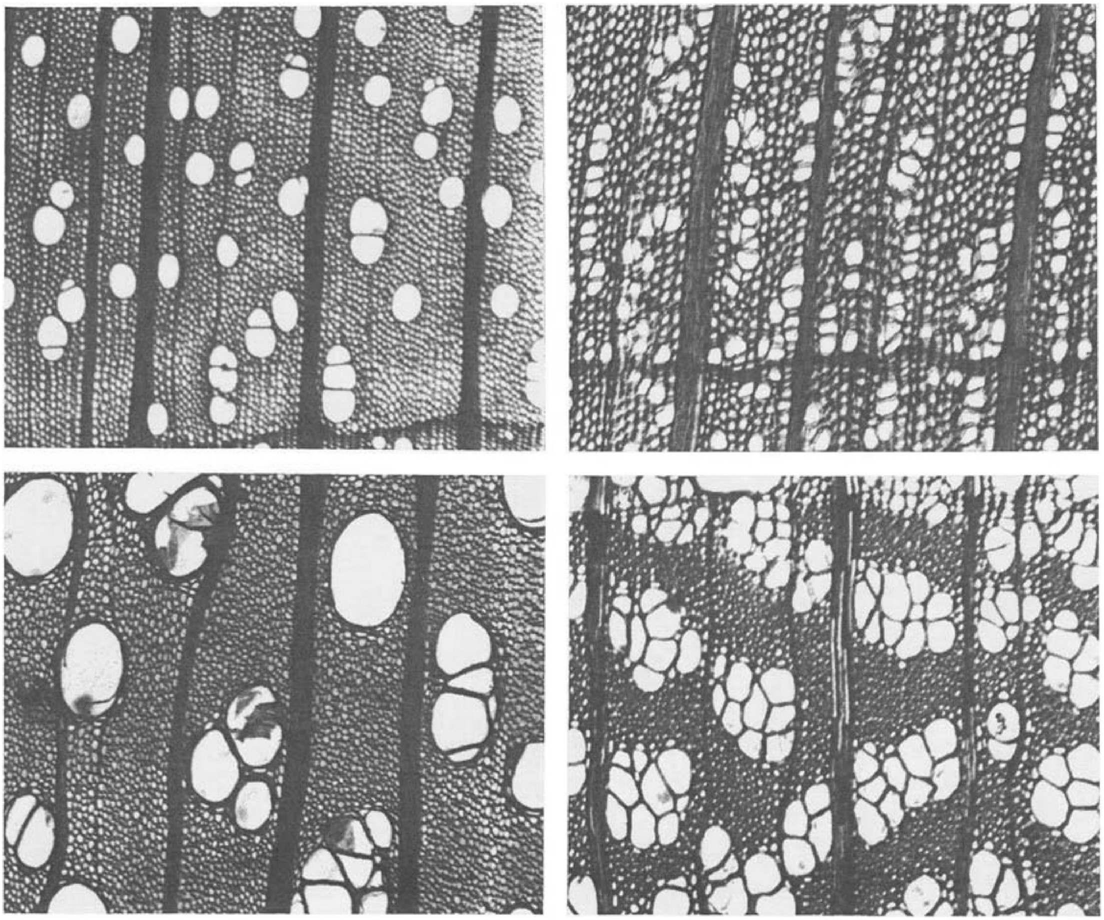


FIGURE 5.2 Solitary and pore multiples in *Acer saccharum* (top left), pore chains in *Ilex opaca* (top right), nested pores in *Nyssa silvatica* (bottom left), and ulmiform pores in *Ulmus americana* (60×).

wide parallel to the growth rings). Lines of banded parenchyma may form a net-like appearance with rays known as *reticulate parenchyma* as in hickory and persimmon (Plate 5.1B). If the parenchyma cells are arranged around the vessels, they are called *paratracheal*. If they partially surround the vessels, they are *scanty*. If they form a partial band around the vessel all on one side, they are *unilateral*. They may totally encircle the vessel (*vasicentric*, Plate 5.1C) and have lateral wings (*aliform*) or long lateral wings that merge with each other (*confluent*).

Ray Appearance

Oaks, maples, and beeches contain rays that are readily visible in all three views. *Aggregate rays* consist of radial and longitudinal cells that are intermixed and occur in addition to smaller rays (red alder and American hornbeam). *Storied rays* are a series of rays that each have and occur at the same height (in the tangential view, *t*) (American mahogany). Some species have rays that are not observed with a hand lens.

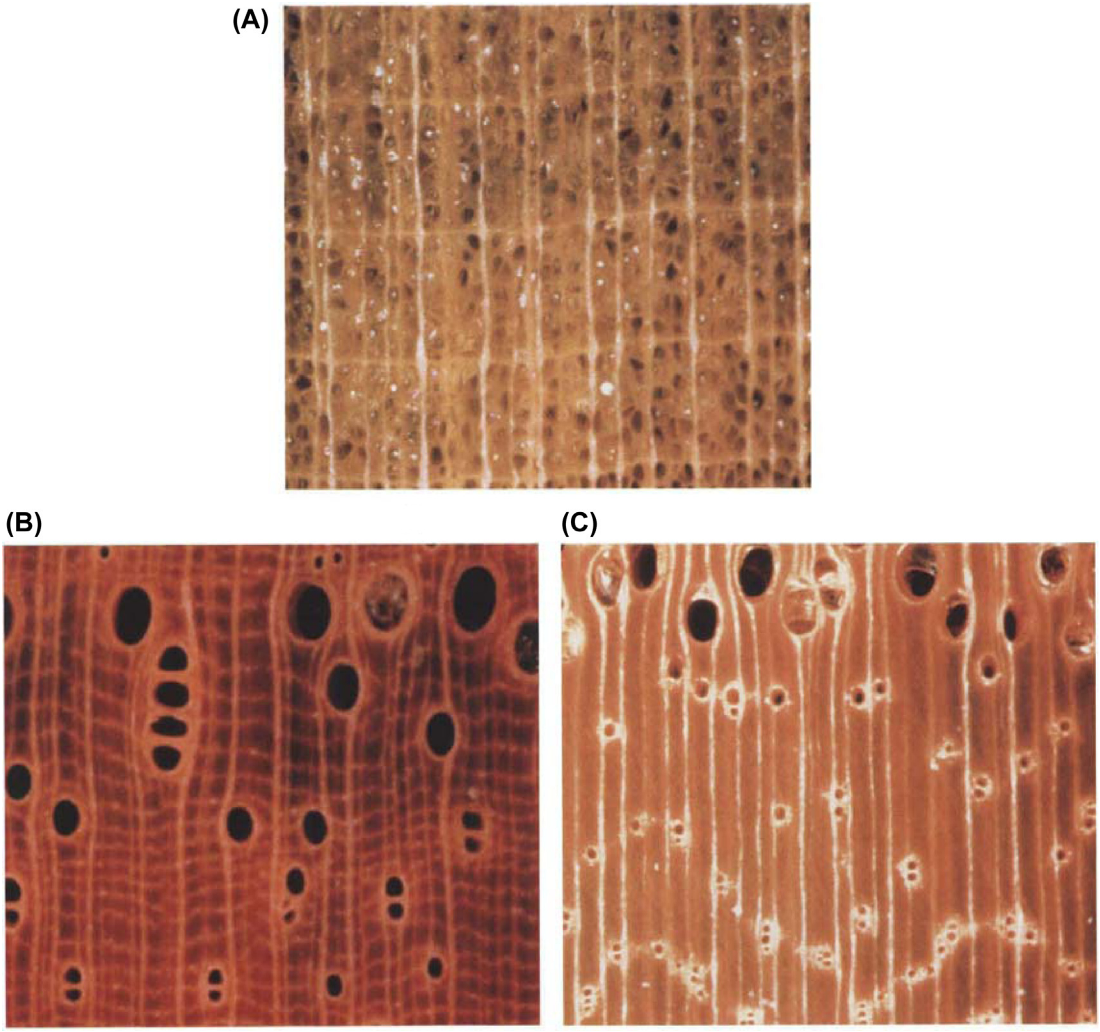


PLATE 5.1 Hardwood parenchyma types: (A) marginal of yellow poplar, (B) reticulate of hickory, and (C) vasicentric of ash.

The ray width relative to vessel diameter, the number of rays over a given area, and the percentage of cross-sectional area covered by rays are three items that may be important. Some rays expand at the growth ring boundary (*x*) in *noded* rays [yellow poplar (Plate 5.1A), beech, and sycamore]. Large rays show as *ray flecks* (*r*).

Color

The heartwood of many hardwood species is characteristic. Black walnut has a dark brown heartwood; the color of black cherry varies from light to deep brown with high luster; ebony is almost black; yellow poplar heartwood has a greenish cast with patches or streaks from red to dark brown; the small black heartwood of persimmon resembles ebony, to which it is related; red gum has a dingy, reddish-brown color; buckeye has a uniform creamy yellow color. Osage orange is very similar to black locust, but the former gives off a water-soluble yellowish dye when extracted with water. A reference collection of known species is useful for color comparisons.

Odor

Teak, sassafras, and Oregon myrtle have distinctive odors. Bass wood (said to be like raw potatoes) and catalpa (said to be like kerosene) have odors that can be helpful in their identification, especially in freshly cut green wood.

Fluorescence

Hoadley (1990) describes the fluorescence of wood using long-wave UV lamp sources. Among US woods, this technique is useful with members of the Leguminosae family, including black locust (to separate it from Osage orange), honey locust, Kentucky coffee tree, and acacia. Wood from *Rhus* and *Ilex* genera also fluoresce.

Resin Canals

Longitudinal resin canals may occur in hardwoods, but they are rare in US species. The *schizogenous* type (Fig. 5.3) occurs by separation of cells and is lined with epithelium cells (as in traumatic resin canals of softwoods); they often occur in a single tangential row. The *lysigenous* type occurs by lysis (dissolution) of cells and is not lined with epithelial cells.

5.2 MICROSCOPIC ANATOMY OF HARDWOODS

Spiral Thickening of Vessels

Some vessel elements (Fig. 5.4) have spiral thickening (*Tilia americana*, sweet bay, maples). This is limited to the elongated tips (*ligules*) of the vessel elements in sweet gum and black tupelo and to latewood vessels and vascular tracheids in elm and hackberry. It is rare in tropical species.

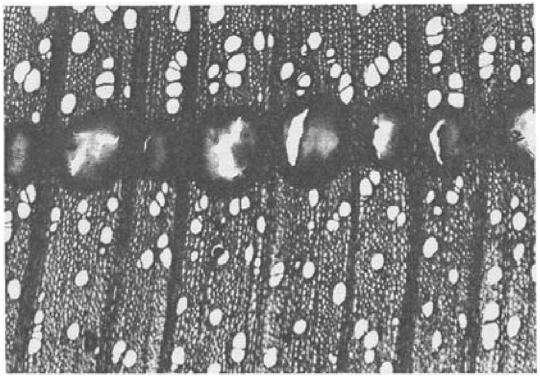


FIGURE 5.3 Traumatic resin canals from *Prunus serotina* filled with a gummy mass.

Vessel Element Perforation Plates (Radial View, *r*)

The perforation plates of vessel elements occur where two vessel elements join end to end. *Simple* perforation plates have a single opening (without bars) as in the maples. *Scalariform* perforation plates have a series of bars across the opening. The number of bars is an important identifying attribute and varies from a few in yellow poplar to many in sweet gum (Fig. 5.4).

Intervessel Pitting

The pitting between side-by-side vessels (Figs. 5.5–5.7) is usually observed on the tangential face, but it may be more visible on the radial face when near the ends of vessels when vessels are isolated from each other. Intervessel pitting may be opposite (Fig. 5.5, forming horizontal rows) or, more commonly, alternate (forming diagonal rows. Fig. 5.6). The pits of the various

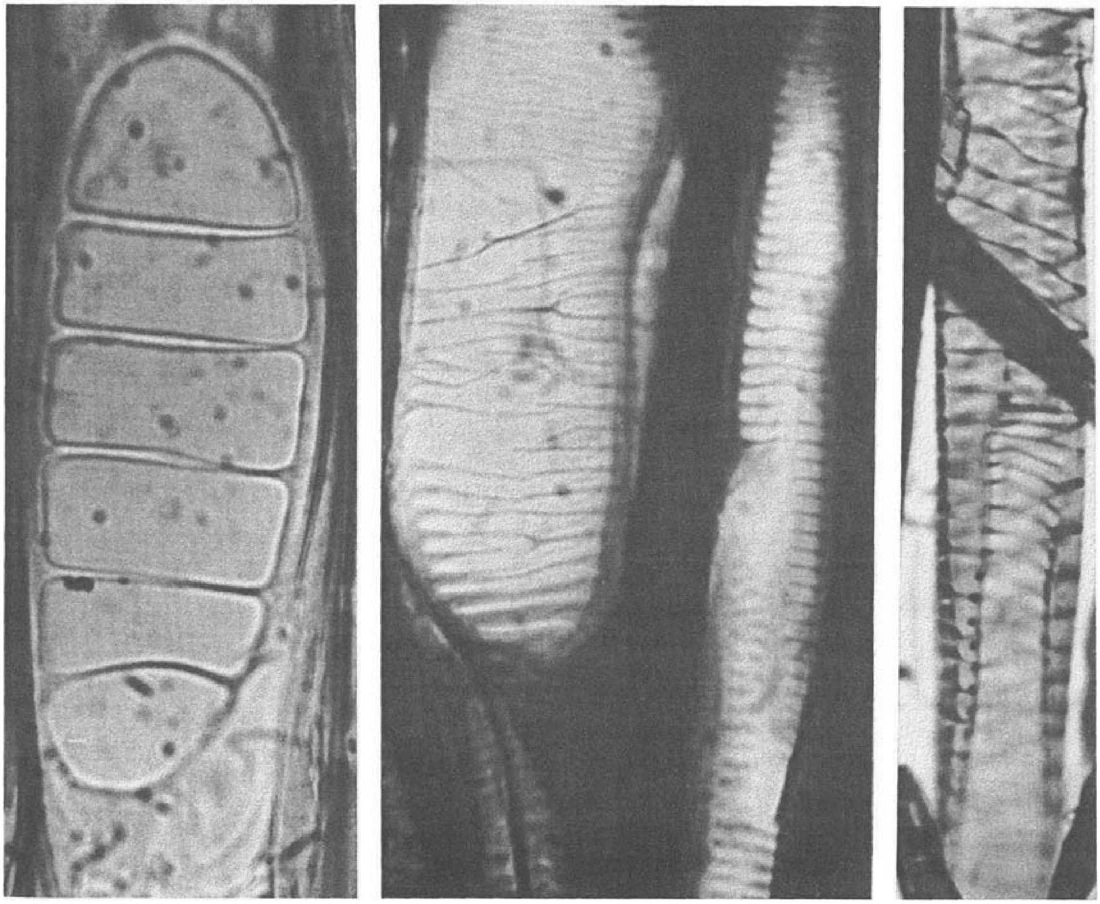


FIGURE 5.4 Scalariform perforation plates of vessels in *Liriodendron tulipifera* left), *Nyssa sylvatica* (center, two examples), and *Ilex opaca* (right, at bottom with spiral thickenings as well) (600×).

species differ in size and shape. This is a key feature for the identification of hardwood fibers. Pits that are long across the vessel diameter and narrow in the longitudinal axis are called *linear* or *scalariform* (Fig. 5.7). The pit outline is also of relevance (angular, rounded). Intervessel pitting is rare in oaks and sweet gum. The pit pairs from vessels to ray parenchyma may be bordered, half-bordered, or simple (Brown and Panshin, 1940). The ray to vessel pitting is compared with intervessel pitting (similar or dissimilar; rounded, oval, elongated); see ray to vessel pitting below. Woods in the Leguminosae family and many tropical species have *vestured* intervessel pitting. This is characterized by outgrowths in the pit chamber to give it a jagged appearance, although it is difficult to see by light microscopy.

Ray Appearance

Hardwoods do not have ray tracheids. *Homocellular* rays consist of *procumbent* cells only (cells with the long axis parallel to the radial direction). *Heterocellular* rays have two types of

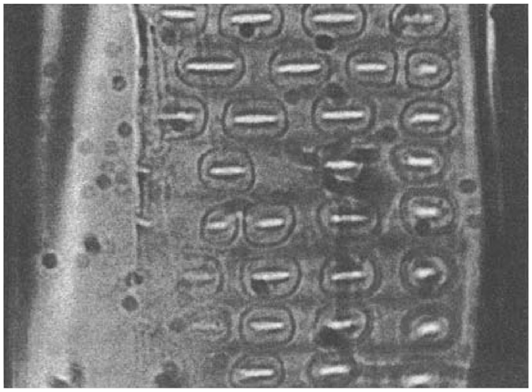


FIGURE 5.5 Opposite intervessel *Liriodendron tulipifera*, 600×.

cells: cells with the long axis arranged longitudinally (*upright*) and procumbent cells (Fig. 5.8). Upright cells are often restricted to the margins (top and bottom) of the rays.

Uniseriate rays are 1 cell wide and may range from 1 to 3 cells to over 12 cells in height. Rays may also be multiseriate and very wide in oaks and maples. *Aggregate* (occasionally called false) rays are closely spaced rays that form a large structure that is visible with the hand lens. Some procumbent cells of a ray may be subdivided into many small erect empty cells (*tile cells*), which occur in some families of the Malvales order. Some hardwoods (sassafras and Oregon myrtle of the Lauraceae family) contain enlarged upright ray cells known as *oil* cells.

Ray to Vessel Pitting

Ray to vessel pitting can be similar to or different from intervessel pitting. Fig. 5.6 shows an example where the ray to vessel pitting is different from the intervessel pitting. If it is similar, its appearance is known by the intervessel pitting. If it is different it may be essentially simple and elongated or it may be simple to bordered. It is unique in *Populus* and *Salix*.

Fiber Tracheids and Libriform Fibers

There are two types of fibers that may intergrade to a degree (Fig. 5.9). Fiber tracheids have bordered pits and tend to have relatively large lumens. Libriform fibers have simple pits and tend to have relatively small diameter lumens. Libriform fibers can be stiff due to the thick cell wall. These differences may be difficult to see by light microscopy.

Tracheids

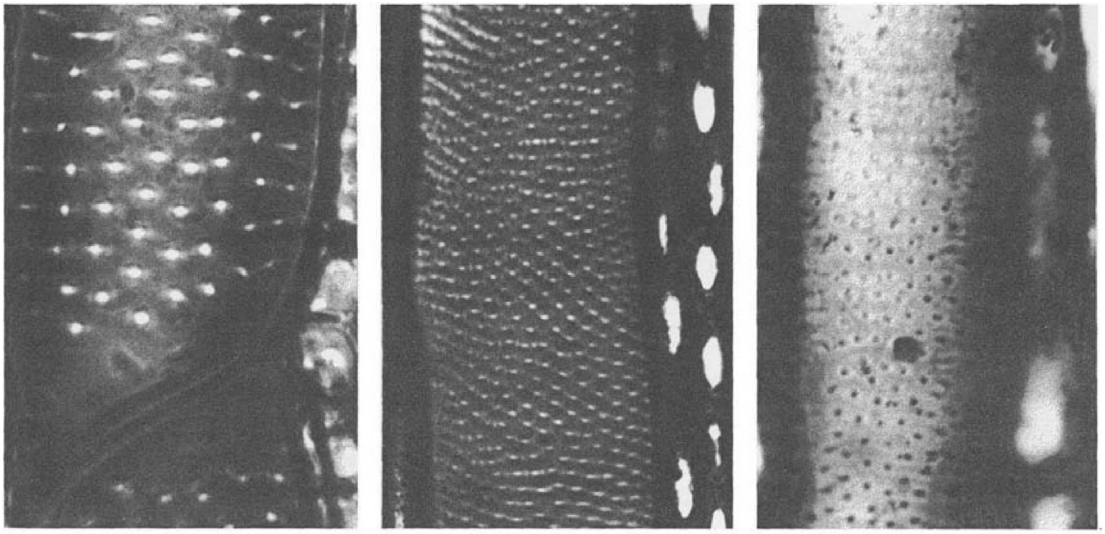
Two relatively rare (in US species) types of tracheids occur. These are not required for identification of large wood samples but may be useful in the identification of slivers and pulp fibers. *Vascular* tracheids of hardwoods may appear to be like the latewood vessel elements but have pitting at the end walls instead of perforation plates (elm, hackberry). *Vasicentric* tracheids (oaks) are shorter than libriform fibers but of larger diameter, have an irregular outline, distinctive pitting, and *crassulae*, thickenings of the cell wall. They occur in horizontal clusters in association with vessel elements, especially in the earlywood. They are found in the oaks, tan oak, and eucalypts.

Future Research

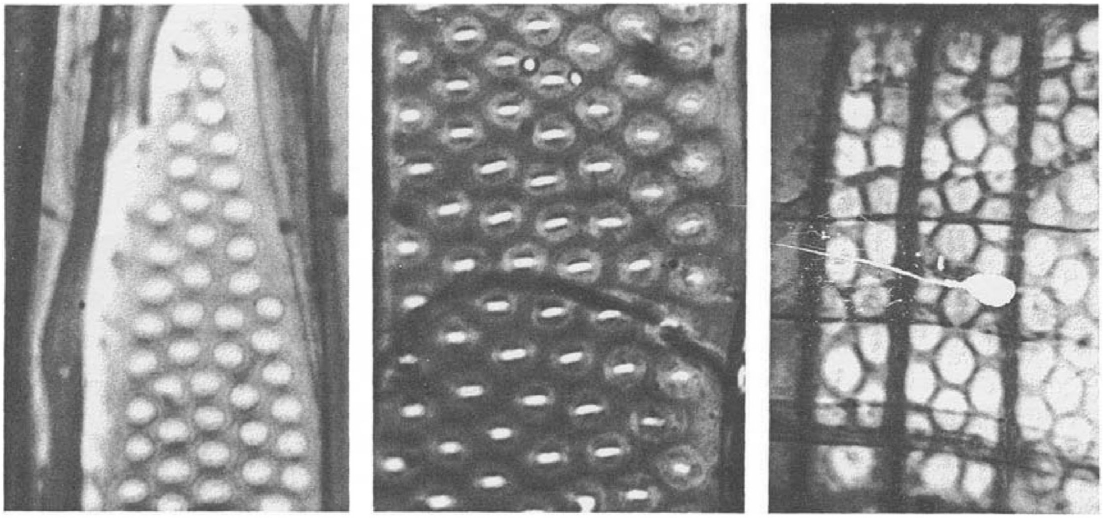
An interesting value for hardwoods would be the parenchyma value by mass (or at least the useful fiber content). This could be obtained by an acid chlorite treatment of wood shavings followed by fiber fractionation (a 200 μm screen is said to isolate fines and parenchyma cells). Each fraction should be examined microscopically to determine the efficiency of the separation. This would give an indication of the useful amount of fiber in hardwood.

Summary

A summary of features for many hardwoods is given in Table 5.1.



Carya ovata, > 12 μm *Betula papyrifera*, > 5 μm *Fraxinus penn.*, > 5 μm



Aesculus octandra, > 12 μm *Populus tricarpa*, > 12 μm *P. tricarpa* ray contact area

FIGURE 5.6 Examples of alternate, intervessel pitting, 600×.

5.3 ANATOMY OF HARDWOOD SPECIES

Hardwoods are listed alphabetically in this section (usually ignoring geographical, color, and other prefixes) because of the numerous families, genera, and variety that occurs. For a listing by family and order see Table 3.4 (Vol. 1).

The *uses* section includes the properties related to the uses of wood. The mechanical

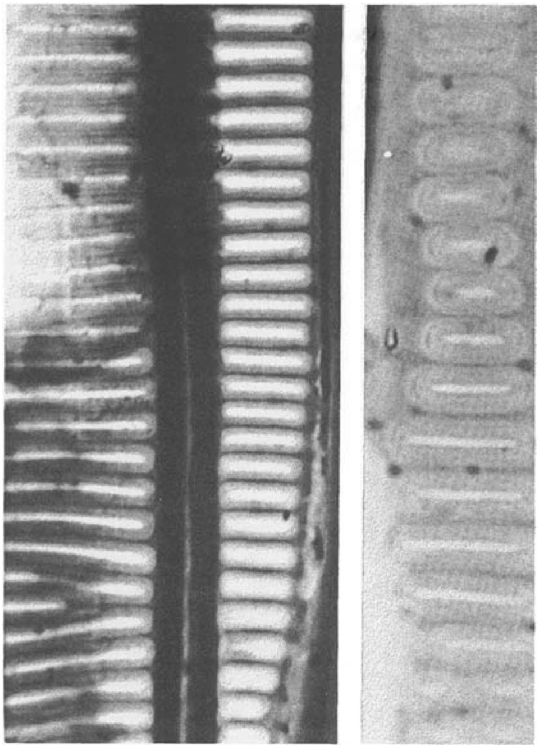


FIGURE 5.7 Scalariform intervessel pitting of *Magnolia acuminata* (left) and less pronounced in *Liquidambar styraciflua* (right), 600×.

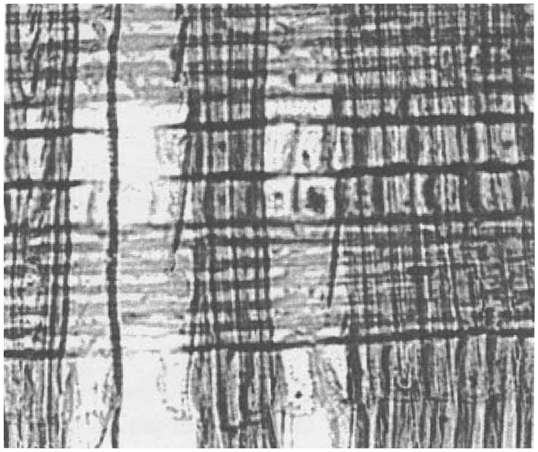


FIGURE 5.8 Heterocellular *sylvatica* (150×).

properties are of relevance to wood chipping. The *color* section includes the overall appearance. Many sapwoods are stained with blue stain, a type of fungi, that modifies the natural color of the sapwood.

Macroscopic features refer to those that can be seen with the unaided eye or with a l0× lens. The words pores and vessels are used synonymously throughout. The presence of tyloses often tends to make the vessels difficult to see on the cross section with the unaided eye, so the appearance and the actual sizes of vessels are not the same. Parenchyma descriptions in this section refer to longitudinal parenchyma. Most of the macroscopic cross sections are courtesy of R.L. Krahmer and A.C. VanVliet; they are all the same magnification, about 15–20×. While the taste of some woods is mentioned, it is not a good idea to apply this for routine sample identification of large numbers of samples.

Red Alder (Fig. 5.10)

Red alder (*Alnus rubra*) grows along the Pacific coast between Alaska and California. It is used commercially along the coasts of Oregon and Washington and is the most abundant commercial hardwood species in these States. European black alder (*Alnus glutinosa*) is native to Europe, North Africa, and Asia; it now grows in the Northeast to North Central United States into Canada. As alder is a legume, the wood has high levels of nitrogen and is a rapidly decaying wood. Vessel elements of aged alder contain an orange-red pigment that may survive pulping and bleaching [Karchesy et. al., 7. *Chem. Soc. Chem. Comm*. 649–650(1974)].

Uses

The main use is for furniture, but it is also used for sash, doors, panel stock, and millwork. It has appreciable use in pulp and paper.

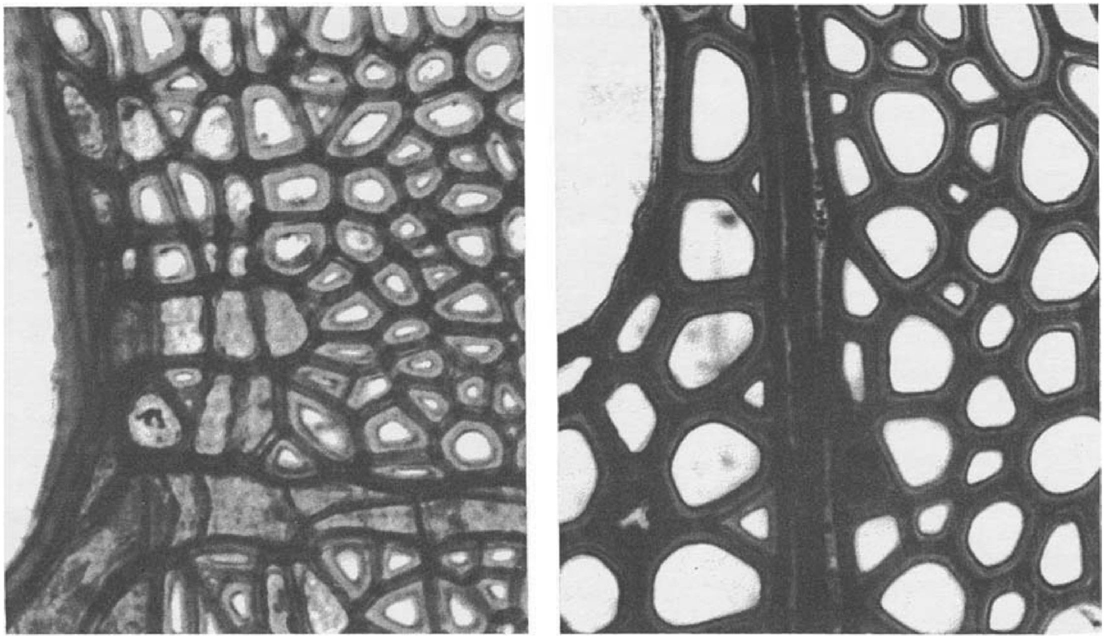


FIGURE 5.9 Libriform fibers of *Fraxinus* (left) and fiber tracheids of *Betula papyrifera* (600×).

Color

The wood of red alder varies from almost white to pale pinkish brown and has no visible boundary between heartwood and sapwood. It is moderately light in weight, intermediate in most strength properties, but low in shock resistance. Red alder has relatively low shrinkage.

Macrostructure

The wood is diffuse porous and the growth rings are delineated by a whitish or brownish line. The latewood vessels are numerous, small, and occur in small clusters or multiples. Longitudinal parenchyma is not visible. The wide, aggregate rays are distinctive.

Similar Woods

Red alder is sometimes confused with birch, but birch is harder and does not have the wide, aggregate rays.

Ash (Figs. 5.11 and 5.12)

Important species include white ash (*Fraxinus americana*), green ash (*Fraxinus pennsylvanica*), blue ash (*Fraxinus quadrangulata*), black ash (*Fraxinus nigra*), pumpkin ash (*Fraxinus profunda*), and Oregon ash (*Fraxinus latifolia*). Another 12 species account for only a few percent of the commercial cut. The first five of these species grow in the eastern half of the United States and are grouped together commercially. Oregon ash grows along the Pacific coast. Commercial white ash is a group of species that consists mostly of white ash and green ash, although blue ash is also included.

Uses

Second-growth white ash is sought as it is especially heavy, strong, hard, stiff, and has high resistance to shock; it is used principally for handles, oars, vehicle parts, baseball bats,

TABLE 5.1 Anatomical Characteristics of Deciduous Woods Useful in Their Identification

Common Name	Ailanthus	Alder, red	Ash	Basswood, American	Beech, American	Birch, paper etc.	Buckeye, Ohio etc.	Butternut	Catalpa	Cherry, black	Chestnut, American	Cucumber tree	Dogwood	Elm, American	Elm, red (slippery)	Elm, rock (hard)	Hackberry, etc.	Hickory, pecan	Hickory, true	Holly, American	Honeylocust	Hophornbeam	Hornbeam, American	Locust, black	Madrone, Pacific		Magnolia, south. etc.	
Scientific Name	*Ailanthus altissima*	*Alnus rubra*	*Fraxinus spp.*	*Tilia americana*	*Fagus grandifolia*	*Betula papyrifera*	*Aesculus glabra*	*Juglans cinerea*	*Catalpa spp.*	*Prunus serotina*	*Castanea dentata*	*Magnolia acuminata*	*Cornus florida etc.*	*Ulmus americana*	*Ulmus rubra*	*U. thomasii*	*Celtis occidentalis*	*Carya spp.*	*C. spp.*	*Ilex opaca*	*Gleditsia triacanthos*	*Ostrya viginiana*	*Carpinas caroliniana*	*Robinia pseudoacacia*	*Arbutus menziesii*		*Magnolia grandiflora*	
Page No		000	000	000	000	000	000	000	000	000	000		000	000	000	000	000	000	000		000			000			000	
Use this for alignment	1	2	3	4	5	6	7	8	9	0	1	2	3	4	5	6	7	8	9	0	1	2	3	4	5	6	7	8
Vessels																												
Ring porous	X		X					X			X			X	X	X	X	x	X		X			X				
Semi-ring porous								X	X	X								X	X									
Diffuse porous		X		X	X	X	X					X	X							X		X	X		X		X	
Spiral thickening				A			S		L	A				L	L	L	L			F	L	A	A	L	F		A	
Arrangement-mostly solitary	-	S	S		X							S	X												S		S	
-of clusters	-	M	M	M	M	M	M	M	N	M	M	M	M	W	W	W	W	M	M	C	N	M	M	N	M		M	
Perforation plates-simple	-		X	X	X		X	X	X	X	X	X		X	X	X	X	X	X		X	X	X	X			X	
-scalariform (T some >10 bars)	-	T		S	S	T					S	S	T							T		S	S		X		X	
Intervessel Pitting																												
Opposite	-	S											X															
Alternate	-	X	X	X	X	X	X	X	X	X	X	X		X	X	X	X	X	X	X	X	X	X	X	X			
Scalariform	-												X														X	
Linear	-												X														X	
Fibers																												
Libriform	-		X				X		X		X			X	X	X	X	X	X		X	X		X				
Fiber tracheids	-	X		X	X	X	S	X		X	X	X	X					X	X	X			X		X		X	
Ray Composition																												
heterocellular					?		?	S	S	S		X	X				X	X	X	X		S	X	S	X		X	
homocellular	X	X	X	X	X	X	X	X	X	X	X	X		X	X	X					X	X		X			X	
Ray-vessel pitting (1, 2, 3)	3	1	1		3	1	2	1	1		3	3	1	3	3	3	2	1	1	1	1	3	3	3	3		3	
Tracheids present	-		C								C			R	R	R	R											
Use this for alignment	1	2	3	4	5	6	7	8	9	0	1	2	3	4	5	6	7	8	9	0	1	2	3	4	5	6	7	8

Continued

TABLE 5.1 Anatomical Characteristics of Deciduous Woods Useful in Their Identification—cont'd

Common Name	*Maple, Hard*	sugar (and black)	Maple, soft red	silver	Mulberry, red	Oak, red group	Oak, white group	Oak. live	Oregon-myrtle	Osage orange	Persimmon	Poplar Family	aspens	cottonwoods	Sassafras	Sugarberry	Sweetgum	Sycamore, American	Tanoak	Tupelo	Walnut, black	Willow, black	Yellow-poplar	*Non U.S. Species*	Eucalypts	Gmelina		
Scientific Name		*Acer saccharum*	*A. rubrum*	*A. saccharinum*	*Morus rubra*	*Q. rubra* etc.	*Q. alba* etc.	*Q. viginiana*	*Umbellularia californica*	*Maclura pomifera*	*Diospyros virginiana*		*Populus spp.*	*P. spp.*	*Sassafras albidum*	*Celtis laevigata*	*Liquidambar styraciflua*	*Platanus occidentalis*	*Lithocarpus densiflorus*	*Nyssa spp.*	*Juglans nigra*	*Salix nigra*	*Liriodendron tulipifera*		*Eucalyptus* spp.	*Gmelina arborea*		
Page No		000	000	000	000	000	000	000		000	000		000	000	000		000	000	000	000	000	000	000		000	000		
Use this for alignment	1	2	3	4	5	6	7	8	9	0	1	2	3	4	5	6	7	8	9	0	1	2	3	4	5	6	7	8
Vessels																												
Ring porous					X	X	X			X					X	X					X							
Semi-ring porous								X			X		X	X					X		X	X						
Diffuse porous		X	X	X					X				X	X				X		X		X	X					
Spiral thickening		A	A	A	L					L						L	T			T								
Arrangement-mostly solitary		X	X	X					S						S			X	X	S			S		—	—		
-of clusters		M	M	M	N	M	M	M	M	N	M		M	M	M	W	M	M		M	M	M	M		—	—		
Perforation plates-simple		X	X	X	X	X	X	X	S	X	X		X	X	X	X		X	X		X	X			X	X		
-scalariform (T >10 bars)									X						S		T	S		T			T					
Intervessel Pitting																												
Opposite																	X			X			X					
Alternate	X	X	X	X	X	X	X	X	X	X	X		X	X	X	X		X	X		X	X			—	—		
Scalariform																	S						S					
Linear																	X			S			S		—	—		
Fibers																												
Libriform		X	X	X	X	X	X	X	X	X	X		X	X	X	X			X			X	X		—	—		
Fiber tracheids		X	X	X		X	S	X							X		X	X	X	X	X		X		—	—		
Ray Composition																												
heterocellular					X				X	X	?				X	X	X			X	?	?	X		X	X		
homocellular		X	X	X	X	X	X	X			X		X	X	X		X	X	X		X		X					
Ray-vessel pitting (1, 2, 3)		1	1	1	3	3	3	3	2	2	1		3	3	3	2	3	1		1	1	2	3					
Tracheids present						C	C	C								R			C						C			
Use this for alignment	1	2	3	4	5	6	7	8	9	0	1	2	3	4	5	6	7	8	9	0	1	2	3	4	5	6	7	8

Key: X indicates characteristic is pronounced. x indicates characteristic is present but not pronounced (when used with X, it is the less likely of the two choices). S indicates a feature is sporadic, ? indicates sources disagree. Spiral thickening (Core et al, 1979, p. 78). *S*, sporadic; *A*, all vessels; *L*, latewood vessels only; *F*, fibers and vessels; *T*, vessel tips only. Vessel arrangement of clusters; *M*, multiples; *C*, chains; *W*, wavy bands; *N*, nested. Ray vessel pitting (Core et al., 1979, p. 68). *1*, essentially like intervessel pitting; *2*, essentially simple; *3*, simple to bordered. Tracheids present; *C*, vasicentric; *R*, vascular.

Panshin and de Zeeuw (1980); Hoadley (1990); and other.

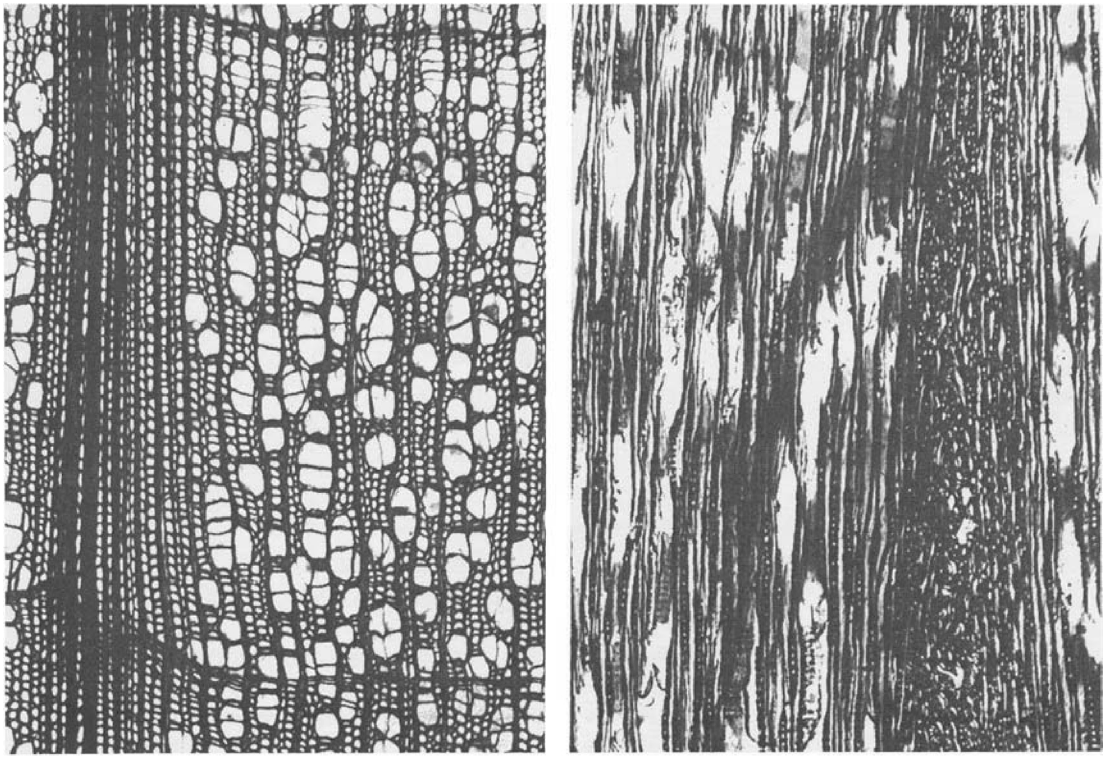


FIGURE 5.10 Red alder (*Alnus rubra*) (50×).

and other sporting and athletic goods. The best handle specifications require 5 to 17 growth rings per inch and a weight of at least 43 Ib/ft3 at 12% MC.

Ash wood of lighter weight, including black ash, is sold as cabinet ash and is suitable for cooperage, furniture, and shipping containers. Some ash is cut into veneer for furniture, paneling, and wire-bound boxes.

Color

The heartwood is grayish brown, sometimes with a reddish tinge; the sapwood is light-colored or nearly white and several inches wide. Second-growth trees have a large proportion of sapwood. The annual rings are very distinct and mostly of moderate width.

Macroscopic Structure

Green ash and white ash are ring-porous woods that are difficult to distinguish anatomically. The earlywood vessels form a ring that is 2 or 3 (4 in wide rings) pores wide; they usually contain tyloses, except in the outer sapwood. Latewood vessels are very small and appear as white specks that are not numerous and are scattered singly or in groups of two. The latewood pores are arranged in short, radial multiples that are sparsely distributed.

The rays are small, normally spaced, and uniform in size; they are not distinct without a lens. The longitudinal parenchyma is paratracheal, being associated with the latewood vessels; they form wavy, tangential lines visible without a lens, especially in the outer latewood of wide

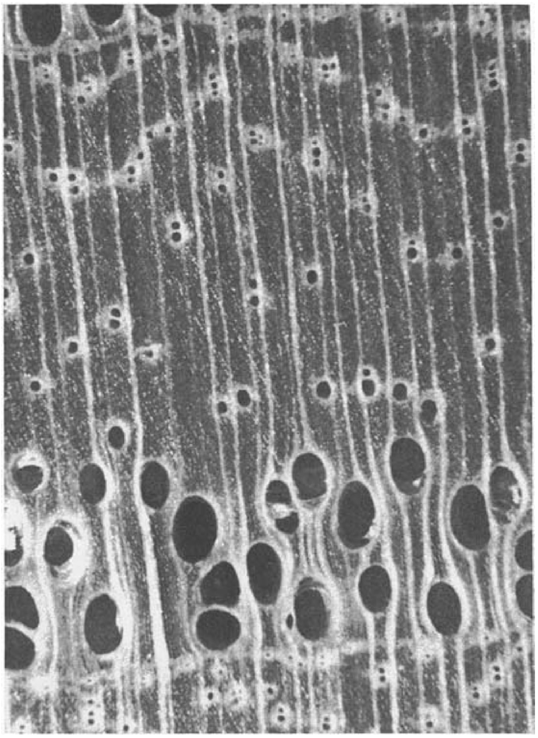


FIGURE 5.11 *Fraxinus* spp.

growth rings. The tangential bands of parenchyma are wider in green ash and narrower in black ash than in white ash. White ash has more luster, darker heartwood, and usually has wider growth rings than brown (black) ash, which may be very slow growing. The latewood pores of white ash are more prominent than those of black ash.

Microscopic Structure

Intervessel pitting of white ash is alternate with rounded pits in outline.

Similar Woods

Hickory is distinguished from ash by the presence of abundant apotracheal parenchyma in the latewood, whereas white ash has paratracheal and paratracheal confluent parenchyma. The earlywood pores of hickory are more distinctive than those in ash. In chestnut, the vessels of the latewood are numerous and in radial bands. In catalpa and sassafras, the latewood vessels are numerous but in tangential bands, whereas in the ashes, they are few and scattered and surrounded by parenchyma so as to appear in tangential bands. Sassafras is readily distinguished by its spicy odor.

Aspen

Aspen is applied to bigtooth aspen (*Populus grandidentata*) and to quaking aspen (*Populas tremuloides*) but not balsam poplar (*Populas balsamifera*) and the species of *Populus* that make up the group of cottonwoods (see Figs. 5.28 and 5.29). The lumber of aspens and cottonwood may be mixed in trade and sold either as poplar ("Popple") or cottonwood. The name poplar should not be confused with yellow poplar (*Liriodendron tulipifera*), also known in the trade as poplar. Aspen lumber is produced mainly in the Northeastern and Lake States. There is some production in the Rocky Mountain States.

Uses

The wood of aspen is lightweight and soft. It is low in strength, moderately stiff, moderately low in resistance to shock, and has a moderately high shrinkage. Aspen is cut for lumber, pallets and crates, pulpwood, particleboard, matches, veneer, and miscellaneous turned articles.

Color

The heartwood of aspen is grayish white to light grayish brown. The sapwood is lighter colored and generally merges gradually into heartwood without being clearly marked. Aspen wood is usually straight-grained with a fine, uniform texture. It is easily worked.

Macroscopic Structure

Aspen is semi-ring porous to diffuse porous. The pores are small and usually not visible to the unaided eye. Growth rings are usually faint.

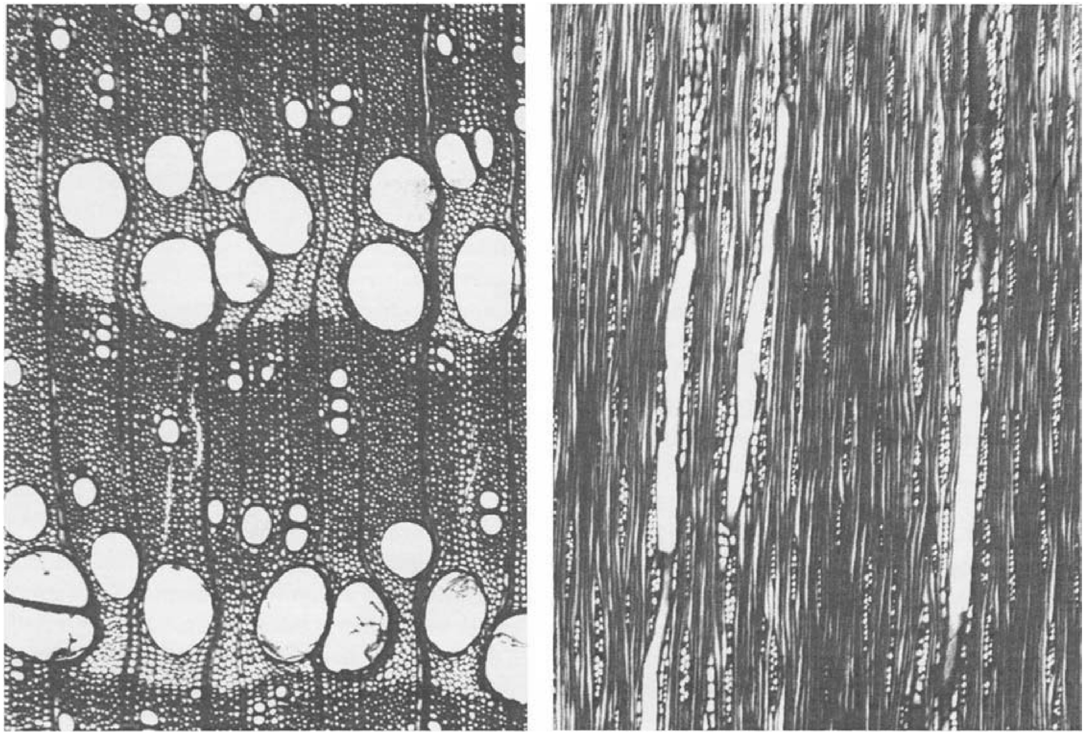


FIGURE 5.12 Green ash (*Fraxinus pennsylvanica Marsh.*) (50×).

Rays are small, uniform in height, and visible only on radial surfaces.

Basswood (Figs. 5.13 and 5.14)

American basswood (*Tilia americana*) is the most important of the several native basswood species; next in importance is white basswood (*Tilia heterophylla*). Other species occur only in very small quantities. No attempt is made to distinguish them in lumber form. Other common names of basswood are linden, linn, and bee tree. Basswood grows in the eastern half of the United States from the Canadian provinces southward. Most basswood lumber comes from the Lake, Middle Atlantic, and Central States. In commercial usage, "white basswood" is used to specify white wood or sapwood of either species.

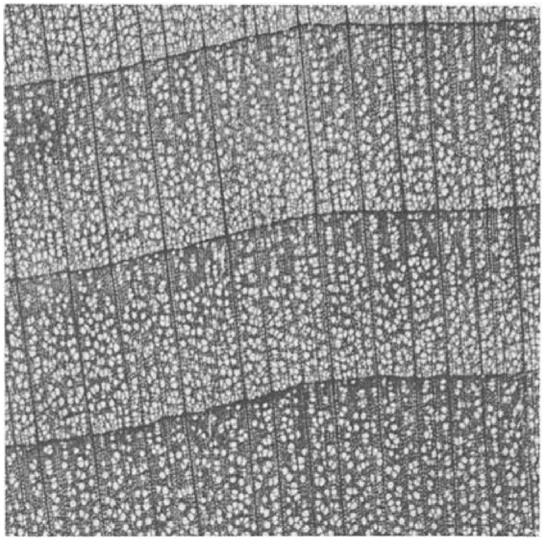


FIGURE 5.13 *Tilia americana* 15× (Koehler, 1917).

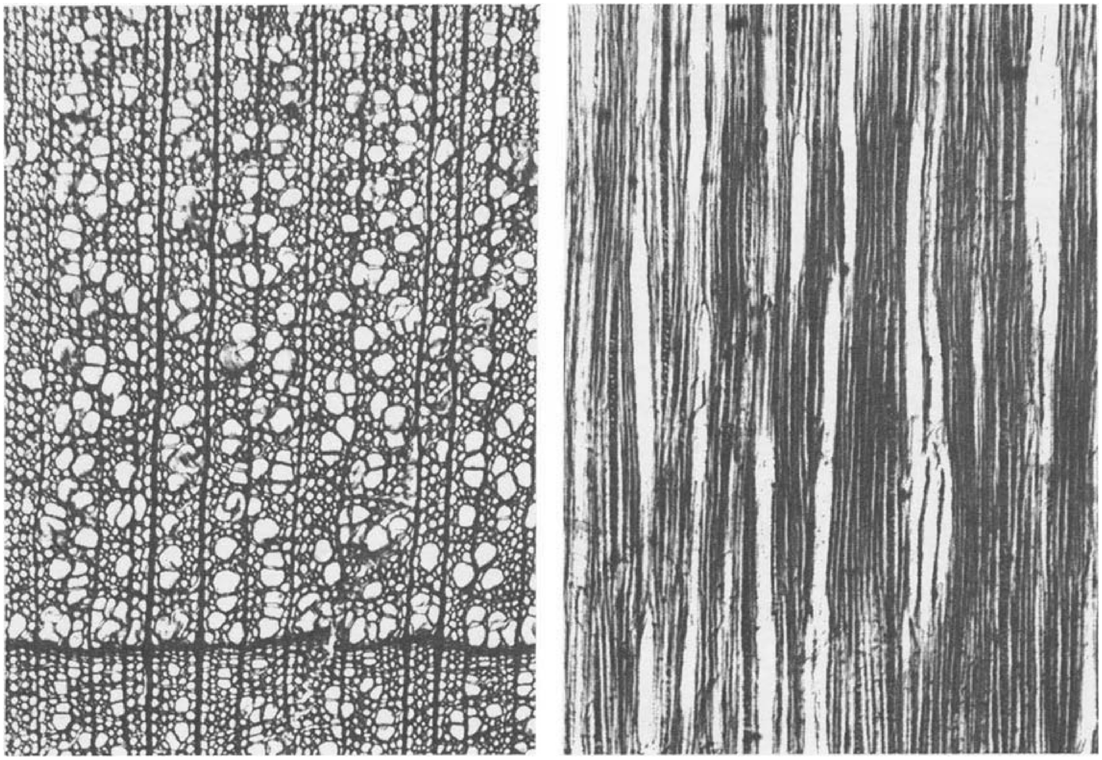


FIGURE 5.14 American basswood (*Tilia americana* L.) (50×).

Uses

When dry, the wood is without odor or taste. It is soft and light in weight; has fine, even texture; and is straight-grained and easy to work with tools. Shrinkage in width and thickness during drying is rated as large, but basswood seldom warps in use. Basswood is used for crates, lumber for furniture, millwork, and core material in plywood.

Color

The heartwood of basswood is pale yellowish brown with occasional darker streaks. Basswood has wide (several inches), creamy white, or pale brown sapwood that merges gradually into the heartwood. The annual rings are fairly distinct and defined by a change in vessel size and a white line of marginal parenchyma.

Macroscopic Structure

Basswood has small pores (distinct with a lens) that may form groups or chains radially, diagonally, or tangentially. The rays of basswood are more pronounced (broader and higher) than those of aspen, are fairly distinct without a lens, and form high, scattered flecks on the radial surfaces. The rays of basswood vary in height, whereas those of aspen are more uniform. Parenchyma may or may not be visible with a lens as very fine tangential lines (apotracheal). The wood has a slight, characteristic odor. *Similar woods*. See yellow buckeye for differentiation of this species.

American Beech (Figs. 5.15 and 5.16)

Only one species of beech, Americana beech (*Fagus grandifolia*), is native to the United States. It grows in the eastern one-third of the United

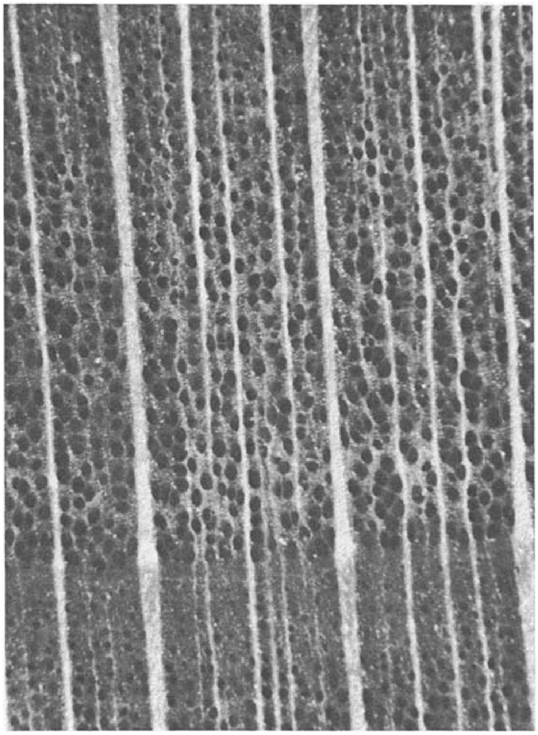


FIGURE 5.15 *Fagus grandifolia.*

States and adjacent Canadian provinces. The highest production of beech lumber is in the Central and Middle Atlantic States.

Uses

The wood of beech is classed as heavy, hard, strong, high in resistance to shock, and highly adaptable for steam bending. Beech has large shrinkage and requires careful drying. It machines smoothly, is an excellent wood for turning, wears well, and is rather easily treated with preservatives. Large amounts of beech go into flooring, furniture, brush blocks, handles, veneer woodenware, containers, and cooperage. When treated, it is suitable for railway ties.

Color

Beech wood varies in color from nearly white sapwood to reddish brown heartwood in some trees. Sometimes there is no clear line of demarcation between heartwood and sapwood. The sapwood may be 3–5 in. thick. The annual rings are distinct. The wood has little figure and is of close, uniform texture. It has no characteristic taste or odor.

Macroscopic Features

Beech is diffuse porous. The vessels are very small and not visible to the unaided eye. They are crowded in the earlywood but gradually decrease in number and size through the growth ring, forming a darker and denser band of latewood. Tyloses are present. The parenchyma form very fine, irregular, light-colored, tangential lines in the latewood that usually cannot be seen distinctly with a lens. The rays are of two sizes, with the broad ones visible on all surfaces. They appear uniformly spaced on the cross section and of uniform height on the radial surface. The cross section shows 5%–10% of the rays to be conspicuously broad, fully twice as wide as the widest vessels. These rays appear as "silver grain" on the radial surfaces. The other rays are narrower than the vessels.

Similar Woods

Beech is distinguished from other rays and tiny pores. The tangential surface shows the wide rays to be less numerous than in sycamore, which has only wide rays.

Birch (Figs. 5.17–5.19)

The important commercial species of birch are yellow birch (*Betula alleghaniensis*), sweet birch (*Betula lenta*), and paper birch (*Betula papyrifera*). Other birches of some commercial importance are river birch (*Betula nigra*), gray birch (*Betula populifolia*), and western paper birch (*Betula papyrifera* var. *commutata*). Yellow birch, sweet birch, and paper birch grow principally in the Northeastern and Lake States. Yellow and sweet birch also grow along the Appalachian Mountains to northern Georgia. They are the source of most

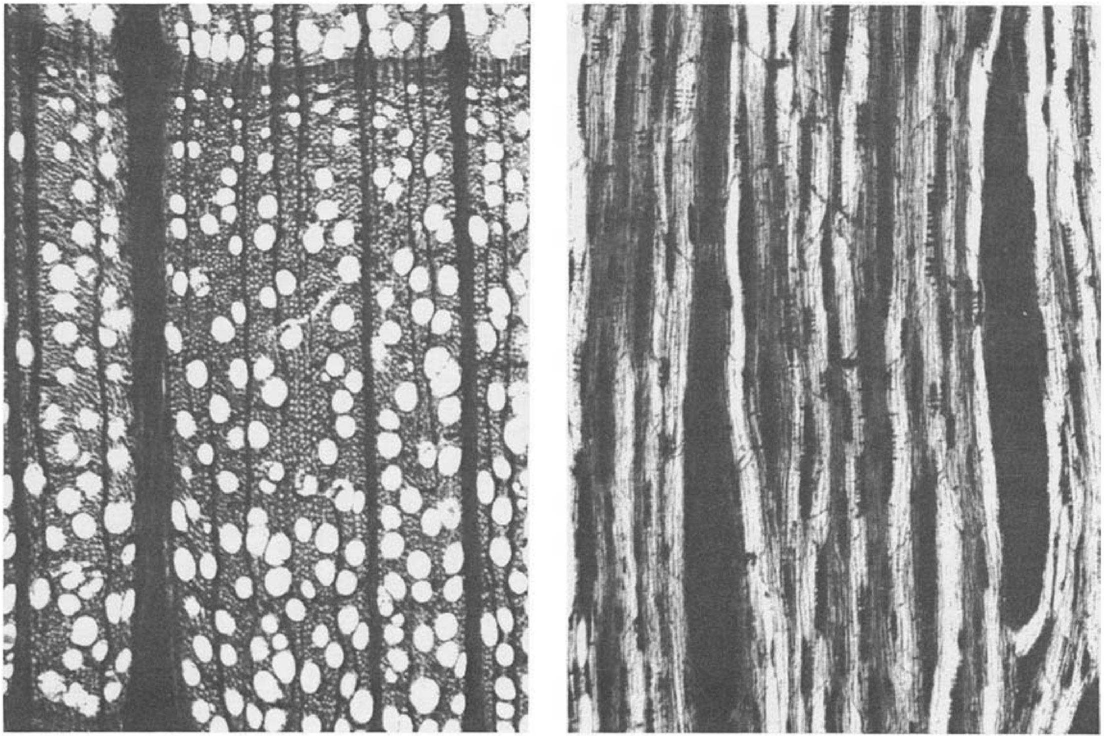


FIGURE 5.16 American beech (*Fagus grandifolia*) (50×).

birch lumber and veneer. The inner bark of yellow and sweet birch has a slight wintergreen flavor. These species are difficult to discern unless the outer bark is present.

Uses

Birchwood is used in furniture, boxes, baskets, crates, woodenware, cooperage, interior finish, doors, and pulp. Birch veneer goes into plywood used for flush doors, furniture, paneling, cabinets, aircraft, and other specialty uses. Paper birch is used for turned products, including spools, small handles, and toys.

Color

Yellow birch has white sapwood (several inches wide, but variable) and light reddish brown heartwood. Sweet birch has light-colored sapwood and dark brown heartwood tinged with red. The annual rings are not distinct to the unaided eye; they are defined by a faint line and a small change in pore size. (Pith flecks are usually absent in yellow birch but abundant in river birch.) Wood of yellow birch and sweet birch is heavy, hard, strong, and has good shock-resisting ability. The wood is fine and uniform in texture. Paper birch is lower in weight, softer, and lower in strength than yellow and sweet birch. Birch shrinks considerably during drying.

Macroscopic Features

Birch is diffuse porous. Yellow birch vessels may be barely visible to the unaided eye (*x*); they occupy less than one-third of the area between rays, except in very narrow growth rings. They may form radial rows of 2–4. Tyloses are absent. The vessels form small groves on the

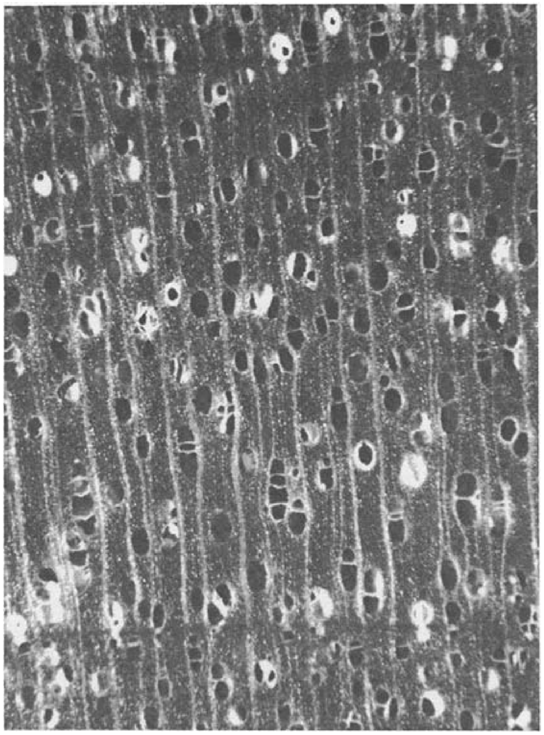


FIGURE 5.17 *Betula* spp.

longitudinal surfaces. Longitudinal parenchyma is not visible. Rays are visible only on the radial surface without magnification as very fine reddish brown "flakes." They appear to be one size and of uniform height along the grain. The rays are narrower than the vessels (*x*). Growth rings are moderately distinct on tangential surfaces. Paper birch has smaller pores, is lighter in weight, and is softer than yellow and sweet birch.

Microscopic Features

The simple vessel perforation plates of maple distinguish it from birches, which have scalariform perforation plates.

Similar Woods

The maples have smaller pores and wider rays than the birches.

Buckeye (Figs. 5.20 and 5.21)

Buckeye consists of two species, yellow buckeye (*Aesculus octandra*) and Ohio buckeye (*Aesculus glabra*). They range from the Appalachians of Pennsylvania, Virginia, and North Carolina westward to Kansas, Oklahoma, and Texas. Buckeye is not customarily separated from other species when manufactured into lumber and can be utilized for the same purposes as aspen, basswood, and sap yellow poplar.

Uses

The wood is uniform in texture, usually straight-grained, light in weight, weak in beam use, soft, and low in shock resistance. It is rated low on machinability, such as shaping, steam bending, boring, and turning. Buckeye is suitable for pulping for paper; its lumber is used principally for furniture, crates, food containers, woodenware, novelties, and planning mill products.

Color

The white sapwood of buckeye merges gradually into the creamy or yellowish-white heartwood. The annual rings are not always distinct and are defined by light-colored lines of marginal parenchyma.

Macroscopic Features

The pores are very small, uniform in size, and distributed evenly throughout the growth ring (diffuse-porous). The rays are very fine (uniseriate), even under a lens. They are storied (arranged in tiers), producing very fine bands or ripple marks running across the tangential surface (not as pronounced in *A. glabra* but made more visible by wetting its surface). Marginal parenchyma is seen with a lens. *Similar woods*. Basswood is differentiated from buckeye by the conspicuous rays of basswood. The fine lines of buckeye on the tangential surface also distinguish it from basswood.

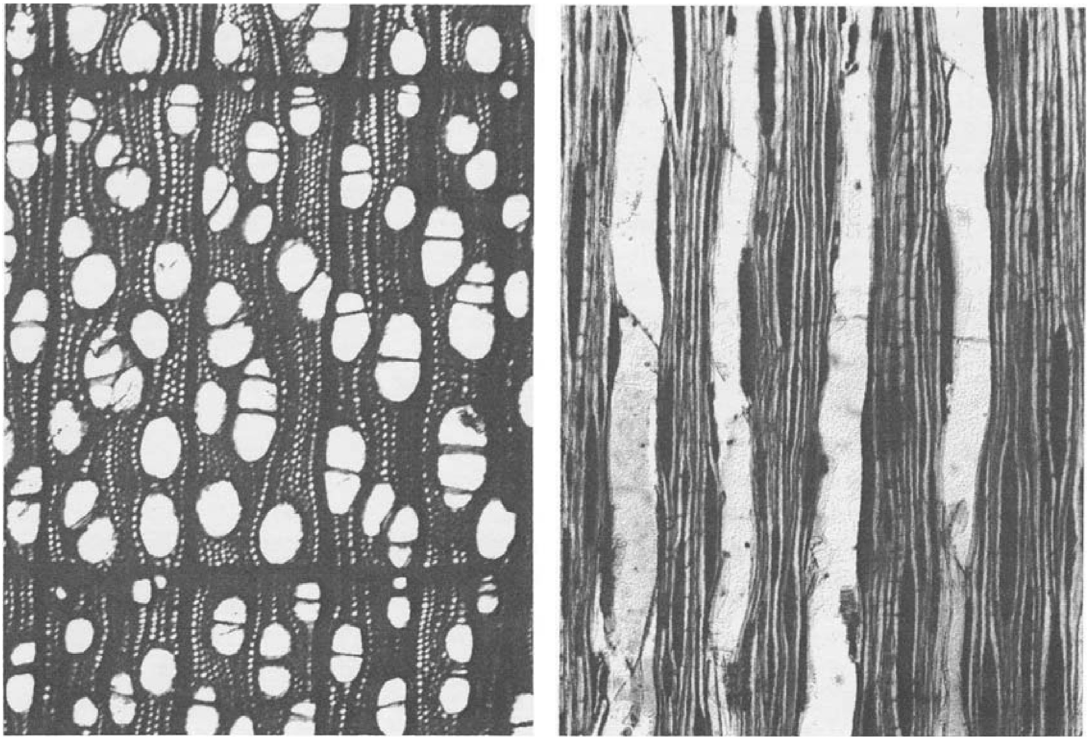


FIGURE 5.18 River birch (*Betula nigra*) (50×).

Butternut (Figs. 5.22 and 5.23)

Butternut (*Juglans cinerea*) is also called white walnut, American white walnut, and oil nut. It is grown from southern New Brunswick west to Minnesota. It extends southward into northeastern Arkansas and eastward to western North Carolina.

Uses

The wood is moderately light in weight, about the same as eastern white pine, rather coarse-textured, moderately weak in bending and endwise compression, relatively low in stiffness, moderately soft, and moderately high in shock resistance. Butternut machines easily and finishes well. In many ways it resembles black walnut, but it does not have the same strength or hardness. Principal uses are for lumber and veneer, which are further manufactured into furniture, cabinets, paneling, trim, and assorted rough items.

Color

The sapwood (rarely over 1 in. wide) is nearly white or grayish brown; the heartwood is light brown, frequently modified by pinkish tones or darker brown streaks. The annual rings are distinct, marked by the abrupt change in pore size.

Macroscopic Features

The wood is semi-ring porous. The pores are relatively large and easy to see, especially in the earlywood. Tyloses are present but not dense. They are not crowded but occasionally form radial rows of 2–6. Rays are very fine, inconspicuous, and indistinct without a lens.

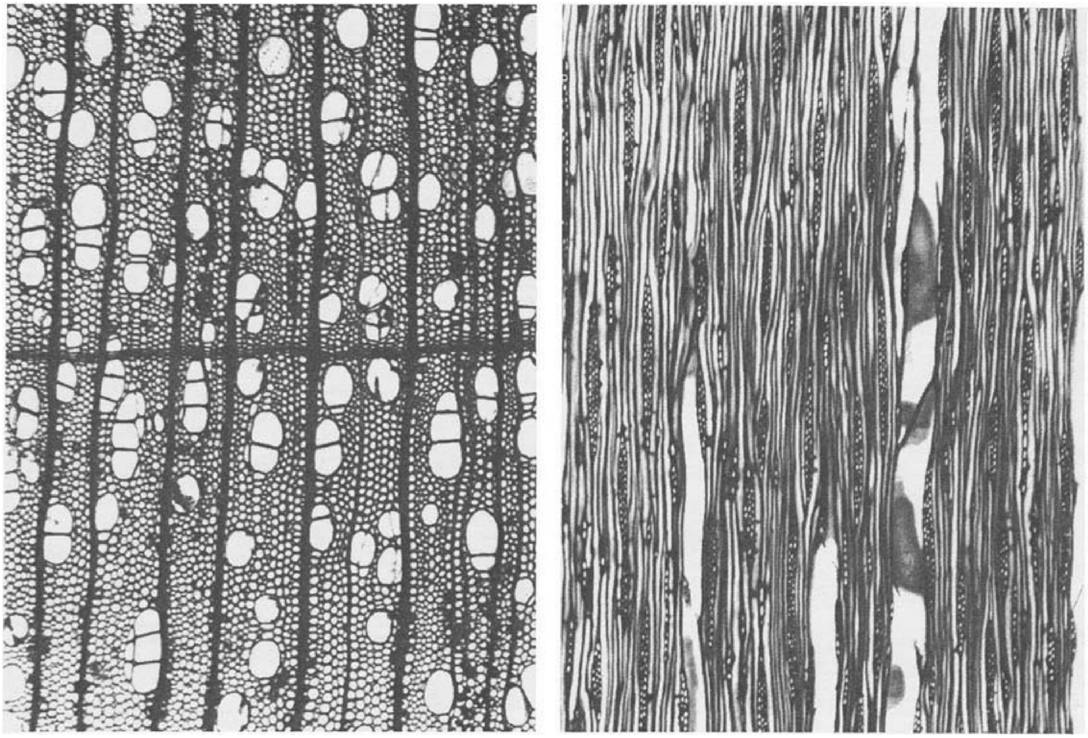


FIGURE 5.19 Paper birch (*Betula papyrifera*) (50×).

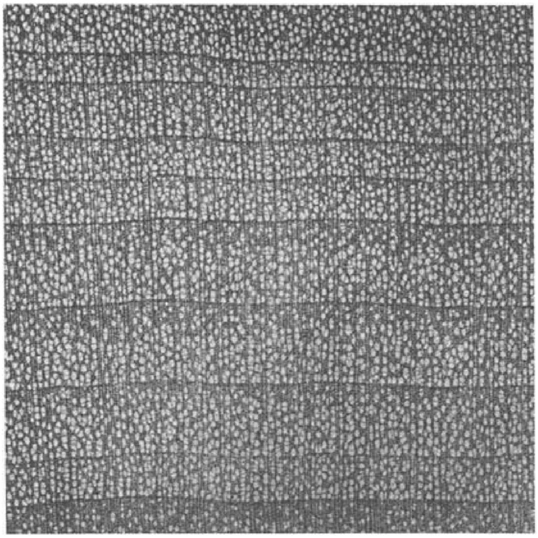


FIGURE 5.20 *Aesculus octandra* 15× (Koehler, 1917).

The apotracheal parenchyma is visible as fine, tangential lines on the cross section, especially in the outer portion of the growth ring.

Black Cherry (Figs. 5.24 and 5.25)

Black cherry (*Prunus serotina*) is also known as cherry, wild black cherry, wild cherry, or chokecherry. It is the only native species of the genus *Prunus* of commercial importance for lumber. It is scattered from southeastern Canada throughout the eastern United States. Production is centered in the Middle Atlantic States.

Uses

The wood has a fairly uniform texture and very satisfactory machining properties. It is moderately heavy. Black cherry is strong, stiff, moderately hard, and has high shock resistance

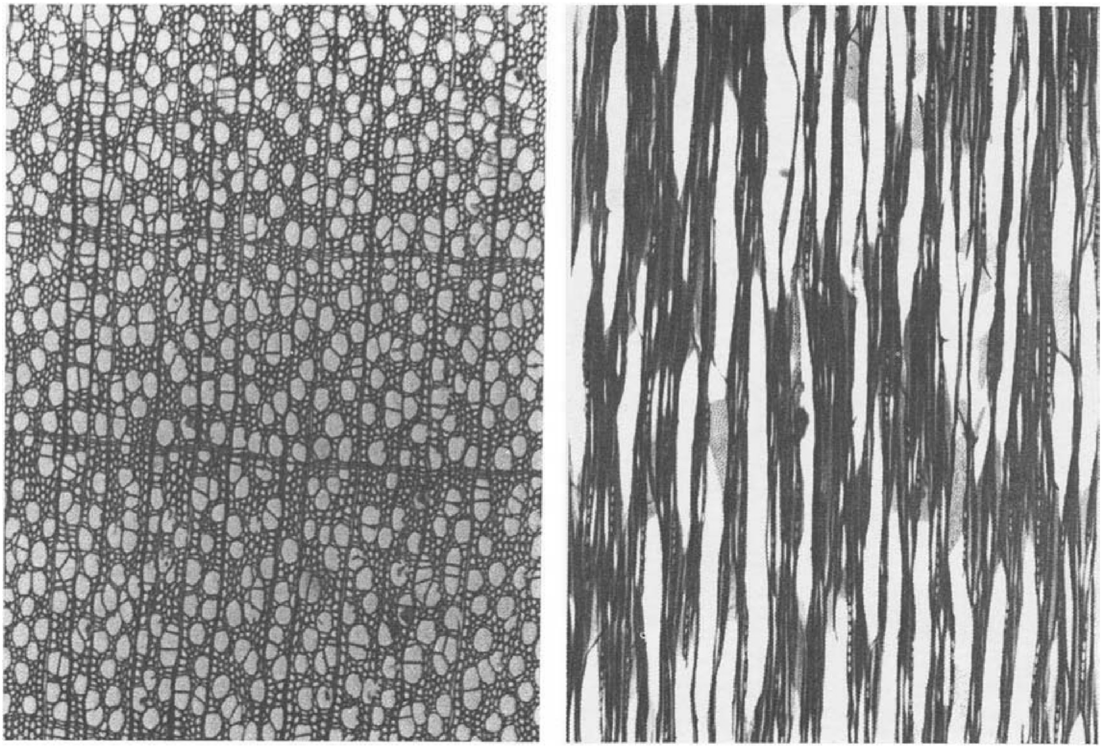


FIGURE 5.21 Yellow buckeye (*Aesculus octandra*) (50×).

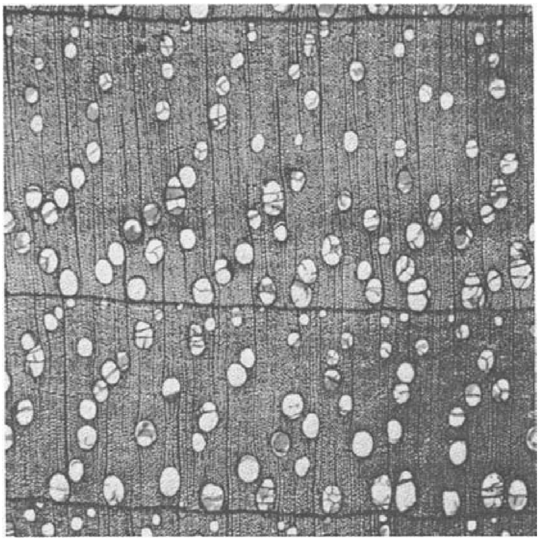


FIGURE 5.22 *Juglans cinera*, 15× (Koehler, 1917).

and moderately large shrinkage. After seasoning, it has good dimensional stability. Black cherry is used principally for furniture, fine veneer panels, and architectural woodwork.

Color

The heartwood of black cherry varies from light to dark reddish brown and has a distinctive luster. The sapwood is narrow (less than 1 in.) in old trees and nearly white. The annual rings are fairly distinct and defined by the change in pore size.

Macroscopic Features

Individual pores are not visible to the unaided eye, but they form tangential lines. The pores occupy one-third or slightly more of the area between rays. Tyloses are absent, but gum may be

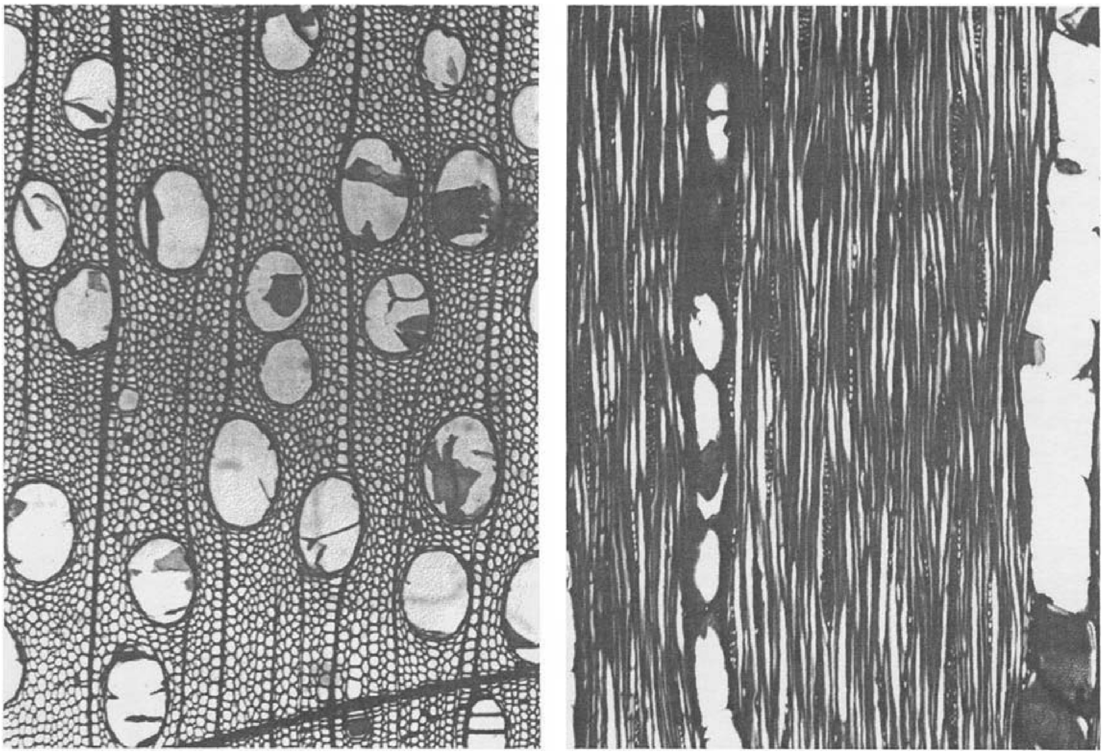


FIGURE 5.23 Butternut (*Juglans cinera*) (50×).

present in some pores. The rays are barely visible to the unaided eye on the cross section (as wide or almost as wide as the widest pores) and tend to produce a distinctive flake pattern on radial surfaces (the identifying characteristic) that are more pronounced than those of black walnut. Parenchyma is not visible. Traumatic resin canals may be present and appear as dark lines on longitudinal surfaces.

Catalpa (Fig. 5.26)

Catalpa (*Catalpa speciosa*), alias northern catalpa, western catalpa, cigar tree, and Indian bean, is widely planted outside its natural range of central to southeastern United States. A minor species is southern catalpa or common catalpa (*Catalpa bignonioides*).

Color

The sapwood is very narrow, rarely over $^1/_2$ in. wide. The heartwood is grayish brown with an occasional tinge of light purple. The wood is moderately light, straight-grained, and without a unique odor or taste. Sometimes it has a faint odor resembling kerosene. The growth rings are usually fairly wide and often variable in width, but slow growth is possible.

Macroscopic Features

The earlywood vessels are large and distinct and filled with glistening tyloses. The pores in

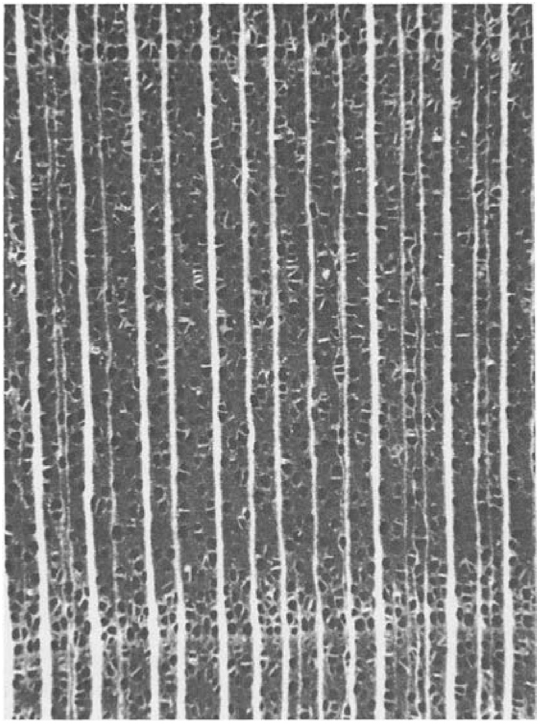


FIGURE 5.24 *Prunus serotina.*

the middle of the growth ring are isolated, in groups of 2–5, or more often in wavy, tangential bands. The pores in the latewood near the end of the growth ring are very small and always in wavy, tangential bands. The normally spaced rays are not distinct nor are the paratracheal parenchyma distinct from the latewood vessels without a lens. Sassafras and black ash resemble catalpa in color and somewhat in structure. Sassafras is separated by its spicy odor. Black ash is separated by its higher density and relatively few vessels in the latewood. The pith of catalpa is often three-sided, whereas in black ash it is round.

American Chestnut (Fig. 5.27)

American chestnut (*Castanea dentata*) is also known as sweet chestnut. It grew in commercial quantities from New England to northern Georgia, but practically all standing chestnut has been killed by blight.

Uses

Chestnut was used for poles, railway ties, furniture, caskets, boxes, crates, and core stock for veneer panels. It appears as "wormy chestnut" for paneling, trim, and picture frames, whereas a small amount is still used in rustic fences.

Color

The heartwood of chestnut is a fairly uniform grayish brown or brown and darkens with age. The sapwood is very narrow (rarely over 0.5 in. wide) and almost white. Chestnut wood is moderately light in weight. It is moderately hard, moderately low in strength, moderately low in resistance to shock, and low in stiffness. It seasons well and is easy to work with tools.

Macroscopic Features

The wood is ring porous and coarse in texture. The growth rings are made conspicuous by several rows of large, distinct vessels (almost entirely plugged with tyloses) at the beginning of each year's growth. The latewood vessels are very small, numerous, and arranged in irregular branched radial bands. The rays are barely distinct with a hand lens. The apotracheal and paratracheal parenchyma are scattered among the pores and are not distinct.

Similar Woods

The radial bands of vessels are found in no other native timber species except oaks, but oaks have large rays. Black ash resembles chestnut, but the vessels of black ash latewood are few, isolated, and never arranged in radial bands.

Kentucky Coffeetree

Kentucky coffee tree (*Gymnocladus dioicus*) grows in the central section of the eastern United States. The sapwood is narrow, usually

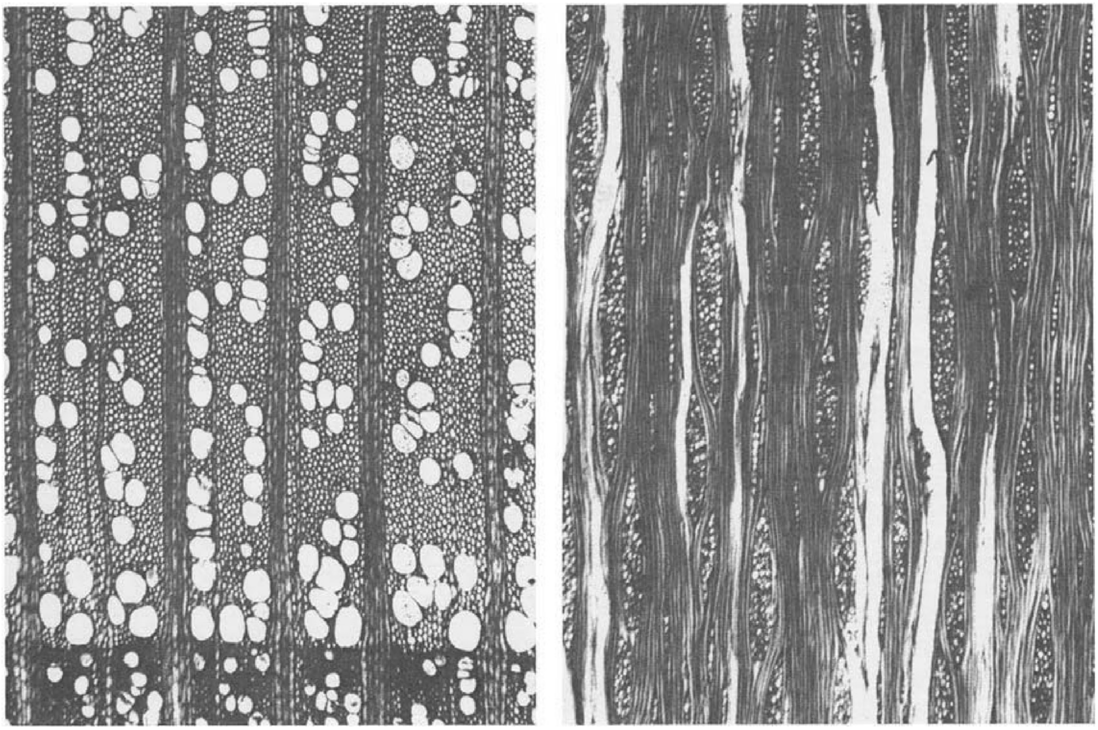


FIGURE 5.25 *Prunus avium* (50×).

less than 0.5 in. but up to 1 in. wide. The heartwood is bright cherry red to reddish brown. The annual rings are distinct and highly variable in width. The wood has the same weight and physical properties of honey locust. Its color and structure are similar to those of honey locust. See honey locust for structure and distinguishing characteristics.

Cottonwood (Figs. 5.28 and 5.29)

Cottonwood includes several species of the genus *Populus*. Most important are eastern cottonwood (*Populus deltoides* and varieties), also known as Carolina poplar and whitewood; swamp cottonwood (*Populas heterophylla*), also known as river cottonwood, cottonwood, and swamp poplar; and black cottonwood (*Populas trichocarpa*). Eastern cottonwood and swamp cottonwood grow throughout the eastern half of the United States. The greatest production of lumber is in the Southern and Central States. Black cottonwood grows in the West Coast States and in western Montana, northern Idaho, and western Nevada. Balsam poplar grows from Alaska across Canada and in the northern Great Lake states. Eastern cottonwood is moderately low in bending and compressive strength, moderately limber, moderately soft, and moderately low in ability to resist shock. Black cottonwood is slightly below eastern cottonwood in most strength properties; both have moderately large shrinkage. Some cottonwood is difficult to work with tools because of fuzzy surfaces. Tension wood is largely responsible for this characteristic.

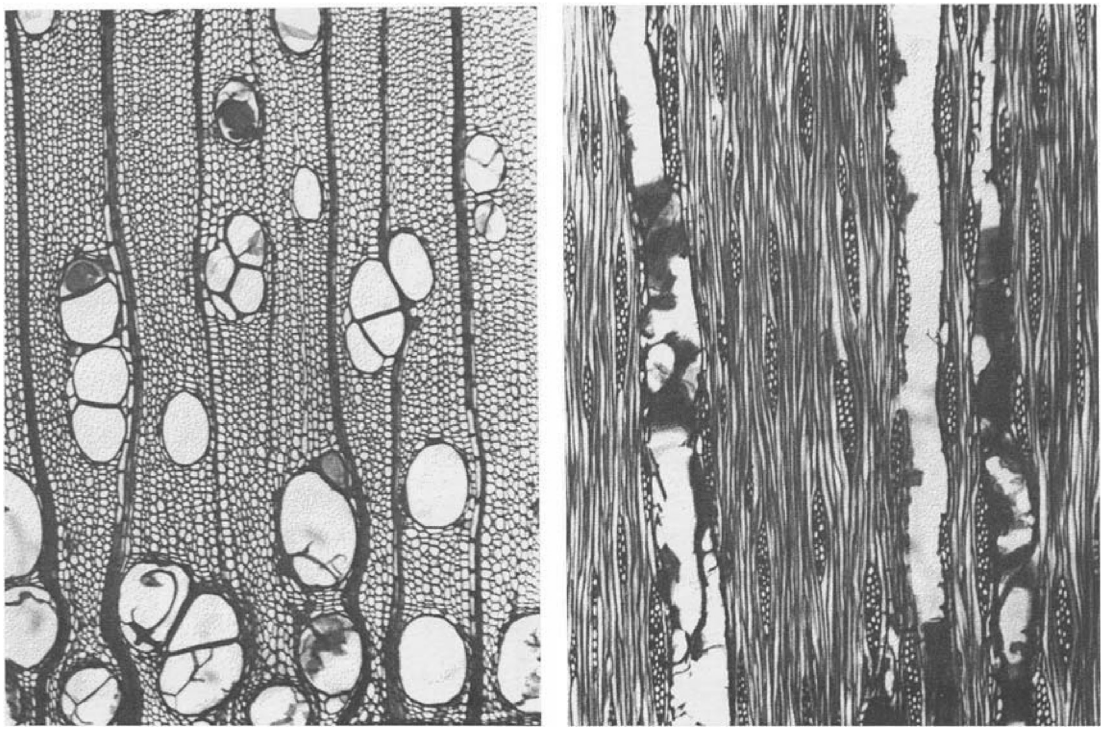


FIGURE 5.26 Catalpa (*Catalpa speciosa*) (50×).

Uses

Cottonwood is used principally for lumber, veneer, pulpwood, particleboard, and fuel. The lumber and veneer go largely into boxes, crates, baskets, and pallets.

Color

The heartwood of the three cottonwoods is grayish white to light brown. The sapwood is whitish and merges gradually with the heartwood. The wood is comparatively uniform in texture and generally straight-grained. It is odorless when well seasoned.

Macroscopic Structure

The annual rings are semi-ring porous (approaching diffuse porous in some samples), distinct, but not conspicuous, and defined by a slight difference in pore size. The vessels are usually visible to the unaided eye. They decrease slightly in size from the earlywood to the latewood. They are numerous and occupy one-half of the area between the rays, except in the widest rings. They are scattered singly or occasionally in radial rows of 2—4. The rays are barely distinct with a lens and normally spaced. Marginal parenchyma is not distinct but forms a narrow, light-colored line.

Similar Woods

Cottonwood is very similar in appearance to black willow. The heartwood color of willow is more brown to reddish. Microscopic examination of sapwood also distinguishes them. Cottonwood pores are larger than those of aspen and are barely visible without magnification. Cottonwood may be confused with other lightwoods such as tupelo, yellow poplar, basswood, and

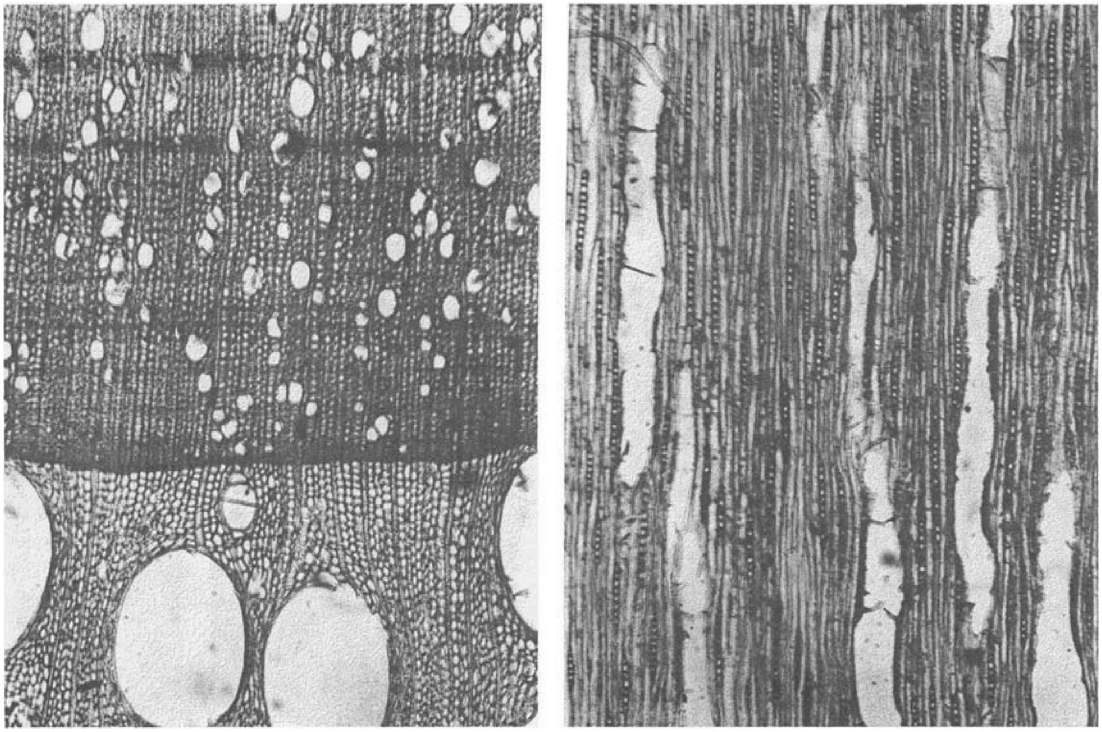


FIGURE 5.27 American chestnut (*Castanea dentata*) (50×).

buckeye. However, the pores of the earlywood of Cottonwood are larger than those of the other species, being nearly visible with the unaided eye.

Dogwood

Dogwood does not usually grow to very large sizes. It appears to be similar to maple. Its grain tends to be interlocked. Its sapwood has a pinkish cast. The heartwood (of large samples) is narrow and dark brown. It is diffuse porous with indistinct annual rings. The vessels are mostly solitary or form short radial multiples in the latewood. The apotracheal banded parenchyma is not visible. The rays are of two sizes and occupy nearly half the cross section. Pacific dogwood (*Cornus nuttallii*) has rays up to about 40 cells high, whereas those of flowering dogwood (*Cornus florida*) may be up to 80 cells high.

Similar Woods

The tendency toward radial multiples of pores separates it from red gum. Swamp tupelo is similar in appearance.

Elm (Figs. 5.30 and 5.31)

Six species of elm grow in the eastern United States: American elm (*Ulmus americana*), slippery elm (*Ulmus rubra*), rock elm (*Ulmus Thomasii*), winged elm (*Ulmus alata*), cedar elm (*Ulmus crassifolia*), and September elm (*Ulmus serotina*). American elm is also known as white elm, water elm, and gray elm; slippery elm as red elm; rock elm as cork elm or hickory elm; winged elm as wahoo; cedar elm as red elm or basket elm;

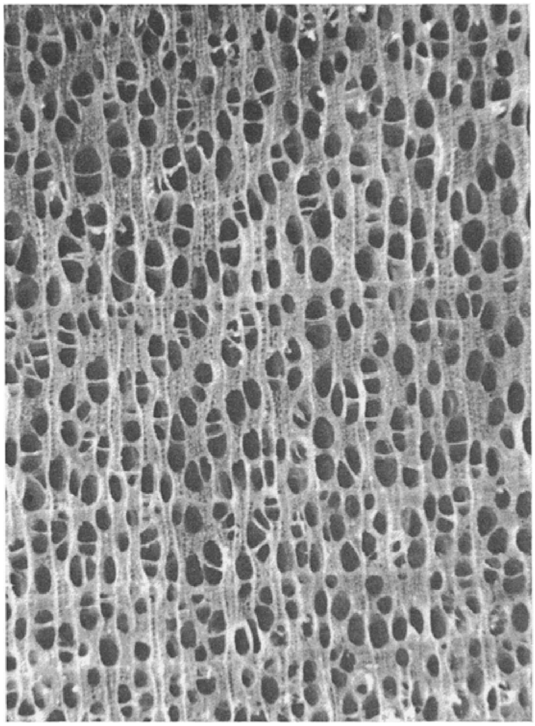


FIGURE 5.28 *Populus trichocarpa.*

and September elm as red elm. More than 80% of rock elm comes from Wisconsin and Michigan. American elm has been almost eradicated by two diseases, Dutch elm and phloem necrosis. Slippery elm is distinguished by the mucilaginous nature of its inner bark, if it is available.

Uses

The elms may be divided into two general classes, hard elm and soft elm, based on the weight and strength of the wood. Hard elm includes rock elm, winged elm, cedar elm, and September elm. American elm and slippery elm are the soft elms. Soft elm is moderately heavy, has high shock resistance, and is moderately hard and stiff. Elm has excellent bending qualities and is used in the bent portion of chairs. Some hard elms tend to have interlocked grain. Elm lumber is used principally in boxes, baskets, crates, slack barrels, furniture, and caskets. For some uses the hard elms are preferred. Elm veneer is used for furniture, fruit, vegetable and cheese boxes, baskets, and decorative panels.

Color

The sapwood of the elms is nearly white (1–3 in. wide) and the heartwood light brown, often tinged with red.

Macroscopic Features

American elm is a ring-porous wood, and the earlywood pores are easily observed in one row (or two to three rows in very wide growth rings), rarely with tyloses. Winged elm usually has a more interrupted, uniseriate row of earlywood vessels at the start of the growth ring. (In rock elm, earlywood vessels are observed only with magnification and tend to have tyloses.) The latewood vessels are arranged in an ulmiform pattern (wavy, tangential bands) characteristic of elms and hackberry. The rays are fine and not distinct without a hand lens. The longitudinal parenchyma are paratracheal but not seen without a hand lens. The wetted heartwood of *U. rubra* has a disagreeable odor.

Microscopic Features

Intervessel pitting of American elm is alternate, angular, and crowded. Rays are normally spaced and 3–4 seriate.

Similar Woods

See hackberry (which has more distinct rays, paler heartwood with a tinge of green, and wider sapwood) for separation from this species.

Hackberry (Fig. 5.32)

Hackberry (*Celtis occidentalis*) and sugarberry (*Celtis laevigata*) supply the lumber known in the trade as hackberry. Hackberry grows east of the Great Plains from Alabama, Georgia, Arkansas, and Oklahoma northward, except

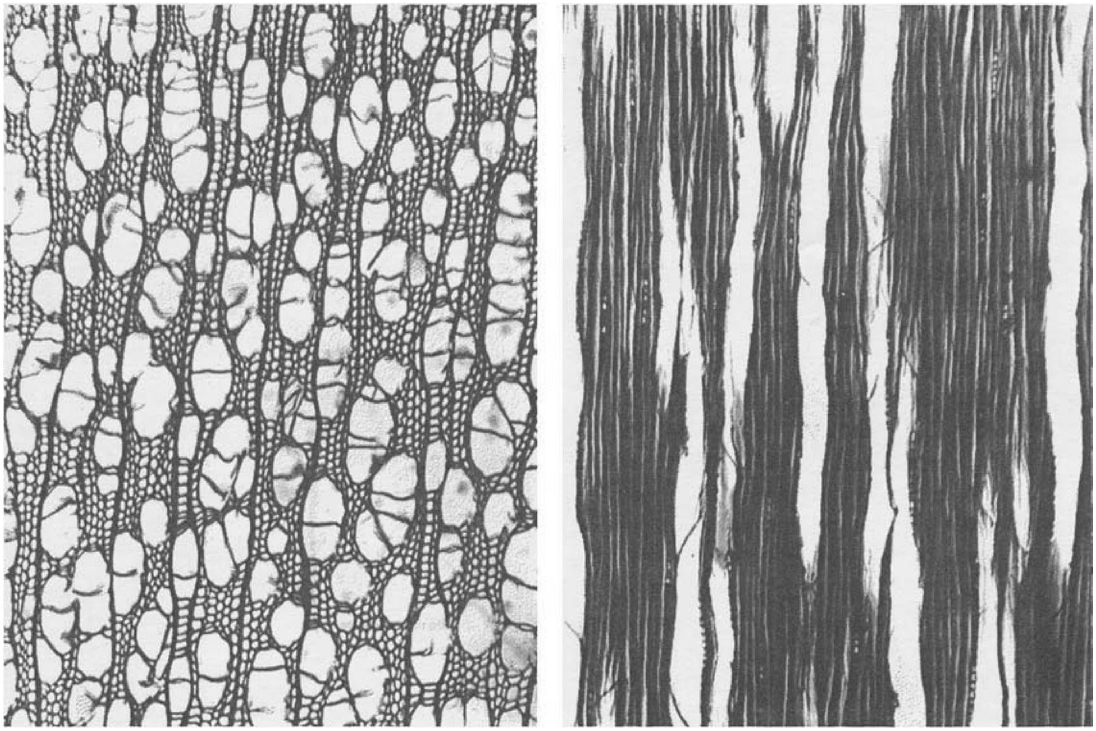


FIGURE 5.29 Black cottonwood (*Populus trichocarpa*) (50×).

along the Canadian boundary. Sugarberry overlaps the southern part of the range of hackberry and grows throughout the Southern and South Atlantic States. The sapwood of both species varies from pale yellow to greenish or grayish yellow and may be over 3 in. wide; it is subject to blue stain. The heartwood is commonly darker and yellowish or greenish gray. The wood resembles elm in structure. Hackberry lumber is moderately heavy. It is moderately strong in bending, moderately weak in compression parallel to the grain, moderately hard to hard, high in shock resistance, but low in stiffness. It has moderately large to large shrinkage. Hackberry lumber keeps its shape well during seasoning. Hackberry is cut into lumber, with small amounts going into dimension stock and veneer. It is used for furniture and some for containers.

Macroscopic Features

Hackberry is a ring-porous wood; the earlywood vessels form a ring that is 2–3 pores wide, except in narrow growth rings. The earlywood pores of the heartwood are partly occluded with tyloses. The latewood vessels are in an ulmiform arrangement. The rays are normally spaced and relatively conspicuous. Longitudinal parenchyma is paratracheal, being intermixed with latewood vessels and vascular tracheids, and visible only with a hand lens. Hackberry is similar to elm but the large earlywood vessels are in more than one row, the ulmiform pattern of latewood vessels is less

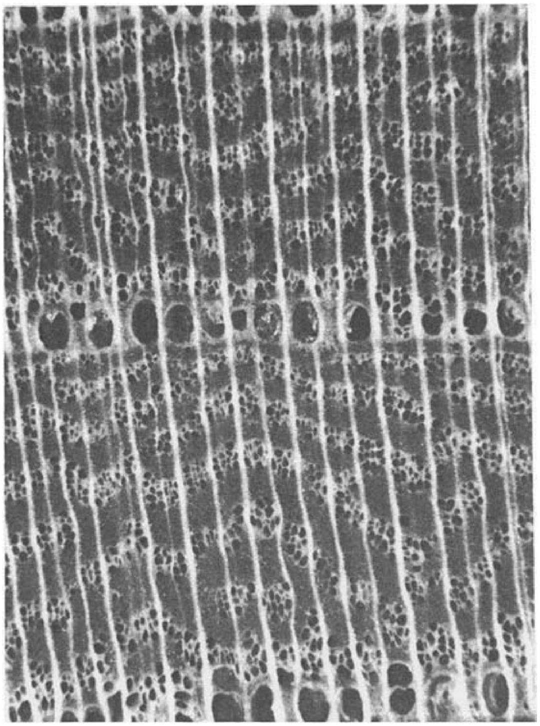


FIGURE 5.30 *Ulmus americana.*

pronounced, the rays are more distinct, and the heartwood may have a greenish tinge.

Hickories (Figs. 5.33 and 5.34)

The hickories are divided into two groups, the pecan hickories and the true hickories, based on the twigs, leaves, and fruit. It is difficult, even with a microscope, to distinguish among the species, or even the groups, except for the water hickory. The hickories range throughout the eastern United States. The wood is very heavy and exceedingly hard and tough.

Color

The sapwood is 1–2 in., occasionally to 3 in., wide. The heartwood is brown to reddish brown. It has no characteristic odor or taste.

Macroscopic Features

Individual pores are visible, but the zone of large pores is not sharply outlined as in the oaks and the ashes. The earlywood has a ring of large vessels of 1–2 (or 3 pores in wide rings) width. The pores decrease in size somewhat gradually toward the latewood. In the latewood, the pores are not numerous, isolated, or in radial rows of 2–3. The rays are very small and seen without magnification on radial surfaces only. The apotracheal, banded parenchyma are distinct with a lens and form numerous fine, light-colored, tangential bands that do not encircle the vessels (as in ash) but usually extending between the vessels or passing around them to one side. The parenchyma forms a net-like appearance with the rays.

Similar Woods

The hickories are distinguished from the other ring-porous woods by the numerous fine, tangential lines of parenchyma and the presence of few pores in the latewood. Persimmon is similar but has finer tangential lines of parenchyma and its rays are in horizontal rows that are plainly visible on tangential surfaces as very fine bands across the grain.

Pecan Hickories

Species of the pecan group include bitternut hickory (*Carya cordiformis*), pecan (*Carya illinoensis*), water hickory (*Carya aquatica*), and nutmeg hickory (*Carya myristiciformis*). Bitternut hickory grows throughout the eastern half of the United States. Pecan hickory grows from central Texas and Louisiana to Missouri and Indiana. Water hickory grows from Texas to South Carolina. Nutmeg hickory occurs principally in Texas and Louisiana. The wood of pecan hickory resembles that of true hickory but tends to be semi-ring-porous. It has nearly white sapwood, which is relatively wide, and somewhat darker heartwood. The wood is heavy and sometimes

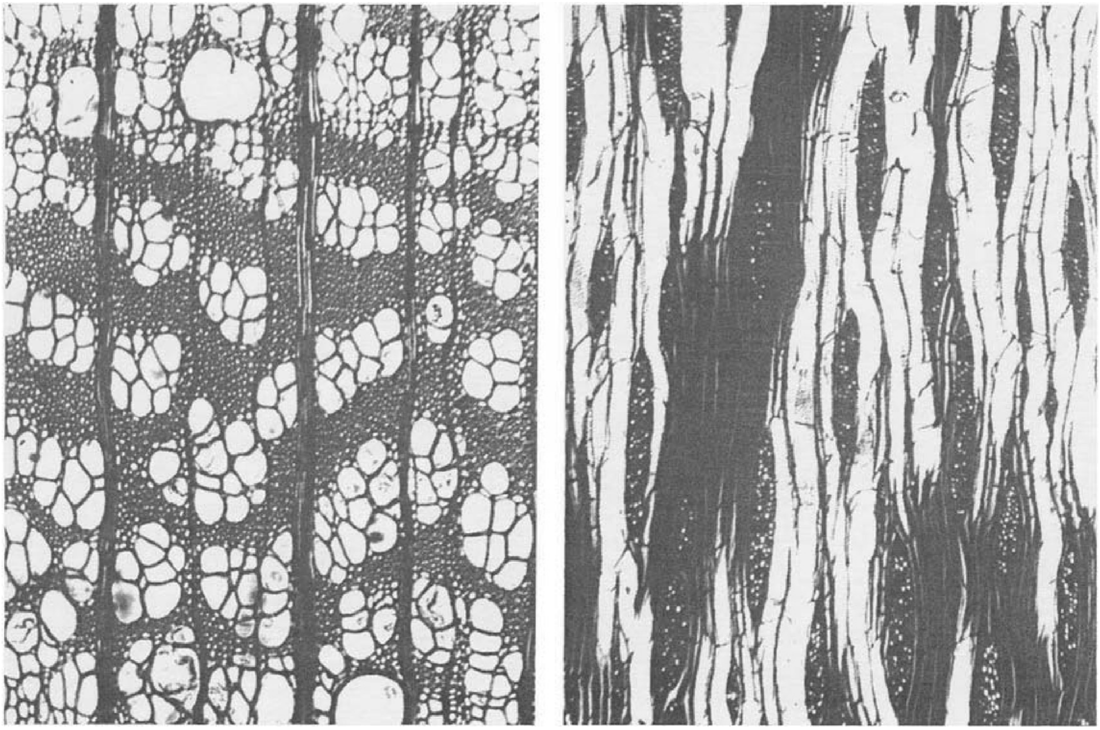


FIGURE 5.31 Rock elm (*Ulmus thomasii*) (50×).

has very large shrinkage. Heavy pecan hickory finds use in tool and implement handles and flooring. The lower grades are used in pallets. Many higher grade logs are sliced to provide veneer for furniture and paneling. Water hickory differs from the other hickories by having less clearly defined annual growth rings and large pores being more scattered (approaching diffuse-porous woods in structure). The fine, light-colored lines of parenchyma are particularly distinct in this species. The wood is somewhat lighter in weight than most hickories.

True Hickories

True hickories are found throughout most of the eastern half of the United States. The species most important commercially are shagbark (*Carya ovata*), pignut (*Carya glabra*), shell bark (*Carya Laciniosa*), and mockernut (*Carya tomentosa*). The greatest commercial production of the true hickories is in the Middle Atlantic and Central States. The Southern and South Atlantic States produce nearly half of all hickory lumber. The wood of true hickory is exceptionally tough, heavy, hard, strong, and shrinks considerably in drying. Both rings per inch and weight are limiting factors where strength is important. The major use for hickory is for tool handles, which require high shock resistance. It is also used for ladder rungs, athletic goods, agricultural implements, dowels, gymnasium apparatus, poles, and furniture. A considerable quantity of lower grade hickory is not suitable because of knottiness or other growth features and low density, for the special uses of high-quality hickory. It appears particularly useful for pallets, blocking, and similar items. Hickory

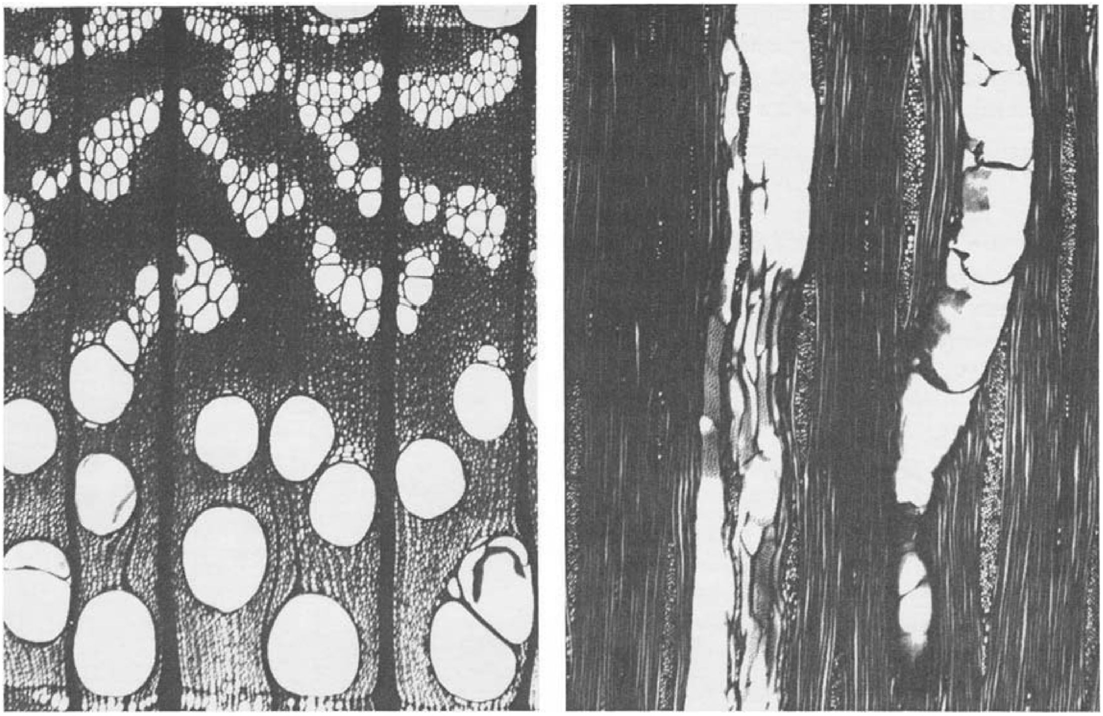


FIGURE 5.32 Hackberry (*Celtis occidentalis*) (50×).

sawdust and chips and some solid wood are used by the major packing companies to flavor meat by smoking. True hickories are ring-porous woods. The latewood vessels are solitary and in short radial multiples sparsely distributed. Rays are normally spaced and uniform. Longitudinal parenchyma is essentially apotracheal, forming short tangential bands at right angles to the rays (parallel to the growth rings).

American Holly (Fig. 5.35)

American holly (*Ilex opaca*) is sometimes called white holly, evergreen holly, and boxwood. The natural range of holly extends along the Atlantic coast, Gulf Coast, and Mississippi Valley.

Uses

The wood has a uniform and compact texture; it is moderately low in strength when used as a beam or column and low in stiffness, but it is heavy and hard and ranks high in shock resistance. It is readily penetrable to liquids and can be satisfactorily dyed. It works well, cuts smoothly, and is used principally for scientific and musical instruments, furniture inlays, and athletic goods as a specialty wood.

Color

Both the heartwood and sapwood are exceptionally white, occasionally with a bluish tinge. The heartwood has an ivory cast.

Macroscopic Structure

The wood is diffuse porous. The margin of the growth ring is made up of dense, fibrous cells. The latewood vessels are quite small and arranged in long radial chains. The scarce longitudinal parenchyma is not visible to the unaided

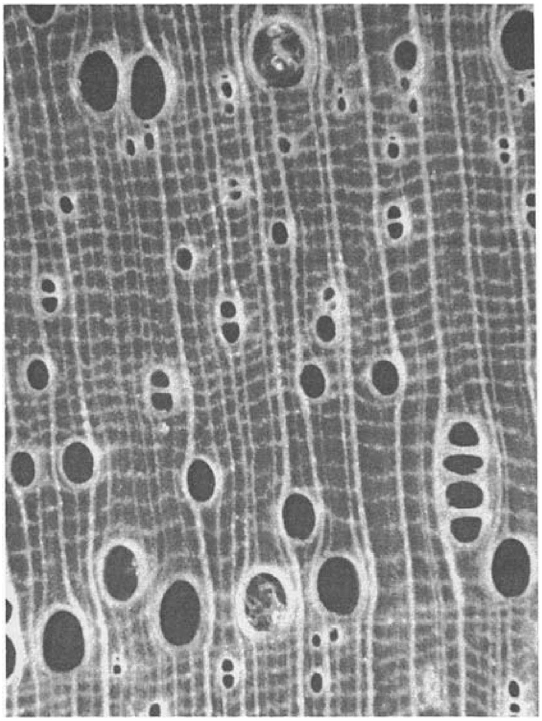


FIGURE 5.33 A pecan hickory; *Carya* spp.

eye. The rays are of two widths, and the wider ones are barely distinct to the unaided eye.

Honey Locust (Fig. 5.36)

The wood of honey locust (*Gleditsia triacanthos*), alias thorny locust, honey shucks, and three-thorned acacia, possesses many desirable qualities, such as attractive figure and color, hardness, and strength, but is little used because of its scarcity. Although the natural range of honey locust has been extended by planting, it is found most commonly in the eastern United States, except for New England and the South Atlantic and Gulf Coastal Plains.

Uses

It is very heavy, very hard, strong in bending, stiff, resistant to shock, and is durable when in contact with the ground. When available, it is restricted primarily to local uses, such as fence posts and lumber for general construction. Occasionally it will show up with other species in lumber for pallets and crating.

Color

The sapwood is mostly 0.75—2 in. wide and yellowish, in contrast to the bright cherry red to reddish brown heartwood. The annual rings are distinct and irregular in width and outline.

Macroscopic Structure

The wood is ring porous. The earlywood pores are conspicuous without a lens and form a wide band (3—5 pores wide) that occupies about one-half of the total width of moderately wide growth rings. In the outer latewood, the pores are very small, with lumens that are not visible without a lens, and form short, wavy, light-colored tangential bands visible without a lens. Honey locust has gummy deposits in the vessels of its heartwood. The rays are of two sizes; the larger size rays are distinct without a hand lens. The paratracheal and paratracheal confluent parenchyma are not distinguished from the latewood pores without a lens.

Similar Woods

Honey locust may be confused with Kentucky coffeetree. The gummy deposits of honey locust vessels are usually lacking in coffeetree, but this is not definitive. Coffeetree also has narrower sapwood and a much larger pith (often less than 0.15 in. in honey locust and greater than 0.20 in. in coffeetree). The pores in the outer latewood of coffeetree are somewhat larger and form more rounded groups than those of honey locust. The rays of coffeetree are less distinct to the unaided eye than those of honey locust and are all of the same width. Honey locust may have small pin knots from the thorns that grow on the trunks, which never occur in coffeetree.

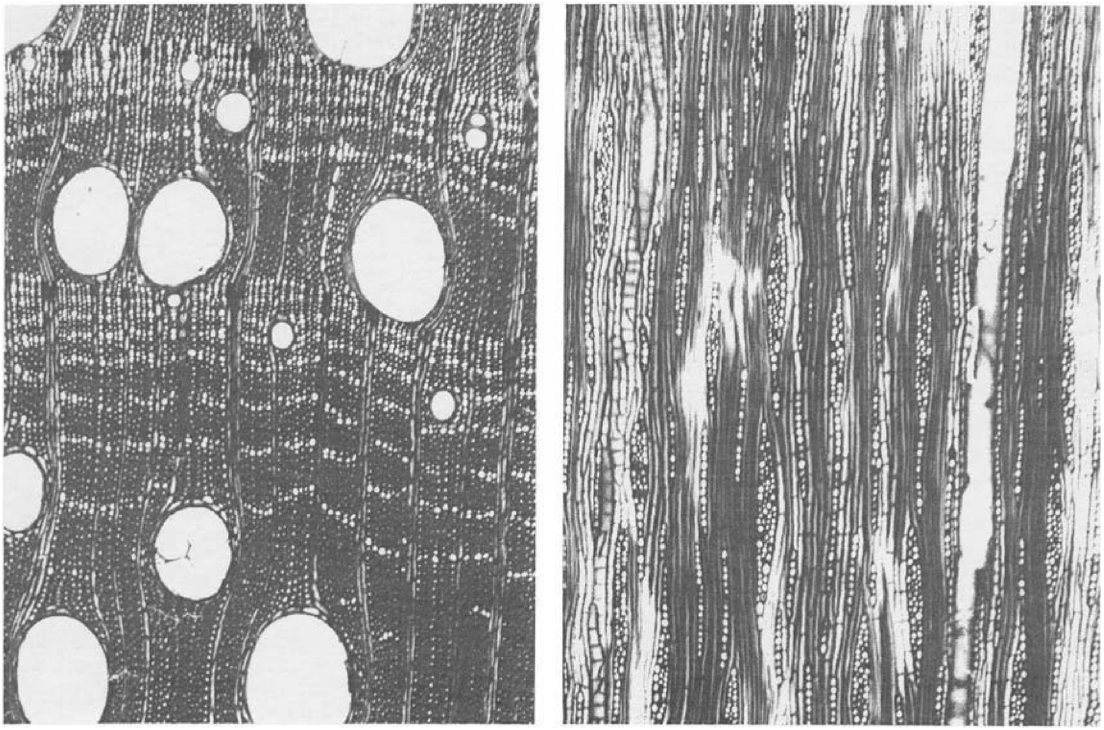


FIGURE 5.34 Shagbark hickory, a true hickory (*Carya ovata*) (50×).

Black Locust (Fig. 5.37)

Black locust (*Robinia pseudoacacia*) is sometimes called yellow locust, white locust, green locust, or post locust. This species grows from Pennsylvania along the Appalachian Mountains to northern Georgia. The greatest production of black locust timber is in Tennessee, Kentucky, West Virginia, and Virginia.

Uses

Black locust is very heavy, very hard, very high in resistance to shock, and ranks very high in strength and stiffness. It has moderately small shrinkage. The heartwood has high decay resistance. Black locust is used extensively for round, hewed, or split mine timbers, and for fence posts, poles, railroad ties, stakes, and fuel. Uses include rough construction, crating, ship treenails, and mine equipment.

Color

Locust has narrow, creamy white sapwood. The heartwood, when freshly cut, varies from greenish yellow to dark brown.

Macroscopic Features

The earlywood vessels are large but quite occluded with tyloses, which makes them appear as a band rather than as other ring-porous woods. A lens shows this band to consist of 2–3 rows of vessels. The latewood vessels are small and occur in wavy tangential bands toward the outer portion of the growth ring. The rays are not visible or barely visible without a lens. The annual rings are distinct and variable in width. Parenchyma is not easily distinguished from the vessels.

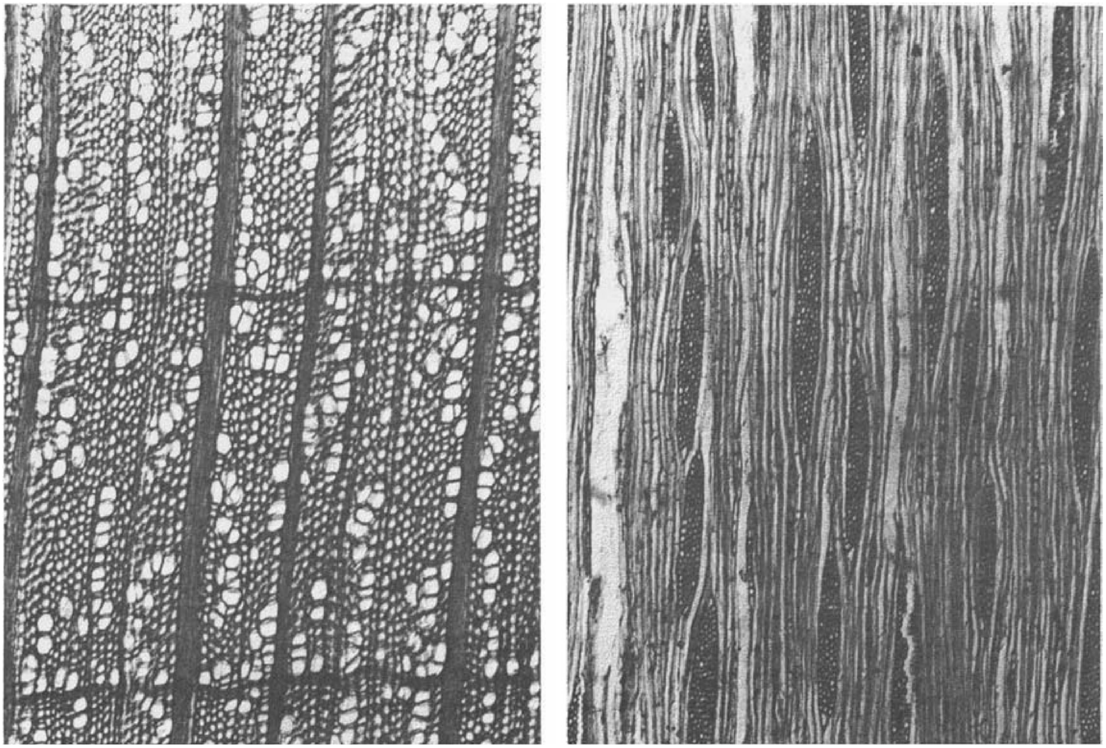


FIGURE 5.35 American holly (*Illex opaca*) (50×).

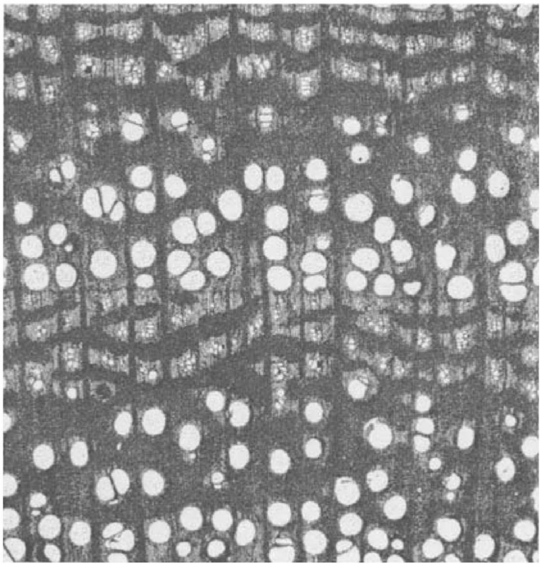


FIGURE 5.36 *Gleditsia triacanthos* (Koehler) 15×.

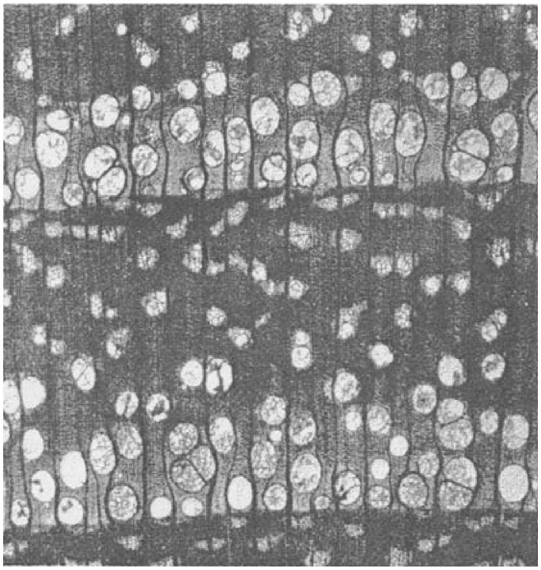


FIGURE 5.37 *Robinia pseudoacacia* (Koehler) 15×.

Similar Woods

Black locust may be confused with Osage orange, but black locust has vessels with distinct outlines in the earlywood and lacks the yellow-orange extractive of Osage orange wood. It is sometimes confused with mulberry.

Magnolia (Fig. 5.38)

Three species comprise commercial magnolia: southern magnolia (*Magnolia grandiflora*), sweet bay (*Magnolia virginiana*), and cucumber tree (*Magnolia acuminata*). Other names for southern magnolia are evergreen magnolia, magnolia, big laurel, bull bay, and laurel bay. Sweet bay is sometimes called swamp magnolia, or more often, simply magnolia. The natural range of sweet bay extends along the Atlantic and gulf coasts from Long Island to Texas and that of southern magnolia from North Carolina to Texas. Cucumber tree grows from the Appalachians to the Ozarks northward to Ohio. Louisiana leads in production of magnolia lumber.

Uses

The wood, which has close, uniform texture and is generally straight-grained, closely resembles yellow poplar. It is moderately heavy, moderately low in shrinkage, moderately low in bending and compressive strength, moderately hard and stiff, and moderately high in shock resistance. Sweet bay is reported to be much like southern magnolia. The wood of cucumber tree is similar to that of yellow poplar, and cucumber tree growing in the yellow poplar

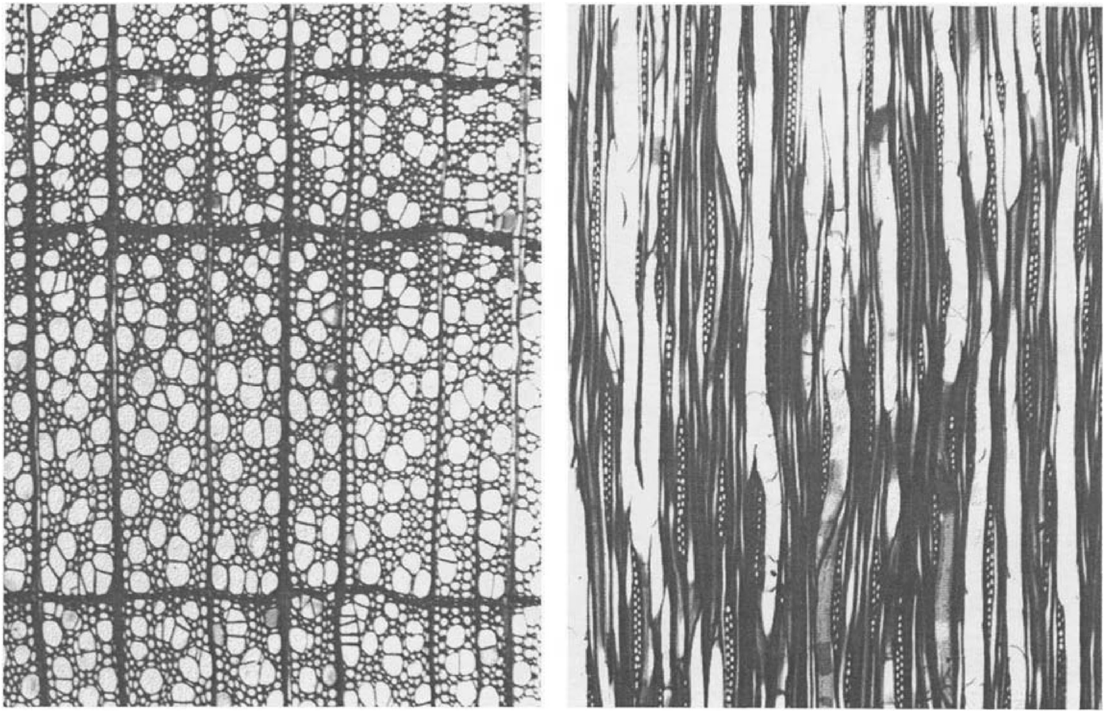


FIGURE 5.38 Cucumber tree (*Magnolia acuminata*) (50×).

range is not separated from that species on the market. Magnolia lumber is used principally in the manufacture of furniture, boxes, pallet, Venetian blinds, sash, doors, veneer, and millwork.

Color

The sapwood of southern magnolia is yellowish white, and the heartwood is light to dark brown with a tinge of yellow or green.

Macroscopic Structure

Sweet bay is a diffuse-porous wood. The vessels are in radial multiples of two to several. The rays are distinct, normally spaced, and uniform. The longitudinal parenchyma is marginal, marking the end of the growth ring as a whitish line.

Microscopic Structure

The anatomy of this wood is very similar to yellow poplar. Sweet bay, however, has scalariform intervessel pitting.

Maple (Figs. 5.39–5.41)

Commercial species of maple in the United States include sugar maple (*Acer saccharum*), black maple (*Acer nigrum*), silver maple (*Acer saccharinum*), red maple (*Acer rubrum*), box elder (*Acer negundo*), and big-leaf maple (*Acer rubrummacrophyllum*). Sugar maple is also known as hard maple, rock maple, sugar tree, and black ample; black maple as hard maple, black sugar maple, and sugar maple; silver maple as white maple, river maple, water maple, and swamp maple; red maple as soft maple, water maple, scarlet maple, white maple, and swamp maple; box elder as Manitoba maple, ash-leaved maple, three-leaved maple, and cut-leaved maple; and big-leaf maple as Oregon maple. The Middle Atlantic and Lake States account for about two-thirds of the maple production.

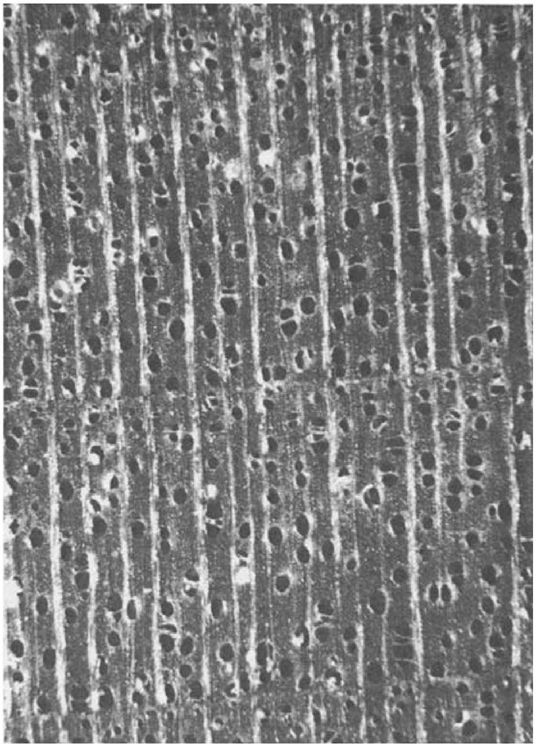


FIGURE 5.39 *Acer macrophyllum.*

Uses

The wood of sugar maple and black maple is known as hard maple and that of silver maple, red maple, and box elder as soft maple. Hard maple has a fine, uniform texture. It is heavy, strong, stiff, hard, resistant to shock, and has large shrinkage. Sugar maple is generally straight-grained but also occurs as "bird's eye," "curly," and "fiddleback" grain. Soft maple, while not as heavy, has been substituted for hard maple in the better grades, particularly for furniture. Maple is used principally for lumber, veneer, crossties, and pulpwood. A large proportion is manufactured into flooring, furniture, boxes, pallets and crates, handles, woodenware, novelties, spools, and bobbins.

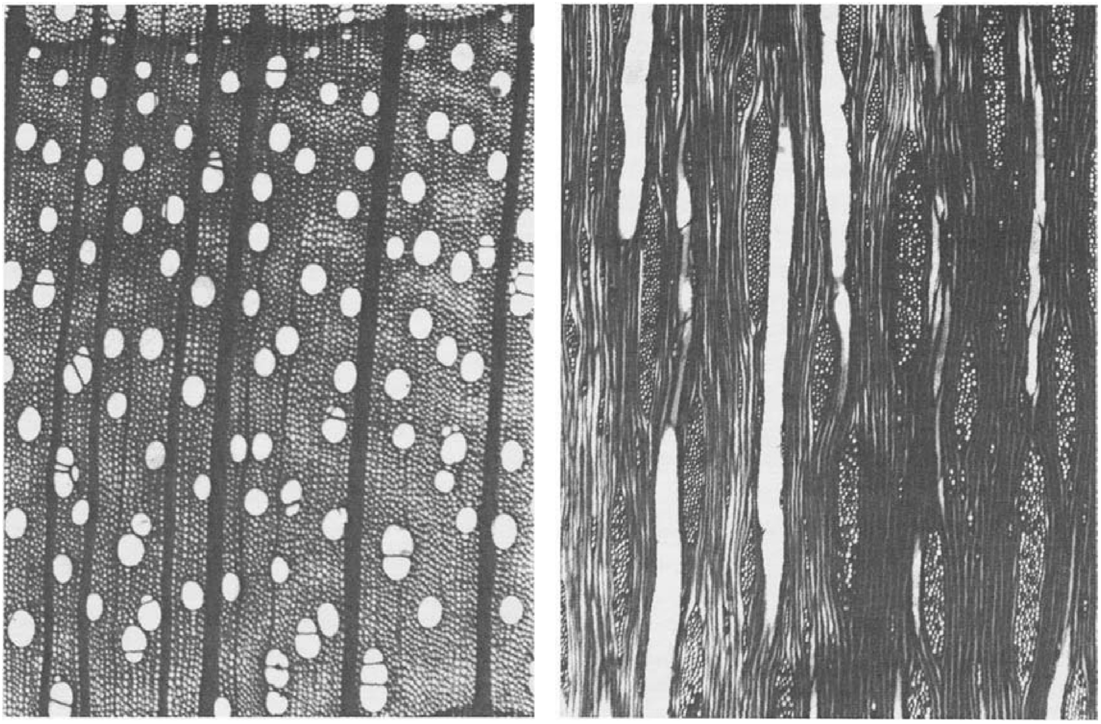


FIGURE 5.40 Sugar maple (*Acer saccharum*) (50×).

Color

The sapwood of the maples is commonly white with a slight reddish brown tinge. It is from 3 to 5 or more inches thick. The heartwood is usually light reddish brown, but sometimes it is considerably darker. The annual rings are not very distinct; they are defined by an indistinct, darker line of marginal parenchyma intermixed with fibers.

Macroscopic Features

Maples are diffuse-porous woods, and the pores are not visible on any surface without magnification. The vessels are solitary (sometimes in radial multiples of 2–3) and evenly distributed within the growth ring. Tyloses are normally absent. Rays are visible. Hard maple is distinguished from soft maple by the two distinct ray sizes of hard maple (which may be up to 8-seriate and as wide as the widest pores) and a lustrous appearance. The rays of soft maples vary in size, the widest of which is almost the same width as the widest vessels (about 5-seriate). Saturated FeS04 in water turns red maple blue-black but gives a green color with sugar maple. Parenchyma is not seen with a lens.

Microscopic Features

Longitudinal parenchyma is marginal, defining growth ring boundaries and intermixed with fibers. Intervessel pitting of red maple is alternate, angular in outline, and crowded. The vessels of soft maple are longer than those of hard maple, whose lengths are seldom more than about three times their diameter.

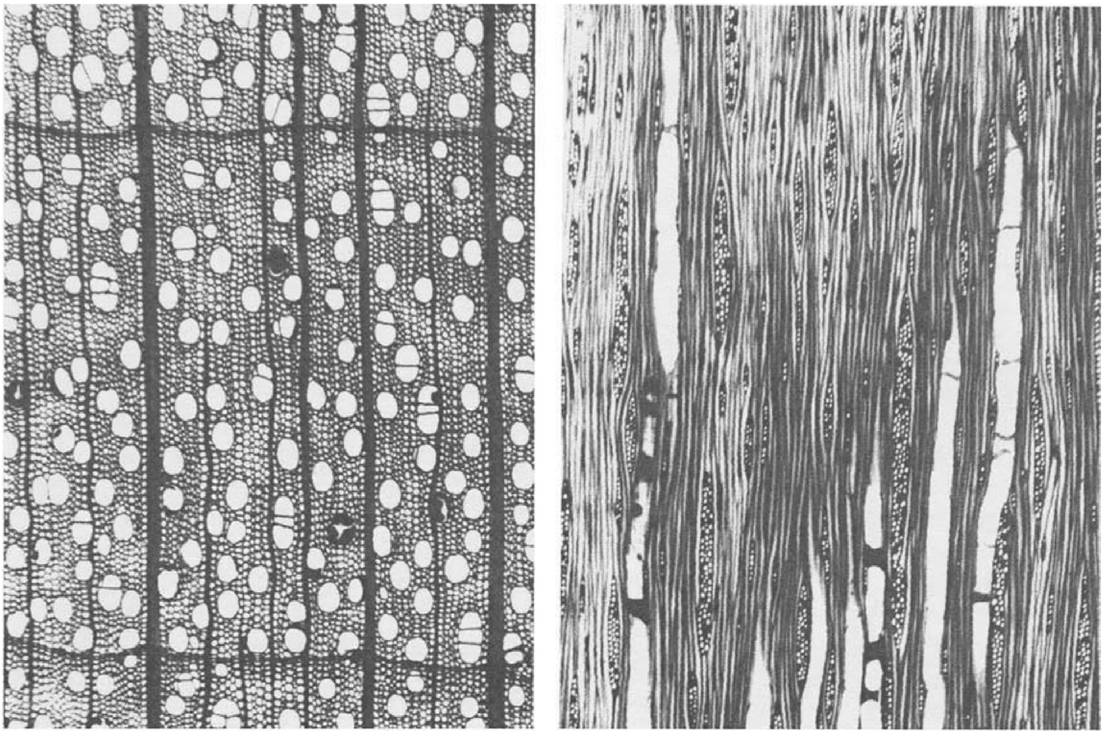


FIGURE 5.41 Red maple (*Acer rubrum*) (50×).

Similar Woods

Maples (simple vessel perforation plates) are distinguished from birches (scalariform perforation plates). The rays of birches are not distinct to the unaided eye, while the vessels are distinct. The rays of beech are much wider than the vessels (*x*).

Red Mulberry (Fig. 5.42)

Red mulberry (*Morus rubra*), alias black mulberry, grows throughout the eastern United States, except in New England. The wood is heavy and straight-grained. The growth rings are distinct and usually moderately wide.

Color

The sapwood is yellowish and about 0.5 in. wide. The heartwood is yellowish brown on freshly cut surfaces, turning to russet brown with exposure to air.

Macroscopic Structure

The wood is ring porous. The earlywood pores are large, distinct, and form a ring of 2–5 pores width. They are densely packed with tyloses that have a unique glistening appearance. The latewood pores form small irregular (nestlike) groups of 3–10, often forming wavy, tangential bands that are observed without a lens. The rays are evident without a lens and form flecks on the radial surfaces. The parenchyma is observed with a lens.

Red Oaks (Figs. 5.43 and 5.44)

Most red oak lumber and other products come from the Southern States, the southern

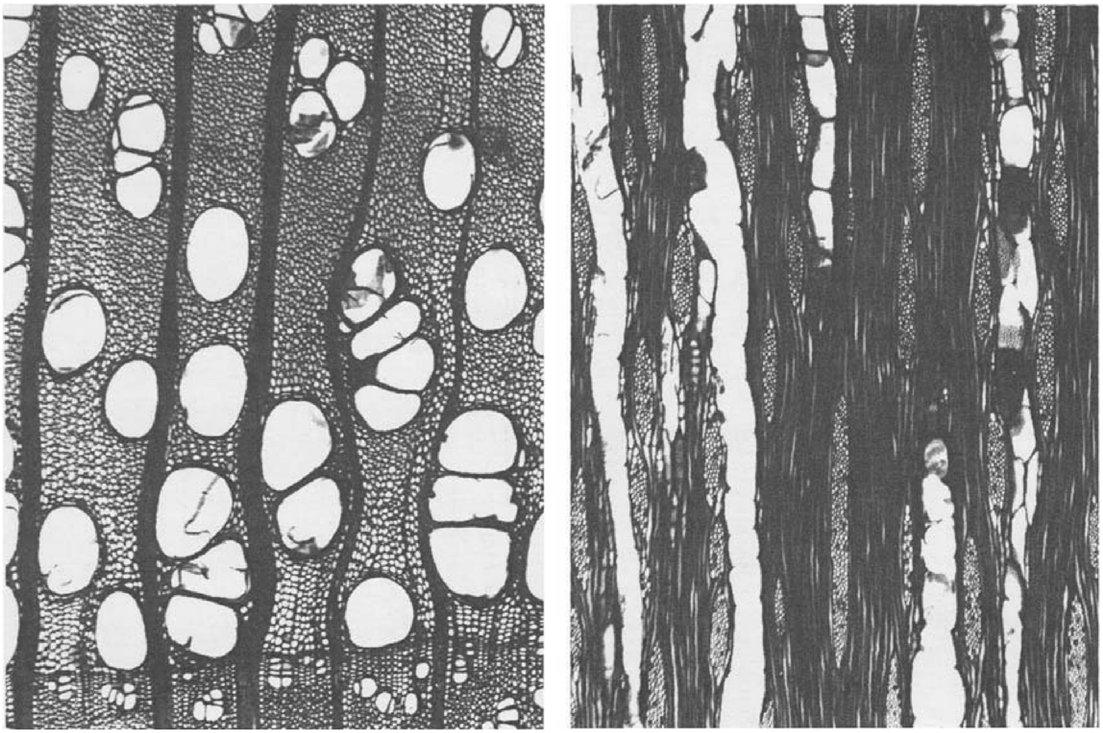


FIGURE 5.42 Red mulberry (*Moms rubra*) (50×).

mountain regions, the Atlantic Coastal Plains, and the Central States. The principal species are: northern red oak (*Quercus rubra*), scarlet oak (*Quercus coccinea*), Shumard oak (*Quercus shumardii*), pin oak (*Quercus palustris*), Nuttall oak (*Quercus nuttallii*), black oak (*Quercus velutina*), southern red oak (*Quercus falcata*), cherrybark oak (*Quercus falcata* var. *pagodifolia*), water oak (*Quercus nigra*), laurel oak (*Quercus laurifolia*), and willow oak (*Quercus phellos*).

Uses

Wood of the red oaks is heavy. Rapidly grown second-growth oak is generally harder and tougher than finer textured old-growth timber. The red oaks have fairly large shrinkage in drying. The red oaks are largely cut into lumber, railroad ties, mine timbers, fence posts, veneer, pulpwood, and fuelwood. Ties, mine timbers, and fence posts require preservative treatment for satisfactory service. Quartersawn lumber is distinguished by the broad and conspicuous rays, which add to its attractiveness. Red oak lumber is remanufactured into flooring, furniture, general millwork, boxes, pallets and crates, caskets, woodenware, and handles.

Color

The sapwood is nearly white and usually 1—2 inches thick. The heartwood is brown with a tinge of red.

Macroscopic Features

The red oaks are ring porous, but may be more semi-ring porous than the white oaks. The earlywood vessels form two or three rows (or four in wide growth rings). Latewood vessels have a dendritic arrangement (groups that are

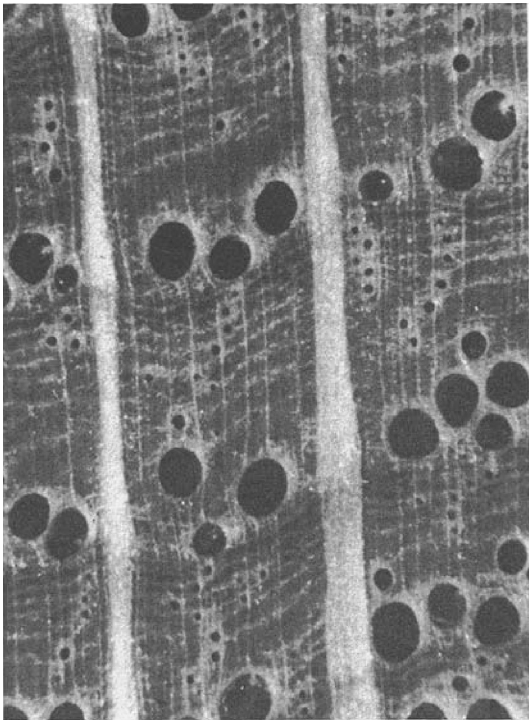


FIGURE 5.43 *Quercus rubra.*

oblique or in a group that widens toward the outer limit of the growth ring) and are surrounded by paratracheal parenchyma. Individual vessels are solitary, rounded, sparsely distributed, and have thick walls. Rays are either uniseriate or extremely broad of the type characteristic of oaks. Longitudinal parenchyma is abundant as paratracheal and apotracheal banded parenchyma. Tyloses are usually absent to sparse.

Similar Woods

Sawed lumber of red oaks cannot be separated by species on the basis of the characteristics of the wood alone. Red oak lumber can be separated from white oak by the number of pores in the latewood and, as a rule, it lacks tyloses in the pores. The open pores of the red oaks make these species unsuitable for tight cooperage, unless the wood is sealed.

White Oaks (Figs. 5.45 and 5.46)

White oak lumber comes chiefly from the South, South Atlantic, and Central States, including the southern Appalachian area. Principal species are white oak (*Quercus alba*), chestnut oak (*Quercus prinus*), post oak (*Quercus stellata*), overcup oak (*Quercus lyrata*), swamp chestnut oak (*Quercus michauxii*), bur oak (*Quercus macrocarpa*), chinkapin oak (*Quercus muehlenbergii*), swamp white oak (*Quercus bicolor*), and live oak (*Quercus virginiana*)

Uses

The wood of white oak is heavy, averaging somewhat higher in weight than that of the red oaks. The heartwood has moderately good decay resistance. White oaks are used for lumber, railroad ties, cooperage, mine timbers, fence posts, veneer, fuelwood, and many other products. High-quality white oak is especially sought for tight cooperage. Live oak is considerably heavier and stronger than the other oaks and was formerly used extensively for ship timbers. An important use of white oak is for planking and bent parts of ships and boats, heartwood often being specified because of its decay resistance. It is also used for flooring, pallets, agricultural implements, railroad cars, truck floors, furniture, doors, millwork, and many other items.

Color

The heartwood of the white oaks is generally grayish brown, and the sapwood, which is from 1 to 2 or more inches thick, is nearly white, although the sapwood is often stained by tannins that leach from the bark.

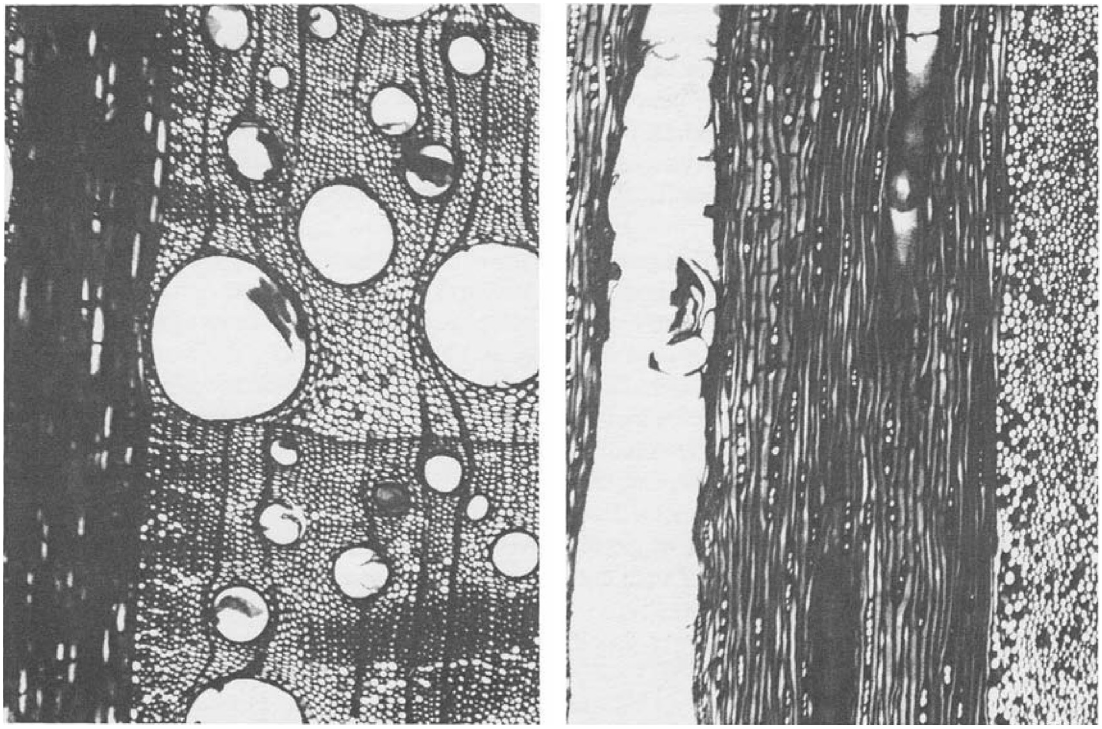


FIGURE 5.44 Red oak group: pin oak (*Quercus palustris*) (50×).

Macroscopic Features

The white oak group is not separable as to species. White oaks are typically ring porous, with the earlywood vessels forming one to two rows (or three in wide growth rings). The pores of the heartwood of white oaks are usually plugged with the membranous growth known as tyloses (although chestnut oak pores are more open). These tend to make the wood impenetrable by liquids, and for this reason most white oaks are suitable for tight cooperage. Latewood vessels have a dendritic arrangement (groups that are oblique or in a group that widens toward the outer limit of the growth ring) (*x*) and are surrounded by paratracheal parenchyma. Latewood vessels are solitary, angular, very small, closely spaced, and thin walled. The red and white oaks are separable based on the appearance of the latewood vessels (see red oaks). Rays are either uniseriate or extremely broad of the type characteristic of oaks. Ray height in red oaks is 1/4 to 1 in., whereas those in white oak may be 0.5–5 in. high, paratracheal and apotracheal. Parenchyma is paratracheal and apotracheal.

Osage Orange (Fig. 5.47)

Osage orange (*Maclura pomifera*) is also called hedge plant, yellow-wood, and mock orange. It grows naturally from Texas to Mississippi and north to Oklahoma but is widely planted outside this region for hedges.

Uses

The wood is very heavy, exceedingly hard, somewhat cross-grained, and without unique odor or taste. It is separated from black locust by its yellowish water-soluble extract of the wood.

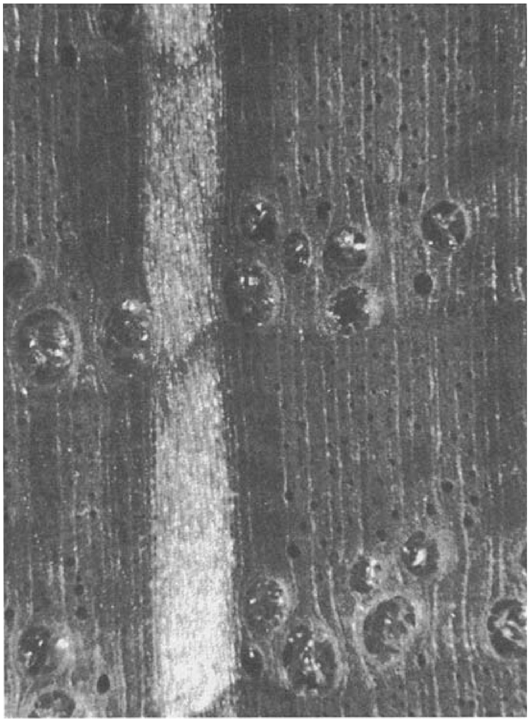


FIGURE 5.45 *Quercus alba.*

Color

The sapwood is very narrow, usually less than 0.5 in. wide. The heartwood on freshly cut surfaces is golden yellow to brown with reddish brown streaks and turns darker with exposure to air.

Macroscopic Features

The wood is ring porous. The large earlywood vessels form a light-colored ring, although the individual vessels are not distinguished due to the presence of tyloses (except near the bark). The latewood pores are very small and are grouped in short, wavy tangential bands. The rays are barely visible without a lens. The paratracheal and paratracheal confluent parenchyma are difficult to distinguish from the latewood vessels with a lens. The annual rings are distinct and irregular in width and outline.

Similar Woods

Black locust is very similar, but black locust lacks the water-soluble yellow dye and has more distinct pores.

Persimmon (Fig. 5.48)

Persimmon (*Diospyros virginiana*), alias date plum or possum wood, grows in the eastern half of the United States, except in the Northeast. The wood is very heavy to extremely heavy, straight or wavy grained. It is easily turned on lathes.

Color

The sapwood is from 2 to 5 in. wide; it is white when freshly cut, but may darken slightly to grayish brown when exposed to air for some time. The heartwood is jet black or blackish brown, irregular in outline, and usually very small. The annual rings are marked by a row of larger pores at the beginning of the earlywood but are not conspicuous because the pores are not numerous and more or less gradually decrease in size toward the outer portion of each ring.

Macroscopic Features

The wood is semi-ring porous with pores barely visible to the unaided eye. The thick-walled vessels are comparatively large, especially in the earlywood, decreasing in size either somewhat abruptly or gradually toward the latewood. Occasionally they are in rows of 2–5; tyloses are lacking. The rays are very fine even under a lens. On the tangential surface they appear in tiers or stories, producing very fine bands running across the grain and visible with the unaided eye. The apotracheal-banded parenchyma are visible with a lens as numerous, very fine, light-colored, irregular, tangential lines no wider

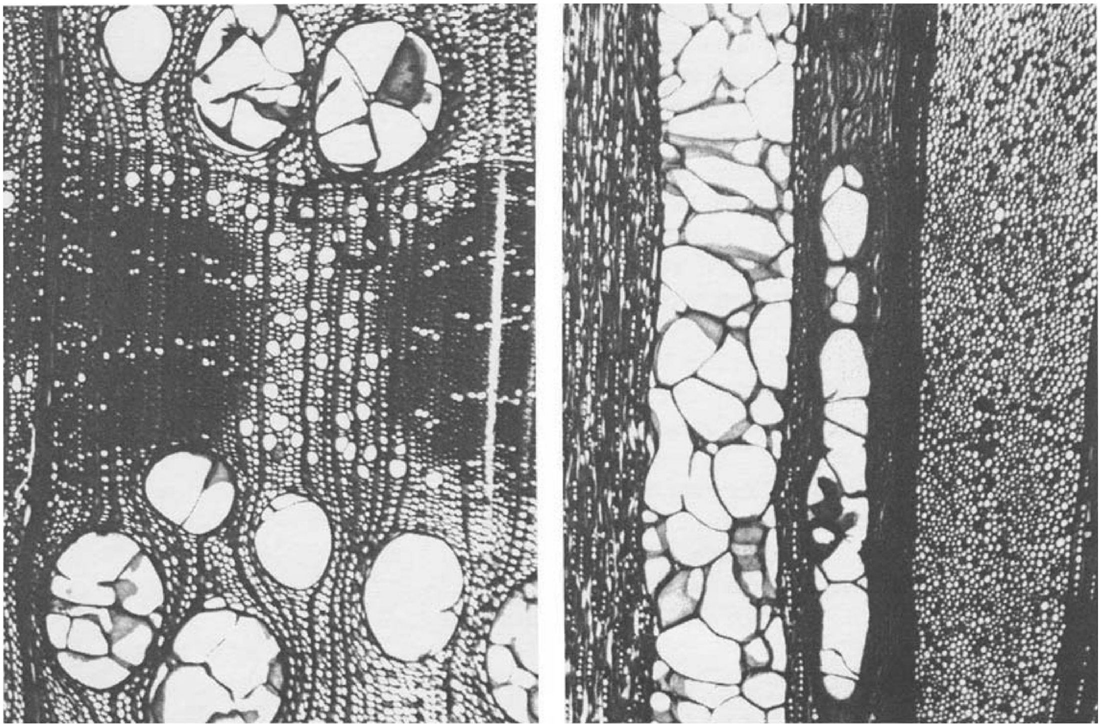


FIGURE 5.46 White oak (*Quercus alba*) (50×).

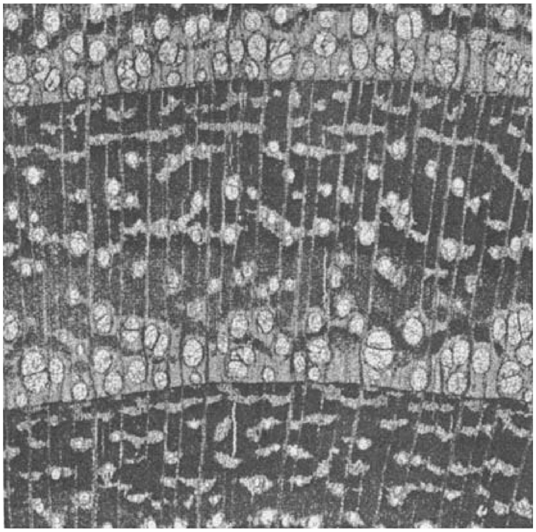


FIGURE 5.47 *Maclura pomifera* (Koehler, 1917) 15×.

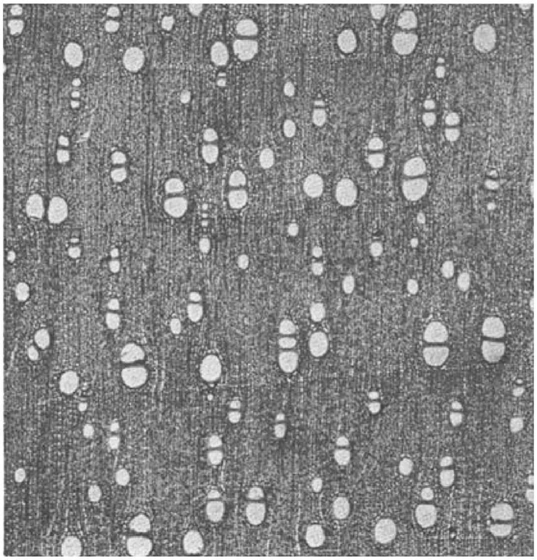


FIGURE 5.48 *Diospyros virginiana* (Koehler), 15×.

than the rays; with the rays, they impart a netlike appearance.

Similar Woods

The heartwood is characteristic among native US woods. The sapwood is similar to that of hickory with the heavy weight, large pores, and fine lines of parenchyma but can be distinguished by the fine horizontal bands on the tangential surface, which are due to the storied arrangement of the rays.

Sassafras (Fig. 5.49)

The range of sassafras (*Sassafras albidum*) covers most of the eastern half of the United States from southeastern Iowa and eastern Texas eastward.

Uses

Sassafras is moderately heavy, moderately hard, moderately weak in bending and endwise compression, quite high in shock resistance, and has high resistance to decay. It was highly prized by the Indians for dugout canoes, and some sassafras lumber is now used for small boats. It is used for fence posts and rails and general millwork, for foundation posts, and some wooden containers.

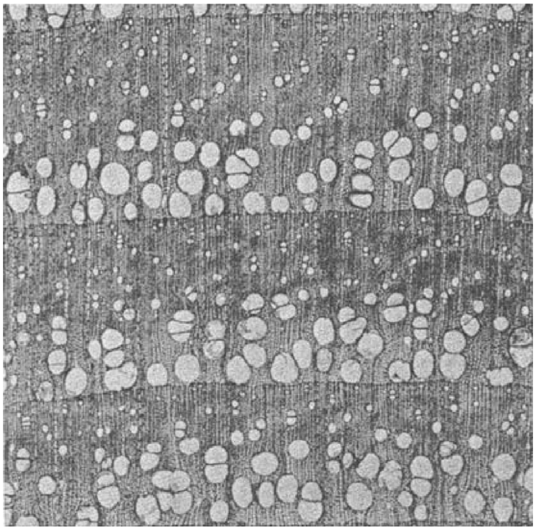


FIGURE 5.49 *Sassafras albidum* (Koehler), 15×.

Color

The sapwood is light yellow and rarely over 0.55 in. wide; the heartwood varies from dull grayish brown to dark brown, sometimes with a reddish tinge. The annual rings are very distinct and of moderate width. The wood has an odor of sassafras on freshly cut surfaces. Sassafras has less luster than catalpa.

Macrostructure

The wood is ring porous. The large pores of the earlywood form a band that is 3—5, or even 7, vessels wide; they are filled with glistening tyloses. The latewood vessels are very small (not visible without a lens), mostly isolated or in radial rows of two or three, and not crowded. The rays are fine but distinct without a lens. The paratracheal confluent and aliform parenchyma are noticeable as a narrow lighter-colored area in the latewood.

Similar Woods

The wood of sassafras is easily confused with black ash, which it resembles in color, grain, and texture. See ash for distinguishing characteristics of other woods.

Sweet gum (Figs. 5.50 and 5.51)

Sweet gum (*Liquidambar styraciflua*), alias red gum and gum tree, grows from southwestern Connecticut westward into Missouri and southward to the gulf. Lumber production is almost entirely from the Southern and South Atlantic States. The lumber from sweet gum is usually divided into two classes: sap gum, the light-colored (white with reddish tinge) wood from the sapwood, and red gum, the reddish brown heartwood.

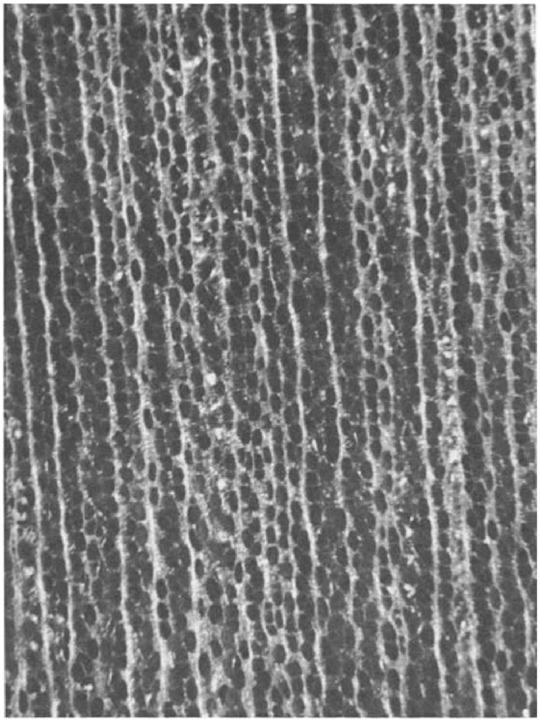


FIGURE 5.50 *Liquidambar styraciflua.*

Uses

Sweet gum must be carefully dried due to its interlocked grain; it causes a ribbon stripe that is desirable for interior finish and furniture. The wood is rated as moderately heavy and hard. It is moderately strong, moderately stiff, and moderately high in shock resistance. Sweet gum is used principally for lumber, veneer, plywood, slack cooperage, railroad ties, fuel, and pulpwood. The lumber goes principally into boxes and crates, furniture, cabinets, interior trim, and millwork. Sweet gum veneer and plywood are used for boxes, pallets, crates, baskets, and interior woodwork.

Color

The sapwood is 1–5 in. thick and subject to blue stain. It is whitish with a pinkish tinge. The heartwood is reddish brown and variable; occasionally it is streaked with a darker color. Traumatic resin canals may be present.

Macroscopic Structure

Sweet gum is a diffuse-porous wood. The pores tend to be solitary, are very numerous, closely spaced, and appear to occupy one-half to two-thirds of the area between rays on the transverse surface. They are visible only with magnification. The appearance of pore pairing occurs in the cross section where the perforation plate between two vessel elements is present. Rays are fine, closely spaced (numerous), and visible on the cross section and radial surface without magnification; they appear to occupy about half of the cross-sectional area. Longitudinal parenchyma is sparse; strands of apotracheal diffuse and paratracheal parenchyma are occasionally present but difficult to see even with a lens. Growth ring boundaries are indistinct and are marked by a few rows of thick-walled and somewhat flattened fibers.

Similar Woods

The heartwood color is characteristic. Black tupelo has less vessel area, vessels in radial multiples, and irregularly distributed vessels. Cherry is usually darker, more lustrous, and has more distinct rays.

American Sycamore (Figs. 5.52–5.54)

American sycamore (*Platanus occidentalis*) is also known as sycamore and sometimes as buttonwood, buttonball tree, water beech, and planetree. Sycamore grows from Maine to Nebraska, southward to Texas, and eastward to Florida. In the production of sycamore lumber, the Central and Southern States rank first.

Uses

The wood has a fine texture and interlocked grain; it shrinks moderately in drying and may

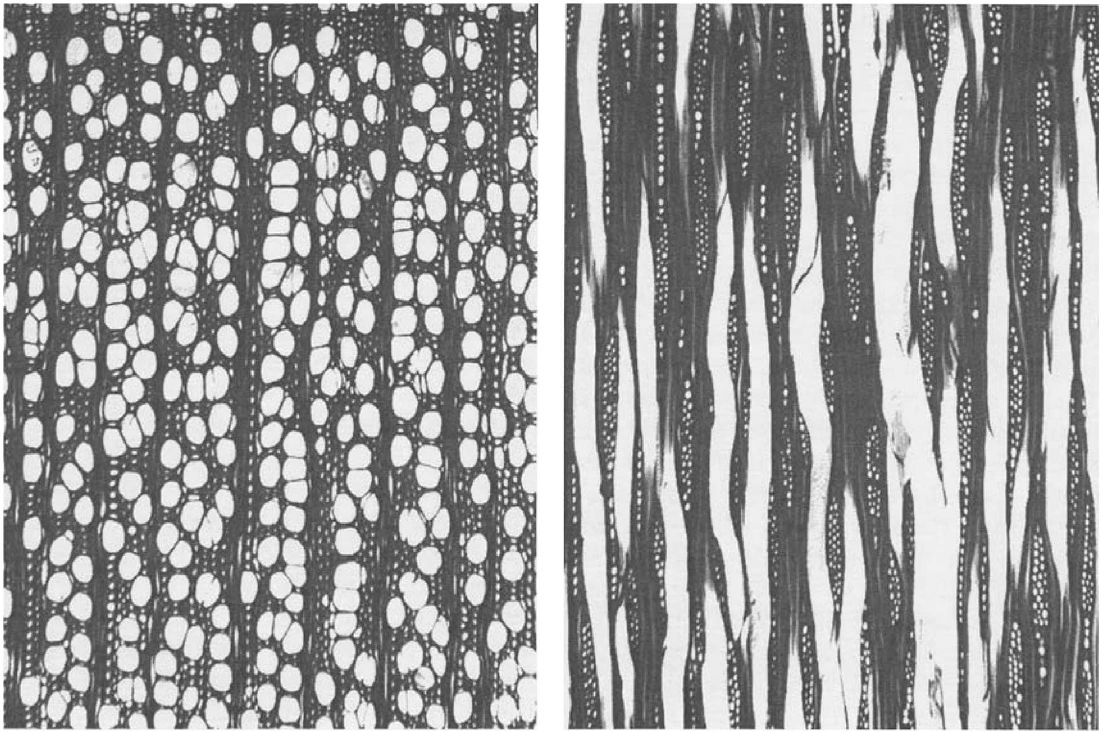


FIGURE 5.51 Sweet gum (*Liquidambar styraciflua*) (50×).

warp; it is moderately heavy, moderately hard, moderately stiff, moderately strong, and has good resistance to shock. Sycamore is used principally for lumber, veneer, railroad ties, slack cooperage, fence posts, and fuel. Sycamore lumber is used for furniture, boxes (small food containers), pallets, flooring, handles, and butcher's blocks. The veneer is used for fruit and vegetable baskets, decorative panels, and door skins.

Color

The heartwood of sycamore is reddish brown and sometimes not sharply delineated from the sapwood; the sapwood is white to yellowish and 1.5—3 in. thick. The annual rings are distinct but are not differentiated into distinct earlywood and latewood.

Macroscopic Features

The wood is diffuse porous. The vessels are very small and not visible to the unaided eye. They are crowded in the earlywood but gradually decrease in number in the latewood. They have some tangential pairing in the latewood. Toward the end of the growth ring they form a narrow, lighter-colored band. Rays are visible on all surfaces. They appear uniformly spaced on the cross section and of uniform height on the radial surface. These rays appear as "silver grain" on the radial surfaces. The parenchyma is not visible even with a lens.

Other Species

Sycamore is not easily confused with other species. Its numerous conspicuous rays and interlocked grain make it easily recognizable. It

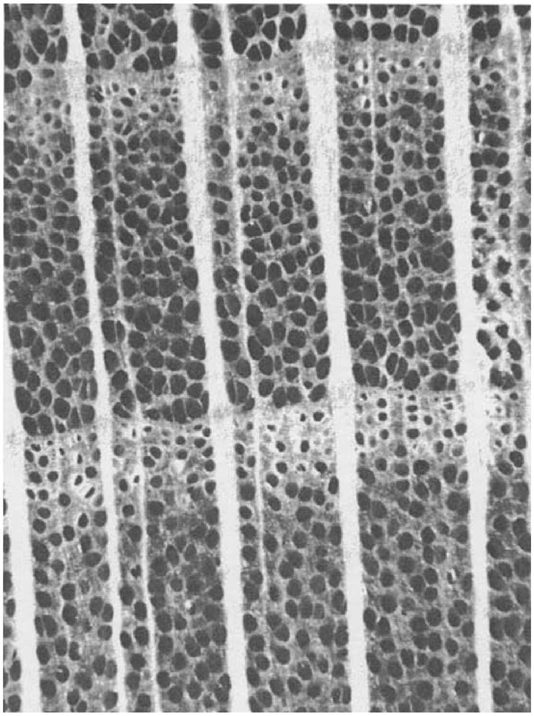


FIGURE 5.52 *Platanus occidentalis.*

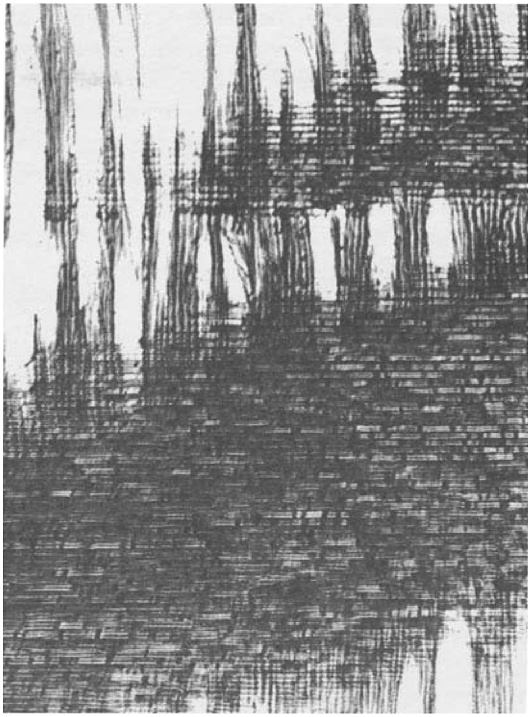


FIGURE 5.53 *Platanus occidentalis*, r view, 50×.

is distinguished from beech by its rays, only a small proportion of which are broad in beech. Beech also has a distinct darker and denser band of latewood.

Tan oak (Figs. 5.55 and 5.56)

Tan oak (*Lithocarpus densiflorus*) has some importance commercially, primarily in California and Oregon. It is also known as tanbark-oak because at one time high-grade tannin in commercial quantities was obtained from the bark. This species is found in southwestern Oregon and south to Southern California, mostly near the coast but also in the Sierra Nevada range.

Uses

The wood is heavy, hard, and, except for compression perpendicular to the grain, has roughly the same strength properties as eastern white oak. Volumetric shrinkage during drying is more than for white oak, and it has a tendency to collapse during drying. It is quite susceptible to decay, but the sapwood takes preservatives and stains easily. It has straight grain and machines and glues well. Because of tan oak's hardness and abrasion resistance, it is an excellent wood for flooring in homes or commercial buildings. It is suitable for industrial applications such as truck flooring. Tan oak treated with preservatives has been used for railroad crossties. The wood has been manufactured into baseball bats with good results. It is also suitable for veneer, both decorative and industrial, and for high-quality furniture. It is used in corrugating medium.

Color

The sapwood of tan oak is light reddish brown when first cut and turns darker with

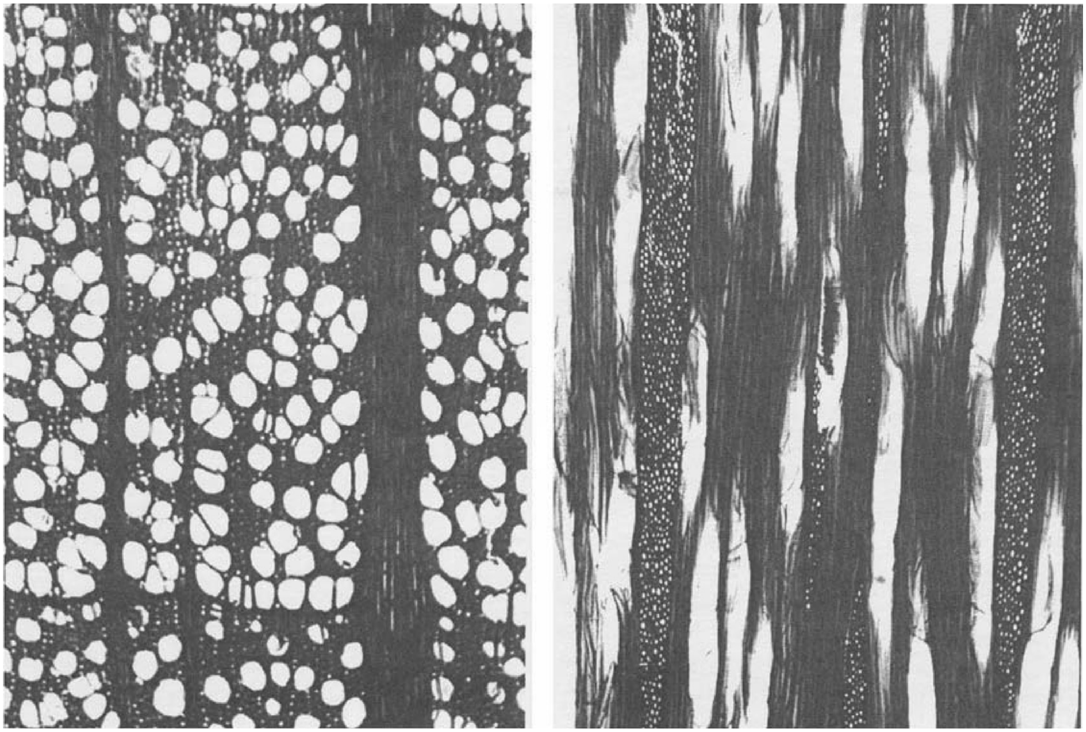


FIGURE 5.54 American sycamore (*Platanus occidentalis*) (50×).

age to resemble the heartwood, which also ages to dark reddish brown.

Macroscopic Features

The wood is semi-ring porous with a gradual transition in pore size. The latewood vessels form oblique groups or clusters. The apotracheal parenchyma is banded and abundant. They are visible with a lens as irregular wide lines. The rays are of two sizes; the large rays are irregularly distributed.

Tupelo (Fig. 5.57)

The tupelo group includes water tupelo (*Nyssa aquatica*), also known as tupelo gum, swamp tupelo, and gum; black tupelo (*Nyssa sylvatica*), also known as black gum and sour gum; swamp tupelo (*Nyssa sylvatica* var. *biflora*), also known as swamp black gum, black gum, tupelo gum, and sour gum; Ogeechee tupelo (*Nyssa ogeche*), also known as sour tupelo, gopher plum, tupelo, and Ogeechee plum. All except black tupelo grow principally in the southeastern United States. Black tupelo grows in the eastern United States from Maine to Texas and Missouri. About two-thirds of the production of tupelo lumber is from the Southern States.

Uses

The wood has fine, uniform texture and interlocked grain that requires careful lumber drying. Tupelo wood is rated as moderately heavy. It is moderately strong, moderately hard and stiff, and moderately high in shock resistance. Buttresses of trees growing in swamps or flooded areas contain wood that is much lighter in weight than that from upper portions of the

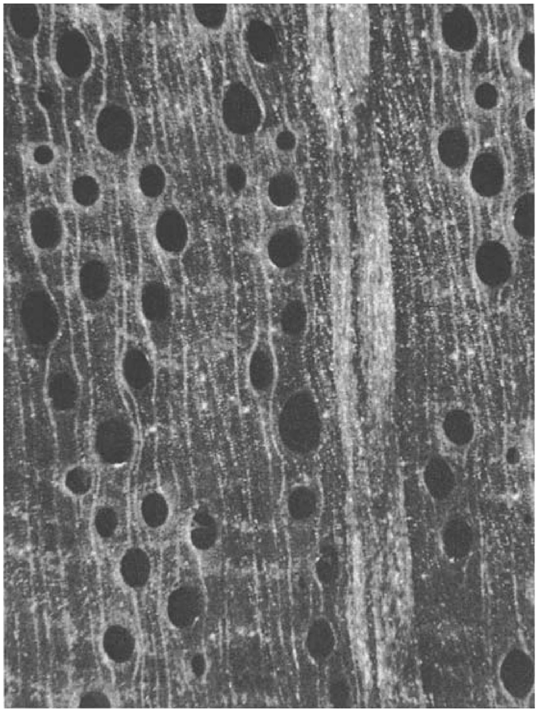


FIGURE 5.55 *Lithocarpus densiflorus.*

same trees; this wood should be separated from the heavier wood to assure material of uniform strength. Tupelo is cut principally for lumber, veneer, pulpwood, and some railroad ties and slack cooperage. Lumber goes into boxes, pallets, crates, baskets, and furniture.

Color

Wood of the different tupelos is quite similar in appearance and properties. The heartwood is light brownish gray and merges gradually into the lighter-colored sapwood, which is generally several inches wide.

Macroscopic Structure

Black tupelo is diffuse porous with small pores like sweet gum. The vessels are numerous and in radial multiples, which may be irregularly distributed. Growth rings are inconspicuous to moderately distinct. Rays are slightly coarser than in sweet gum but are numerous and closely spaced; they are inconspicuous against the background color but appear to occupy half of the surface (in the cross section, x). The longitudinal parenchyma occurs in scattered paratracheal—scanty and apotracheal—diffuse arrangements but are very difficult to see. See sweet gum for its distinction from black tupelo.

Microscopic Structure

Intervessel pitting of black tupelo is opposite, pits are nearly square in outline, and there are up to six pits per row.

Black Walnut (Fig. 5.58)

Black walnut (*Juglans nigra*) is also known as American black walnut. Its natural range extends from Vermont to the Great Plains and southward into Louisiana and Texas. About 75% of the timber is produced in the Central States.

Uses

Black walnut is normally straight-grained, easily worked with tools, and stable in use. It has a faint characteristic odor that is manifested when it is worked. It is heavy, hard, strong, stiff, and has good resistance to shock. Black walnut wood is expensive and well suited for natural finishes. The outstanding uses of black walnut are for furniture, architectural woodwork, and decorative panels. Other important uses are gunstocks, cabinets, and interior finish. It is used either as solid wood or as plywood.

Color

The characteristic heartwood of black walnut varies from light to dark brown; the sapwood is nearly white and up to 3 in. wide in open grown trees but typically less than 1 in. wide. Annual rings are distinct and marked by the change in pore size.

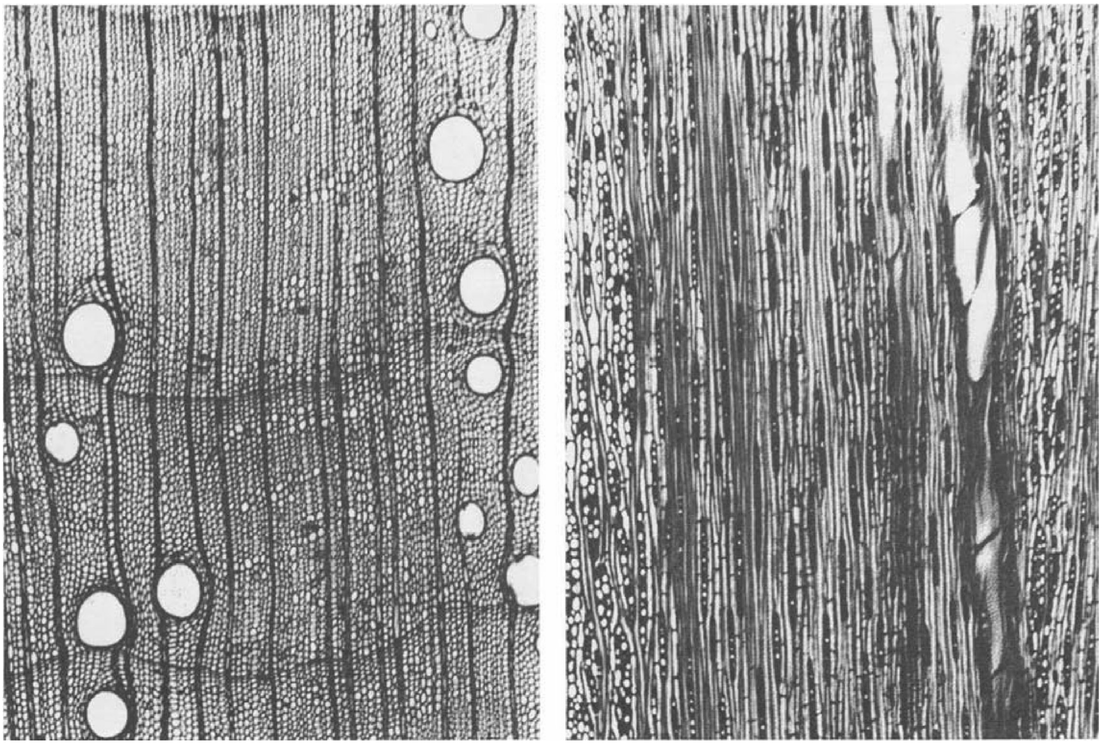


FIGURE 5.56 Tan oak (*Lithocarpus densiflora*) (50×).

Macroscopic Features

Black walnut is not easily confused with any other native species. The wood is semi-ring porous. Pores are barely visible in the cross section (with tyloses) to the unaided eye but are easily seen as darker streaks or grooves on the longitudinal sections. The pore arrangement is similar to that of hickories and persimmon, but the pores are smaller in size. The rays are very fine, inconspicuous, and not distinct without a lens. The apotracheal parenchyma is readily visible in the sapwood as several lighter-colored, irregular, tangential bands but are indistinct in the heartwood without a lens.

Microscopic Features

The netlike (*reticulate*) thickening that occurs sporadically in the latewood vessels (*gash pits*) distinguishes it from butternut and English walnut of the same genus. Black walnut has crystals in strand parenchyma (that tend to dull woodworking tools) but butternut does not.

Black Willow (Fig. 5.59)

Black willow (*Salix nigra*) is the most important of the many willows that grow in the United States. It is the only one to supply lumber to the market under its own name. Black willow is most heavily produced in the Mississippi Valley from Louisiana to southern Missouri and Illinois.

Uses

The wood of black willow is uniform in texture, with somewhat interlocked grain. The

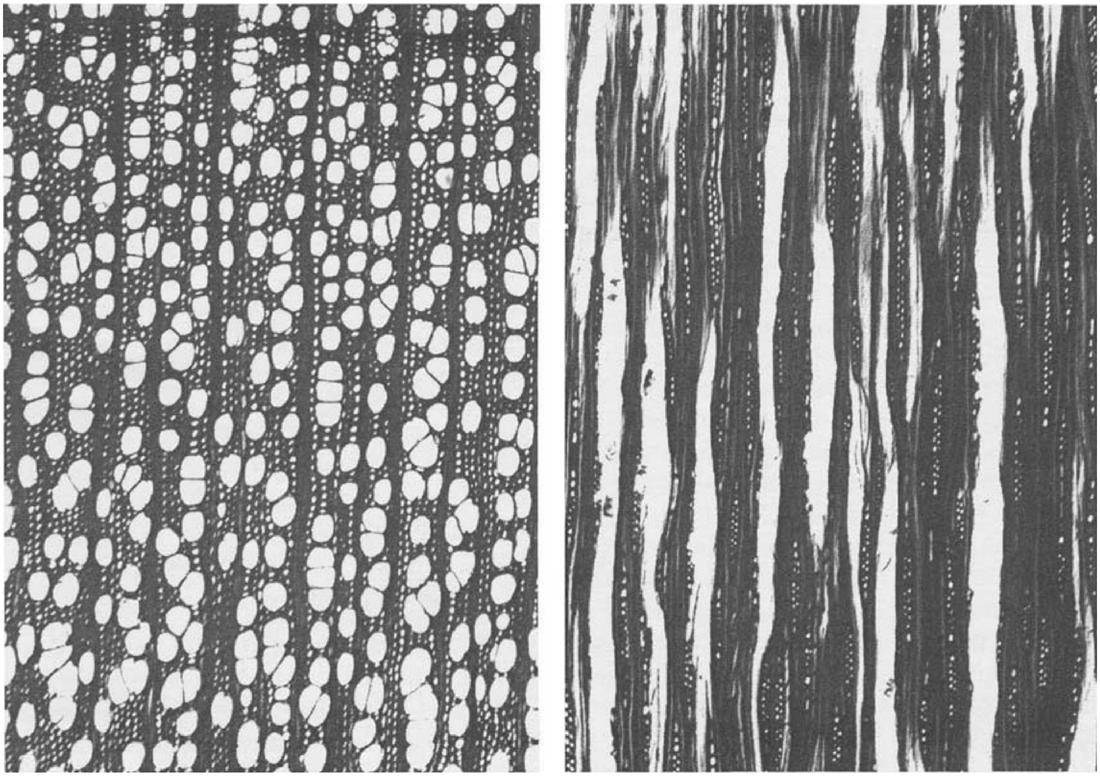


FIGURE 5.57 Water tupelo (*Nyssa sylvatica*) (50×).

wood is light in weight. It has exceedingly low strength as a beam or post and is moderately soft and moderately high in shock resistance. It has moderately large shrinkage. Willow is cut principally into lumber. Small amounts are used for slack cooperage, veneer, excelsior, charcoal, pulpwood, artificial limbs, and fence posts. Black willow lumber is remanufactured principally into boxes, pallets, crates, caskets, and furniture. Willow lumber is suitable for roof and wall sheathing, subflooring, and studding.

Color

The heartwood of black willow is grayish brown or light reddish brown frequently containing darker streaks. The sapwood is whitish to creamy yellow.

Macroscopic Structure

The wood is semi-ring porous. The latewood vessels are small, numerous, and solitary or in radial multiples of 2–4. The marginal parenchyma is not conspicuous. The rays are narrow, normally spaced, and visible with a lens.

Yellow Poplar (Figs. 5.60 and 5.61)

Yellow poplar (*Liriodendron tulipifera*) is also known as poplar, tulip poplar, tulipwood, and hickory poplar. Sapwood from yellow poplar is sometimes called white poplar or whitewood. Yellow poplar grows from Connecticut and New York southward to Florida and westward to Missouri. The greatest commercial production of yellow poplar lumber is in the South.

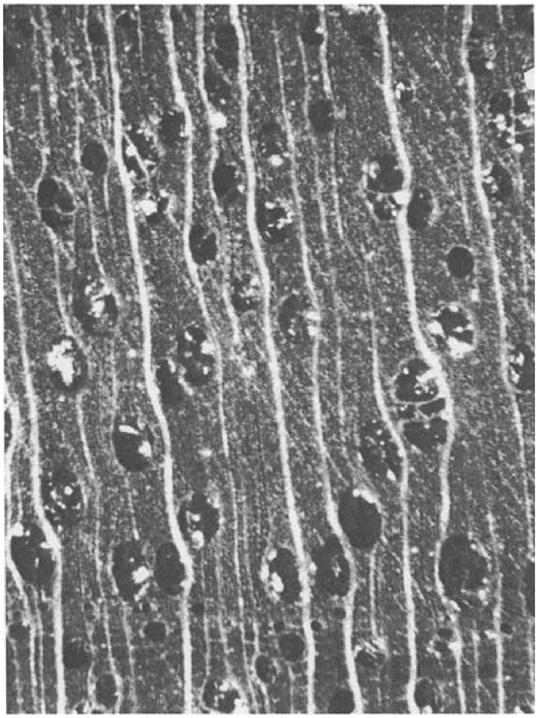


FIGURE 5.58 *Juglans nigra.*

Uses

The wood is generally straight-grained and comparatively uniform in texture. Old-growth timber is moderately light in weight and is reported as being moderately low in bending strength, moderately soft, and moderately low in shock resistance. It has moderately large shrinkage when dried but is not difficult to season and stays in place well after seasoning. Much of the second-growth yellow poplar is heavier, harder, and stronger than old growth. Selected trees produce wood heavy enough for gunstocks. Lumber is used in furniture, interior finish, siding, core stock for plywood, cabinets, and musical instruments, but use for core stock is decreasing as particleboard use increases. Yellow poplar is frequently used for crossbands in plywood. Boxes, pallets, and crates are made from lower grade stock. Yellow poplar plywood is used for finish, furniture, piano cases, and various other special products. Yellow poplar is used for pulpwood and slack cooperage staves. Lumber from the cucumber tree

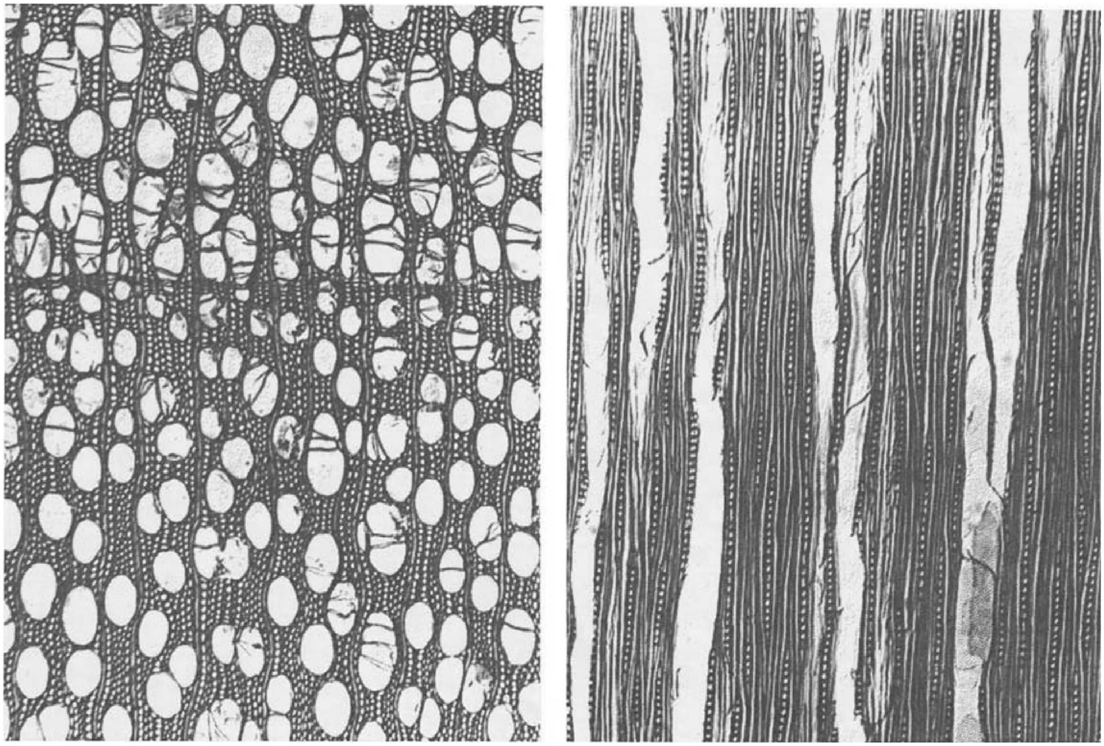


FIGURE 5.59 Black willow (*Salix nigra*) (50×).

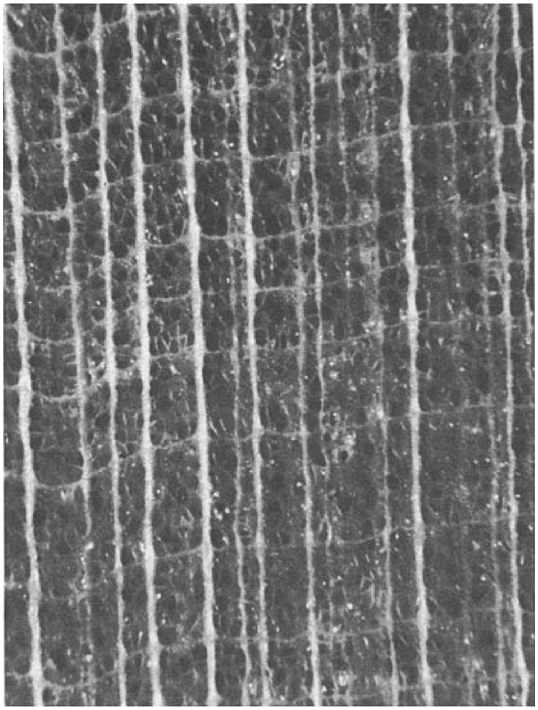


FIGURE 5.60 *Liriodendron tulipifera.*

(*Magnolia acuminata*) sometimes may be included in shipments of yellow poplar because of its similarity.

Color

Yellow poplar sapwood is white and often several inches thick; it merges gradually into the heartwood. The heartwood is yellowish brown, sometimes streaked with purple, green, black, blue, or red.

Macroscopic Structure

Yellow poplar is a diffuse-porous wood. The pores are numerous and in radial multiples that are frequently diagonal. Rays are normally spaced, much fewer than in sweet gum, and visible to the unaided eye. Longitudinal parenchyma is marginal, forming a continuous white line of several rows in the outer portion of the latewood. The vessel distribution is variable, frequently being less numerous in the outer latewood.

Microscopic Structure

Intervessel pitting is opposite, pits are rectangular in outline.

Similar Woods

Yellow poplar can usually be distinguished from other woods by its greenish tinge. Sweet bay (magnolia) is very similar but can be separated by use of a microscope. Non–North American Species.

Eucalyptus (Fig. 5.62)

Eucalypts (*Eucalyptus* spp.) constitute a genus with over 500 species of greatly differing properties; some are suitable for pulping, while others are not. *Eucalyptus marginata* is called jarrah and is native to the coastal belt of southwestern Australia. The heartwood is a uniform pinkish to dark red, often with a rich, dark red mahogany hue, turning to a deep brownish red with age and exposure. The sapwood is pale in color and usually very narrow in old trees. The texture is even and moderately coarse. The density is 44 lb/ft3. The grain is often interlocked or wavy. Gum veins and pockets are a common defect. The heartwood is extremely resistant to preservatives. *Eucalyptus diversicolor* is called karri and is a large tree limited to Western Australia. It is 57 Ib/ft3 and paler in color than jarrah but otherwise similar in appearance. *Eucalyptus grandis* is the principal hardwood species used for pulping in Brazil; it is more difficult to pulp than *Eucalyptus globulus*. Other species include (Tasmanian) blue gum (*Eucalyptus globules* Labill.), blackbutt (*Eucalyptus pilularis* Sm.), and robusta (*Eucalyptus robusta* Sm.).

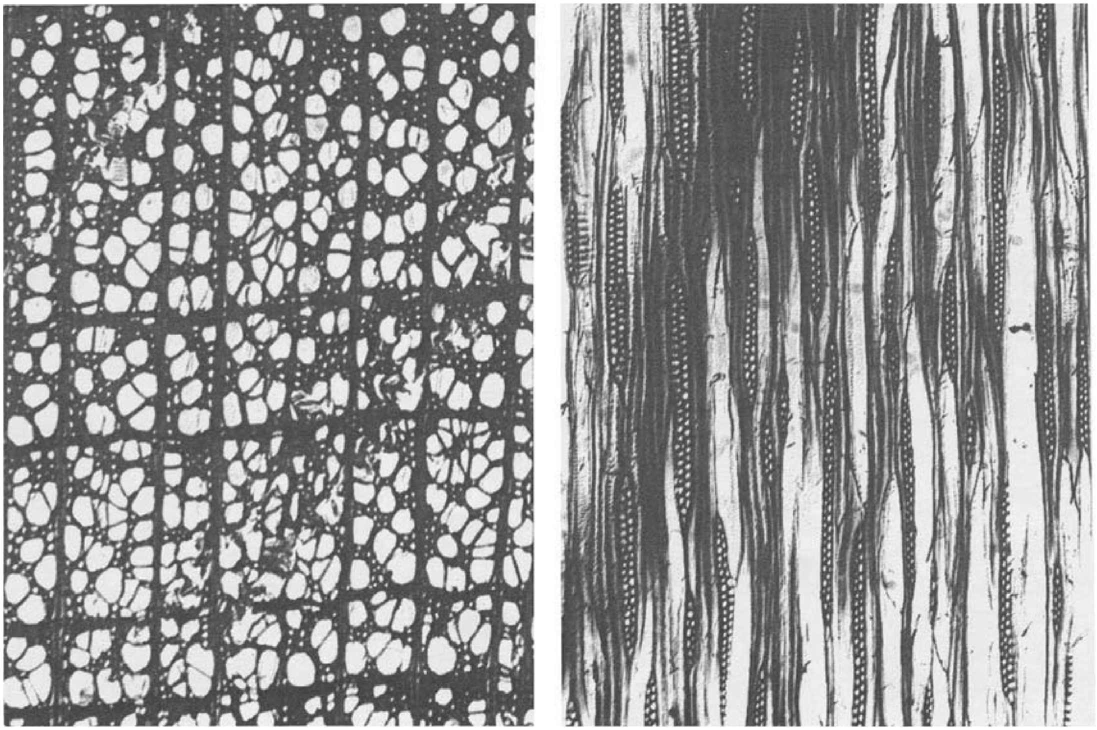


FIGURE 5.61 Yellow poplar (*Liriodendron tulipifera*) (50×).

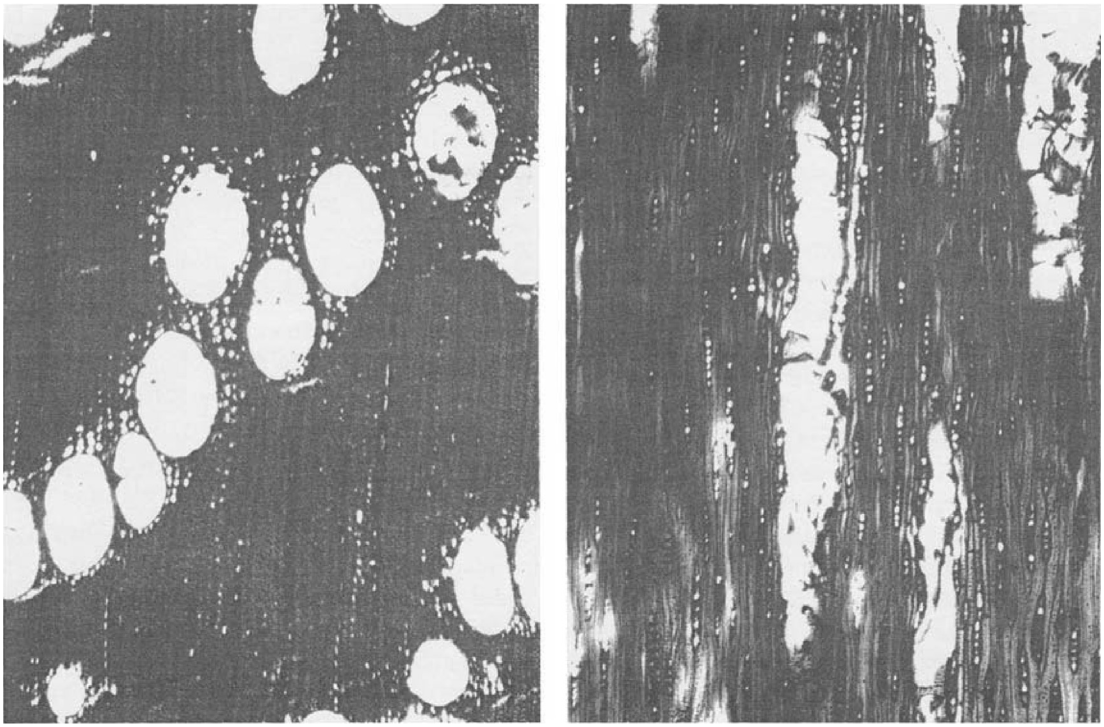


FIGURE 5.62 A eucalypt (*Eucalyptus grandis*) (50×).

Gmelina

Gmelina (*Gmelina arborea*) has some limited use in pulp and paper. It is distributed in India, Burma, and eastward to Vietnam. It is a common plantation species. It takes 20 years for it to grow to 100 feet high with a diameter of 2 feet. The grain is interlocked and wavy. The texture is moderately coarse. The wood is pale straw yellow. The fibers are 0.8–1.3 mm long with diameters of 25–35 μm.

CHAPTER

6

Wood Fiber Anatomy and Identification

6.1 FIBER ANALYSIS

Introduction

The references for this chapter are found in Chapter 3 (Vol. 1).

It is useful to look at wood in terms of its fiber anatomy and properties because this is how it is used by the pulp and paper industry.

There are many excellent references available for fiber analysis (see Annotated Bibliography section in Chapter 3, Vol. 1), and much of the information presented in earlier chapters can be used. This chapter gives an overview of fiber morphology from wood and shows what features to look for in fibers for their identification. Information is also given to help determine pulping and bleaching methods used to prepare the pulp.

It is fundamental that the properties on paper depend on the fiber properties and the method of fiber preparation (pulping, bleaching, and fiber processing). It is difficult to separate wood before pulping (latewood from earlywood, fast-growth wood from slow-growth wood, compression wood from normal wood, juvenile wood from mature wood, etc.), so variability of wood must be overcome by varying the processing of the wood and pulp. The availability and price of wood are as important as the properties of the wood itself.

Fiber Anatomy Considerations

Identification of fibers is difficult because there is much less information available than in the wood; identification is often down to a few members within a genus, rather than to a particular species. Other species, such as Douglas fir with spiral thickening, are unique and can be identified as to the species. The situation is complicated by the fact that many papers can contain two, three, or more types of fibers, especially if the paper contains appreciable amounts of recycled fiber. Panshin and de Zeeuw (1980, pp. 657−666) include a key for fiber identification.

It is important to have authentic fiber samples of contributing species on hand for comparison with unknown samples. For example, if one is using a lot of "precommercial" thinnings with a high percentage of juvenile wood, fiber length will be shorter than published values. It takes a large investment of time to become proficient at fiber identification, and many references containing micrographs should be used. This chapter allows one to visualize the major differences in pulps that contribute to the papermaking properties and is useful for simple identifications, such as determining when various places in a mill are affected by the changeover of a digester line from one species to another. In mechanical pulps, one can learn about the relative morphology of the contributing species by looking for fiber bundles.

Biermann's Handbook of Pulp and Paper: Raw Material and Pulp Making
https://doi.org/10.1016/B978-0-12-814240-0.00006-9

Weight Factors

When attempting quantitative analysis of fiber mixtures, the number of a particular type of fiber is multiplied by its *weight factors* because some types of fibers appear to be present in larger amounts than others, such as those with low surface areas. Weight factors are given in T 401 (based largely on Graff, J.H., *Paper Trade J.* 110(2):37(1940)). The weight factors for coastal Douglas fir and loblolly pine are 1.40, for most hardwoods 0.50, and for bleached straw 0.35. The higher the relative surface area (per given mass of pulp), the lower the weight factor. Parham and Gray (1990) give weight factors on page 35 (largely from Einspahr, D.W. and J.D. Hankey, *Tappi* 61(12): 86−87(1978)). One could determine one's own weight factors for a particular application. Weight factors are a crude method of taking number averages and converting them to weight averages.

Fiber Pitting

Pitting, in general, is very useful in the determination of isolated fibers. However, one must keep in mind that pulping operations and refining are bound to affect the way a pit looks under the microscope. Intervessel pitting of hardwoods and ray cross-field pitting in softwoods are the principal means of identification. Ray cross-field pitting shows whether ray parenchyma and/or tracheids are present; it also indicates the height of the rays.

Fiber and Wood Staining

Chemical stains can help with the analysis by identifying the type of pulping method used to generate the fibers. This might be more important in brown papers that might have some recycled newsprint rather than in white printing papers, but these might have some bleached CTMP pulp. Hoadley (1990) references examples of species determination of wood using chemical stains, including box elder and other maples, red gum and black tupelo, elms, pond and sand pines, spruces and pines, and other groups. Separation of red and white oaks and red and sugar maples is discussed in Panshin and de Zeeuw (1980). Eastern spruce and balsam fir are separated by the method of Kutscha et al. in *Wood Sci. and Tech.* 12:293−308(1978). Separation of heartwood and sapwood is referenced (Kutscha and Sachs, 1962). Iodine is used to detect the presence of starch, which might be present in sapwood but not in heartwood or paper such as in the detection of forged currency. It is used with iodide to form the soluble I_2^- species in water (0.3% I_2 and 1.5% KI in water). *Safranin O* is a general stain for cellulosic materials (red). It is used as a 0.5−1% solution in water or 50% ethanol. Pulp stains are described in detail in Graff (1940), Isenberg (1967), and TAPPI Standard T401 om-82. Graff (1940) describes three types of stains: (1) spot stains or groundwood reagents using chemicals such as aniline sulfate, phloroglucinol and hydrochloric acid, and p-nitroaniline for detection of mechanical pulps in paper; the first class is said here to be of limited value; (2) the iodine/iodide metallic salt stains, including the Herzberg stain, the "A" stain, and the "C" stain; these give qualitative information about fibers; and (3) aniline dyes for the determination of the degree of cooking, bleaching, and purity of pulps. *Phloroglucinol* is specific for lignin, causing it to turn red. It is used as a 2% solution in 18.5% HCl. Isenberg (1967) suggests mixing 1 g in 50 mL of EtOH to which is added 25 mL of concentrated HCl; this is made up immediately before use. One use is to show mechanical pulps in white papers.

Mechanical softwood and hardwoods are differentiated with the use of 2% aniline sulfate made acidic (1 drop concentrated H_2SO_4 per 50 mL) followed by 0.02% methylene blue after removal of the first dye by blotting. Softwoods are yellow and hardwoods are bluish green. The Maule reaction can also be used. Mechanical pulp bleached with dithionite no more than a few months old is determined by detecting traces of SO_2 or sulfite as H_2S liberated by stannous chloride. Several stains are available to determine the level of bleaching (or cooking) of pulps, such as Bright stain. These can be used to check the uniformity of bleaching (and pulping) in the mill (Isenberg, 1967). Stains even exist for the identification of dirt, although scanning electron microscopy and energy dispersive X-ray analysis (SEM-EDAX) has made many of these methods somewhat obsolete.

Other Techniques

Monosaccharide analysis (although tedious) will give a good indication of the ratio of hardwoods to softwoods because galactose and mannose come from softwoods. Dissolving pulps will have low levels of hemicelluloses, of course.

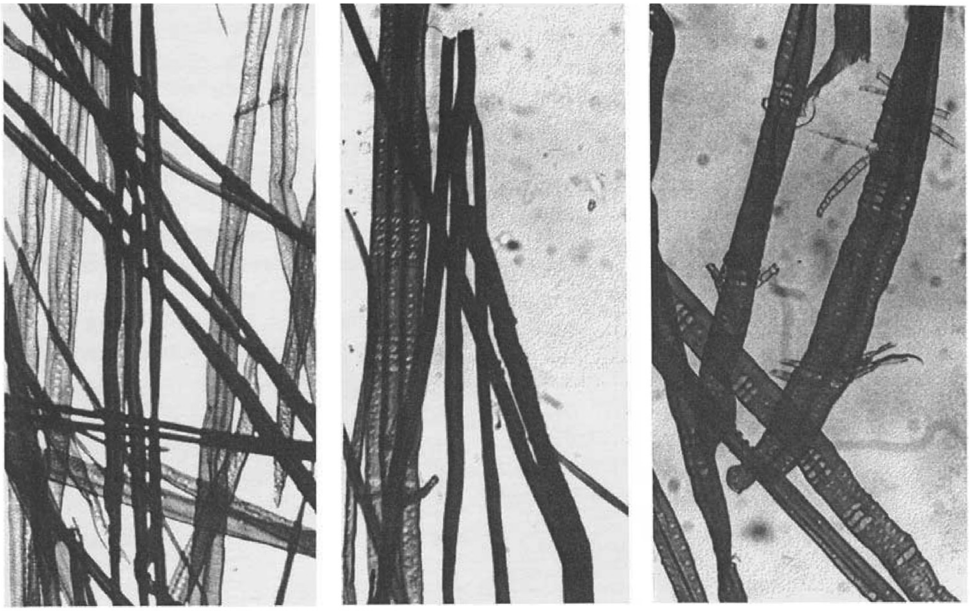
6.2 SOFTWOOD FIBER

Fibers over 2 mm long are most often softwood fibers. Table 4.3 is a general guide to softwood fiber analysis, and Table 4.4 contains a summary of some important softwood fiber properties. Fig. 6.1 shows six types of softwood fibers. Parham and Gray (1990) claim that Douglas fir, redwood, bald cypress, podocarp, Parana pine, sugar pine, white pine, and hard pine should be distinguishable under most circumstances, although these separations require a high degree of skill. Spruce, larch, and hemlock may not be able to be distinguished from each other as with true fir and western red cedar. If the source of the pulp is known then regional information can be used (i.e., European or American, eastern or western, etc.). Ray cross-field pitting in softwoods is the principal means of identification. Examination of many ray cross-field pits shows whether ray tracheids are present, marginal, or interspersed and may indicate the average height of the rays.

For example, Fig. 6.2 shows some fibers with ray cross-field pitting on the tracheids. The western white pine shows the fenestriform ray cross-field pitting that is characteristic of the white pines, and the small pits are from ray tracheids. Ponderosa pine has pinoid ray cross-field pitting with pits that are variable is size and up to 7 pits per cross-field. The Sitka spruce fiber shows piceoid ray cross-field pitting of uniform size with 3 or more pits per cross-field common.

6.3 HARDWOOD FIBER

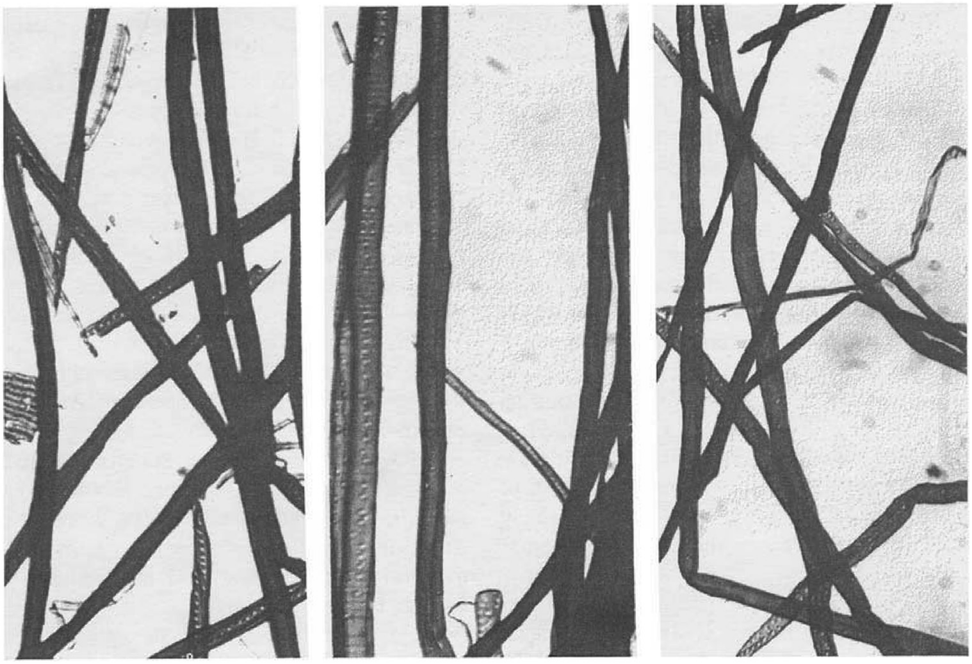
Table 5.1 is a general guide to hardwood pulp analysis. Whole fibers less than 2 mm long usually originate from hardwoods. Hardwood fibers are accompanied by vessels or vessel fragments, depending on the pulping process. The fibers shown in this chapter were isolated by a laboratory pulping process that leaves the vessels largely intact. Furthermore, parenchyma cells have not been removed as occurs to various degrees in pulp processing. Fig. 6.3 shows fibers from hardwoods.



Douglas—fir

Southern pine

Eastern white pine



Sitka spruce

Western hemlock

Western cedar

FIGURE 6.1 Various softwood fibers isolated in the laboratory (60×).

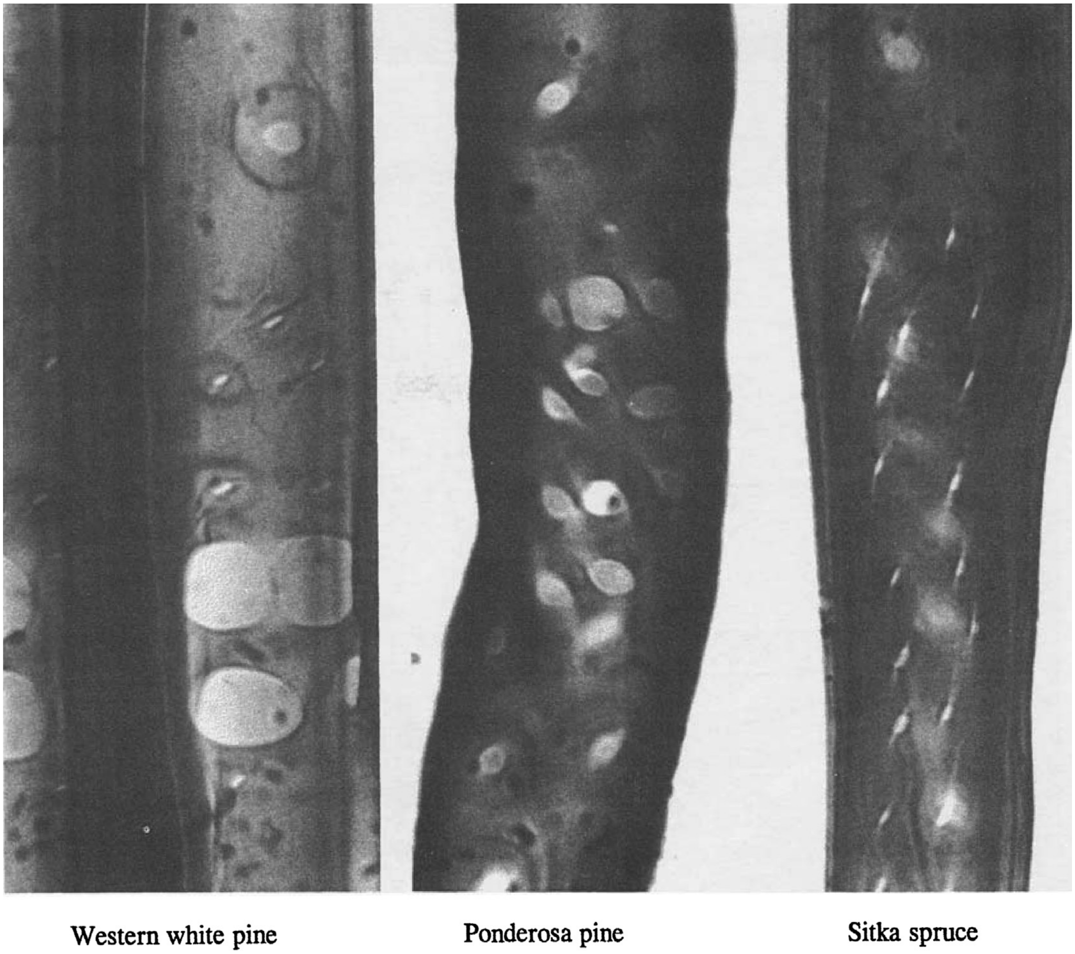
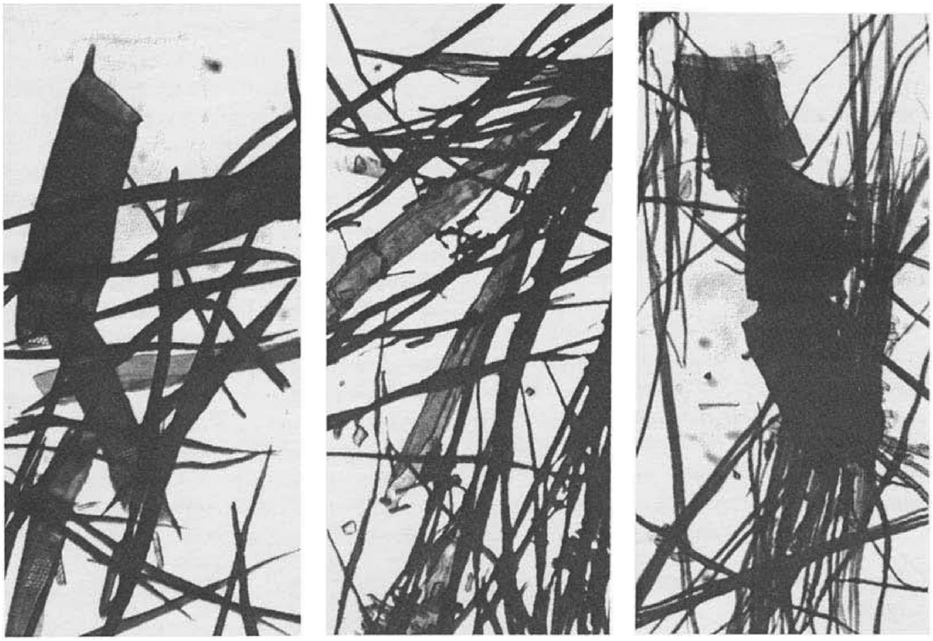
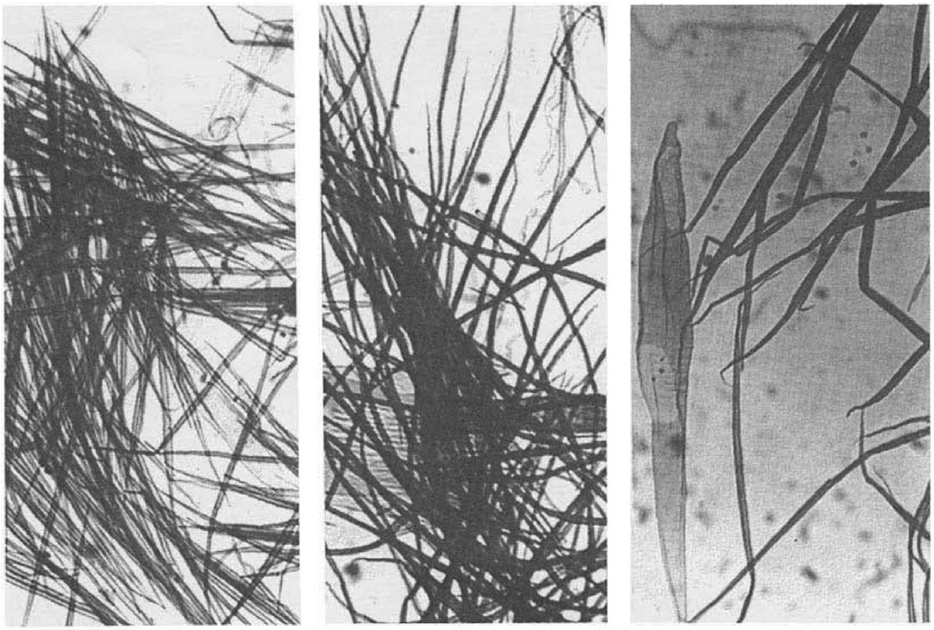


FIGURE 6.2 Portions of fiber tracheids of three softwoods (600×).

Hardwood libriform fibers or fiber tracheids are not helpful in species determination unless helical thickening is observed. Vascular or vasicentric tracheids (the shape of vasicentric tracheids is observed in red oak [upper right] in Fig. 6.3) indicate the presence of certain species. However, vessel elements offer much information based on their overall size, shape, intervessel pitting, and ray contact pitting. The intervessel pitting of *Populus* (observe black cottonwood in Fig. 6.3) and *Salix* genera is easy to recognize. Ring-porous woods may be difficult to determine because the large vessels are generally fragmented during processing.



Black cottonwood Swamp tupelo *Eucalyptus grandis*



red maple red oak yellow birch

FIGURE 6.3 Various hardwood fibers isolated in the laboratory (60×).

CHAPTER

7

Properties of Wood

7.1 INTRODUCTION

Wood is an anisotropic (properties vary with different crystallographic orientations), heterogeneous, and hygroscopic material. It is composed of cells, and the cell walls are composed of microfibrils of cellulose (40%—50%) and hemicellulose (15%—25%) impregnated with lignin (15%—30%). It is the most widely used engineering construction material owing to the fact that the energy requirements of wood for producing a usable end product are significantly lower than those of competitive materials, such as steel, concrete, or plastic. Wood has a wide range of physical and mechanical properties among the many species of wood.

7.2 WOOD STRUCTURE

Microstructure

Fig. 7.1 shows the characteristic cell structure and the differences between hardwoods and softwoods. Fig. 7.2 shows gross and fine structure of typical softwood (red pine, *Pinus resinosa*) and typical hardwood (northern red oak *Quercus rubra*).

Softwood (Fig. 7.3) mainly consists of long, thin-walled tubular cells called tracheids. The length of a longitudinal tracheid is about 3—5 mm and its diameter is about 20—80 µm and constitutes about 90% volume of the softwood (Fig. 7.4). The large open space in the center of the cell is termed lumen and is used for water conduction. The earlywood cells have thin walls, a relatively large diameter, and also a large-sized lumen (Table 7.1). The latewood cells have thick walls, a smaller diameter, and a smaller lumen (Table 7.2). The type and rate of growth vary between earlywood and latewood cells. Because void volume and density are related and density is related to lumber strength, latewood is sometimes used to judge the strength or quality of some species. Earlywood is lighter in weight and color, softer, and weaker than latewood; it shrinks less across the grain and more lengthwise along the grain than does the latewood. Wood rays which run in transverse directions from the bark to the center of the tree consist of an aggregate of small parenchyma cells, which are bricklike in shape and used for food storage.

Hardwoods (Fig. 7.3) have vessels of large diameter for the conduction of fluids. These vessels are thin-walled structures consisting of individual elements called vessel elements. These are formed in the longitudinal direction of the tree stem. The wood of hardwood trees is classified as follows, depending on how the vessels are arranged in the growth rings:

- Ring-porous—In a ring-porous hardwood, the vessels formed in the earlywood are larger than those formed in the latewood.
- Diffuse-porous—In a diffuse-porous hardwood, the vessel diameters are essentially the same throughout all the growth rings.

https://doi.org/10.1016/B978-0-12-814240-0.00007-0

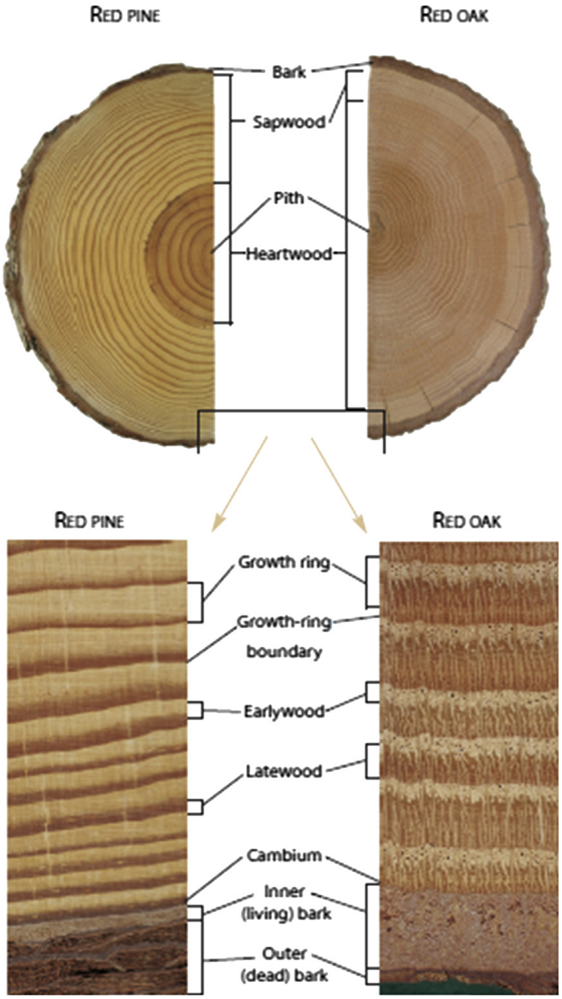


FIGURE 7.1 Stem cross sections (top) and detail (bottom) show gross and fine structures of a typical softwood, red pine (*Pinus resinosa*), and a typical hardwood, northern red oak (*Quercus rubra*). In red pine, narrow rays are too small to be seen without magnification, while portions of the large rays in the red oak are visible to the naked eye. *Reproduced with permission Hoadley (2000).*

The longitudinal cells in the hardwood tree stem are fibers. These are elongated cells having close pointed ends and are usually thick-walled. The length of these fibers are about 0.7–3 mm and average diameter is 20 μm. The food storage cells of hardwood are the ray (transverse) and longitudinal parenchyma, which are box or brick-shaped. The rays for hardwoods are usually much larger in comparison with softwood, having several cells across their width.

A cubic centimeter of wood can contain more than 1.5 million wood cells. These cells form a strong composite when packed together. Each individual wood cell is even more structurally advanced. Each individual cell has four distinct cell wall layers. These are Primary, S1, S2, and S3 layers. Each layer is composed of a combination of three chemical polymers: cellulose, hemicellulose, and lignin (Fig. 7.5). The cellulose and hemicellulose are linear polysaccharides, whereas lignin is an amorphous phenolic. Hemicellulose forms short branched chains and cellulose forms long unbranched chains. Lignin encrusts and stiffens these polymers. As carbohydrate and phenolic components of wood are assembled in a layered tubular or cellular manner with a large cell cavity, specific gravity of wood can vary to a great extent. Wood excels as a viable building material because the layered tubular structure provides a large volume of voids. It has an advantageous strength-to-weight ratio and other inherent advantages, such as low cost, corrosion and fatigue resistance, and ease of modification at the job site.

Macrostructure

The cross section of a tree is divided into three broad categories (Fig. 7.6):

- Bark
- Cambium
- Wood

The bark refers to all the tissues outside of the vascular cambium. It overlays the wood and consists of the inner bark and the outer bark. The inner bark in older stems is living tissue. It includes the innermost area of the periderm. Inner bark

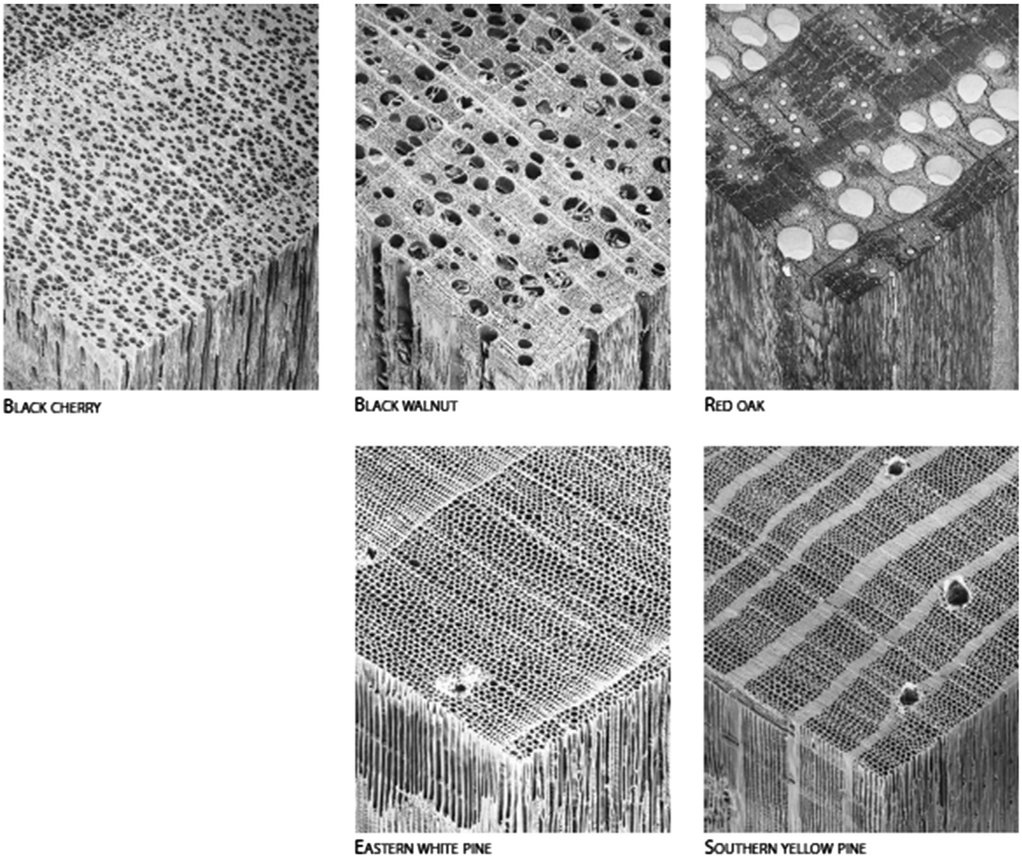


FIGURE 7.2 Characteristic cell structure and the differences between hardwoods and softwoods are visible in these photos made with a scanning electron microscope. Cross-sectional surface is uppermost, radial plane is lower left, and the tangential plane is lower right. *Reproduced with permission Hoadley (2000).*

stores the nutrients and transports them down through the tree. The outer bark in older stems includes the dead tissue on the surface of the stems, along with parts of the innermost periderm and all the tissues on the outer side of the periderm. The outer bark on trees which lies external to the last formed periderm is also called the rhytidome. Primary functions of bark are protection from injury or disease and nutrient conduction. The thickness and appearance of bark vary substantially depending on the species and age of the tree. Just inside this layer is a very thin, invisible layer, the cambium. It produces new growth in girth of the tree. It produces the inner bark on the outside.

The cambium is a thin, continuous ring of reproductive tissue. It is located between the wood and the bark and is the only portion of the tree where new wood and bark cells are produced and is usually only 1 to 10 cells thick, depending on the season of the year. All material inside the cambium layer is wood. This conducts and stores nutrients and provides the tree with structural support. At the center of the wood, where tree growth begins, is the pith or heart center.

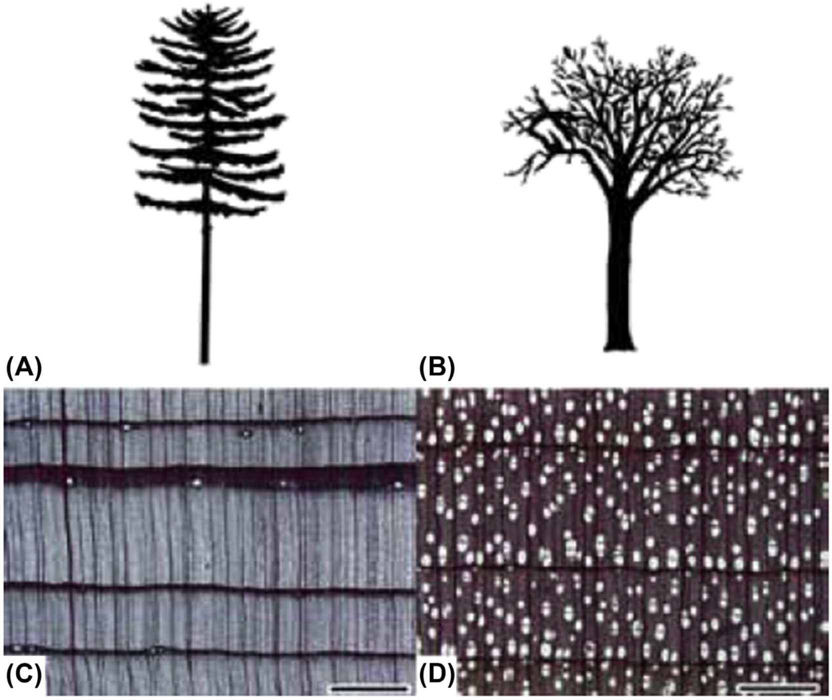


FIGURE 7.3 (A) The general form of a generic softwood tree. (B) The general form of a generic hardwood tree. (C) Transverse section of *Pseudotsuga mensiezii*, a typical softwood; the 13 round white spaces are resin canals. (D) Transverse section of *Betula allegheniensis*, a typical hardwood; the many large, round white structures are vessels or pores, the characteristic feature of a hardwood. Scale bars = 780 μm. *Based on USDA Report (2010). Centennial Edition, Wood handbook—Wood as an engineering material. General Technical Report FPL-GTR-190.*

Wood is divided into two general classes:

- Sapwood—The sapwood consists of both active and inactive cells and is located on the outside of the tree, next to the cambium. Primarily, it functions in food storage and the transport of sap from the roots to the leaves where it is turned into nutrients. Width of the sapwood may vary from a few centimeters in Douglas fir and spruces to more than 30 cm in ponderosa pine.
- Heartwood—The heartwood is the inactive layer beneath the sapwood. It is often darker than the sapwood, although for many species there is not much difference in color. It is composed mostly of inactive cells that differ both physically and chemically from sapwood cells. The heartwood cells do not function in sap transportation or food storage. In most species, the heartwood contains extractive substances, which are deposited in the cell during the conversion from sapwood to heartwood. These deposits frequently give the heartwood a much darker color than sapwood. However, in several species the heartwood is not dark and appears nearly the same as sapwood. The extractives also serve to make the heartwood of several species more resistant to attack by insects and decay fungi. Because all heartwood was once sapwood, there is generally not much

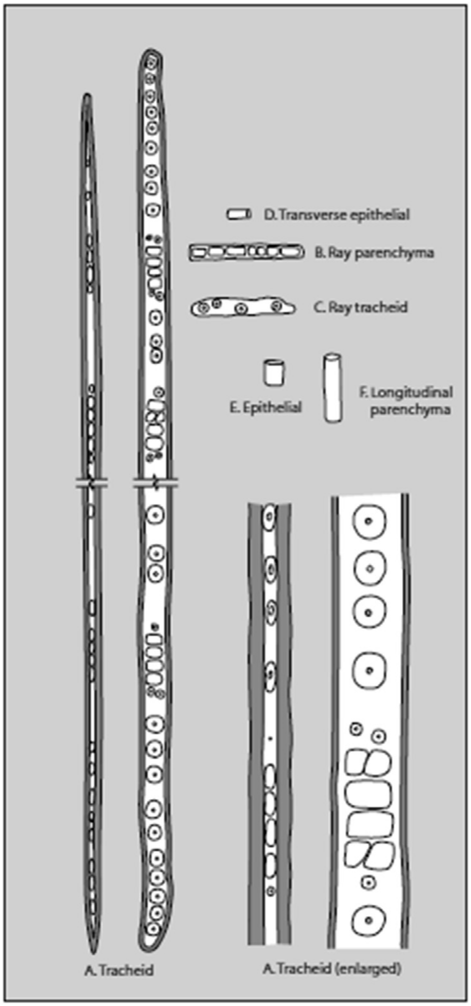


FIGURE 7.4 Some coniferous cell types. Tracheid (A, enlarged view A) comprise more than 90% of the wood volume. The remainder is mostly ray tissue, either ray parenchyma cells (B) or ray tracheids (C). Some species also have a very small percentage of epithelial cells (D, E), which line resin canals, or longitudinal parenchyma cells (F). *Reproduced with permission Hoadley (2000).*

difference in their dry weight or strength. The central core of the tree is the pith. It is formed by the stem, which pushes growth upward each year. It also starts new growth upward and downward, at twigs and roots.

TABLE 7.1 Earlywood or Springwood

Formed during spring season
Formed early in a year
Consists of xylem tissues with wider vessels
Produced more in amount
Less dense
A broad zone of wood
Not as strong as latewood

TABLE 7.2 Latewood or Autumnwood

Formed during winter season
Formed after the earlywood
Consists of xylem elements with narrow vessels
Produced less in amount
More dense
A narrow zone of wood
Stronger than earlywood because of larger volume of wall materials

Fig. 7.7 shows the macroscopic view of a transverse section of a Quercus alba trunk. Beginning at the outside of the tree is the outer bark (ob), next is the inner bark (ib), and then the vascular cambium (vc), which is too narrow to see at this magnification. Interior toward the vascular cambium is the sapwood, which is easily differentiated from the heartwood that lies toward the interior. At the center of the trunk is the pith (p), which is barely discernible in the center of the heartwood.

The marked difference between the earlywood and latewood cells forms the characteristic growth rings common to most species. These growth rings, depending on species and site conditions, vary in width. Fig. 7.8 shows a tree cross section with 24 distinct annual rings; a smaller set of rings pertaining to a branch is visible also.

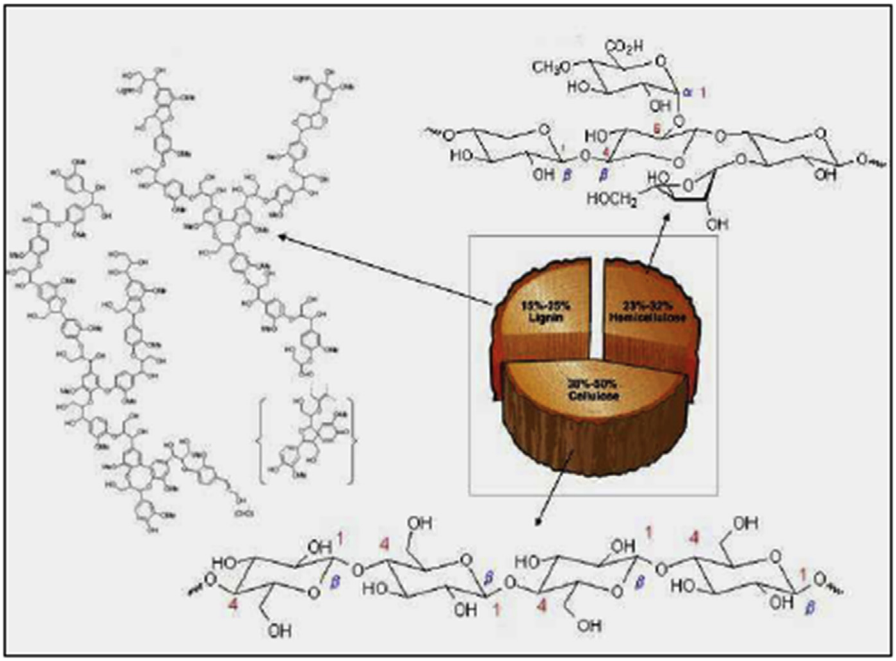


FIGURE 7.5 Chemical structures of wood constituents. *Reproduced with permission Brostow et al. (2010).*

In many species of softwood, such as Douglas fir and southern pine, there is a significant contrast between the earlywood and latewood, and growth rings are plainly visible. In other species, such as spruces and true firs, the change from earlywood to latewood is not much obvious, and rings are more difficult to see. Fig. 7.9 shows transverse sections of woods showing types of growth rings.

Growth in trees is affected by the soil and environmental conditions with which the tree must exist and contend. Environmental conditions can also affect growth rings. Rings formed during short or dry seasons are narrower in comparison with those formed under more favorable growing conditions.

Earlywood is lighter in color and weight, weaker and softer than latewood; it shrinks more lengthwise along the grain and shrinks less across the grain than does the latewood. Growth in trees is affected by the soil and environmental conditions with which the tree must exist and contend. Growth is accomplished by cell division. As new cells get formed, they are either pushed to the inside to become wood cells or to the outside to become bark cells. Sometimes, new cells are also retained in the cambium to account for increasing cambial circumference as the diameter of the tree increases. Furthermore, as the diameter of the tree increases, additional bark cells are pushed outward, and the outer surface becomes cracked and ridged, forming the bark patterns characteristic of each species.

Wood is characterized by the presence of conspicuous layers known as growth rings. This pattern is due to the mechanism of tree growth which takes place by superposition of structurally different layers. In the temperate zones there is, as a rule, one such wood layer (and one bark

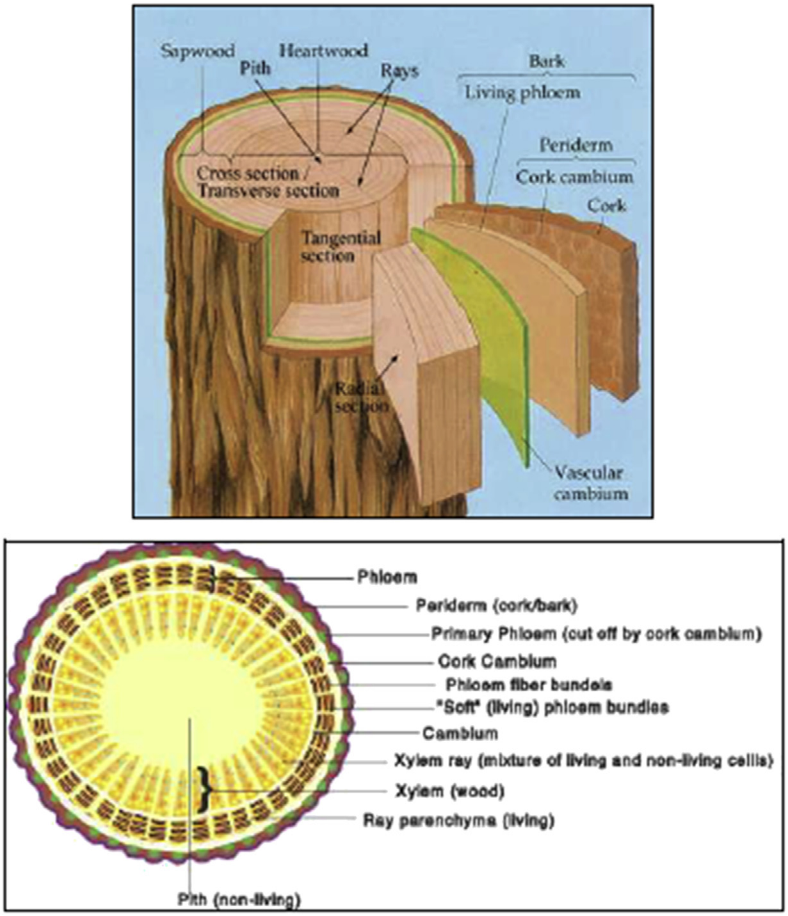


FIGURE 7.6 Structure of tree trunk. *Reproduced with permission Brostow et al. (2010).*

layer) added during each season of growth. There are abnormal cases in which more than one such layer may be produced during a year, whereas in other cases certain rings may be locally discontinuous.

Depending on the species and site conditions, the growth rings vary in width. Rings produced during short or dry seasons are thinner as compared with those produced when growing conditions are more favorable. Also, rings produced in shady conditions are generally thinner in comparison with those produced by the same species in sunny conditions. It is generally believed that the age of a tree may be determined by counting these rings. The annual rings appear like concentric bands and can be counted to date the tree (Fig. 7.8). However, this method can lead to errors because abnormal environmental conditions can cause a tree to produce multiple growth increments or even stop growth entirely for a period.

The trunk of the tree increases in width as the tree grows. Soon, the trunk grows much larger than the branches that grow out of it. It is

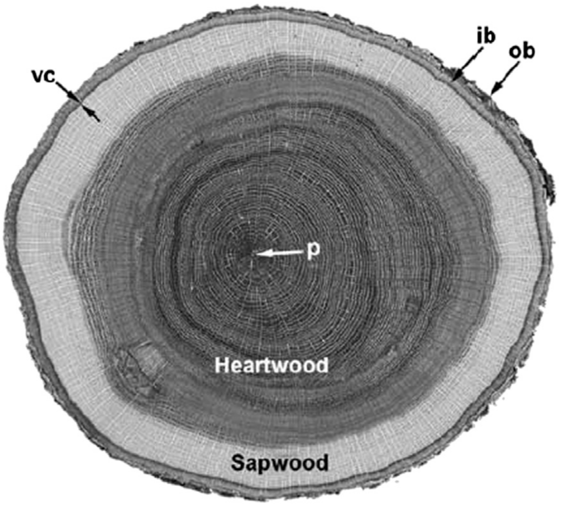


FIGURE 7.7 Macroscopic view of a transverse section of a Quercus alba trunk. Beginning at the outside of the tree is the outer bark (ob). Next is the inner bark (ib) and then the vascular cambium (vc), which is too narrow to be seen at this magnification. Interior toward the vascular cambium is the sapwood, which is easily differentiated from the heartwood that lies toward the interior. At the center of the trunk is the pith (p), which is barely discernible in the center of the heartwood. *Based on https://www.fpl.fs.fed.us/documnts/pdf2013/fpl_2013_wiedenhoeft001.pdf.*

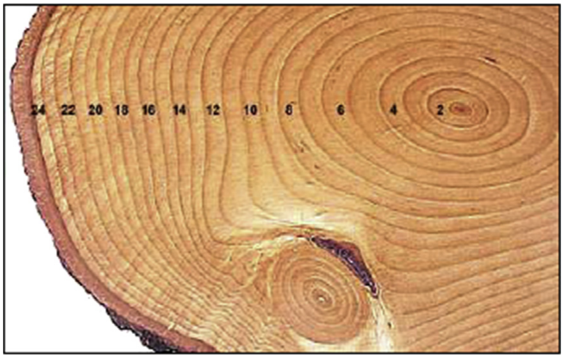


FIGURE 7.8 A tree cross section with 24 distinct annual rings; a smaller set of rings pertaining to a branch is also visible. *Reproduced with permission Brostow et al. (2010).*

common to see knots emerging from around the branches of these trees, thickening in size as the tree keeps on growing. With the branches of the tree continuing to grow, they are quickly overtaken by the tree trunk where a solid knot is formed and contains live wood. The knot contains very thick and tough wood, which is much more than the wood surrounding it and may end up as a big bulge around a branch that sprouts from its middle.

Knots are classified in two categories:

- Intergrown knots—An intergrown knot is termed "tight" knot because it is tightly bound to the wood around it. These knots are produced by living branches. An intergrown knot is the base of a living branch within a tree. It is surrounded by a halo of circular growth rings.
- Encased or loose knots—An encased knot is formed when a tree grows around a dead branch. It is surrounded by a dark ring of bark, and its center is often decayed. An encased knot is termed as a "loose" knot, as the bark prevents the knot from tightly binding to the wood around it.

Knots formation results in grain deviations. This is quite important as the straight-grained wood is stronger by approximately 10–20 times parallel to grain than perpendicular to grain. The size of the knot is a major predictor of sawn timber strength.

Reaction wood is formed in place of normal wood as a response to gravity, where the cambial cells are orientated other than vertically. It is usually found on leaning stems and branches and is an example of self-optimization and the axiom of uniform stress in trees. Reaction wood is of two different types representing two different approaches to the same problem by woody plants: Reaction wood is called tension wood in angiosperms. Tension wood forms on the side of the part of the plant that is under tension, pulling it

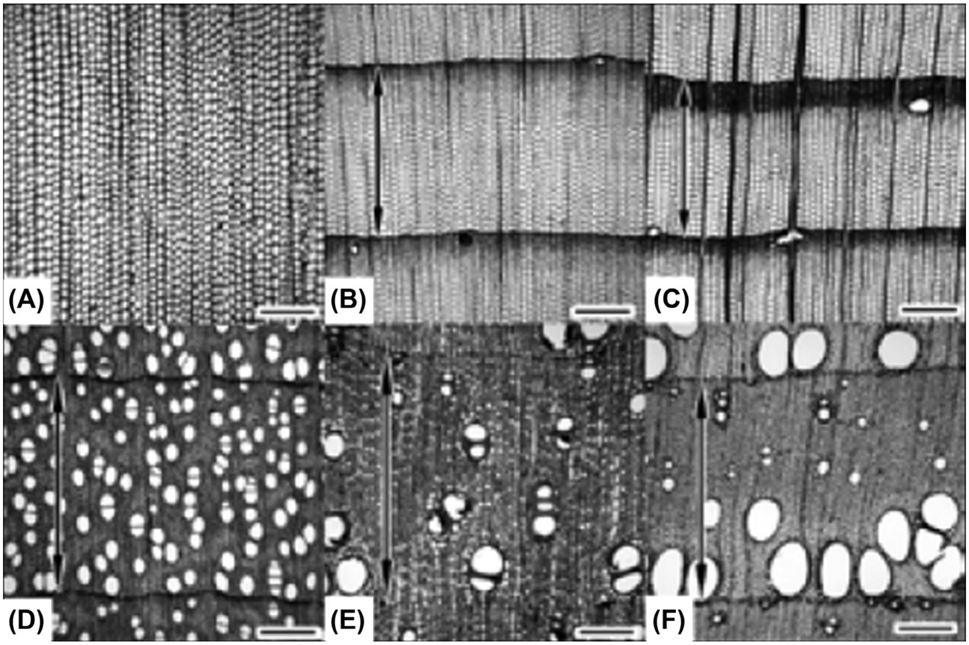


FIGURE 7.9 Transverse sections of woods showing types of growth rings. (A—C), softwoods. (A), no transition within the growth ring (growth ring absent) in *Podocarpus imbricata.* (B), gradual transition from earlywood to latewood in *Picea glauca.* (C), abrupt transition from earlywood to latewood in *Pseudotsuga menziesii.* (D—F), hardwoods. (D), diffuse-porous wood (no transition) in *Acer saccharum.* (E), semiring-porous wood (gradual transition) in *Diospyros virginiana.* (F), ring-porous wood (abrupt transition) in *Fraxinus americana.* Scale bars = 300 μm. *Based on https://www.fpl.fs.fed.us/documnts/pdf2013/fpl_2013_wiedenhoeft001.pdf.*

toward the affecting force (upward, in the case of a branch). It has a higher proportion of cellulose content than normal wood. Tension wood may have as high as 60% cellulose. In case of gymnosperms, reaction wood is called compression wood. Compression wood forms on the side of the plant that is under compression, thus lengthening/straightening the bend. Lignin content is higher in compression wood than normal wood. Compression wood has only about 30% cellulose compared with 42% in case of normal softwood. Its lignin content can be as high as 40%. Most of the chemical, physical, mechanical, and anatomical properties of reaction wood differ clearly from those of normal wood. The specific gravity of compression wood is frequently 30%—40% higher in comparison with normal wood, but the tensile strength is several times lower.

7.3 WOOD PROPERTIES

Physical Properties

Physical properties are the quantitative characteristics of wood and its behavior to external influences other than applied forces. Physical properties discussed here are directional properties, moisture content, dimensional stability, thermal and pyrolytic properties, density, electrical conductivity, chemical resistance, and decay resistance.

Directional Properties

Wood is an orthotropic and anisotropic material with unique and independent properties in different directions. Because of the orientation of the wood fibers and the manner in which a tree increases in diameter as it grows, properties vary along three mutually perpendicular axes: longitudinal, radial, and tangential. The longitudinal axis is parallel to the fiber (grain) direction, the radial axis is perpendicular to the grain direction and normal to the growth rings, and the tangential axis is perpendicular to the grain direction and tangent to the growth rings. The wood properties differ in each of these three directions, but differences between the radial and tangential directions are normally little compared with their mutual differences with the longitudinal direction. As a consequence, most wood properties for structural applications are given only for directions parallel (longitudinal) and perpendicular (radial and tangential) to grain.

Moisture Content

Water is an essential agent in the life process of a tree. It is present in large quantities in the tree and in the green log after felling. The moisture content of wood is defined as the weight of water in wood given as a percentage of ovendry weight. The weight of water equals the weight of wet wood minus the weight of ovendry wood. This moisture content in living trees comes from sap, which consists of water and dissolved mineral salts. Moisture content in living trees can vary from 200% in the sapwood of some trees to 30% in the heartwood of others. Water is required for the growth and development of living trees and constitutes a major portion of green wood anatomy. In living trees, moisture content depends on the species and the type of wood. In most species, the moisture content of sapwood is higher than that of heartwood. Water is present in wood either as free water or bound water. Free water occurs within a cell cavity as a liquid. It is the easiest and first to be removed during drying. This free water moves toward the end surfaces through connecting cells and laterally through the pits of neighboring cells. It is evaporated from the wood faces as well as the ends. The point at which all free water is removed from the cell cavity is known as the fiber saturation point and is reached at around 30% moisture content. When the cell walls are completely saturated, and there is no free water in the cell cavity, the wood is at its fiber saturation point. This occurs when the moisture content is between 25% and 32%, depending on the species. Wood is a hydroscopic material that absorbs moisture in a humid environment and loses moisture in a dry environment. As a result, the moisture content of wood is a function of atmospheric conditions and depends on the relative humidity and temperature of the surrounding air. Under constant conditions of temperature and humidity, wood reaches an equilibrium moisture content (EMC) at which it is neither gaining nor losing moisture. The EMC represents a balance point where the wood is in equilibrium with its environment. In case of structural applications, the moisture content of wood is always undergoing some changes as temperature and humidity conditions change. These changes are generally gradual and short-term fluctuations which affect only the surface of the wood. The time required for wood to reach the EMC is found to be dependent on the size and permeability of the member, the difference between the moisture content of the member, the temperature, and the EMC potential of that environment. Changes in moisture content cannot be completely stopped but can be retarded by coatings or treatments applied to the surface of wood.

Dimensional Stability

Information on the physical properties including dimensional stability and shrinkage/swelling behavior of wood is most important to maximize the value added on wood products. Information on the swelling behavior of wood is generally obtained by studying the dimensional changes of wood when exposed to different relative humidities and temperatures and in contact with water and other liquids. The dimensional stability of wood varies with species, density, direction of measurement, relative humidity, temperature, chemical composition in terms of lignin, microfibril angle, type and amount of extractives. Swelling and shrinkage are often used to define or classify the relative dimensional stability of wood. Several methods have been studied to estimate wood swelling of tropical species. Dimensions measured using a micrometer at different complete EMCs and at ovendry conditions have been used to compute the swelling of nine hardwoods from Peru. Significant variation in weathering performance and dimensional stability of 10 tropical hardwoods from Bolivia has been reported. The samples were exposed to different relative humidity levels at 27°C, and dimensional changes were measured in radial, tangential, as well as longitudinal directions. The use of wood is restricted due to its swelling and shrinkage at different relative humidities and temperatures. Dimensional changes due to moisture exchange in wood can lead to several defects, such as warping, checking, or splitting, which may compromise with the performance of the wood piece or product. Hence, most of the challenges of using wood in architecture or engineering involve understanding the relationship of wood and moisture and its effect on wood properties. Dimensional stability is a coefficient which shows the resistance of the wood to environmental changes such as moisture or temperature. All wood change in sizes (shrink or swell) under certain conditions, and the minimal changes (lower number on the scale) show higher dimensional stability. Fig. 7.10 shows the comparison of different types of wood. The comparative data show which species show more resistance to impacts of water. As compared with American cherry, popular red oak is not that dimensionally stable. Bamboo has very high dimensional stability. It is also included in the figure despite the fact it is not a wood.

Thermal Expansion

Thermal expansion is the tendency of matter to change in shape, volume, and area in response to a change in temperature. Temperature is a monotonic function of the average molecular kinetic energy of a substance. Monotonic function is a function which is either entirely nonincreasing or nondecreasing. A function is monotonic if its first derivative (which need not be continuous) does not change sign. The kinetic energy of the molecules of a substance increases when the substance is heated. Thereby, the molecules start to vibrate and move more and usually maintain a greater average separation. The degree of expansion divided by the change in temperature is called the material's coefficient of thermal expansion. It is found to generally vary with temperature. Thermal expansion of dry wood is positive in all directions. It expands when heated and contracts when cooled. The linear expansion coefficients of dry wood parallel to grain are generally independent of species and specific gravity and range from approximately 0.0,000,017 to 0.0,000,025 per degree F. The expansion coefficients perpendicular to grain are proportional to density and range from 5 to 10 times greater than parallel to grain coefficients. Wood is a good insulator and does not respond swiftly to changes in temperature in the environment. Therefore, its thermal expansion and contraction lag substantially behind temperature changes in the surrounding air. The moist wood, when heated, has a tendency to expand because of normal thermal expansion and shrinkage due to moisture loss from increased temperature. Unless the initial moisture content in wood is very low (3%–4%), the net dimensional change on heating is negative. Wood having moisture level of about 8%–20% will expand when first heated, then shrink slowly to a volume smaller than the initial volume as moisture is lost in the heated condition.

Density and Specific Gravity

The density of a material is defined as the mass per unit volume under some specified condition.

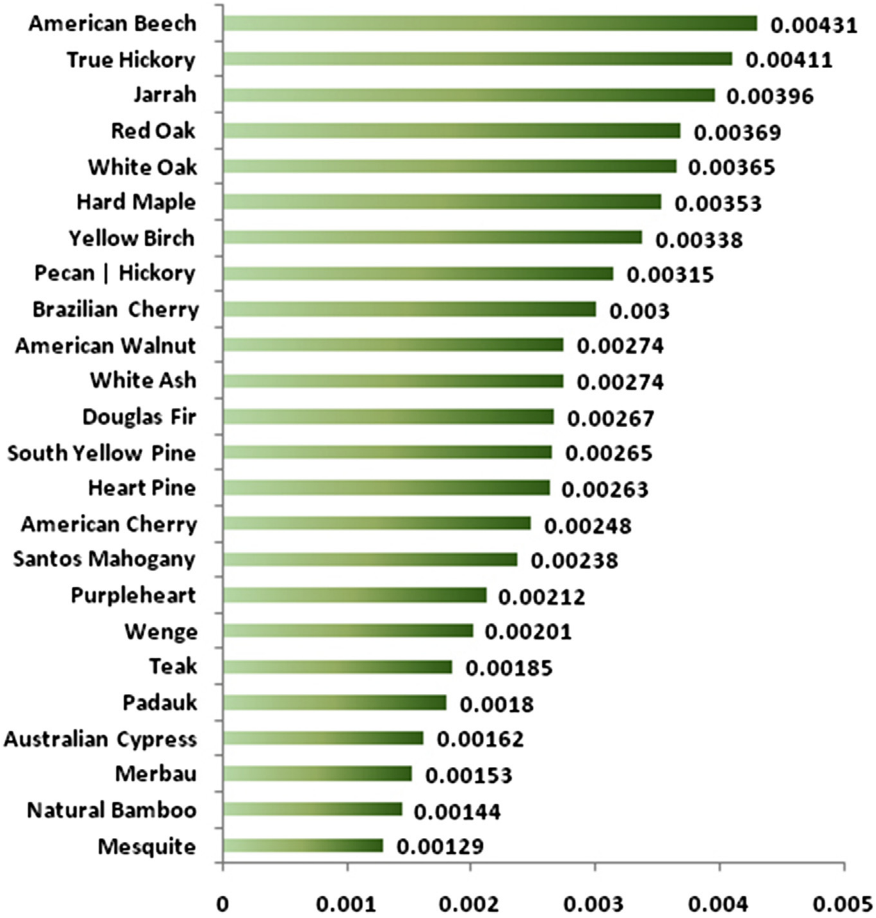


FIGURE 7.10 Dimensional stability of various wood species. *Based on USDA Report, Wood as an Engineering Material (Agriculture Handbook 72, Forest Products Laboratory).*

For a hygroscopic material such as wood, density depends on the following two factors:

- Weight of the basic wood substance
- Weight of the moisture retained in the wood

Wood density varies with moisture content and must be given relative to a specific condition for having practical meaning. Values for density are generally based on the wood weight and volume at one of the following three moisture conditions:

1. Ovendry, where the moisture content is zero
2. Green, where the moisture content is greater than 30%
3. In-use, where the moisture content is specified between ovendry and green.

The density of ovendry wood varies within and among species. While the density of most species is between 20 and 45 lb/ft^3, the densities extend from approximately 10 lb/ft^3 for balsa to more that 65 lb/ft^3 for some types of imported woods. Average densities for green wood and wood at different moisture levels are given in several reference publications. For applications in bridge, a density of 50 lb/ft^3 is generally used as an average density for all species and moisture contents.

Specific gravity is a dimensionless ratio of the weight of an ovendry volume of wood to the weight of an identical volume of water. It provides a relative measure of the amount of wood substance contained in wood sample. In research activities, specific gravity can be reported on the basis of both weight and volume ovendry. For most of the engineering applications, the basis for specific gravity is generally the ovendry weight and volume at a moisture level of 12%. For instance, a volume of wood at some specified moisture content with a specific gravity of 0.50 would have a density of 500 kg/m^3.

Pyrolytic Properties

Wood can undergo thermal degradation or pyrolysis under suitable conditions. The byproducts of pyrolysis may burn, and if enough heat is generated and retained by the wood, the wood can be set on fire. In the presence of a pilot flame (independent source of ignition), the minimum rate of heating needed for ignition is 0.3 calorie per square centimeter, whereas in the absence of a pilot flame, the minimum rate of heating needed for ignition is 0.6 calorie per square centimeter. This is almost double the rate of the pilot flame situation. Still, heavy timber construction deserves an extremely favorable fire insurance rating because it will generally not produce enough heat energy for maintaining combustion unless an external heat source is present. Timber gradually produces a char layer from the residue of wood combustion. This char acts as a thermal insulator. On heavy timbers this char layer will ultimately inhibit combustion by establishing a thermal barrier between the uncharred wood (interior to char) and the heat of the fire (exterior to char). Heavy timber is essentially self-extinguishing, but steel, which has a thermal conductivity 100 times that of wood, will absorb heat until it reaches a temperature at which it yields under structural load without actually burning.

Electric Resistivity

Electrical resistivity is also known as specific electrical resistance. It is an intrinsic property which quantifies how strongly a given material opposes the flow of electric current. A low resistivity indicates a material that is capable of readily allowing the flow of electric current. Wood is a good electrical insulator, but significant variations in conductivity are observed. These variations in electrical resistance can be related to variations in grain orientation, moisture level, and temperature. The conductivity of wood in the longitudinal axis is approximately two times that in the radial or tangential axes. The electrical conductivity of wood usually doubles for each 10°C increase in temperature. Generally, variations in conductivity related to wood density and species are considered small. The correlation between electrical resistivity and moisture content is the basis for electrical resistance—type moisture meters, which estimate moisture level by measuring the resistance of the wood between two electrodes. Meters for determining moisture level need to be calibrated for temperature and species and are effective only for moisture levels of 5%—25%. They are generally not reliable for high resistivities at moisture levels below 5 or 6% for estimating the moisture level of green timber or for estimating moisture level of treated timbers (most treatments alter conductivity).

Decay Resistance

Wood-destroying organisms require oxygen, suitable temperature, moisture, and a food source. If the wood is kept dry (moisture content less than 20%), it will not decay. On the other hand, if submerged in water at sufficient depths, wood will generally not decay. Problems with wood decay can result whenever wood is intermediary to either of these two extremes. To prevent problems with decay where moisture cannot be controlled, the engineer can use either naturally durable species or treated timber. The natural durability of wood to the mechanisms and processes of deterioration is related to the anatomical characteristics and wood species. Generally, the outer zone or sapwood of all species has little resistance to deterioration and fails rapidly in adverse conditions. For heartwood, natural durability depends on species. Heartwood forms as the living sapwood cells gradually die. In some species, the sugars present in the cells are converted to highly toxic extractives which are deposited in the wood cell wall. Several species produce durable heartwood, including western red cedar, redwood, and black locust. However, durability varies within a tree and between trees of a given species. To improve the durability, wood can be treated with an EPA-registered, toxic preservative chemical treatment.

Chemical Resistance

Wood is very much resistant to many chemicals, which gives it a significant advantage over many alternative building materials. Wood is often considered superior to alternative materials, such as concrete and steel, partly because of its resistance to mild acids (pH more than 2.0), acidic salt solutions, and corrosive agents. Generally, iron holds up better on exposure to alkaline solution as compared with wood, but wood can be treated with many of the common wood preservatives to greatly improve its performance in this respect. Heartwood is much more durable in comparison with sapwood to chemical attack because heartwood is more resistant to penetration by liquids. Several types of preservative treatments, such as creosote or pentachlorophenol in heavy oil, can also substantially increase the ability of wood to resist liquid or chemical penetration, or both. Chemical solutions may induce two types of action, namely normal reversible swelling by a liquid and irreversible chemical degradation. In the former case, removal of the liquid will return wood to its original condition. In the latter case, permanent changes will take place within the wood structure from oxidation, hydrolysis, or delignification.

Strength Properties

Strength properties describe the ultimate resistance of a material to applied loads. With wood, strength varies greatly depending on species, loading condition and load duration, and a number of assorted material and environmental factors. They include material behavior related to compression, tension, shear, bending, torsion, and shock resistance. As with other wood properties, strength properties vary in the three primary directions, but differences between the tangential and radial directions are relatively small and randomized when a tree is cut into lumber. As a consequence, mechanical properties are collectively described only for directions parallel and perpendicular to grain.

Compression

Compression across the grain is related very closely to hardness and transverse shear. There are two ways in which wood is subjected to this type of stress, namely with the load acting over the entire area of the specimen and with a load concentrated over a portion of the area. The latter is the condition more commonly met with in practice, as for instance, where a post rests on a horizontal sill or a rail rests on a crosstie. However, the former condition gives the true resistance of the grain to simple crushing.

Wood can be subjected to compression in the following ways:

- Parallel to grain
- Perpendicular to grain
- At an angle to grain

When compression is applied parallel to grain, the stress is produced which deforms the wood cells along their longitudinal axis. Each cell acts as an individual hollow column which receives lateral support from its own internal structure and from adjacent cells. At failure, large deformations can take place from the internal crushing of the complex cellular structure. The average strength of loblolly pine and Douglas fir in compression parallel to grain is about 3511 and 3,784 lb/in^2, respectively.

When compression is applied perpendicular to grain, stress is produced that deforms the wood cells perpendicular to their length. Wood cells actually get collapsed at relatively low stress levels when loads are applied in this direction. But once the hollow cell cavities are collapsed, wood is quite strong in this mode because no void spaces are found. Before complete collapse of cell takes place, wood will actually deform to about half its initial thickness, resulting in a loss in utility long before failure. In case of compression perpendicular to grain, failure is based on the accepted performance limit of 0.04 inch deformation. Using this convention, the average strength of loblolly pine and Douglas fir in compression perpendicular to grain is about 661 and 700 lb/in.^{2}, respectively.

Compression applied at an angle to grain produces stress, which acts both parallel and perpendicular to the grain. Therefore, the strength at an angle to grain is intermediate to these values and is determined by a compound strength equation.

Tension

Tension results when a pulling force is applied to opposite ends of a body. This external pull is communicated to the interior, so that any portion of the material exerts a tensile force upon the remainder. The ability to do this depends upon the property of cohesion. The result is stretching of the material in the direction of the applied force. The action is the opposite of compression.

The tensile strength of wood parallel to the grain depends upon the strength of the fibers and is affected by their arrangement and also by the dimensions and nature of the wood elements. It is greatest in case of straight-grained specimens having thick-walled fibers. Cross grain of any type reduces the tensile strength of wood as the tensile strength at right angles to the grain is just a small fraction of that parallel to the grain.

Failure of wood in tension parallel to the grain takes place sometimes in flexure, particularly with dry material. The tension portion of the fracture is almost the same as though the piece were pulled in two lengthwise. The fiber walls are torn across obliquely and usually in a spiral direction. There is practically no separation of the fibers along their walls, regardless of their thickness. The tension failure is apparently not affected by the moisture condition of the specimen, at least not as much as the other strength values. Tension at right angles to the grain is intently related to cleavability. When wood fails in this way, the thin fiber walls are torn in two lengthwise, whereas the thick-walled fibers are generally pulled apart along the primary wall.

The mechanical properties for wood loaded in tension parallel to grain and for wood loaded in tension perpendicular to grain differ substantially. Parallel to its grain, wood is relatively stronger in tension. Failure takes place by a complex combination of two modes, cell wall failure and cell-to-cell slippage. Slippage takes place when two adjacent cells slide past one another, while cell wall failure involves a rupture within the cell wall. In both modes, there is little or no visible deformation before the complete failure. The average strength of loblolly pine and Douglas fir in tension parallel to grain is approximately 11,600 and 15,600 lb/in^2, respectively.

In contrast to tension parallel to grain, wood is very weak in tension perpendicular to grain. Stress in this direction acts perpendicular to the cell lengths and produces splitting or cleavage along the grain that substantially affects structural integrity. Deformations are usually low before failure because of the geometry and structure of the cell wall cross section. Strength in tension perpendicular to grain for loblolly pine and Douglas fir averages 260 and 300 lb/in^2, respectively. But because of the excessive variability associated with tension perpendicular to grain, situations which induce stress in this direction should be recognized and avoided in design.

Shear

There are three types of shear which act on wood:

- Vertical
- Horizontal
- Rolling

Vertical shear is normally not taken into consideration because other failures, such as compression perpendicular to grain, almost always occur before cell walls break in vertical shear. In most cases, the most important shear in wood is horizontal shear, acting parallel to the grain. It produces a tendency for the upper portion of the specimen to slide in relation to the lower portion by breaking intercellular bonds and deforming the wood cell structure. Horizontal shear strength for loblolly pine and Douglas fir averages 863 and 904 lb/in^2, respectively.

In addition to horizontal and vertical shear, a less common type called rolling shear may also develop in wood. Rolling shear is caused by loads acting perpendicular to the cell length in a plane parallel with the grain. The stress produces a tendency for the wood cells to roll over one another. Wood shows low resistance to rolling shear, and failure is usually preceded by large deformations in the cell cross sections. Test procedures for rolling shear in solid wood are of recent origin, and few test values are available. Rolling shear strength or green, clear wood specimens generally average 18% to 28% of the shear strength parallel to grain.

Bending

When wood specimens are loaded in bending, the portion of the wood on one side of the neutral axis is stressed in tension parallel to grain, whereas the other side is stressed in compression parallel to grain. Bending also results in horizontal shear parallel to grain and compression perpendicular to grain at the supports. A common failure sequence in simple bending is the formation of minute compression failures followed by the development of macroscopic compression wrinkles. This effectively results in a sectional increase in the compression zone and a section decrease in the tension zone, which is eventually followed by tensile failure. The ultimate bending strength of loblolly pine and Douglas fir are reached at an average stress of 7300 and 7665 lb/in^2, respectively.

In contrast to tension parallel to grain, wood is very weak in tension perpendicular to grain. Stress in this direction acts perpendicular to the cell lengths and produces cleavage along the grain, which significantly affects structural integrity. Deformations are usually low before failure because of the geometry and structure of the cell wall cross section. Strength in tension perpendicular to grain for loblolly pine and Douglas fir averages 260 and 300 lb/in^2, respectively.

Torsion

Not much information is available on the mechanical properties of wood in torsion. The torsional shear strength of solid wood is usually taken as the shear strength parallel to grain where needed. Two-thirds of this value is presumed as the torsional strength at the proportional limit.

Shock Resistance

Shock resistance is the ability of a material to quickly absorb then dissipate energy by deformation. Wood is notably resilient in this respect and is a preferred material when shock loading is considered. Several parameters are used to describe energy absorption, depending on the eventual criteria of failure considered. Work to proportional limit, maximum load, and toughness describe the energy absorption of wood materials at progressively more stern failure criteria.

7.4 ANNOTATED BIBLIOGRAPHY

Brostow W, Datashvili T and Miller H (2010). Wood and wood derived materials, Journal of Materials Education Vol. 32 (3—4): 125—138.
This chapter points out the role of wood in the development of “green” technologies. To provide a perspective, the authors discuss forests and woodlands in the past and their role in the growth of civilization. Wood structure and the role of wood as a fuel are described. Manufacturing of paper from wood, composites containing synthetic polymers and wood, and wood as an art material are discussed.
Forest Products Laboratory (2010). Centennial EditionWood handbook—Wood as an engineering material. General Technical Report FPL-GTR-190. Madison, WI: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory. 508 p.
Information on wood as an engineering material and a discussion on the properties of wood and wood-based products of particular concern to the engineer and architect are presented. It also includes a discussion of designing with wood and wood-based products along with some pertinent uses.
Green David, Wm Winandy JE, Kretschmann, DE (1999). Mechanical properties of wood. Wood handbook: wood as an engineering material. Madison, WI: USDA Forest Service, Forest Products Laboratory, 1999. General technical report FPL; GTR-113: pp. 4.1—4.45
The mechanical properties of wood are presented in this chapter. Because wood is a natural material and the tree is subject to many constantly changing influences, wood properties vary considerably, even in clear material. This chapter provides information on the nature and magnitude of variability in properties. This also includes a discussion of the effect of growth features on clear wood properties. The effects of manufacturing and service environments on mechanical properties are discussed, and their effects on clear wood and material containing growth features are compared.
Hoadley, B. (2000). Understanding Wood. The Taunton Press: Newtown, Connecticut.
This book is widely held as a definitive reference work and the cornerstone of every woodworker’s library.
Kollman, FFP, Côté, WA Jr (1968). Principles of wood science and technology I—solid wood. New York: Springer-Verlag. 592 p.
This is an excellent book dealing with principles of wood science and technology. It looks at wood anatomy, biology, chemistry, physics, and mechanical technology and discusses the progress made in wood seasoning, wood preservation methods, wood machining, surfacing, and gluing, etc.
Kubler, H, Liang, L, Chang, LS (1973). Thermal expansion of moist wood. Wood and Fiber. 5(3): 257—267.
Thermal expansion of moist wood at tangential and longitudinal directions are presented in this chapter.
Kukachka BF (1970). Properties of imported tropical woods. Res. Pap. FPL—RP—125. Madison, WI: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory. 67 p.
An excellent description on properties of imported tropical woods is presented in this report. Species descriptions are arranged alphabetically by generic names.
Lin RT (1967). Review of dielectric properties of wood and cellulose. Forest Products Journal. 17(7): 61.
A comprehensive review on dielectric properties of wood and cellulose are presented.
McKenzie WM, KarpovichH. (1968). Frictional behavior of wood. Munich: Wood Science Technology. 2(2): 138.
This work deals with determining the more important variables affecting friction between

wood and steel and also investigates friction between wood and nonferrous materials.

Murase Y (1980). Frictional properties of wood at high sliding speed. Journal of the Japanese Wood Research Society. 26(2): 61–65.

Much of the works on the friction of wood is concerned with the friction between wood and steel. In this study, the frictional properties of wood at high sliding speed are presented.

Panshin AJ and deZeeuw C (1980). Textbook of Wood Technology, fourth ed., p. 705. McGraw-Hill, NewYork.

This is an excellent textbook on wood technology dealing with structure, identification, properties, and uses of the commercial woods of the United States and Canada.

Simpson WT (1993). Specific gravity, moisture content, and density relationships for wood. Gen. Tech. Rep. FPL–GTR–76. Madison, WI: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory. 13 p.

Specific gravity, moisture content, and density relationships for wood are discussed in this report.

Steinhagen HP (1977). Thermal conductive properties of wood, green or dry, from −40 degrees to +100°C: a literature review. Gen. Tech. Rep. FPL–GTR–9. Madison, WI: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory. 10 p.

A literature review on thermal conductive properties of wood, green or dry, from −40 degrees to +100°C are presented.

TenWolde A, McNatt JD, Krahn, L (1988). Thermal properties of wood panel products for use in buildings. ORNL/Sub/87–21,697/1. Oak Ridge, TN: Oak Ridge National Laboratory. 38 p.

Thermal properties of wood panel products for use in buildings are discussed in this report.

Weatherwax RC, Stamm, AJ (1947). The coefficients of thermal expansion of wood and wood products. Transactions of American Society of Mechanical Engineers. 69(44): 421–432.

This report deals with the coefficients of thermal expansion of wood and wood products.

Winandy JE (1994).Wood Properties In: Arntzen, Charles J., ed. Encyclopedia of Agricultural Science. Orlando, FL: Academic Press: 549–561. Vol. 4, October 1994.

This is a very good review dealing with wood structure, properties, factors affecting properties of wood and properties and grades of sawn lumber.

CHAPTER

8

Wood-Based Products and Chemicals

8.1 INTRODUCTION

Wood, wood wastes, residues, and other biomass sources have been the subject of extensive surveys, economic studies, and technical investigations as alternatives to petroleum and coal, as a source of energy, and also as a feedstock for a number of basic chemicals from synthesis gas and from fermentation ethanol. The use of wood for the production of chemicals is, however, of a rather moderate size as petroleum constitutes an excellent and versatile starting material for the chemical and polymer industry. Only in a few areas, wood-based chemical products have been able to compete successfully with the petroleum-based ones. The most important of these is based on cellulose, which can be purified and further transformed into regenerated cellulose, i.e., rayon or derivatized into a large variety of cellulose esters and ethers. In some sulfate (kraft) and sulfite mills in the world, the dissolved lignin is recovered by evaporation or precipitation and further processed into products such as dispersing agents. From softwood kraft mills, the volatile extractives are recovered as turpentine, and the remaining portion of the extractives form the so-called tall oil. Both these fractions can be further refined. The flavoring agent vanillin is produced from sulfite liquor by oxidation with air. Several other uses of wood for the production of chemicals have been also explored, some of which are old technologies.

8.2 PROCESSES

A variety of potential processes to obtain chemicals from wood are being examined.

Low-Energy Processes

The first type is *low-energy processes*. These processes use less high heat to convert wood to chemicals. This includes processes that are typically called extraction, near-neutral biochemical conversion, and fermentation. A variety of methods are being developed. These include fermentation, extraction, and others. Many of these methods remove the hemicellulose from wood and use it as a starter for chemical building blocks. Removal of hemicellulose has the advantage of leaving the lignin and cellulose behind to produce pulp and other forest products. This process is called the value prior to pulping pathway. Value prior to processing is another similar but broader concept. This is sometimes abbreviated VPP. Table 8.1 shows the potential benefits, and Table 8.2 shows the various steps involved in the low-energy process.

This extraction process presently can only be performed using hardwoods and the kraft process. Fermentation is greatly used to produce bioproducts. This process has been used for several years in agriculture to produce a great variety of chemicals and food products. For example, ethanol from biomass is produced

Biermann's Handbook of Pulp and Paper: Raw Material and Pulp Making
https://doi.org/10.1016/B978-0-12-814240-0.00008-2

TABLE 8.1 Potential Benefits of the Low-Energy Processes

Potentially being able to extract hemicelluloses before pulping would create an additional revenue stream for a mill with potentially the same pulp mill production as before the extraction.
Reduction of black liquor solids sent to the recovery boiler, potentially allowing the production of more tonnage.

from the fermentation of glucose in corn starch. Typically fermentation means the breakdown and conversion of organic substances, mainly carbohydrates, into other substances through the actions of a microorganism. Different types of materials are produced through fermentation. Examples are beer, wine, and vinegar (approximately 5% acetic acid).

Biomass products other than wood have been fermented for many years. Two types of sugars are typically present in biomass:

1. Five-carbon sugars—These sugars are known as pentoses. Xylose is the most common of these in hardwoods
2. Six-carbon sugars—These sugars are known as hexoses. Glucose is the most common of these. Wood has been more difficult to ferment in comparison with several other types of biomass. Cellulose is a polymer that is more difficult to break down into fermentable glucose as compared with starch-based materials. Furthermore, the purity of cellulose is a potential problem. However, hemicellulose can be relatively easily hydrolyzed into 5-carbon mono sugars that can be fermented. Tethys Research LLC is looking for enzymes capable of breaking down the wood structure into its major components (FBRI, 2008). A variety of companies are exploring new fermentation technologies. Certain components of wood are difficult to ferment, especially cellulose. Additionally, certain chemicals which are present in biomass, such as phenolics, may inactivate fungi and bacteria and prevent fermentation. A major attribute of these low-energy processes is the ability to filter or separate different chemicals.

TABLE 8.2 Steps Involved in the Low-Energy Process

Wood chips and hot water are combined, and various compounds are extracted, including hemicelluloses.
The extracted compounds are hydrolyzed to yield xylan and other products.
The xylan, a complex polysaccharide, is reacted to yield acetic acid from its acetyl groups.
The five-carbon sugars are fermented to other products.
The wood chips are used for pulping or burned for energy.

High-Energy Processes

The second type of processes is high energy because these processes consume the entire biomass by heating it. These methods are also sometimes called thermochemical conversion methods. The processes used here are called gasification or pyrolysis, a difference being that pyrolysis involves heating the biomass in the absence of oxygen (Table 8.3). It has been suggested that both types of processes could occur at the same facility.

TABLE 8.3 High-Energy Processes

Gasification A process in which biomass or waste is heated in a vessel to produce a gas (syngas) that can then be used as a fuel to produce electricity or as an intermediate for chemicals or fuels production
Pyrolysis A process in which biomass or waste is heated in a vessel to form a char and a gas and/or liquid that can be used to produce electricity or other fuels

The high-energy route to products is quite different from the extraction and fermentation processes. A major difference is that all the biomass is consumed in the process. These are sometimes called the whole wood processes. It might also be called a high-temperature process and a high-energy process. A high-temperature treatment results in syngas or pyrolysis oil. The two primary processes are known as gasification and pyrolysis. Gasification takes place in the presence of some oxygen, whereas pyrolysis occurs in the absence of oxygen. Gasification produces a gas as a product, whereas pyrolysis produces a liquid. This process does not have any limitation like in case of the extraction process, which may only use kraft pulping process and hardwoods.

8.3 CHEMICAL COMPOSITION OF WOOD

Chemicals which can be in practice obtained from wood depend greatly on its chemical composition. Wood is a mixture of three types of natural polymers—cellulose, lignin, and hemicelluloses. The approximate ratio of cellulose, lignin, and hemicelluloses is 50:25:25. It depends on the following:

- Species
- Biological variations such as genetic differences within species
- Growing conditions

Cellulose and hemicelluloses are carbohydrate polymers made up from molecules of simple sugars, whereas lignin is a polymer of phenylpropane units. Cellulose is a long-chain polymer of glucose. It differs from starch, which is also a glucose polymer, only in the configuration of the glucose molecules. The fibrous nature of the wood cells is the result of the linear, oriented, crystalline arrangement of their most plentiful component, cellulose. Hemicelluloses are branched polymers of five-carbon sugars such as xylose or six-carbon sugars other than glucose. They are shorter and amorphous in nature and serve with the lignin to form the matrix in which the cellulose fibrils are embedded. Although the cellulose structure is the same in different species, the hemicelluloses are found to vary significantly among species and particularly between hardwoods and softwoods. Hardwood hemicelluloses generally contain large amount of pentoses, whereas softwood hemicelluloses generally contain more hexoses. Lignin, which is the third cell wall component, is a three-dimensional polymer produced from phenylpropane units which have randomly grown into a complicated large molecule having many different kinds of linkages between the building blocks. The structure of lignin also varies between hardwoods and softwoods. In hardwood lignins, the phenyl groups are more highly substituted with methoxyl groups as compared with those in softwood lignins. The hardwood lignins are less cross-linked and get more easily dissolved in pulping. Lignin acts as cement between the wood fibers and as a stiffening agent within the fibers. Lignin is dissolved by various chemical processes in the production of chemical wood pulps, leaving the cellulose and hemicelluloses behind in fibrous form. Some hemicelluloses are lost in the process because of their greater solubility, lower molecular weight, and easier hydrolysis. In addition to the polymeric cell wall components which make up the major portion of the wood, different species contain varying amounts and kinds of extraneous materials called extractives. In softwoods, significant amounts of resins consisting of both fatty acids and so-called resin acids are found. These are obtained from the simple terpenes such as turpentine and pine oil. Tannins are polyhydroxylic phenols which are found in the heartwood and bark of several species. Rubber in the form of a latex is obtained from the inner bark of certain trees. Aromatic oils and water-soluble sugars may also be obtained from various species. Cedar oil and maple sugar are common examples.

8.4 CHEMICALS DERIVED FROM WOOD

Before the advent of cheap fossil fuels such as coal, petroleum, and natural gas, the destructive distillation of wood to produce charcoal was an important industry. The gas produced in wood carbonization can be used as a low Btu fuel. It was sometimes used during World War II to power internal combustion engines when gasoline was unavailable. A number of volatile organic chemicals can be recovered from the distillate of wood pyrolysis. Acetic acid, methyl alcohol, and acetone were obtained earlier from wood distillation exclusively. Methyl alcohol was termed "wood alcohol." In addition, several wood tar oil fractions used for medicinals, disinfectants, and weed killers were isolated.

Extractives

The resinous material from pine trees provided the raw material for the naval stores industry, which is the oldest chemical industry in North America. First used for tarring of ropes and caulking of seams in wooden ships, these crude exudates were later distilled to provide turpentine and rosin, which have a variety of industrial uses. The latex obtained from rubber trees was the only source of rubber for many years. For many applications, natural rubber is still preferred today over synthetic rubbers. Extracts of the heartwood of certain hardwoods and also the bark of various species provided tannins, which were found important in tanning leather. In addition to cellulose, the most widely used polymer today, which is mainly used in its natural fibrous state after extraction from the wood, substantial quantities of chemicals called "silvichemicals" are still in use today despite the overwhelming predominance of petroleum-based chemicals.

Extractives from wood and bark have much more potential than their present use represents. Cellulosic polymers could become more important if energy costs can be reduced and properties improved. Production of oleoresin in pines can be stimulated by the application of herbicides. Hydrocarbon polymers can be obtained by cultivation of new plants as commercial crops. Low molecular weight phenols can be obtained from the by-product lignin in pulping liquors. From kraft black liquor, saccharinic acids could be recovered. Essential oils, chlorophyll, and protein can be obtained from foliage.

Regenerated Cellulose and Cellulose Derivatives

The chemical fragments of the cell wall polymers which end up in solution after pulping can be recovered from the pulping liquors and used. Generally, alkaline pulping liquors are burnt in the recovery boiler to recover the pulping chemicals. But sulfite pulping liquors are usually treated to yield useful by-products. The sulfonated lignin can be precipitated as lignin sulfonates and used as adhesives, binders, dispersants, and tanning agents, etc. The spent sulfite liquor can be fermented with yeast for producing ethanol, fodder yeast, and food supplements. By mild alkaline oxidation of lignin sulfonates, vanillin can be obtained for flavoring and odorant applications. Alkali lignin from kraft black liquor may be precipitated and used as an extender for resins, for rubber reinforcement, and for stabilization of emulsion. Volatile products from kraft black liquor include dimethyl sulphide, dimethyl sulphoxide, and dimethyl sulfone. These products are useful as solvents and chemical reactants.

The hydrolysis of wood to simple sugars by chemical reaction with water in the presence of acid catalysts has been known for the last 150 years and has been used on a commercial scale in the United States during World War I, in Germany during World War II, and at present in the USSR. Glucose is the major product and can be further converted to ethanol or yeast.

Fig. 8.1 shows thermal and chemical techniques for the conversion of wood (or other biomass) into chemical products.

High-purity chemical cellulose or dissolving pulp is the starting material for polymeric cellulose derivatives such as cellophane and rayon (both regenerated cellulose), cellulose esters such as acetate and butyrate for fiber, film and molding applications, and cellulose ethers such as ethylcellulose, hydroxyethylcellulose, and carboxymethylcellulose (CMC) for use as gums.

The processing of cellulose for production of regenerated cellulose and cellulose derivatives requires high-purity cellulose, i.e., dissolving pulp or cotton linters. Dissolving pulp can be produced either by prehydrolysis kraft or acid sulfite pulping. In both these processes, the conditions must be selected in such a way that the remaining amount of hemicellulose in the fibers is reduced to a very low level. Also, bleaching to high brightness is essential for removing all of the lignin. The pulp yield in these processes is very low—in the order of 35%, making it a rather expensive product. A more energy-efficient way of separating the wood components from each other has been suggested and is usually referred to as the "wood explosion" process (Fig. 8.2). Wood is treated with steam at high temperatures in the range of 190–240°C for a few minutes and then the pressure is released rapidly. This forces the material to "explode" and the individual fibers and fiber bundles are formed, whereas volatile extractives can be collected separately. Wood acids are liberated, and acid hydrolysis of the polysaccharides takes place along with simultaneous hydrolysis and condensation reactions of the lignin under the conditions of the steam treatment. Most of the hemicelluloses get degraded into sugars (low molecular weight) and oligosaccharides. These

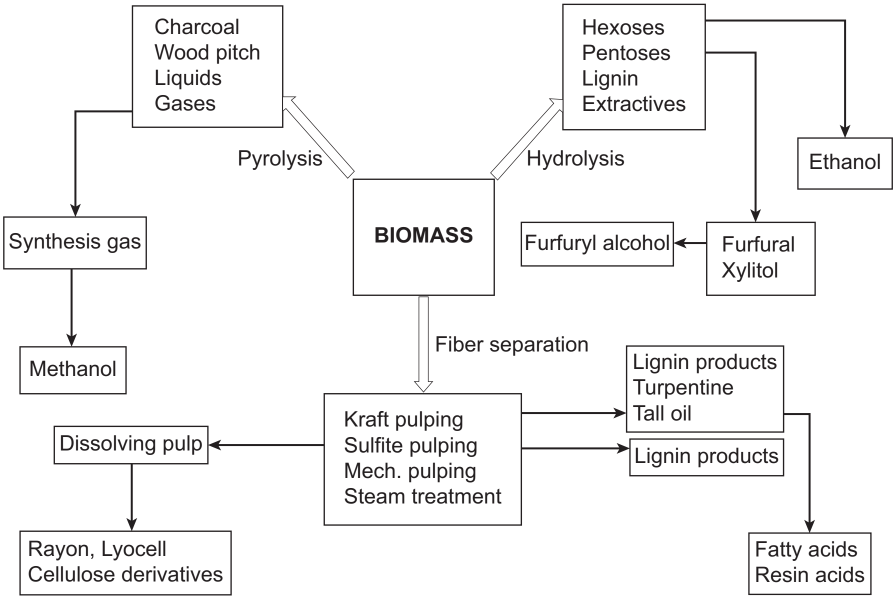


FIGURE 8.1 Processes for the conversion of wood into chemical products. *Reproduced with permission Gellerstedt (2009).*

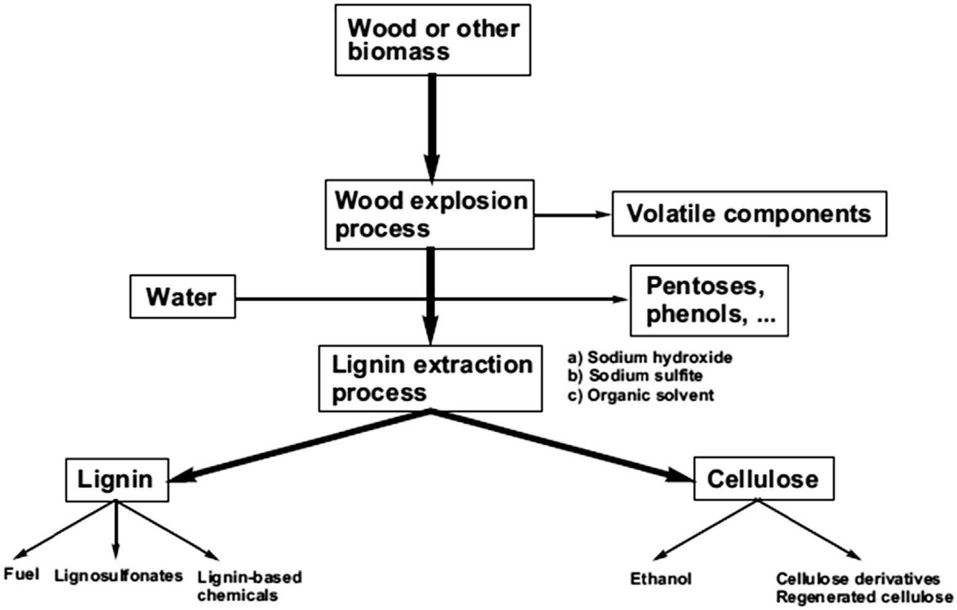


FIGURE 8.2 Wood explosion process. *Reproduced with permission Gellerstedt (2009).*

can be removed by washing with water. A redistribution of lignin in the fiber walls also takes place and results in a rather facile elimination of a large portion of the lignin by extraction of the fibrous material using aqueous alkali, sodium sulfite, or an organic solvent. The remaining material consisting of cellulose with a low to medium degree of polymerization (DP) along with the remaining lignin and some degraded carbohydrates like furfural-derived polymers can be easily bleached, giving a rather pure cellulose. But this process suffers from the difficulty in obtaining a homogeneous reaction in the biomass material and which results in high amounts of shives. Therefore, the process has not yet reached the commercial scale. From cellulose, a large variety of derivatives, esters, and ethers can be produced. The largest volume is regenerated cellulose, which is produced as rayon fibers, cellophane, and lyocell fibers. Several major difficulties are faced in the production of cellulose-based products. These are listed as follows:

- Heterogeneity of the starting material
- Reproducibility of the experimental conditions
- Heterogeneous phase of the reaction
- Purification difficulties
- Effluent disposal and the product quality control

In addition, there has been no real driving force to further develop the technologies used because of the strong competition from the petroleum-based industry. Thus, a successive decline in the production of cellulose-based fibers has been encountered during the last 2 decades. Table 8.4 shows the global fiber market in 2016 [(Global fiber consumption in 2016 by type of fiber in percent (basis = 99 mn tons)].

The traditional process of manufacturing regenerated cellulose fibers and films is by treating

TABLE 8.4 Global Fiber Market in 2016 (Global Fiber Consumption in 2016 by Type of Fiber in Percent (Basis = 99 mn tons)

Synthetic fibers	62.7%
Cotton	24.3%
Wool	1.1%
Wood-based cellulose fibers[a]	6.6%
Other natural fibers	5.3%

[a] *Wood-based and cotton linter–based cellulose fibers.*

From http://www.lenzing.com/en/investors/equity-story/global-fiber-market.html.

the cellulose with strong alkali (mercerization) for reducing the DP to a suitable value followed by reaction with carbon disulfide. The solution that is produced is termed viscose, and the name of the process is also viscose. Chemically, the mercerization converts the cellulose I to cellulose II, which is later converted to cellulose xanthate by reaction with carbon disulfide. The xanthate is then dissolved in aqueous sodium hydroxide solution and allowed to equilibrate to get the substitution as evenly distributed as possible. Finally, the xanthate is pressed through a spinnerette into a solution of sulfuric acid where the acid regenerates the cellulose as fine filaments resulting in rayon fibers. Fig. 8.3 shows the process. Cellophane can be made in a similar manner by pressing the viscose solution through a fine slit.

Another developed alternative to the viscose process is a direct dissolution of the cellulose in NMMO (N-methyl-morpholine-N-oxide, Fig. 8.4) and subsequent precipitation of the cellulose filaments in an NMMO–water mixture. These fibers are termed lyocell fibers and like the rayon fibers, their major use is in textiles. Lyocell is known in the United States under the brand name Tencel. Although it is related to rayon, it is manufactured by a solvent spinning technique, and the cellulose undergoes no major chemical change. It is a very strong fabric with industrial uses such as in automotive filters, ropes, abrasive materials, protective suiting material, and bandages. It is primarily used in the garment industry, mainly in women's clothing. Fig. 8.5 shows the process for manufacturing of lyocell fiber.

CMC is one of the most important cellulose derivatives. The process of manufacturing CMC involves mercerization of the starting cellulose, usually dissolving pulp, followed by reaction with sodium monochloroacetate to form an ether linkage. Then it is neutralized, washed, and beaten and is dried as its sodium salt (Fig. 8.6). The degree of substitution (DS) is usually around 0.60–0.95. CMC has a wide area of use. Highly purified CMC is used in food as a viscosity modifier or thickener and to stabilize emulsions in various products, including ice cream. It is also a constituent of many nonfood products, such as toothpaste, diet pills, laxatives, water-based paints, detergents, textile sizing, and various paper products. A somewhat less pure, highly viscous, and water-soluble form of CMC is used in various industrial applications such as dispersing agent, flow property regulator, and thin film developer in, e.g., paper coating colors.

In the manufacturing of ethyl hydroxyethyl cellulose (EHEC), the cellulose is first mercerized and then reacted with ethylene oxide to form hydroxy-polyethoxy ether groups along the

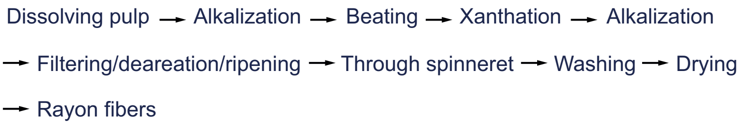


FIGURE 8.3 Process steps involved in manufacturing of rayon.

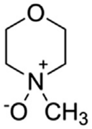


FIGURE 8.4 Structure of N-Methylmorpholine N-oxide.

cellulose chain. Typically, a DS ~1.2 is obtained. In a second reaction step, ethyl chloride is used to introduce ethyl ether groups with a DS of around 0.8–1.0. Fig. 8.7 shows the various process steps. In water, EHEC forms colloidal solutions that are used for water retention in cement and other applications in the construction industry. Other important uses are as dispersing and thickening agents and also as a stabilizer in water-based latex paints. Fig. 8.8 shows the structure of EHEC.

Several products based on cellulose acetate are manufactured commercially, having different degrees of substitution along the cellulose chain. Major uses of cellulose acetate are as lacquers, photographic films, fibers, and fabrics (Table 8.5). Normally, the reaction is carried out in acetic acid with acetic anhydride as the acetylation reagent and sulfuric acid as the catalyst. The reaction conditions not only determine the DS but also the solvent and catalyst.

Another cellulose ester of commercial interest is cellulose nitrate, which can also be produced with a variety of DS (Table 8.5). The process involves treatment of dissolving pulp with a mixture of nitric acid and sulfuric acid in which the treatment conditions determine the DS of the product. The crude product is washed with water and then treated with boiling sodium carbonate solution to adjust the DP before beating and dewatering to form the final product. In Sweden, Bofors Explosives AB in Karlskoga is manufacturing cellulose nitrate. The

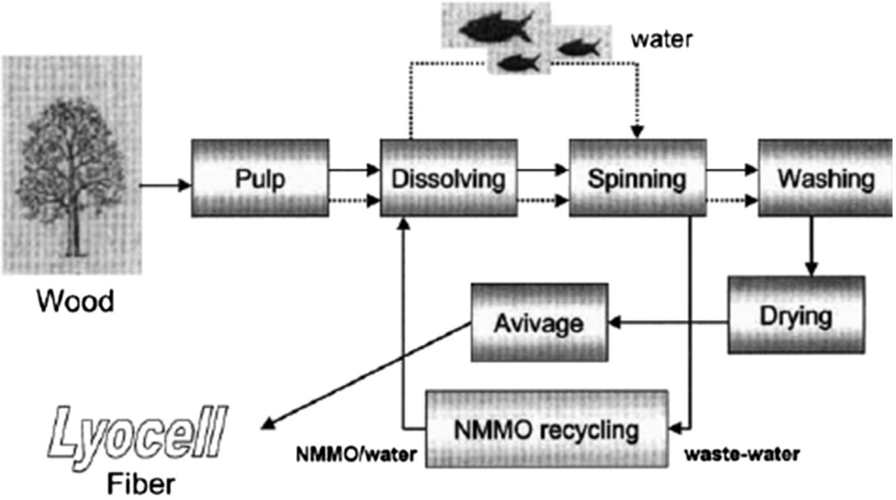


FIGURE 8.5 Process for manufacturing of lyocell fiber. *Reproduced with permission Rosenau et al. (2001).*

Dissolving pulp → Beating → Mercerization → Etherification →

Neutrilization → Washing → Beating → Drying → Sodium CMC

FIGURE 8.6 Process steps involved in manufacturing of carboxymethyl cellulose.

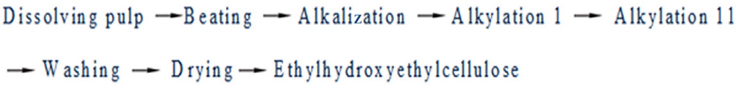


FIGURE 8.7 Process steps involved in manufacturing of ethyl hydroxyethyl cellulose.

DS is around 2.2–2.5 with more than 50% of the substitution in the positions 2 and 3. The products are gunpowder and explosives, made by mixing of low and high nitrated cellulose together with a solvent like ethanol.

A different way of substituting the cellulose is by graft polymerization. Although several modes of adding reactive compounds to cellulose have been studied, not much success has been achieved. One major problem faced in these experiments is the relative ease by which homopolymers are formed together with the desirable copolymerization. Therefore, comparatively large losses of the grafting compound can be obtained.

Lignosulfonates

In kraft mills, a partial precipitation of kraft lignin from the black liquor can be obtained by addition of carbon dioxide or mineral acid to a pH of around 9–10. About 80% of the lignin can be recovered and further processed into sulfonated or oxidized lignin products. Beside energy, other uses of lignin have been suggested as the availability of lignin is high and potentially large volumes of organic material can be produced. In spite of many efforts, the market for lignin-based products has only developed slowly and still the major use is as a macromolecule in solution. A major problem of lignin is the large heterogeneity because the various technical pulping processes give rise to molecules ranging from virtually monomeric phenols to high-molecular weight polymers. As a result, the physical properties of a certain lignin product cannot be well defined and, so the technical performance is such that only rather low value-added uses can be found. The heterogeneity of lignins is expressed as polydispersity. It is calculated as Mw/Mn with typical values for lignosulfonates of 5–7 and for kraft lignins of 2–3.

At present, approximately 1,000,000 tons/y of lignosulfonates are produced in the world, with the major producer being Borregaard LignoTech (Norway) with production facilities in six different countries. Lignosulfonates consist of a mixture of sulfonated lignin, sugar acids, sugars, inorganic chemicals, and resins. Most of the lignosulfonates are obtained from the spent

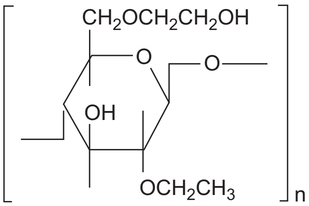


FIGURE 8.8 Structure of ethyl hydroxyethyl cellulose.

TABLE 8.5 Typical Application Areas of Different Types of Cellulose Acetates and Cellulose Nitrates

CELLULOSE ACETATES
Plastics, lacquers (22–32% acetyl content; DS, 1.2–1.8)
Fibers. Photographic films (36–42% acetyl content; DS, 2.2–2.7)
Fabrics, foils, fibers (43–45% acetyl content; DS, 2.8–3.0)
CELLULOSE NITRATES
Plastics, lacquers (10.5–11.1% nitrogen content; DS, 1.8–2.0)
Lacquers. Adhesives (11.2–12 0.2% nitrogen content; DS, 2.0–2.3)
Explosives (12.0–13.7% nitrogen content; DS, 2.2–2.8)

Based on Gellerstedt (2009).

pulping liquor of sulfite pulping processes but some are also produced by postsulfonation of lignins obtained by sulfate pulping (kraft process). Recovered coproduct lignosulfonates can be used with little or no additional treatment or they can be converted to specialty materials with the physical and chemical properties adjusted for specific end-use markets.

One metric ton of pulp produces 330–540 kg of lignosulfonate. The global lignosulfonates market was valued at US$691.9 mn in 2015 and is anticipated to reach US$960.2 mn in 2024, expanding at a CAGR of 3.8% between 2016 and 2024. Sodium lignosulfonates are used as plasticizers for concrete. Lignosulfonates reduce the amount of water needed, making concrete stronger. Other uses of lignosulfonates are as a dispersant, binder, emulsifier, chelating agent, or food additives (vanillin). In the production process (for making sulfite pulp), the water-soluble lignosulfonate is formed by extensive sulfonation and partial hydrolysis of the native lignin macromolecule. Simultaneously, some condensation reactions will occur within the lignin. In addition, a certain degradation of the wood polysaccharides takes place, giving rise to monomeric sugars and the formation of small amounts of furfural and hydroxymethyl furfural. Normally, the counterion is calcium. From this mixture, a variety of products can be produced, with the major changes being the amount of sugars (which can be reduced) and the counterion used (calcium, magnesium, sodium, and ammonium).

Tall Oil

In kraft pulping of softwood, the nonvolatile extractives, mainly soaps of resin acids and fatty acids, are separated from the black liquor after the cooking. The free acids are liberated by the addition of sulfuric acid which forms crude tall oil. The yield of tall oil might reach ~50 kg/ton of pulp in areas having high density of pine. The distillation products of tall oil are rosin, fatty acids, and resin. The rosin products are mainly used in the sizing of paper, as adhesives, and in printing inks, whereas a major use of the fatty acids are in alkyd resins.

Turpentine

Some turpentine and rosin are obtained by using steam distillation or by extraction of pine stumps. Arabinogalactan, which is a hemicellulose gum extracted from larch, is used in place of gum arabic. Phenolic acids extracted from the bark of various conifers are used as extenders for synthetic resin adhesives and as binders and dispersants. Waxes obtained from Douglas fir bark can be used for general wax applications, and natural rubber remains an important material.

Turpentine is produced in many countries by direct solvent extraction of wood, whereas in pulp producing countries sulfate turpentine is predominant. The crude sulfate turpentine market was valued at USD 213.87 million in 2015 and is projected to grow at a CAGR of 4.10% to reach USD 279.5 million by 2022. Major uses of turpentine are as a raw material for the manufacturing of chemicals and resins and as fragrances and flavors. The single largest use of turpentine is for the production of pine oil, which chemically involves a hydration of α-pinene to α-terpineol. Another major use is for the production of resins, which when starting with α-pinene and using a Lewis acid as catalyst gives rise to the adhesive in tape.

Turpentine is a volatile oil and is distilled from pine resin, which is obtained by tapping trees of the genus Pinus. The solid material which is left behind after distillation is known as rosin. Both these products are used in many different types of applications. Turpentine, rosin, and derivatives of these which are obtained via tapping of living pine trees whether plantations or natural stands are known collectively as gum naval stores. The turpentine and rosin are known as gum turpentine and gum rosin, respectively. This differentiates them from turpentine and rosin which are recovered as by-products from chemical pulping of pines and which are termed as sulfate naval stores and wood naval stores. These are similar materials obtained from aged pine stumps. Turpentine has been used as a solvent or cleaning agent for paints and varnishes, especially in those countries where the pine trees are tapped. There are also some specialized uses in the pharmaceutical industry. Most turpentine nowadays is used as a source of chemical isolates, which are converted into a wide range of products. Several of these, including the biggest single turpentine derivative, synthetic pine oil, are used for flavor and fragrance, although there are also many important nonaromatic applications such as polyterpene resins. Pine oil is used as cleaning agents, in disinfectants, and other products having a "pine" odor. Derivatives such as camphor, citral, linalool, citronellal, menthol, isobornyl acetate, and several others are used either as such or for the elaboration of other fragrance and flavor compounds. Many of the flavors and odors in use today, which are associated with naturally occurring oils, may well be derived, instead, from turpentine. The chemical composition of turpentine is found to vary significantly, depending on the species of Pinus from which it is harvested. The terpene composition is relatively simple in case of some pines and consists mainly of two common terpenes: alpha and beta pinenes (Fig. 8.9). Other pine species contain different terpenes, which may have a significant effect on the composition and use of the turpentine. The resin of the North American pine, *P. contorta*, contains phellandrene, which is found in plants of the parsley family and has a grassy fragrance. The resin of the Mediterranean species, *P. pinea*, and some North American species contain limonene. *P. ponderosa* resin contains a sweet-smelling terpene, which is known as 3-carene. Two pines endemic to Pacific coastal regions of North America, *P. jeffreyi* and *P. sabiniana*, do not have terpene components in their resin. Instead, they contain aldehydes, which are much diluted with a gasoline-like material, heptane, which has no fragrance but is explosive. Aldehydes mixed with heptane provide the characteristic vanilla-like smell associated with *P. jeffreyi* forests. Table 8.6 shows the principle uses of turpentine and rosin.

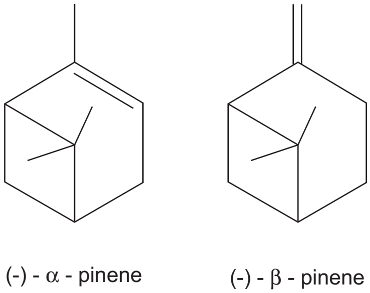


FIGURE 8.9 Structure of alpha and beta pinene.

Ethanol

Acid sulfite cooking is one of the most notable technologies for biorefinery and bioethanol production. In the acidic sulfite pulping process, a portion of the wood polysaccharides are hydrolyzed into hexoses and pentoses, which are found in the spent pulping liquor. Several sulfite pulp mills have used SSL for ethanol production. *Saccharomyces cerevisiae* can ferment hexose, but it is not able to ferment oligosaccharides and pentoses. Further hydrolysis steps such as acid or enzyme treatments are required for ethanol fermentation for utilizing oligosaccharide in SSL, which would require additional stages and equipment. Since long, fermentation of the hexoses to ethanol has been used in some sulfite mills. In Sweden, the Domsjö mill outside Örnsköldsvik produces around 14,000 tons/year of bioethanol. The unique process also produces complementary products such as carbonic acid, biogas, and energy. The bioenergy produced by the process is used internally and makes Domsjö virtually independent of fossil energy sources. The raw material consists largely of pine and spruce. As part of a major international development project, significant efforts are being made in

TABLE 8.6 Principle Uses of Turpentine and Rosin

TURPENTINE
Chemicals and pharmaceuticals
Gums and synthetic resins
Paint, varnish, and lacquer
Products for railroads and shipyards
Shoe polish and related materials
Rubber
Printing inks
Adhesives and plastics
Asphaltic products
Furniture
Insecticides and disinfectants
ROSIN
Paper and paper sizing
Chemicals and pharmaceuticals
Ester gums and synthetic resins
Paint, varnish, and lacquer
Soap
Linoleum and floor coverings
Adhesives and plastics
Oils and greases
Rubber
Printing inks
Shoe polish and related materials

Sweden for finding suitable ways of converting wood waste such as branches and other nonpulpable parts into ethanol by using direct acid hydrolysis. The following three alternative methods have been examined:

- Hydrolysis with concentrated sulfuric acid or hydrochloric acid at 20–40 °C [the concentrated hydrochloride acid process (CHAP) method]
- Hydrolysis with diluted acid at high temperature [the Canada-America-Sweden-Hydrolysis (CASH) method]
- Enzymatic hydrolysis.

Of these, the CASH method appears to be the most promising. Such an ethanol plant can easily be incorporated in a normal pulp mill, thus making effective use of the raw material, energy, water, and effluent treatment facilities.

Borregaard is the world's largest producer of second-generation bioethanol, with a production of around 20 million liters per year. The bioethanol that is produced in Borregaard's biorefinery is produced by extracting sugar from wood, which is then fermented to produce ethanol. At present, Borregaard delivers bioethanol from its Sarpsborg facility for heavy goods vehicles and buses in the Oslo region. By mixing bioethanol with normal petrol, the highest possible numbers of motorists will be able to drive on environmentally sound Norwegian bioethanol. The company has developed a new process for production of ethanol and chemicals from various biomasses (including waste products from agriculture) and is in the process of building a NOK 130 million pilot plant to develop this process.

Vanillin

The world production of vanillin is around 3500 tons/year, with the predominant producer being Borregaard, Norway. For 50 years, Borregaard has produced vanillin based on wood. Their vanillin plant has been running for 50 years. Vanillin is one of the most valuable products they make from wood. Borregaard products from renewable raw materials are good alternatives to petroleum-based products. Borregaard is today one of the world's leading suppliers of vanillin and produces 1500 tons per year based on the spruce log.

Vanillin is used as a food and beverage flavoring agent. Vanillin is a vital ingredient in several flavors and fragrances, particularly in the beverage industry. Although overshadowed in volume by synthetic alternatives, it still remains an important ingredient in today's markets. Most of the vanillin is obtained by treatment of lignosulfonate with alkali at higher temperatures under oxidative conditions although synthetic routes from phenol also exist. In addition, vanillin can be obtained from natural sources such as vanilla beans. The formation of vanillin from lignosulfonate has been investigated using a phenolic β-O-4 structure, with a sulfonic acid group in the β-position as a model compound. On treatment with alkali, the structure was degraded into vanillin and acetaldehyde, whereas the β-substituent was released as a phenol. Thus, it can be assumed that phenolic end groups in the lignosulfonate give rise to vanillin. The modified lignosulfonate that is obtained after treatment can be further processed into commercial lignosulfonate products. Fig. 8.10 shows the structure of vanillin.

Researchers from the University of Maine have identified seven chemicals—lactic acid, acetic acid, furfural, itaconic acid, succinic acid, methanol, and hydrogen—having potential for production from wood. The first five would more likely be created through low energy processes and six and seven through high-energy processes. These chemicals come from a range of technologies, many of which are still emerging technologies for wood/biomass.

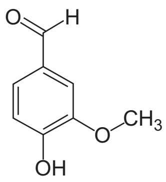


FIGURE 8.10 Structure of vanillin.

8.5 FUTURE PERSPECTIVES

The large societal consumption of nonrenewable resources such as petroleum will surely result in successively higher energy costs. Also, a large net increase of the concentration of carbon dioxide in the atmosphere can be seen. The only alternative to petroleum, available worldwide, is biomass present in wood and annual plants, which can be converted into chemicals as already described. A commercial production of fuel ethanol, based on sugarcane bagasse, corn, or wheat has already started in a few countries. This development is expected to continue and, successively other biomass will also be included. However, the rate will be much dependent on political decisions such as tax rates.

The development of chemicals from biomass is likely to grow. There are several reasons why this shift will continue. A major impetus will be increasing cost of petroleum and natural gas feedstocks as the world economy improves. In the long term, the supplies of these fossil fuel feedstocks are limited and will ultimately be depleted. Another major reason is that such a shift may have a positive impact on the environment. Policymakers will favor using biomass because it is expected to reduce environmental impacts, partly because of decreasing greenhouse gases. Other reasons are more subtle. Biomass is a very flexible feedstock—many products can be produced. Also, some chemicals are simply lost today because the water-soluble components of wood are partially lost in leachate from wood chip piles and pass into the waste stream from mills.

Using wood for chemicals has a long history. It appears that an incremental approach to development of markets for chemicals from woody biomass will occur. Some states enjoy a large forest product industry and a substantial forest resource. Some states have large hardwood timber resource, an input required for several processes for obtaining useful chemicals. The production processes that are successful will be processes that are economically desirable in terms of the market for the product and the cost to produce it. The number of chemicals potentially produced from biomass is huge, but much research remains on the optimal way to produce these chemicals. The market for these materials will be a major component in their viability.

8.6 ANNOTATED BIBLIOGRAPHY

Allan, GG (1978). Polymeric cellulose derivatives. Special paper, 8th World Forestry Congress.

Barton GM (1978). Chemicals from trees - outlook for the future. Special paper, 8th World Forestry Congress.

The chemical utilization of plant materials for liquid fuels or organic chemicals is reviewed. The possibility of producing chemicals from plants rather than from fossil sources such as petroleum or coal is discussed.

Benigni JD and Goldstein IS (1971) Neutral hydrolysis of alkali lignin to monomeric phenols. J. Polymer Science, C36, p. 467–475.

Browning, BL (1963) ed. The chemistry of wood. Interscience, 687 p. New York.

Cowie JG (2008). The value prior to pulping (VPP) platform for biomass utilization. Presentation to the American Association for the Advancement of Science. February 18, 2008.

The concept of extracting hemicellulose before pulping and utilizing the extract to create new value streams as having high promise is discussed.

Dickerson C and Rubin J (2008). Maine Bioproducts Business Pathways. Margaret Chase Smith Policy Center and Forest Bioproducts Research Initiative, School of Economics, University of Maine, Orono.

This paper discusses both the near-neutral extraction process and a thermochemical process that can be utilized in a Kraft pulp mill based biorefinery to produce ethanol and acetic acid as initial products. The potential investment is analyzed and production costs for a biorefinery based on studies that have looked specifically at this type of evolution, as well as cellulosic biorefineries that are based on other types of processes has been estimated. Also potential “second stage” fuels that could be produced, as well as the modes of transportation that can be used to get the fuels and products to the existing infrastructure have been identified.

Forest Bioproducts Research Initiative (2008). Website http://www.forestbioproducts.umaine.edu/Tethy_Technology.php.

Gellerstedt G (2009) Cellulose Products and Chemicals from Wood, Wood Chemistry and Wood Biotechnology, Vol. 1, Edited by Monica Ek, Göran Gellerstedt, Gunnar Henriksson, Walter de Gruyter GmbH & Co. KG, Berlin, p. 173, ISBN 978-3-11-021340-9.

Thermal and chemical techniques for the conversion of wood (or other biomass) into cellulose products and chemicals are discussed.

Goheen DW (1971). Low molecular weight chemicals. In: Lignins, K.V. Sarkanen and C.H. Ludwig, eds. John Wiley, p. 797–831. New York.

Goheen DW (1972) Silvichemicals - what future? American Institute of Chemical Engineers Symposium 69, p. 20–24.

Goldstein IS (1978) Chemicals from wood: outlook for the future. Eight World Forestry Congress, Jakarta, Indonesia.

Description of past, present and potential future chemicals derived from wood is presented in this paper. Predictions about the future of chemicals from wood has been made

Goldstein IS, Holley DL and Deal EL (1978). Economic aspects of low-grade hard-wood utilization. For. Prod. J. 28(8):53–56.

Three potential applications are discussed for wood not suitable for structural purposes, nor for pulping, because of size, species, defects, or bark content. The potential value as fuel, for conversion into chemicals, and conversion into fibreboard is compared to the cost of such material delivered as whole-tree chips to a central location. The potential availability of such wood is discussed with particular reference to the Piedmont of North Carolina.

Hillis WE (1978). Extractives. Special paper, 8th World Forestry Congress.

Laver, ML (1978). Chemicals from bark. Special paper, 8th World Forestry Congress.

MacKay DG, Cole BJW, Fort RC and Mares A (2009) Potential markets for chemicals and pharmaceuticals from woody biomass in Maine. Forest Research LLC. Orono, ME, USA. 26 p.

A broad overview of some of the potential chemicals and pharmaceuticals, including a food additive, with a focus on activities currently taking place in Maine is presented here. It identifies some key chemicals and pharmaceuticals that might be produced, and describes some market characteristics for these chemicals.

Roberts DR (1973) Inducing lightwood in pine trees by paraquat treatment. USDA Forest Service Research Note SE-191, April. Asheville, N.C.

Rosenau T, Potthast A, Sixta H, P Kosma P (2001). The chemistry of side reactions and byproduct formation in the system NMMO/cellulose (Lyocell process), Progress in polymer science 26 (9), 1763—1837.

This chapter focuses on lyocell fiber production and the analytical techniques to moniter side reactions in the lyocell process.

Sakanen KV (1976) Renewable resources for the production of fuels and chemicals, Science, Vol. 191, p. 773—776.

The sources of renewable resources for energy generation are summarized. The forms of energy generation possible from biomass are discussed. The production of chemicals and polymers from biomass is somewhat limited but still of conservation value. The chemical and by-product potential of renewable resources is evaluated. Production of chemicals by gasification is also briefly considered.

Winandy JE, Rudie AW, Williams RS, and Wegner TH (2008) Integrated biomass technologies: A future vision for optimally using wood and biomass. Forest Products Journal. Vol. 58, No. 6. p. 6—16.

Exciting new opportunities for sustainably meeting many global energy needs and simultaneously creating high value biobased consumer and construction products from wood, forest and agricultural residues, and other biobased materials are discussed. In addition, to traditional value added biobased products, such as lumber, paper, paperboard, and composites, opportunities for biorefining to produce electricity, transportation fuels, chemical feedstocks, syngas, and nanocrystalline cellulose are also presented.

www.prnewswire.com/.../lignosulfonates-market-to-grow-to-us9602-million-by-2024.

www.wrcbtv.com/.../crude-sulfate-turpentine-market-by-type-application-and-region-gl.

CHAPTER

9

Calculations of Wood, Paper, and Other Materials

9.1 WOOD MOISTURE CONTENT AND DENSITY

Moisture Content

There are several definitions regarding wood and properties of wood that are useful to understand. One of the most fundamental of these is the moisture content of wood. The moisture content of wood is a measure of the water content relative to either the total wet weight of material (the *green* weight of wood) or the weight of ovendried wood material (the *ovendry* basis). The ovendry weight is determined by drying the wood to constant weight at 103–105°C (217–221°F). The pulp and paper industry almost invariably reports the moisture content of wood and other materials in terms of the total weight of material. Note that the maximum moisture content in this case is 100% for the case of pure water. The other forest product industries almost invariably report moisture contents in terms of the weight of ovendry wood. Here moisture contents over 100% are possible and commonly encountered. The two definitions are as follows (keep in mind the relationship: weight of water in wood = wet weight of wood − ovendry weight of wood):

$$\mathrm{MC_{GR}} = \frac{\text{weight of water in wood}}{\text{wet weight of wood}} \times 100\% \tag{9.1}$$

$$\mathrm{MC_{OD}} = \frac{\text{weight of water in wood}}{\text{ovendry weight of wood}} \times 100\% \tag{9.2}$$

The moisture content of wood (green basis) is typically 50% but varies from 30% to 60%. This corresponds to 0.43–1.5 kg water per kg dry wood (43%–150% $\mathrm{MC_{OD}}$). The two moisture contents are interchangeable as shown in Eqs. (9.3) and (9.4) and Fig. 9.1.

$$\mathrm{MC_{GR}} = \frac{\mathrm{MC_{OD}}}{100\% + \mathrm{MC_{OD}}} \times 100\% \tag{9.3}$$

$$\mathrm{MC_{OD}} = \frac{\mathrm{MC_{GR}}}{100\% - \mathrm{MC_{GR}}} \times 100\% \tag{9.4}$$

Biermann's Handbook of Pulp and Paper: Raw Material and Pulp Making
https://doi.org/10.1016/B978-0-12-814240-0.00009-4

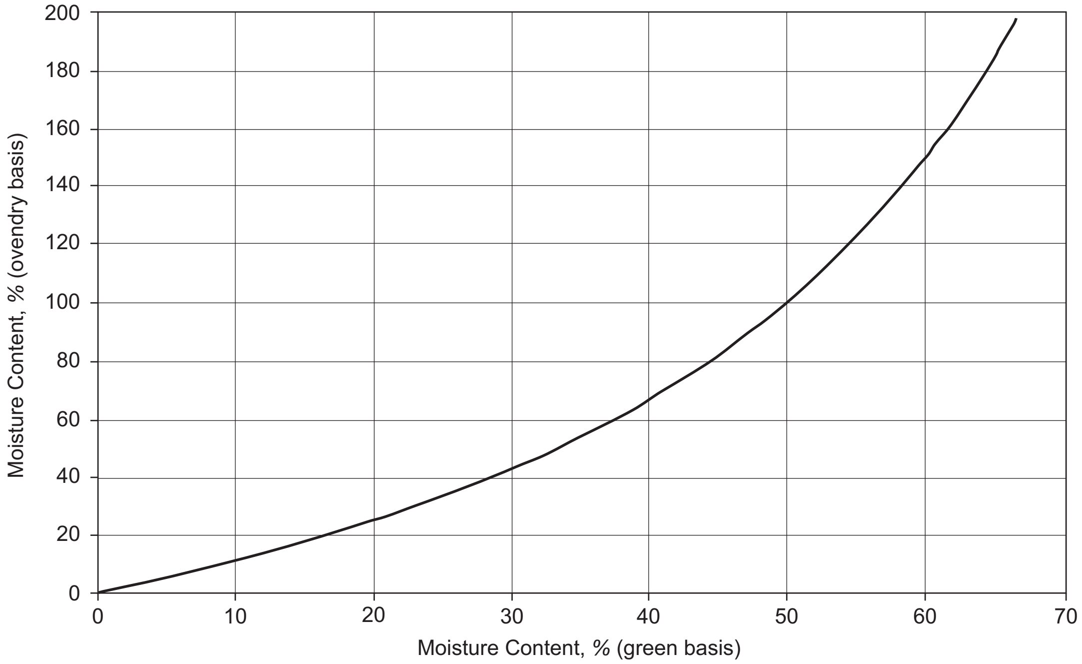


FIGURE 9.1 Comparison of green and ovendry basis moisture contents.

EXAMPLE 1

Convert 20% MC_{OD} to MC_{GR}.

Solution

One could use Fig. 9.1 and come up with about 17% MC_{GR}. Or else, one could use Eq. (9.3) and solve it for 16.7% MC_{GR}. If one uses the two definitions in Eqs. (9.1) and (9.2), it is not necessary to remember Eqs. (9.3) and (9.4). For example, 20% MC_{OD} means 20 parts water to 100 parts dry wood; this, in turn, means 20 parts water for 120 parts wetwood or 16.7% MC_{GR}.

Fiber Saturation Point

Below MC_{GR} of about 25%, free water disappears and the remaining water is chemically adsorbed to the wood, by hydrogen bonding of water with the hydroxyl groups of cellulose and hemicelluloses. The moisture content corresponding to the disappearance of *free water* is called the fiber saturation point (FSP). As the moisture content of wood decreases from 25% toward 0%, the energy required to remove an aliquot of water increases from 540 cal/g (the heat of vaporization of water) to about 700 cal/g (125%) midway and approaches 1100 cal/g (200%) near 0% MC.

Consequently, *air dry* wood is not really dry because wood is a hygroscopic material (as are pulp and paper). This means that wood absorbs or gives off moisture with the atmosphere until an equilibrium moisture content (EMC) is achieved. Fig. 9.2 shows the EMC value of wood as a function of ambient temperature and relative humidity. There is a *hysteresis* effect with the moisture content of wood, pulp, paper, and any lignocellulosic material. The actual EMC in a given environment will depend on whether the material is losing or gaining water to achieve the EMC. Paper below 6% MC put into an environment of 72°F and 50% relative humidity might achieve 7% EMC, whereas paper above 9% MC might achieve 8% EMC in this environment.

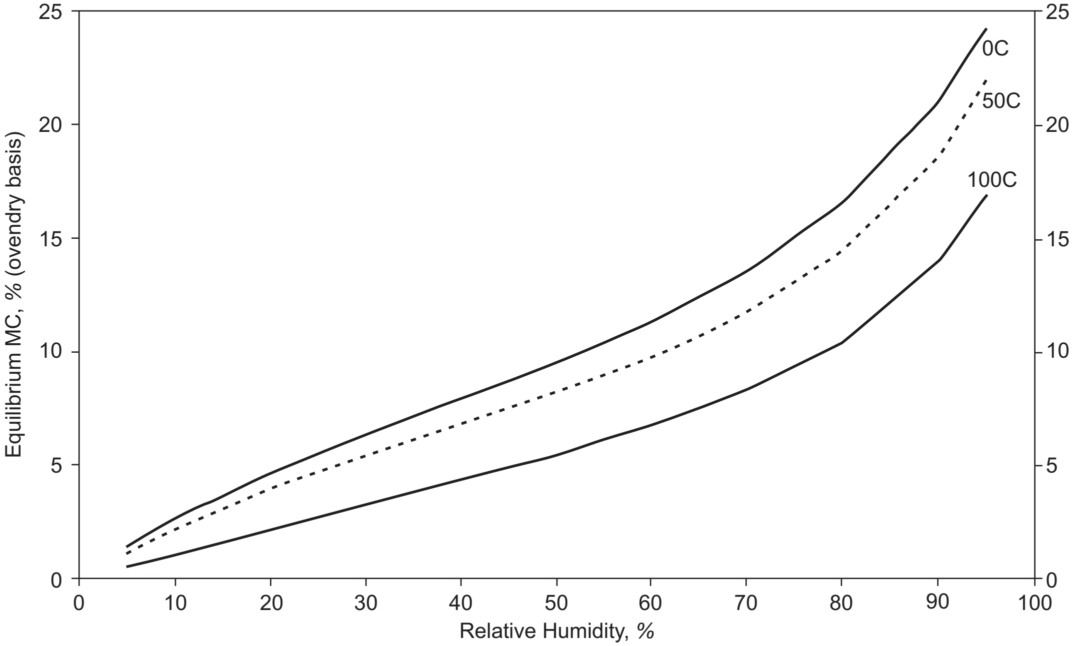


FIGURE 9.2 Equilibrium moisture content (MC) of wood versus relative humidity.

A difference in the physical properties of these papers results. TAPPI T 402 specifies that paper should be put in a warm, dry room before conditioning at standard testing conditions.

Wood shrinkage with decreasing moisture content: As the moisture content of wood decreases from the FSP to 0% moisture content, the wood shrinks. *Shrinkage* is defined as the change in a dimension of wood (from the FSP to a specified moisture content) from the swollen state relative to the swollen dimension. Wood tends to shrink from the FSP to the ovendry moisture content by the following rule-of-thumb amounts.

Longitudinal	0.5%
Radial	4%
Tangential	6%
Volumetric	9%

In fact, the volumetric shrinkage varies from 7% to 15% depending on species, growth rate, and so forth, and is loosely related to the specific gravity of wood as shown in Fig. 9.3, which gives shrinkage values for several species as examples.

Wood Specific Gravity

The specific gravity (sp gr) of wood is the ovendry weight of wood divided by the weight of displaced volume of water. This produces a unitless number. The displaced volume of water can be measured by calculating the volume of the wood if it is of even shape such as a rectangular block. If the wood is of uneven shape, it may be coated with a thin layer of wax, and the water it displaces when immersed is measured. Although the ovendry weight of wood is always used, it is possible to use a volume corresponding to any moisture content; however, the green volume is that most commonly used, and this gives the special term *basic specific gravity*. The basic specific gravity of woods is commonly between 0.35 and 0.60 but can vary from 0.2 to 0.7. The basic specific gravity of cell wall material is approximately 1.50.

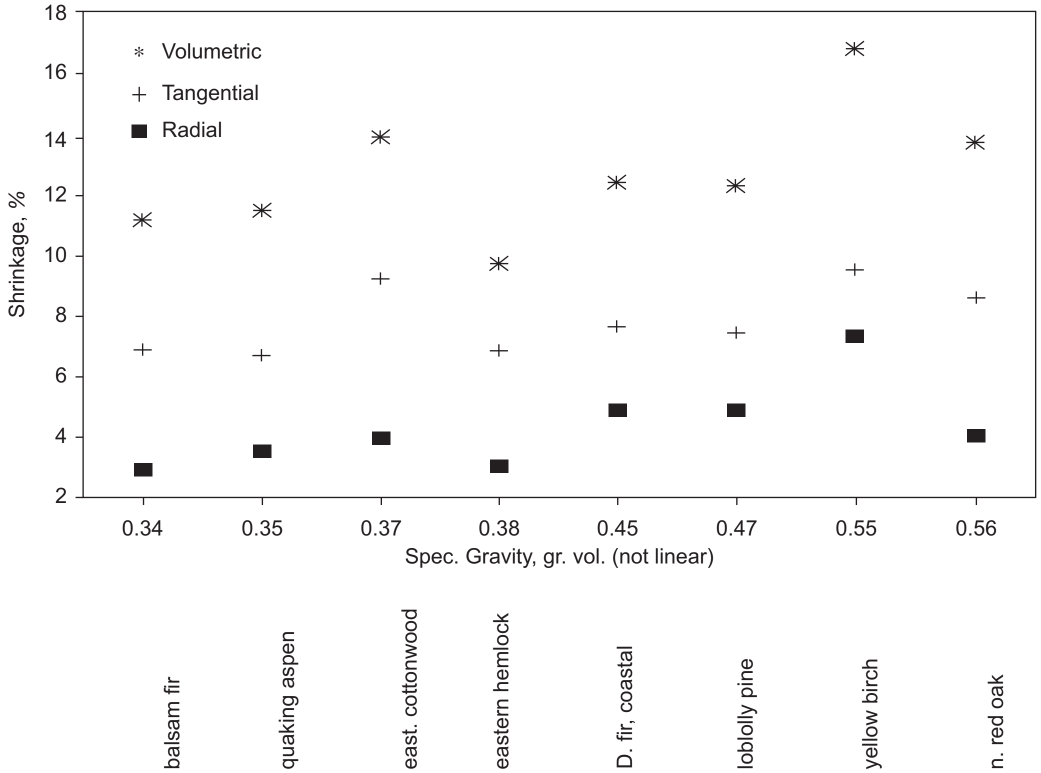


FIGURE 9.3 Shrinkage values for several species of wood.

The density of a material is defined as the mass per unit volume, mass/volume. When the units of pounds or ounces are used, one actually obtains a weight density. For wood, it is customary to take the total mass (or weight) divided by the volume, both at the same moisture content. Because pulp and paper mills seldom process wood below the FSP, it is preferable to use the basic specific gravity when calculating amounts of wood material.

EXAMPLE 2

A sample of wet Douglas fir wood 2 cm thick, 5 cm wide, and 10 cm long weighs 90.21 g. It is then dried at 105°C to constant weight (to insure complete water removal) and reweighed after cooling in a desiccator. The ovendry weight is 44.37 g. What are the MC_{GR}, MC_{OD}, and basic specific gravity of the wood sample?

Solution

$$MC_{GR} = \frac{90.21\text{ g wet weight} - 44.37\text{ g ovendry weight}}{90.21\text{ g wet weight}} \times 100\% = 50.8\%$$

$$MC_{OD} = \frac{90.21\text{ g wet weight} - 44.37\text{ g ovendry weight}}{44.37\text{ g ovendry weight}} \times 100\% = 103.3\%$$

$$\text{sp gr} = \frac{44.37\text{ g dry wood material}}{\dfrac{2\text{ cm} \times 5\text{ cm} \times 10\text{ cm}}{1\text{ g/cm}^3\text{(density of water)}}} = 0.444$$

Problem

A sample of wood with green dimensions of $3 \times 5 \times 10$ cm weighs 105 g green (wet) and 62 g when ovendry. Calculate:

1. Specific gravity
2. MC_{OD}
3. MC_{GR}
4. Ovendry weight in kg/m^3

Answers: 0.413; 69.4%; 41.0%; 413 kg/m^3

9.2 PULPWOOD MEASUREMENT

It is the responsibility of the woodyard operations to obtain a steady supply of suitable wood. Wood sources are as follows:

1. Roundwood (logs at least 4 in. diameter)
2. Chips
3. Slabs
4. Edgings
5. Sawdust and planar shavings

Measurements of wood can be based on weight (with moisture content correction to determine a reliable estimate of ovendry weight), by solid wood volume (for example, the cunit), by gross, stacked volume (for example, the cord), or as volume of chips (for example, the unit). Traditionally, a measure of the gross roundwood volume was used because barking and chipping were done at the mill.

The standard measure was the cord, a pile of wood with 4 ft long logs stacked 8 ft across and 4 ft high, or 128 ft^3 of stacked wood. The amount of solid wood in a cord must be determined by sampling the cord and measuring the solid wood, decayed wood, bark, and air contents.

The cunit is 100 ft^3 of solid wood material of pulp logs. Purchased wood chips are measured in *units* (200 ft^2 of chips) or *bone-dry units* (*BDU*, 2400 lb ovendry wood). The unit and BDU are the terms first used in the US West Coast where mills were first started using residual chips. One unit of Douglas fir chips is approximately the same as one BDU. (It takes about 6 kWh/t [0.33 hp-day/ton] dry wood basis to chip wood for pulping.) A reasonable approximation is that 1 ft^3 of wood will make about 2.6 ft^3 of chips. Thus, if one knows the basic specific gravity of the wood, one will have a reasonable figure for the density of the wood chips. Sections 2.4 and 2.5, Volume 1, describe units of wood measurement. Some conversion factors are listed in Table 2.2, Volume 1.

EXAMPLE 3

A mill produces 700 metric tons of wetwood chips at 50% moisture content (green basis) per day. How many railroad cars are needed to transport them?

Conversion factors: 1 kg wet chips = 0.5 kg dry chips
1 rail car holds 18 units.
1 unit = 200 ft^3
10 pounds dry chips = 1 ft^3
1 kg = 2.2 pounds
1 metric ton = 1000 kg
Others of your choosing.

Solution

$$700{,}000 \text{ kg wet chips} \times \frac{0.5 \text{ kg dry chips}}{1 \text{ kg wet chips}} \times \frac{2.2 \text{ lb}}{1 \text{ kg}} \times \frac{1 \text{ ft}^3}{10 \text{ lb dry chips}} \times \frac{1 \text{ unit}}{200 \text{ ft}^3} \times \frac{1 \text{ rail car}}{18 \text{ units}} = 21.4 \text{ rail cars}$$

Problem

A sawmill produces 87.3 BDU (1 bone-dry unit is 2400 pounds of ovendry wood equivalent) of chips per day with 50% moisture content (green basis). (The solid wood specific gravity is 0.44.)

The chip bulk density is 10 pounds dry wood per cubic foot. These rail cars have a rated capacity of 30 units (1 unit is 200 ft^3). How many rail cars are needed per day? (Give the final result to three significant digits.) Answer: 3.49 rail cars.

9.3 TENSILE STRENGTH AND BREAKING LENGTH OF MATERIALS

It is useful to have a short discussion on *force, weight*, and *mass*. *Mass* is a measure of the amount of material present in an object, that is, the quantity of matter. It is not influenced by gravitational fields, and an object's mass is constant either on the earth's surface or in outer space. *Force* is that which changes the motion (i.e., the momentum) of an object. (*Pressure* or *stress is force per unit area*.) A force may act on a body without changes in motion if an equal force in the opposite direction is also acting. For example, we feel the force of gravity against the ground, but the ground exerts an equal force on us in the opposite direction of gravity to keep us stationary. If one walks off a cliff, the force of gravity continues to act, but the force of the ground in the opposite direction is no longer there, and one begins to accelerate at the rate of 9.81 m/s^2 (32 ft/s^2). (This means after 1 s the velocity is 32 ft/s, after 2 s 64 ft/s, after 3 s 96 ft/s, etc. Because air is a viscous fluid, it exerts force on a moving object, and when a person in free fall reaches a speed of about 180 ft/s [120 miles per h], the air resistance force is equal to the force of gravity, and then one stops accelerating. This is known as *terminal velocity*. The terminal velocity of an object depends on its mass, shape, and surface area; the terminal velocity of a feather of low mass and high surface area might be substantially less than 1 ft/s.)

Weight is the measure of the force a gravitational field exerts on an object. The relationship is: weight = m-g; that is, weight equals mass times acceleration of gravity. The units of mass are kg (or g) and slug, and the units of weight are newton and pound for the metric and English systems, respectively. In practice, weight always refers to the force exerted by gravity at the earth's surface.

Let us examine how these terms are used (and often misused) in speaking. An 80-kg person at the surface of the earth will be 80 kg on the surface of the moon (whose gravitational pull is 1/6th of that on the earth's surface). Because 1 kg = 2.2 lb (at the earth's surface), this person weighs 176 pounds on the earth. But this person weighs 176/6 or 29.3 pounds on the surface of the moon. Pounds are a unit of weight, and kilograms are a unit of mass, and they are not comparable. People get around this by defining the $pound_{force}$ (lb_f) and the $kilogram_{force}$(kg_f). Thus, an object that weighs 2.2 lb is the same as the force exerted by gravity at the earth's surface on a 1-kg object or 1 kg_f ($1\ kg_f = mg = 1\ kg \times 9.81\ m/s^2 = 9.81\ N$). Unfortunately, when the kg is used as a force the subscript is usually omitted. It is vastly preferable to use the units of N rather than kg_f; one reason is that one must be very careful when using dimensional analysis with kg_f.

When materials are subjected to tensile forces, they behave in the manner as shown in Fig. 9.4; that is, they undergo changes in dimensions called deformation or strain. The exact shape of

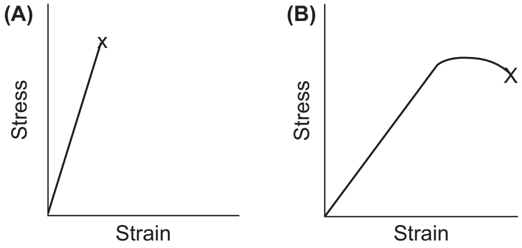


FIGURE 9.4 Stress strain diagrams of (A) a brittle, nonductile material such as glass or cast iron and (B) a ductile material such as aluminum or paper.

the curve depends on whether the material is brittle or ductile. Of course, any type of force causes deformations; however, we will consider only tensile forces here. *Strain* is defined as the deformation per unit (original) length. For example, a 10-cm-long rod that stretches 0.1 cm under a tensile load would have a deformation of 0.1 cm/10 cm = 0.01 = 1%; notice that strain is unitless. *Stress* is force per unit area. *Strength* is a measure of the stress that causes failure. The energy absorbed in the process (*toughness*) is the integral of force times distance and, therefore, is the area under the curve. Brittle materials such as glass can withstand high forces but fail with low strain; therefore, brittle materials are *strong* but not *tough*.

The *breaking length*, L, is a measure of tensile strength by calculating the length of a piece of material such that it breaks under its own weight. The breaking length evens out the differences in density and geometry so that comparisons are made on a "pound-for-pound" basis. This is particularly useful in the paper industry because tensile strengths are usually reported in units of force per width of paper. To calculate the breaking length, we need to know the specific gravity of a material and the tensile strength in units of force/area.

In the metric system the tensile strength is often given in units of N/cm^2 or MPa = 10^6 Pa = 10^6 N/m^2 = 100 N/cm^2. Let us work out the conversion of N/cm^2 tensile strength into breaking length. First, calculate the force exerted by a column of the material 1 km high per square centimeter, which is stress/km/cm^2, which we will designate as x.

$$x = \text{sp gr} \times \frac{1\text{ g}}{1\text{ cm}^3} \times \frac{1\text{ kg}}{1000\text{ g}} \times \frac{10^5\text{cm}}{1\text{ km}} \times \frac{9.81\text{ N}}{1\text{ kg}}$$

$$x = \text{sp gr} \times 981\text{ N}\cdot\text{cm}^{-2}\cdot\text{km}^{-1} \tag{9.5}$$

The breaking length in kilometers, L_{km}, is determined by dividing the tensile strength by stress per kilometer of material (with both stresses in identical units). This is done in the following equation:

$$L_{\text{km}} = \frac{\text{tensile strength in N}\cdot\text{cm}^{-2}}{\text{sp gr} \times 981\text{ N}\cdot\text{cm}^{-2}\cdot\text{km}^{-1}} \tag{9.6}$$

If the tensile strength is reported in Pa, then making the substitution of 9.81 MPa/km for 981 N$-$cm$^2-$km^{-1} in the previous equation gives the following equation for breaking length:

$$L_{\text{km}} = \frac{\text{tensile strength in MPa}}{\text{sp gr} \times 9.81\text{ MPa}\cdot\text{km}^{-1}} \tag{9.7}$$

The tensile strength of wood and many other materials is often reported in units of lb/in.^{2} (psi). The following equation can be used to determine the breaking length in kilometers.

$$L_{\text{km}} = \frac{\text{tensile strength in psi}}{\text{sp gr} \times 1422\text{ psi}\cdot\text{km}^{-1}} \tag{9.8}$$

By using the conversion factors given in the three previous equations, we can compare the breaking length of a variety of materials. Table 9.1 is a comparison of many materials to give an overall picture of the strength of available materials. Specific gravity and tensile strength values of small, knot-free, wood samples at 12% MC_{OD} were obtained from the *Wood Handbook*. See Section 2.7, Volume 1, for the maximum theoretical tensile strength of cellulose fibers, which is about 100 km. Table 9.1 shows that the tensile strength of pulp fibers is quite high in comparison with many materials.

EXAMPLE 4

The tensile strength of black willow is about 15,800 psi parallel to the grain. It has a specific gravity of 0.41. What is its breaking length?

Solution

Using Eq. (9.8) the solution is

$$L = \frac{15{,}800\text{ psi}}{0.41 \times 1422\text{ psi}\cdot\text{km}^{-1}} = 27.1\text{ km}$$

TABLE 9.1 The Breaking Lengths of Various Materials

Material	Tensile Strength (psi)	Specific Gravity	Breaking Length (km)
WOOD, PARALLEL TO WOOD GRAIN			
Black willow	15,800	0.41	27.1
Yellow poplar	22,400	0.46	34.2
Sweetgum	17,300	0.52	23.4
Overcup oak	14,700	0.63	16.4
Interior Douglas fir	18,900	0.48	27.7
Eastern white pine	11,300	0.35	22.7
Engelmann spruce	13,000	0.34	26.9
Western larch	19,400	0.55	24.8
WOOD, PERPENDICULAR TO GRAIN			
Yellow poplar	540	0.42	0.9
Sweetgum	760	0.52	1.0
Interior Douglas fir	390	0.48	0.6
Engelmann spruce	350	0.35	0.7
PAPER, ETC.			
Newsprint			2—5
Bleached softwood			8—10
Cellophane	21,000 maximum	1.50	9.85
OTHER MATERIALS			
Aluminum	13,000	2.7	3.4
Aluminum alloy, aircraft	75,000	2.7+	19.5
$A1_2O_3$, ceramic	50,000	3.8	8.4
Acrylics, plexiglas	10,000 maximum	1.2	5.9
Epoxy	10,000 typical	1.2	5.9
E-glass	500,000	2.4	160
Graphite fiber	100,000	1.9	37.0
Nylon, monofilament	50,000	1.15	30.6
Phenol formaldehyde	6000	1.27	3.3
Steel (0.15% C)	50,000	7.85	4.5
Wood fiber	210,000 maximum	1.50	100

9.4 PAPER PROPERTIES

Table 9.2 shows some properties of paper samples tested by Oregon State University (OSU) students in a 1976 laboratory exercise. These results can be used for comparison between grades of paper. They also supply data for example exercises. Table 16.8 (Chapter 16, Vol. 2) gives some conversion factors of paper properties from English to metric units. Definitions of some paper properties are given in Chapter 2, Volume 2.

EXAMPLE 5

The breaking length of the filter paper listed in Table 9.2 in the machine direction is given as 2.60 km. What was the original force in pounds to break a 15-mm-wide specimen?

Solution

Using Eq. (9.8) and a specific gravity of 0.47 for this paper, one obtains a tensile strength of 1737 psi. The width of the paper is 15 mm or 0.591 in. The caliper of the paper is determined by the relationship: density = mass/volume. For 1 m^2 of paper, the mass is the basis weight (in g/m^2) and the volume (in cm^3) = $(100\ cm)^2 \times$ caliper (cm). Therefore,

$$\begin{aligned} 0.47\ g/cm^3 &= 84\ g/(10{,}000\ cm^2 \times \text{caliper}) \\ \text{caliper} &= 0.0178\ cm \\ &= 0.178\ mm \\ &= 0.00704\ in. \end{aligned}$$

So, $1737\ psi \times 0.591 \times 0.00704\ in.$

$= 7.22\ lb.$

EXAMPLE 6

The burst index is given in Table 9.2 for kraft bag as $3.0\ kPa\ m^2\ g^{-1}$. What is the burst strength in psi?

Solution

The burst index is obtained by dividing the burst strength by the basis weight. To solve for the burst strength, it is necessary to take the burst index and multiply by the basis weight. The burst strength obtained by this method is in kPa. It is necessary to convert kPa to psi to obtain the desired units. The conversion factor is available in Table 6.8 under flat crush. Although a flat crush was not performed here, the conversion factor from kPa to psi is always the same. Therefore,

$$3\ kPa \cdot m^2 \cdot g^{-1} \times 65 g \cdot m^{-2} = 195\ kPa;$$

$$195\ kPa \times \frac{1\ psi}{6.895\ kPa} = 28\ psi$$

This exercise shows that, to convert tensile or burst indexes to tensile or burst strength, the basis weight must be known. It is possible to convert a tensile or burst index back and forth from the English to the metric system without knowing the basis weight.

EXERCISES

Wood

1. A sawmill is *nominally* rated at 150,000 board feet (a board foot is 1/12 of a ft^3) of 2 × 4 in. lumber per day. The *actual* dimensions of a *two by four* are 1.5 × 3.5 in. (The actual board feet production is only 65.6% of 150,000; why?) Douglas fir wood is used with a specific gravity of 0.44 and a moisture content of 120% on an ovendry basis. One uses log volume tables to learn that typically (at this mill) for every 100 lb of solid wood coming in, 50 lb come out as lumber, 33.3 lb come out in the form of chips, and 16.7 lb come out in the form of sawdust. Chips have a bulk density of 10 lb/ft^3 (ovendry wood material), and sawdust 8 lb/ft^3. Rail cars have a rated

TABLE 9.2 Results of OSU Student Testing of Laboratory Samples From 1976

Paper Sample	Basis Weight (g/m$^{2)}$	Density (g/m^3)	Tensile Strength (Breaking Length, km)		Tear Strength (mN·m^2·g^{-1})		MIT Fold (Double Folds)		Burst Index (kPa·m^2·g^{-1})	Gurley Porosity s/(100 cm^2)	Cobb Size (g/m^2)	Elrepho Brightness	Printing Opacity
			MD	CD	MD	CD	MD	CD					
Onionskin, yellow	47	0.63	4.56	1.90	4.4	6.6	21	4	1.4	44	10	32	95
Cascade duplicator	76	0.79	4.60	2.80	6.4	6.9	28	12	1.5	25	50	81	92
Filter paper	84	0.47	2.60	1.70	7.8	7.5	7	4	0.9	9	-	76	81
Vellum tracing	70	0.96	11.40	5.40	6.9	7.3	740	740	5.0	∞	20	82	57
Pamphlet cover	103	0.58	6.50	3.30	8.8	9.8	58	34	2.6	12	34	36	100
Lightweight letterhead	36	0.65	7.03	4.73	20.3	22.0	454	529	3.0	1150	54	84	66
Kraft wrapping postal	63	0.55	8.21	4.50	10.5	14.0	322	228	3.5	6	27	20	99
Straw corrugating medium	126	0.51	5.20	3.30	8.0	8.2	4	8	1.7	60	38	25	99
Black lifeproof	103	0.47	5.05	2.43	5.6	3.1	5	3	0.8	22	-	5	99
Yellow duplicating	75	0.84	8.45	3.46	6.3	7.5	158	59	2.9	36	17	28	91
Recorder paper	46	0.82	8.49	5.32	5.3	5.2	514	437	4.1	315	17	70	75
Letterhead	76	0.68	6.97	4.03	3.1	3.5	150	99	3.2	52	17	88	87
Manila envelope	105	0.69	6.20	4.00	12.1	13.0	450	211	3.3	15	29	37	92
Summit bond	75	0.67	5.10	3.10	8.4	6.1	29	25	1.3	16	28	78	91
Newsprint	58	0.68	4.00	3.20	6.3	7.4	21	5	1.2	74	76	54	95
Kraft bag	65	0.44	6.90	3.00	13.8	17.4	350	100	3.0	11	30	19	99
Notepad	58	0.72	7.20	2.90	8.2	10.5	25	9	2.1	8	36	78	82
Action paper	45	0.44	5.90	2.20	6.7	8.4	41	36	1.4	44	35	35	77
Strathmore report cover	181	0.73	5.90	3.00	10.8	12.2	129	77	2.4	235	45	9	100
Straw bond	71	0.76	8.10	2.90	10.0	13.6	146	67	2.9	368	35	82	83
Index card	180	0.80	5.50	3.20	6.9	6.0	14	15	2.3	77	21	77	99
Green notepad	72	0.66	5.00	3.20	6.4	6.1	34	27	1.9	19	25	51	97
Gibraltar onionskin	32	0.48	8.00	3.20	6.9	9.1	730	120	3.0	185	10	78	60
Simpson vellum	104	0.57	5.10	1.20	9.7	12.7	4	4	1.0	17	23	71	99
Fore duplicator	72	0.85	7.10	3.70	5.7	6.5	145	103	2.5	27	21	47	96

MD - Machine direction; CD - Cross direction capacity of 18 units (3600 ft^3). Chips are worth $160 per BDU, and sawdust $60 per BDU. Calculate the following:

Lumber	Volume ____ft^3; wet weight _____tons; dry weight _____tons.
Chips	Ovendry (OD) weight _____tons; _____BDU; green weight ______tons. Number of rail cars needed ______; chips per car _____tons.
Sawdust	OD weight _____tons; ______BDU.
Revenue to mill	$_____ for chips; $_______ for sawdust; $ _______total.

2. Given: a piece of wood with a specific gravity of 0.42 and a moisture content (MC_{GR}) of 45%. Calculate the following on a green volume basis:

	kg/m^3	**lb/ft^3**
Ovendry weight	_____	______
Green (wet) weight	_____	______
Weight of water contained	_____	_____

3. Douglas fir wood with a basic specific gravity of 0.45 is converted into chips that have a bulk density of 10 lb/ft^3 (ovendry weight of chips). Assume the moisture content on a green basis is 45%. Calculate:

Volume of chips from 1 ft^3 of solid wood	_____ft^3
Volume of chips from 1 m^3 of solid wood	_____m^3
Ovendry weight of wood from 1 ft^3 of solid wood	_____lb
Green weight of wood from 1 ft^3 of solid wood	_____lb
Ovendry weight of wood from 1 m^3 of solid wood	_____kg
Green weight of wood from 1 m^3 of solid wood	_____kg

Breaking Length

4. Show that 9.81 MPa/km is equal to 981 N cm^{-2} km^{-1}.

5. A plastic material has a tensile strength of 3000 psi and a density of 0.85. What is its breaking length? Is it intrinsically stronger than paper?

6. Calculate the breaking force (lb/15 mm) of the newsprint listed in Table 9.2.

Miscellaneous Paper Tests

7. Calculate the caliper of the kraft bag listed in Table 9.2.

CHAPTER

10

Nonwood Fiber Use in Pulp and Paper

10.1 INTRODUCTION

The pulp and paper industry is growing rapidly. Therefore there has been a huge demand for pulp and papermaking raw material. In the recent years, there has been an increase in the use of nonwood fibers being used as a raw material for this purpose. Some nonwood fibers are used for papermaking because of their fine papermaking qualities, but the majority of nonwood fibers is used to overcome the shortage of wood fibers The use of nonwood fibers is more widespread in countries with shortage of wood.

There are many problems with the use of nonwood fibers in pulp and paper industry. Right from supply of raw material to the properties of finished paper, the majority of nonwood raw material has proven to be economically inferior to wood. But during the last few years, the technological developments in almost all the fields of papermaking have made nonwood more competitive with wood as a raw material for papermaking.

Although till recently the use of nonwood fibers for pulp and papermaking was concentrated in countries with limited wood supply, it is now showing an increasing trend even in countries with adequate wood supply because of environmental considerations (Table 10.1). With time, this trend is expected to grow further, and the future of nonwood plant fibers as pulping and papermaking raw material looks bright.

The demand for nonwood plant fibers for papermaking is expected to increase in the highly industrialized nations of Europe and North America because of the environmental concerns such as depleting forest resources and disposal of agricultural residues. Europe has an additional problem with the shortage of short-fibered hardwood pulp, which can be replaced by some nonwood fibers. This will require knowledge of the processes and developments already in place in the countries already using these raw materials in the paper industry. Already, a number of nonwood fibers are commonly used in many countries for papermaking. Straws are by far the largest source of nonwood fibers followed by bagasse and bamboo. Generally, nonwood plant fiber pulps can be grouped into two categories:

- Common nonwoods or hardwood substitutes cereal straws, sugarcane bagasse, bamboo (shorter fiber species), reeds and grasses, esparto, kenaf (whole stalk or core fiber), corn stalks, sorghum stalks, etc.
- Specialty nonwoods or softwood substitutes cotton staple and linters; flax, hemp, and kenaf bast fibers; sisal; abaca; bamboo (longer fiber species); hesperaloe; etc.

As with wood, the chemical and physical properties are different within the two groups, depending on the nonwood fiber raw material. The current uses of nonwood pulps include

Biermann's Handbook of Pulp and Paper: Raw Material and Pulp Making
https://doi.org/10.1016/B978-0-12-814240-0.00010-0

TABLE 10.1 Users of Nonwood Fibers in Papermaking

- China
- India
- Pakistan
- Mexico
- Peru
- Indonesia
- Colombia
- Thailand
- Brazil
- Venezuela
- United States
- Greece
- Spain

TABLE 10.2 Papers Produced From Nonwood Pulps

- Printing and writing papers
- Linerboard
- Corrugating medium
- Newsprint
- Tissue
- Specialty papers

TABLE 10.3 Average Annual Yields of Different Papermaking Raw Materials

Plant	Pulp Yield (tons/year/ha)
Wheat straw	1.9
Rice straw	1.2
Bagasse	4.2
Bamboo	1.6
Kenaf	6.5
Hemp	6.7
Elephant grass	5.7
Canary grass	4.0
Scandinavian softwood	0.7
Fast-growing softwood	4.0
Temperate softwood	1.7
Fast-growing hardwood	7.4

Based on Pierce (1991).

virtually every grade of paper produced as listed in Table 10.2.

Table 10.3 shows average annual yields of different papermaking raw materials.

Typically, common nonwood pulps or hardwood substitutes are produced in integrated pulp and paper mills, and softwood kraft or sulfite pulp is added to provide the strength requirements to the paper. However, specialty nonwood pulp may be used instead of softwood kraft or sulfite pulp, thus producing a 100% nonwood paper. And, in some cases, wastepaper pulp may be blended in the furnish. The nonwood portion of the furnish typically varies from 20% to 90% and can be even up to 100%, depending on the paper grade and required quality. The possible combinations are endless and can be adjusted to meet market requirements. Furthermore, it is possible to add small quantities (up to 20%–30%) of common nonwood pulps to primarily wood pulp–based papers without impairing paper properties or paper machine runnability. This provides wood-based mills deficient in hardwood but located within a region with available nonwood fiber resources such as corn stalks or cereal straw with the option of adding on a nonwood pulping line to supplement their fiber requirements.

The specialty nonwoods have physical properties superior to softwoods and can be used in lower amounts in the furnish when used as a softwood substitute. Specialty papers such as currency, cigarette papers, tea bags, dielectric paper, etc. may be made from a furnish of 100% nonwood specialty pulps. Specialty pulps also may be used in combination with wood pulp to produce lightweight and ultralightweight printing and writing papers. Combinations of common and specialty nonwood pulps will allow the production of virtually any grade of paper to meet any quality requirements demanded in the global market. Adding possible combinations, which include wood pulp, nonwood pulp, and recycled wastepaper pulp, increases the possibilities for developing paper with specific sheet properties designed to meet specific customers' requirements.

Tables 10.4–10.6 lists the physical and chemical properties of some nonwoods in comparison with those of woods. The dimensions of nonwood fibers are between those of hardwoods and softwoods. The cellulose content of most of nonwoods listed in Table 10.4 is comparable with that of woods commonly used for papermaking, whereas the lignin content is much lower than that of woods. Hence, the delignification of nonwoods is relatively easy and consumes less chemicals.

Taxonomy

All seed plants (members of the phylum Spermatophyta) are divided into two subphyla: Gymnospermae (gymnosperms, those with naked seeds) and Angiospermae (angiosperms, those with seeds enclosed within the ovary of the flower).

Angiospermae are arranged into two groups: the *monocots* (*monocotyledons*) and *dicots* (*dicotyledons*). Monocotyledoneae have one leaf in the seed (a seed leaf is a cotyledon; a peanut consists of two cotyledons with a small embryo in the middle, so peanuts are dicots) and include mostly herbaceous plants such as grasses, palms, lilies, and corn. A few plants with a wood-like stem, such as bamboo that are used in pulp and paper, are members of this class.

TABLE 10.4 Comparison of Fiber Properties of Nonwood Fibers With Those of Woody Raw Materials

	Kenaf	Straw	Bagasse	Bamboo	Eucalyptus	Birch	Spruce
Fiber length (mm)	1.3[a]	1.3	1.7	2.3	1.0	1.9	3.6
Fiber width (μm)	27[a]	12.9	20	14.4	18	25	35

[a] *Dimensions for whole stem kenaf from bast and core in the ratio of 35% and 65%, respectively.*
Based on Ashori (2007).

TABLE 10.5 Comparison of Chemical Properties* of Nonwood Fibers With Those of Woody Raw Materials

	Kenaf	Straw	Bagasse	Bamboo	Eucalyptus	Birch	Spruce
Holocellulose (%)	76.5	78.1	77.8	76.6[a]	74[a]	81[a]	71[a]
Hemicellulose (%)	32.6	24.1	27.9	19.5[a]	18[a]	40[a]	27[a]
Lignin (%)	16.2	18.4	20.8	23.4[a]	26[a]	19[a]	29[a]

* *Expressed on dry matter.*
[a] *Extractive free basis.*
Based on Ashori (2007).

TABLE 10.6 Chemical Composition (%) of Cereal Straws

	Rice	Barley	Wheat	Rye	Oat
EXTRACTIVES					
EtOH–benzene	4.6	4.7	3.7	3.2	4.4
Cold water	10.6	16.0	5.8	8.4	13.2
Hot water	13.3	16.1	7.4	9.4	15.3
1% NaOH	49.1	47.0	41.0	37.4	41.8
Lignin	11.9	14.5	16.7	19.0	17.5
Pentosans	24.5	24.7	28.2	30.5	27.1
α-Cellulose	36.2	33.8	39.9	37.4	39.4
Ash	16.1	6.4	6.6	4.3	7.2
Nitrogen	0.6	1.1	0.4	0.7	0.5

After Aronovsky (1943).

Dicotyledoneae have two leaves in the seed and include kenaf, hemp, flax, and the hardwoods. The numerous Dicotyledoneae are further divided into subclasses, orders, suborder, families, and some subfamilies.

Monocots have parallel veins in their leaves, and dicots have branching veins in the leaves.

Anatomy

The primary vascular tissue (xylem and phloem) exists in small bundles (Fig. 10.1). The phloem consists of fibers, sieve tube elements, companion cells, and parenchyma. In monocots these bundles are scattered in the stem throughout the ground tissue, whereas in dicots the bundles are all about the same distance from the center and form a ring of bundles around the pith. In dicots, the bundles unite as the stem grows outward; in many species the bundles are no longer distinct (Fig. 10.2). The scattering of the xylem remains in those monocots that undergo secondary growth.

The outer layer of cells is the epidermis. The layer just inside the epidermis is the cortex. The layer inside the cortex but outside the vascular tissue is the pericycle. Epidermal cells have sinuous or toothed margins and may have

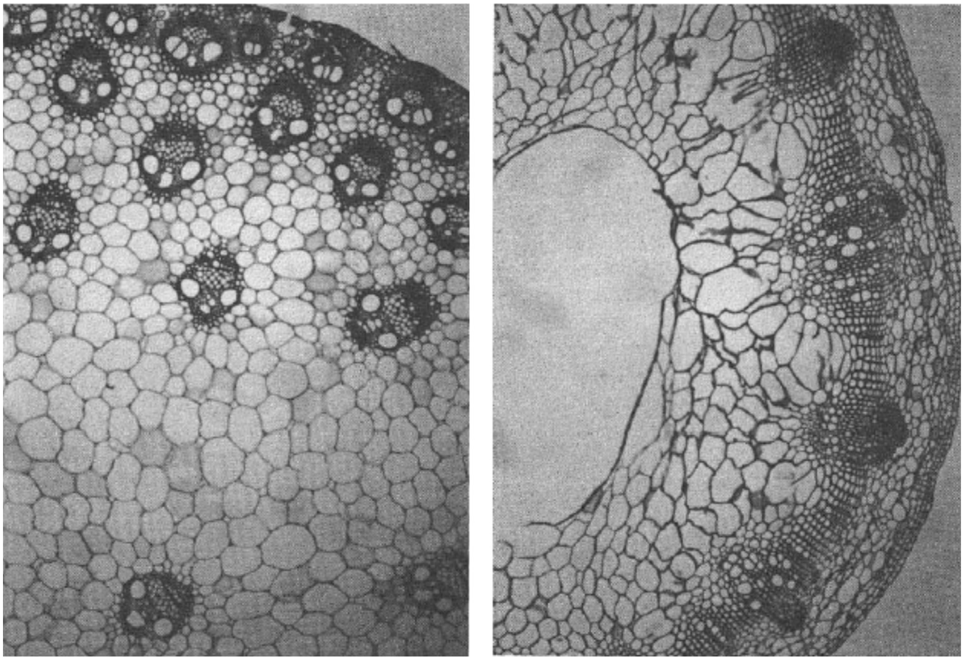


FIGURE 10.1 Portions of a typical monocot stem (left) and herbaceous dicot stem (right) (50×).

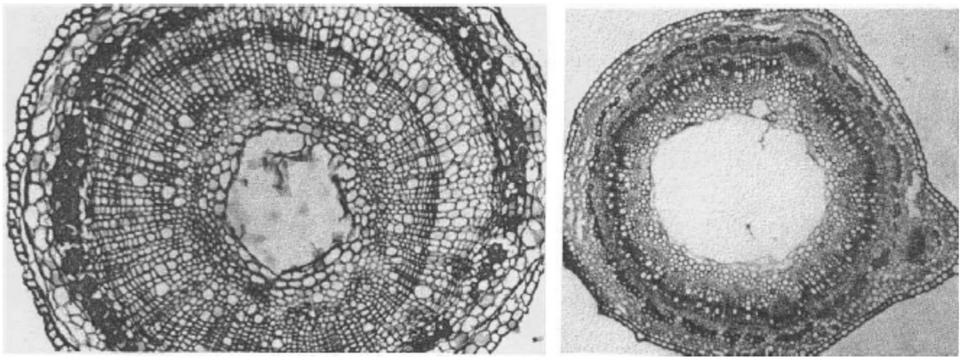


FIGURE 10.2 Stem cross sections of *Cannabis* (left, 100×) and *Linum* (right, 40×)

projections (in cells called trichomes) that are helpful in identification of samples.

Useful Fibers

Useful fiber (that provides the strength for paper made from the pulp) is derived from the vascular tissue of monocots of barley, *Hordeum* spp.; rice, *Oryza* spp.; esparto, *Stipa tenacissima*; wheat, *Triticum* spp.; bamboo, *Phyllostachys* (Fig. 10.3); sugarcane, *Saccharum officinarum*; and others.

Bast fibers from the phloem of dicots are derived from hemp, *Cannabis sativa*; kenaf, *Hibiscus cannabinus*; flax, *Linum usitatissimum* (Fig. 10.3); and others. Fibers may be obtained

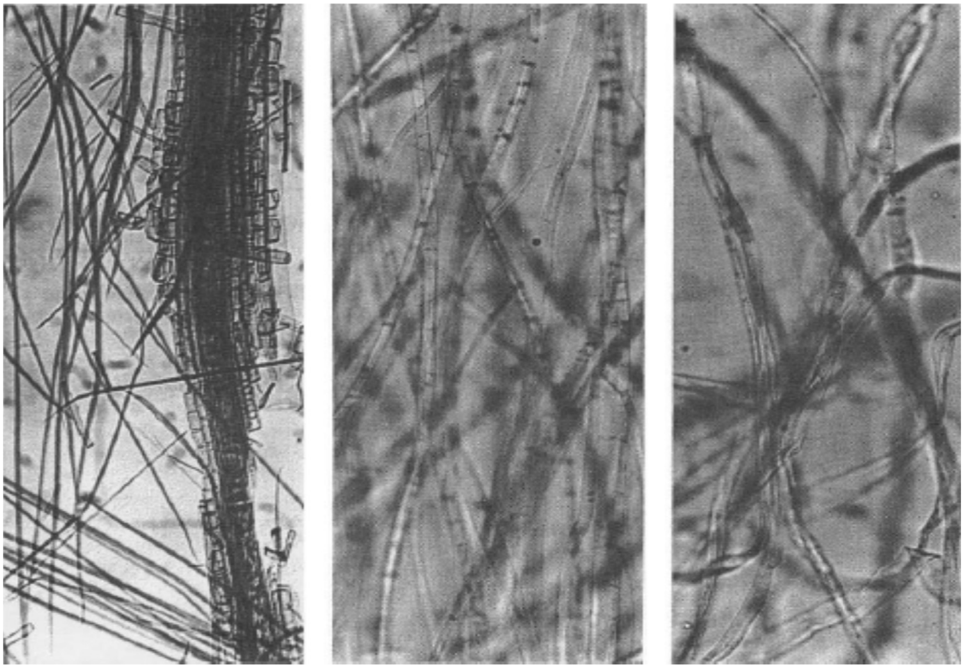


FIGURE 10.3 Fibers of bamboo (left, with parenchyma, 60×), linen (center, 150×), and cotton seed hairs (right, 150×).

from the pericycle or cortex of some dicots. Cotton is the seed hair of the cotton plant (Fig. 10.3). Fiber from the vascular tissue of leafs is obtained from sisal (*Agave sisalana*) and manila hemp (*Musa textilis*).

Nonwood Fiber Identification

A variety of nonwood fibers can be identified by a series of specialized stains. For example, several are available for hemp and flax. Acidified potassium dichromate swells flax somewhat faster than hemp. Cyanine stains these materials differently. Other separations exist for cotton, linen, and wood; cotton, flax, jute, and hemp; animal and plant fibers; etc. (Standard T 401 and others).

Straw Morphology Considerations

Fig. 10.4 shows a cross section of the straw stem. The usable fibers are the dark fibers near the edge of the stem, consisting of phloem and other tissues.

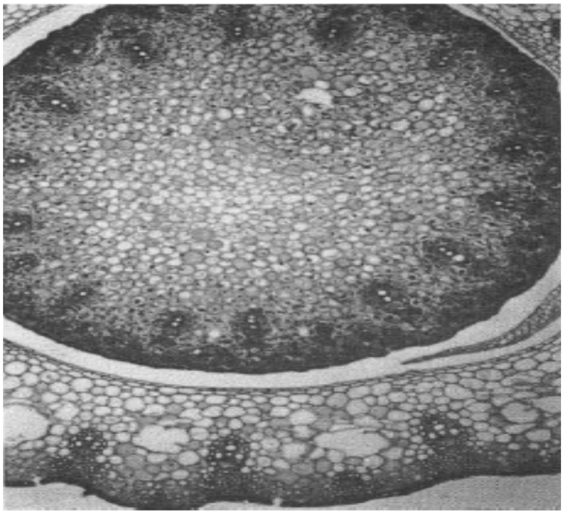


FIGURE 10.4 Stem cross section of wheat (with part of a leaf) (50×).

According to Huamin (1988), parenchyma cells occupy 38% of wheat straw based on the cross-sectional area of the stem, so the mass percentage may be lower. These cells are small and thin walled, contribute to decreased pulp freeness, and do not add much to the strength of paper. They cook more slowly than the fiber cells and use more cooking chemicals. The lignin, cellulose, and xylan composition of the various cell types is very similar.

Petersen (1991) found that the α-cellulose content of the internode of straw of four grains to be 37%–42%, whereas the leaves had only 28%–30% α-cellulose. The fibers are about 15%–20% longer in the nodes compared with the leaves. The author suggests that whole straw should not be pulped anymore than one would pulp trees with leaves and all. The internode is 35% of orchard grass (including the inflorescence) and 43%–48% of many other grasses.

Depithing

Bagasse, and some other nonwood fibers, must be depithed before use. The pith contains small cells (parenchyma) that do not add to the pulp strength and reduce the freeness considerably.

10.2 PULPING METHODS FOR NONWOOD FIBERS

Introduction

Annual plants have been used since the early 1800s, except for cotton, which has been used much longer, of course. Straw has traditionally been pulped by boiling solutions of lime for board grades of paper; this led to a bright yellow pulp. Sodium hydroxide was used to make bleachable grades of pulp and board grades. The soda anthraquinone (AQ) method is replacing the soda method, and the results of the soda/AQ for straw are said to be similar to those for kraft pulping of straw. Other methods of pulping include neutral sulfite and chlorine systems. In general, pulping of nonwood plants is cheaper than that of wood. They are low in lignin, and thus, do not require as much chemical. However, the cost advantage achieved in pulping and bleaching is offset in washing, papermaking, and chemical recovery. In washing, because black liquor is highly viscous, larger washing equipment is required for nonwood fiber. Moreover, because of its high viscosity, to achieve a fair amount of washing, a lot of water is required, thus, reducing the solid content of the black liquor and increasing the load on the evaporators.

Alkali, Chlorine

The Pomilio process (Stephenson, 1951) was the most popular method at one time, being used in 20 mills. Developed around 1925, this process involved treating pulp with 8% NaOH (on dry pulp) in 60 ft cylindrical reaction towers where temperatures up to 130°C could be reached at the bottom. The digestion time was about 90 min. A chlorination step follows. The overall yield is 36%–40%. The high use of chlorine and cellulose hydrolysis makes this method obsolete.

Sulfite

Stephenson (1951) discussed a neutral sulfite (NSSC) method that enjoyed a lot of use in Europe. Sodium sulfite (10%) and 5% NaOH on pulp are combined with straw for a 6-h cook at 160°C. The pulp yield is about 55%. Hypochlorite (5% on pulp) bleaching reduces the yield to 42%. Aronovsky (1948) suggested an NSSC process for pulping wheat straw. This process uses 8% sodium sulfite and 2%–3% sodium carbonate (on dry straw), with a liquor to straw ratio of 7:1 and a cooking time of 2 h at 170°C. The pulp yield is 52%–55% and can be brightened to 70% with 5%–7% total chlorine. Bleaching above this brightness requires a three-stage process. The freeness was said to be 400–500 mL.

Aronovsky (1949) found that the neutral sulfite process was unsuitable at atmospheric pressure, in agreement with other unpublished results, but atmospheric pulping for 1 h with 12% kraft chemicals in a hydrapuler at 90–98°C was very effective. In other work (1947), he also suggested 2% lime and 2% sodium sulfite to give an exceptionally free pulp, although it would seem that calcium sulfite might precipitate. Acid sulfite methods of pulping straw give poor results because of the relatively labile carbohydrates of straw. Relatively weak and brittle pulps result, and the process is unsuitable for materials with high silica contents.

Soda

England used the soda process to make much of its straw pulp at one time. In 1945, the United Kingdom pulped nearly 350,000 tons of straw for paper (FAO, 1952). Esparto uses less alkali and gives a higher yield than the cereal straws. Typically, esparto straw was pulped with 12% NaOH (on straw) for 5 h at 160°C. Hypochlorite bleaching gave a yield of 36%–40%. Anon. (1948) discussed the French process developed by Huguenot for pulping straw. The continuous process involves pulping chopped straw with NaOH at 90–100°C for 30–50 min. The pulp then goes to a digester pulper at 80°C, where it is agitated for 4–7 h. This process is also said to be suitable for wastepaper. More information on soda pulping on nonwood plants is found in Chapter 2, Volume 1.

Alkali–Oxygen Pulping, NACO Process

Ceragioli (1975) describes alkali–oxygen pulping of straw. The author claims that sodium carbonate does not reduce the strength of pulp as does sodium hydroxide in the presence of oxygen. With carbonate, magnesium addition to protect carbohydrates from degradation appears to be unnecessary. A sodium carbonate—based pulping system has a simplified chemical recovery system. The NACO process (US patent 4,612,088 issued in 1986) uses oxygen and alkali (sodium carbonate and some sodium hydroxide) to pulp nonwood fibers (and upgrade secondary fiber) on a relatively small scale (Anon., 1984). A continuous, pressurized reactor (Turbo-Pulper) was developed as part of the process. The process has been used commercially since 1986 in Italy at a mill for about 100 ton per day (IPZP Foggia) for nonwood pulp and 50 tons per day for upgrading old corrugated container (OCC). Unbleached straw pulp has a brightness of 50%—52% ISO and kappa number of 15%—16% with a yield of 48%. The brightness can be increased to 72% with one hypochlorite (H) stage or 82% with two H stages (6%—7% as active chlorine). Ozone bleaching gives a brightness of 75%—78%. Pulping is carried out at 7%—8% consistency, 90 psig, and 130—135°C for a minimum of 1 h.

Organosolv Pulping of Nonwood

The Organosolv process has certain advantages. It makes possible the breaking up of the lignocellulosic biomass to obtain cellulosic fibers for pulp and papermaking, high-quality hemicelluloses, and lignin degradation products from generated black liquors, thus avoiding emission and effluents The Organosolv processes use either low-boiling solvents (for example, methanol, ethanol, acetone), which can be easily recovered by distillation, or high-boiling solvents (for example, ethyleneglycol, ethanolamine), which can be used at a low pressure and hence at available facilities currently used in classical pulping processes. Thus, it is possible to use the equipment used in the classic processes, for example, the soda and kraft processes, hence saving capital costs. Using this process, pulps with properties such as high yield, low residual lignin content, high brightness, and good strength can be produced. Moreover, valuable by-products include hemicelluloses and sulfur-free lignin fragments. These are useful for the production of lignin-based adhesives and other products because of their high purity, low molecular weight, and easily recoverable organic reagents. In recent years, research into the Organosolv pulping processes has led to the development of several Organosolv methods capable of producing pulp with properties near those of kraft pulp. Prominent among the processes that use alcohols for pulping are those of Kleinert. Other processes based on other chemicals also worthy of special note are ester pulping, phenol pulping, Acetocell, Milox, Formacell, and NAEM. Organosolv pulping processes, by replacing much or all of the water with an organic solvent, delignify by chemical breakdown of the lignin before dissolving it. The cleavage of ether linkages is primarily responsible for lignin breakdown in Organosolv pulping. The chemical processing in Organosolv pulping is fairly well understood. High cooking temperatures and thus high pressures are needed when alcohols are used in cooking. However, organic acids require lower temperatures, and the pressure is closer to atmospheric pressure. The ethanol Organosolv process was originally designed to produce clean pulping and was further developed into the Alcell process for pulp production. The Alcell process is a solvent-pulping process that employs a mixture of water and ethanol (C_2H_5OH) as the cooking medium. The process can be viewed as three separate operations: extraction of lignin to produce pulp; lignin and liquor recovery; and by-product recovery. The raw materials are cooked in a 50:50 mixture of water and ethanol at around 175—195°C for 1 h. The typical liquid to biomass solid ratio is 4—7 and a liquor pH of about 2—3. The system employs liquor-displacement washing at the end of the cooking to separate the extracted lignin. The sulfur-free lignin produced with this process has very high purity and has the potential of high-value applications. Furthermore, this process generates the furfural, which is used as the solvent for lubricating oil production. It is claimed that the process produces pulps with a higher yield, which bleach more easily and are free of sulfur emissions. The Alcell process enjoys a significant capital cost advantage compared with the kraft process because it does not require a recovery furnace or other traditional chemical recovery equipment (such as lime kilns and causticizers).

In general, pulping of nonwoods is easier compared with woods. Nonwoods have a low lignin content and therefore require less chemicals during cooking, where the raw material is chemically treated under high temperature and pressure to separate the lignin from the fibers. Although kraft or sulfate is the preferred pulping procedure for wood, nonwoods are generally cooked by soda and sulfite, as well as sulfate processes. In China, sulfite is the preferred mode of pulping.

One of the biggest developments in the pulping of bagasse and straw was the rapid-cooking, horizontal-tube, continuous digester invented in the mid-1950s. Until this invention, rotating and tumbling digesters were running at 4–6 h cycles. These were batch digesters that could cook a certain amount at a time. The continuous digester was able to cook bagasse and straw in less than 10 min. In this kind of digester, raw material was added at the top, and cooking liquor was introduced at the bottom continuously. Cooked pulp was obtained at the bottom, whereas spent liquor came out at the top. The first commercial rapid-cooking, horizontal-tube, continuous digester was installed in Cuba in 1959. Since then there has been a shift away from batch digesters in bagasse pulping. This shift greatly accelerated the growth of bagasse pulping (MacLeod, 1988).

High-energy costs and inferior pulp quality, in general, renders the mechanical pulping of jute less attractive in spite of the obvious advantages of higher yields and less pollution. A study on biomechanical pulping of jute demonstrates the advantages of biological pretreatment before refining (Sabharwal, 1995). Because of the coarseness and stiffness of the fiber bundles, processing of kenaf remains a problem (Tao et al., 1995). Similarly, nodes of bamboo are harder to cook because they are highly lignified. Significant research with these fiber sources is required before they are used efficiently.

Most nonwood plants are high in silica content. This high content of silica causes many problems. Washing is difficult because of poor drainage of pulp and high viscosity of black liquor. Washers twice the normal size are required for washing these pulps. One development in this regard has been the lime–alkali–oxygen pulping process. In the alkali–oxygen process used for straw, adding lime solves the silica problems. When lime is added to the cooking liquor, silica reacts to form calcium silicate, which is insoluble in water. The silica thus remains in the pulp, which is an advantage during the peroxide bleaching stage (Yilmaz, 1995 a,b). Another problem suffered by nonwood plant pulping has been low yield. Studies on AQ pulping have been quite promising in this regard. AQ pulping improves yield by up to 5% and kappa number by up to 5% (Hart et al., 1994).

Some nonwood plant materials contain a significant content of pith. For example, approximately 33%–35% of the ovendry weight of sugarcane bagasse is pith, whereas corn stalks have a pith content of approximately 21%. Pith, found in the center of the plant stalks, consists of only small amounts of usable papermaking fiber. Most of its mass consists of parenchyma cells, used by the plant for storage of water and food. These thin-walled cells offer little resistance to chemical penetration, relative to the other parts of the plant, so they preferentially absorb pulping chemicals and are completely dissolved; the result is high chemical consumption and low yields. In addition, the fine nature of residual pith after pulping significantly reduces the drainage rate of the resulting pulps, making washing and dewatering difficult. Finally, it has been noted that pith cells, if left in the final pulp, can result in reduced sheet opacity. Given these difficulties, it has long been accepted that a pulping facility using nonwoods with a high pith content must have a fiber preparation section featuring wet or dry depithing. Indeed, a large amount of the literature on bagasse pulping has been dedicated to the design and operation of depithing processes. This depithing requirement can be detrimental to the success of a modern nonwood facility.

For some time, research at North Carolina (NC) State has been focused on finding simpler, less costly processes to produce bleached pulp and paper from nonwood raw materials. Much of the initial efforts were focused on corn stalks because of the abundance of these residues in North America. Part of the research on corn stalks involved removing the need for mechanical depithing before pulping. The end result was the development of a new, simplified pulping and bleaching process—EAZP. The EAZP process was developed as a unique, highly simplified pulping and bleaching process for nonwoods, and it was awarded a patent in 2001. The process is based on two shortcomings identified in traditional approaches to nonwood pulping. Traditional pulping methods tend to be too severe, using high alkali charges and high temperatures. Such conditions are often not warranted, given the low lignin contents and low level of lignin condensation in many nonwoods. The result, in many cases, is actually higher kappa numbers, lower brightness levels, and poor bleachability. Traditional methods do nothing to passivate or chemically remove pith, making mechanical depithing necessary. The process, carried out on raw materials that have not been depithed, involves a mild delignification step, followed by acid chelation, ozonation, and a final pressurized peroxide treatment (other bleaching stages may be substituted for the latter). The acid and ozonation steps may been combined, resulting (for corn stalks) in a three-stage process that converts raw materials into papermaking pulps with a brightness of 85% ISO or greater.

Taizen Co., Ltd. has succeeded in developing nonwood fiber pulping technology that enables the production of high-quality chemimechanical pulp with minimum environmental impact at low cost. This patented technology has been tested on various nonwood fibers, including rice straw, wheat straw, kenaf, bagasse, oil palm fiber, bamboo, pineapple fiber, etc. The Taizen system has been proven to work for pulping of all the nonwood fiber materials that have been tested. Taizen's method is chemimechanical pulping. The basic concept of chemimechanical pulping is simultaneous fiber separation and alkali treatment to weaken the bond between fibers. Nonwood plant fibers contain less lignin than wood, so that defibration becomes easy during weak alkali treatment. Most of the lignin and hemicelluloses stay intact within the fiber wall. The result is a high pulp yield compared with conventional chemical pulping. The environmental impact of the process is low because dissolved organic materials are minimal and chemical usage is little. Like wood pulp, nonwood pulp also requires bleaching. Bleaching involves treatment of cellulosic fiber with chemicals as to increase brightness that is achieved by either lignin removal (delignification) or lignin decolonization. Bleaching cleans the pulp of dirt and foreign matter that escaped digestion, as well as removing hemicellulose and other extractives. In the 1950s, the development in the manufacture of chlorine dioxide and dioxide led to the adoption of the five-stage bleaching sequence that is still used extensively in the industry; i.e., (1) chlorine, (2) alkaline extraction, (3) chlorine dioxide, (4) alkaline extraction, and (5) chlorine dioxide. The sequence allows the production of very bright pulp with minor losses in fiber length. Bleaching by colonization is achieved by either an oxidizing agent or a reducing agent. Chlorine gas, sodium hypochlorite, chlorine dioxide, oxygen gas, and hydrogen peroxide are oxidants, whereas sodium hydrosulfite is a reductant. The alkali is used to remove the solubilized lignin from the cellulose. The bleaching is divided into two stages, i.e., the prebleaching stage and the brightening stage. Biobleaching, which utilizes fungal strains such as *Phanerochaete chrysosporium* and *Coriolus versicolor*, has been developed. The purpose of prebleaching is to remove as much lignin from pulp as possible to minimize the volume of the more expensive chemicals. Brightening stages that follow prebleaching removes less of lignin but bring out the brilliance of pulp. Therefore bleaching sequence is a combination of the prebleaching and brightening stages. Bleaching of bagasse and other nonwood fibrous raw materials has not been easy. Because of the rapid discoloration during storage, most of them have a low initial brightness. This results in mechanical pulp with low initial brightness. Studies conducted on this front have shown that enzymatic pretreatment can improve brightness by 2% ISO (Prasad et al., 1996).

10.3 CONSIDERATIONS FOR NONWOOD FIBER USE

Both ash and silica interfere with the pulping (and chemical recovery of pulping chemicals) of many nonwood fibers. The cellulose, hemicellulose, lignin, and extractive contents are fundamental to pulping. Silica is present at elevated levels; whereas wood has less than 0.1%, many annual crops such as straws have 0.5%–5% or more.

The Chemistry of Silica

An introduction to the chemistry of silica will serve as a basis for the behavior of silica during pulping operations. Silicon has an atomic weight of 28.09 and has a valence of 4 in the oxide forms. Silicon dioxide (SiO_2, also called silica or silicic anhydride) is 46.75% silicon and occurs in nature as a variety of minerals such as the quartz minerals and cristobalite. The Si–O bond is partially ionic (about 50%). SiO_2 occurs in crystalline and amorphous forms. The crystallized form is said to be inert to alkali.

SiO_2 is insoluble in acids and water. It is attacked by HF and ultimately converted to the volatile gas SiF_4. (This is the basis of some straw pretreatments with HF for silica removal.) The amorphous form is solubilized in alkali as the salts of silicic acid. Silicic acid has the formula of $HjSiO_3$ and is the basis of silica gel desiccant and opal. The soluble ion under alkaline conditions is SiO_3^{2-} or $[SiO_2(OH)_2]^{2-}$.

Dean (1985) lists the two acid ionization constants of silicic acid and the solubility product of $CaSiO_3$ at 25°C. The pK_1 for silicic acid is 9.77 and the pK_2 is 11.80. (Methods that precipitate silica from black liquor using CO_2 must reduce the pH to about 9.0 to obtain near-complete precipitation of silica.) The pk_{sp} for $CaSiO_3$ is 7.60; $K_{sp} = 2.5 \times 10^{-8}$ corresponding to a solubility of 0.0184 g/L.

The Chemical Composition of Straw

Aronovsky et al. (1943) analyzed a variety of straw materials as well (Table 10.6). The moisture contents were 6.6%–8.4%. Barley is known to have a relatively high content of pectins and gums, making a high water extractive level, although others have reported much lower results for water soluble materials. Among the straws, the low ash content, high cellulose content, and long fibers of rye grain make it particularly useful for pulp.

Mineral Composition, Especially Silica

Delga (1947) investigated the mineral (and elemental) composition of cereal stalks. They are high in soluble ash (1.54%—4.7%). Potassium was 0.77%—3.44%, and silicon (not silica) was 0.35%—0.73%. The highest level of sodium occurred in oat straw (0.85%), whereas the highest level of calcium was 0.26% in rye grain straw. Sulfur and phosphorus contents were low. Oat straws grown in two different soils did not vary in composition. Fahmy and Fadl (1958) found Egyptian wheat straw to contain 8.34% ash and 3.44% silica. The leaf (sheath) is more concentrated with 14.9% ash and 6.90% silica, whereas the stem is 5.90% ash and 2.24% silica. Wet or dry sorting of the prehydrolyzed raw material was said to remove the silica-rich epidermis with a 4% loss of material. Some work indicates that ethanol—benzene extraction allows silica to be removed with the second extraction step.

Silica is about 2.5%—3.5% in bamboo; it is more concentrated in the nodes, where it may occur as nearly pure silica, than in the internode region. Bagasse is about 1.5% silica. The silica content of straw leaves is higher than that of the stems. These facts point out that if straw can be preprocessed to remove leaves and nodes, then many advantages may be realized.

Pulping and Silica Content

Fahmy and Fadl (1959) determined that the duration of alkaline pulping of wheat and rice straws was the most important parameter of the ash and silica content of the final pulp. Other variables have very little influence. For example, rice straw cooked at 150°C for 0.5 h was lower in ash than that cooked for 4 h, with the effect more pronounced for leaves than that for stalks. This may partly be due to a lower pulp yield with increased cooking time. Bleached pulps from rice stalks cooked at 120°C for 0.5 h had 0.064% silica and 0.15% ash.

Sodium sulfite pulping of bamboo with kraft green liquor removes less than 10% of the silica from straw compared with the 60%—70% removed during kraft pulping. The sulfite process leads to high-strength and high-yield pulps.

Alkali Chemical Recovery and Silica

Black liquor from straw pulping has about 5500 Btu/lb (on solids) compared with 6600 Btu/lb for black liquor from wood. A lower residual alkali (about 3—4 g/L) causes lignin and silica to precipitate during liquor concentration, making scaling and high viscosities big problems. Liquor has much higher viscosity than wood pulp. A long time ago, Rinman developed a technique of adding some $Ca(OH)_2$ to the pulping liquor so that calcium silicate would precipitate onto fibers during cooking.

Grubshein (1961) pointed out that during causticization some of the sodium silicate is converted to insoluble calcium silicate. This decreases the causticizing efficiency and increases the lime mud volume. He concluded that the answer is removal of silica from the black liquor by one of two methods: (1) treat the black liquor with lime or (2) treat the black liquor with flue gases to lower the pH and precipitate silicic acid. Method 1 is covered in the patent by Gruen (1953), who suggested that the precipitation with CaO occur near or above the boiling point of the black liquor for a short period of time (5—10 min) to decrease the amount of organic material precipitated. The process was patented in Germany by Schwalbe (1929). (One mill in South Africa uses ferric oxide and alumina to precipitate silica.) The CO_2 method is more common because costly lime is not used. Also, scaling will be lower in subsequent evaporation. The use of CO_2 precipitation with kraft liquors would probably increase the TRS emissions in the recovery boiler because this process is akin to direct contact evaporation. The experimental findings of Lengyel (1960) indicate that 6−8 g/L silica in black liquor can be evaporated without corrosion provided that addition of excess NaOH is used to dissolve incrustations that form. Silica at this level does not overly interfere with causticization but does increase the quantity of lime mud by about 100% and begins to retard the sedimentation rate. Corrosion and scaling are aggravated by allowing the black liquor to stand motionless for prolonged periods of time. Black liquor with more than 8 g/L silica should be treated with CO_2 (favored) or CaO (less favored). Lime mud can be purged if calcium silicate builds up in the system.

Sawheny (1988) reports that silica precipitates from soda black liquor from pH 10.2 to 9.1. At the lower pH, large amounts of lignin also precipitate. The solubilities are also temperature dependent. In pilot plant tests, involving several species of nonwood plants, careful carbonation (with a bubble reactor) of black liquor containing 6 g/L silica followed by filtering in a filter press resulted in 90% of the silica being removed as a solid containing 70% silica. The author claims rapid precipitation/sedimentation of large silica particles. Ibrahim (1988) indicates that precipitation of silica from black liquor is most effective if the black liquor is preconcentrated to at least 8% solids. Either CaO or CO_2 would precipitate over 95% of the silica under these conditions. (The concentration is often about 4% solids off the brown stock washers.) Long settling time (6 h) was needed. The long time period often means that the pH drops and lignin may continue to precipitate. The precipitate should be washed to recover useful alkali. Centrifugal separation of the silica precipitate was the most efficient precipitation method. The best precipitation of silica was achieved at pH 9−10 (at 50°C) with a flue gas (with CO_2 concentration of 6%−8%) application of 50−150 m^3 per m^3 of black liquor.

10.4 USE OF NONWOOD PLANT FIBERS IN SPECIFIC PAPER AND PAPERBOARD GRADES

Any grade of paper can be produced from several nonwood plant fibers and in blends with wood fibers. Some grades of paper have been made from 100% nonwood fibers. Abaca or manila hemp is the best papermaking fiber available. It has excellent properties for making strong products such as tea bags, large sausage casings, currency paper, cigarette, and filter paper, which require high wet strength, often combined with high porosity. Tea bags are the largest market for abaca specialty paper. In addition, abaca is preferred in stencil paper, electrolytic paper, cigarette plug wraps, vacuum-cleaner bags, medical tissue, and other nonwoven disposable products. Bagasse pulps are now used in practically all grades of paper, including bag, wrapping, printing, writing, toilet tissue, toweling, glassine, corrugating medium, linerboard, bleached boards, and coating base stocks. Newsprint has been successfully produced on a commercial scale using a kenaf peroxide chemithermomechanical pulp (CTMP). Pulp blends with 25% kenaf CTMP can be used as reinforcing pulp in recycled newsprint. Kenaf CTMP of 30%−50% can be blended with a loblolly pine kraft pulp and made into linerboard with acceptable strength properties. Flax and true hemp are used to make cigarette paper around the world. Sisal can be made into very strong products such as linerboard, wrapping, and bag paper. Cotton linters are used for premium quality letterhead paper, currency paper, dissolving pulp, and other specialty products. Bagasse and straw are best at contributing excellent formation to papers and can replace hardwood chemical pulps pound-for-pound for printing and writing paper. Pulps made from nonwoody annual plants (e.g., rice and wheat straw, bagasse, flax, or kenaf) are suitable as reinforcing fibers in pulps made from wastepaper. Wheat straw has been shown to be suitable furnish for writing and printing paper. Traditionally hemp bast fibers have been used as raw material for specialty papers such as bible, cigarette, currency, insulating, and condenser tissue paper. Esparto, with a little addition of softwood pulp for strength, makes good writing, postage stamp, and cheque papers. It is specially preferred for those applications that need a clear watermark with an accurate register. In China, sabai grass is used for carbon body paper (Chandra, 1998; MacLeod, 1988; Atchison, 1993; Mayers and Bagby, 1995; Pekarovikova et al., 1994; Zomers et al., 199; Ilvessalo-Pfaffli, 1995).

10.5 ADVANTAGES AND DISADVANTAGES OF USING NONWOOD FIBER FOR PAPERMAKING

Some nonwood fibers used as raw materials for papermaking have high annual yields per hectare. As can be seen in Table 10.3, the average annual yield per hectare of kenaf is about two times higher than that of fast-growing softwoods. Nonwoods have lower lignin content than do woods, and generally it is easier to delignify nonwoods, as they have lower activation energies. Pulping of nonwood materials is favorable compared with wood fiber in several ways. However, there are many disadvantages too (see Tables 10.7 and 10.8).

TABLE 10.7 Advantages of Using Nonwood Fiber

Chipping is not required.
Debarking is not required.
Most of the nonwood fibrous raw materials contain very little lignin as compared with woody materials. So these materials can be pulped with simple chemical systems such as caustic soda.
The alkali charge is normally lower than what is required for woody raw materials to achieve the same degree of delignification.
Because of the thin structure, the impregnation of cooking chemicals is easier.
Shives are not present.
Require lesser refining energy for achieving the same degree of freeness.
Bleaching is easier than wood fibers. Most nonwood fibers can be bleached to high brightness using lower chemical charges in short bleach sequences.
In pulping, nonwood fibers require less energy than wood fibers.

10.6 OTHER FIBER TYPES

Animal Fibers (Fig. 10.5)

Wool and human hair fibers have scales on the surface. Silk is formed by the secretion of proteins from two main glands of the silkworm caterpillar (*Bombyx mori*). Silk often can be seen as two separate component strands, and it is usually of uneven diameter.

Polymer Fibers

Synthetic fibers (Orion and Dacron are shown in Fig. 10.6) can be quite long.

TABLE 10.8 Disadvantages of Using Nonwood Fiber

The availability of a constant, year round supply of fiber is a main concern for paper mills. Given that most nonwoods are annual plants, the crops have short harvesting seasons, requiring storage of the harvested crop over several months.

The storage conditions and moisture content of straw are important because it is susceptible to molds and rot and subject to spontaneous combustion. Weather straw consumes more chemicals for pulping and produces lesser pulp of relatively lower strength.

Agricultural residues are bulky and are more difficult to handle than wood chips.

Agricultural residues are a by-product of food and feed production and not harvested in optimal conditions for fiber production, thus give a lower pulp yield.

Collection, transportation, and storage of agricultural residues need special attention, and the cost of transport and storage is high because of the bulky nature (most nonwood fiber sources are high in volume and low in density when compared with wood), which dictates local processing.

A large storage capacity is required for supporting continuous pulp production.

The ash content of nonwood plants is high. It varies between 1% and 20%. In softwoods and hardwoods the ash is generally less than 1%. The fiber length of nonwoods is usually shorter. This limits the range of paper qualities that can be produced.

Cereal straw is also highly dependent on agricultural subsidies; making a long-term availability unreliable, particularly in the Nordic countries.

The large amount of fines and the shorter fiber length affect the drainage properties of pulp. Slow draining requires either a reduction in processing speed or a lengthening of the drying section, which significantly increases processing (and energy) costs.

Because of the low density of the crops, they need more pulping liquid and need more volumes in process equipment.

High pollution levels are associated with current, low-technology production methods. Pollution from nonwood fiber mills can be up to 20 times than that from wood pulp mills and could prove an inhibiting factor in this sector.

Nonwood raw materials contain higher amounts of silica than woods.

During pulping, the silica is dissolved, enters the black liquor, and results in various problems in the chemical recovery loop, including increased black liquor viscosity at high solid concentrations.

Hard scales in the evaporator and hard deposits in the recovery boiler reduce the efficiency of some equipment and actually can plug it.

Formation of colloidal gels in the recausticizing system lowers the settling rate.

Formation of glassy material in the lime kilns.

Reduced slacking rate. These problems make chemical recovery difficult, less efficient, and more costly as compared with recovery for black liquor from woods.

Because of the high water retention capacity of nonwood fibers, particularly straw, each separation step requires about three times as much separation capacity as for hardwood processing. This means a significant increase in capital investment.

The large amount of fines and the shorter fiber length affect especially the drainage properties of pulp. Slow draining requires either a reduction in processing speed or a lengthening of the drying section, which increases processing cost.

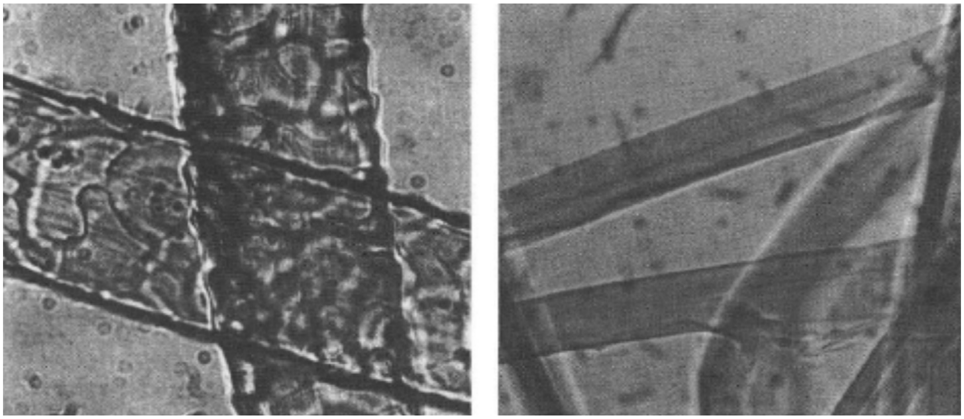


FIGURE 10.5 Wool (left) and silk (right) fibers (600×).

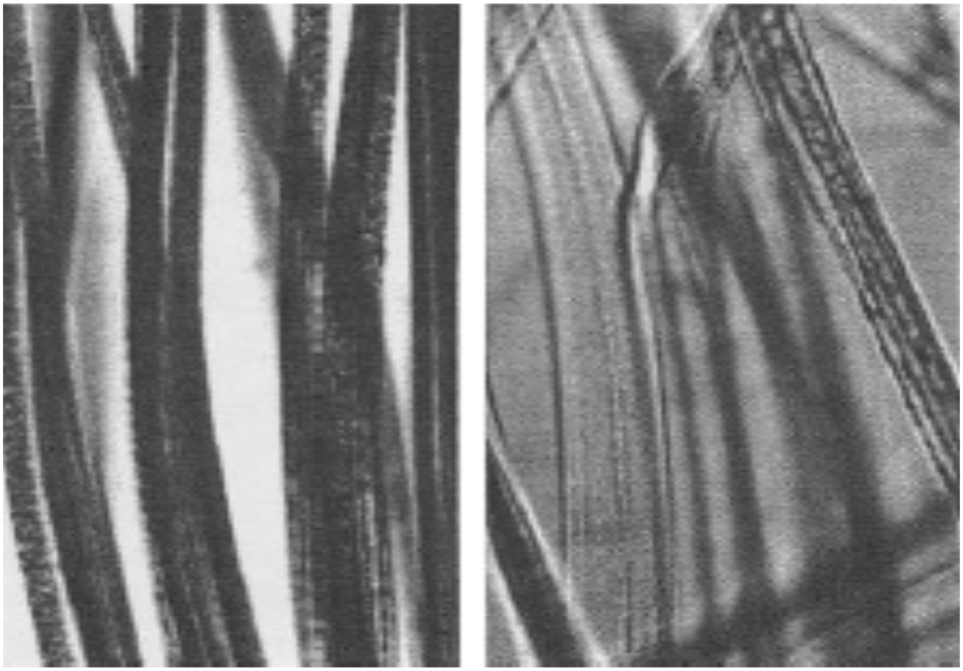


FIGURE 10.6 Orion and Dacron fibers (150×).

10.7 ANNOTATED BIBLIOGRAPHY

Alireza Ashori (2006) Nonwood Fibers—A Potential Source of Raw Material in Papermaking, Polymer-Plastics Technology and Engineering, 45:10, 1133–1136, DOI: 10.1080/03602550600728976.

Anon., Continuous manufacture of pulps from annual plants, *Papeterie* 70(9):271, 273–276 (September 1948).

Anon., Italian mill tires new pulp process, PP/(January):48, 49, 52(1984).

Anon., Tappi Standard T 259 om-83, Species identification of nonwood plant fibers, l1 p., 5 references. This reference has numerous micrographs. It has information on the fiber types obtained from species of commercial importance.

Anon., Tappi Standard T 401 om-88. Fiber analysis of paper and paperboard, 12 p., 32 references. This method describes preparation of slides with the use of stains for the identification of fibers from wood and nonwood plants.

Aronovsky, S.I., G.H. Nelson, and E.G. Lathrop, *Paper Trade J,* 117(25):38–48(1943).

Aronovsky, S.I., A.J. Ernst, and H.M. Sutcliffe, Pulping with sodium sulfite to produce strawboard, *Tech, Assoc, Papers* 30:321–323 (June, 1947).

Aronovsky, S.I., G.H. Nelson, A.J. Ernst, H.M. Sutcliffe and E.G. Lathrop, *Paper Trade J.* 127(11):154–162(1948) and *Tech, Assoc. Papers* 31:291–299(1948).

Aronovsky, S.I. and E.G. Lathrop, A new mechano-chemical process for pulping agricultural residues, *Tappi* 32(4): 145–149(April, 1949).

Atchison, J.E., World capacities for nonwood plant fiber pulping increasing faster than wood pulping capacities, *Tappi Proceedings, 1988 Pulping Conference*, pp 25–45.

Atchison, J.E. Twenty-five years of global progress in non-wood plant fiber repulping. Tappi J. 1996, 79 (10), 87—95

Atchison, J. E.; 1993, Making right choices for successful bagasse newsprint production, *Part 2*, TAPPI 76(1):187—193.

Byrd, M.V. and Hurter, R W, US Patent 6,302, 997, Issued October 16, 2001.

Byrd, M.V. and Gratzl, J.S., "Nonwood Fibers Offer Opportunities and Challenges," Paper Age, 114(7):20—22(1998).

Byrd, M. V. (2005). "A simplified pulping & bleaching process for pith-containing nonwoods: trials on whole corn stalks," *2005 TAPPI Engineering, Pulping and Environmental Conference*, TAPPI Press, Philadelphia, PA, USA.

Casey, J.P., *Pulp and Paper: Chemistry and Chemical Technology*, 2nd, Ed., Vol. 1, Interscience, New York, 1960. pp. 398—425 discuss the pulping of various nonwood fibers.

Ceragioli, G., Wheat straw pulping by alkali oxygen processes—cooking variables and pulp processes, pp. 227—252 (1975).

Chandra M (1998). Use of nonwood plant fibers for pulp and paper industry in Asia: potential in China, Thesis, Master of forestry in wood science and forest products USA, Virginia.

Dean, J. A., *Lange's Handbook of Chemistry*, 13th ed., McGraw-Hill, New York, 1985. 13.

Delga, J., Chemical composition of the stalks of cereals, *Mem. services chim. etat* (Paris) 33: 7—73 (1947).

Fahmy, Y. and M. Fadl, Digestion of wheat straw for the economical production of purified pulps of low silica content, *Textil-Rundschau* 13(12):709—719(1958).

Fahmy, Y. and M. Fadl, Solubility of ash and silicic acid during alkaline pulping of cereal straws. *Das Papier* 13(13/14):311—314(1959).

FAO, Tropical Woods and Agricultural Residues as Sources of Pulp, Rome, Italy 1952, 190 p. Sulfite pulping of Parana-pine (23 p.), chemical pulps from Australian eucalyptus (6 p.), and agricultural residues (47 p.) are some highlights of this work.

Grubshein, B.D., Recovery of lime in the alkaline pulping of straw and reed, *Bumazh*. Prom. 36(8):12—13(1961). Russian.

Gruen, B. H. E., U.S. patent 2,628,155 (February 10, 1953).

Hart PW., Brogdon BN and Hsieh JS (1994), Anthraquinone pulping of nonwood species, TAPPI Nonwood Plant Fiber Progress Report No. 21, pp. 183—192.

Huamin, Z., Separation of fibrous cells and parenchymatous cells from wheat straw and the characteristics in soda-AQ pulping, *1988 International Non-wood Fiber Pulping and Papermaking Conference*, China, pp 469—478.

Hurter, AM 1990 a, Utilization of annual plants and agricultural residues for the production of pulp and paper, TAPPI Nonwood Plant Fiber Pulping Progress Report No. 19, pp. 49—70.

Hurter, AM 1990 b, Some economic considerations in the implementation of a nonwood pulp and paper project, TAPPI Nonwood Plant Fiber Pulping Progress Report No. 19, pp. 217—230.

Ibrahim, H 1988, Silica is no longer a problem in the recovery of heat and chemicals from nonwood plant fibers black liquor, *1988 International Non-wood Fiber Pulping and Papermaking Conference*, China, pp 877—889.

Ilvessalo-Pfaffli, Marja-Sisko; 1995, Fiber Atlas: identification of papermaking fibers, Springer-verlag, New York.

Lengyel, P., Silica removal from black liquors, *Zellstojfu*. Papier 9(3):89—94(1960).

Mayers, G. G., and Marvin O. Bagby; 1995, Feasibility of using kenaf chemithermomechanical pulp in printing and writing paper, TAPPI 78(5):156—161.

Misra, D.K., Pulping and bleaching of nonwood fibers, in *Pulp and Paper: Chemistry and Chemical Technology*, Vol. 1, 3^{rd} ed., Gasey, J.P., Ed., Wiley, New York, 1980, pp. 504–568.

Paavilainen, L. Non-wood fibers in paper and board grades – European perspective. Non-wood Fibers Short Course. Tappi Press: Atlanta, GA, p 23, 1997.

Petersen, P.B., Industrial application of straw, *1991 Wood and Pulping Chemistry*, Tappi Press, Atlanta, pp. 179–183.

Pekarovicova, A, H. Jameel, and T. W. Joyce; 1994, TCF bleaching of wheat straw organocell pulp, Cell. Chem. Tech. 28: 551–561.

Pierce, B. Recycled how many times? Timber Producer 1991, (April), 18–21.

Prasad, D. Y., N. R. M. Rao, K. S. Rajesh, T. T. Prabhuraj, and T. W. Joyce; 1996, Enzymes improve the bleachability of bagasse mechanical pulp, TAPPI 79(8):133–138.

Sawheny, R.S., Desilicanization of black liquor-a glance, *1988 International Non-wood Fiber Pulping and Papermaking Conference*, China, pp 933–942.

Schwalbe, G.G., Process for desalination of alkaline silicious spent liquors, German Patent 522,730 (1929).

Stephenson, J.N., Ed. *Preparation of Stock for Paper Making*, Vol. 2, McGraw-Hill, New York, 1951. pp. 1–91 discuss pulping of nonwood fibers.

MacLeod, Martin; 1988, Nonwood fibers: number 2, and trying harder, an interview with Dr. Joseph E. Atchison, TAPPI 71(8): 50–54.

Sabharwal, H. S.; 1995, Refiner mechanical and biomechanical pulping of jute, Holzforschung, 49(6):537–544.

Tao, W, J. P. Moreau, and T. A. Calamari; 1995, Properties of nonwoven mats from kenaf fibers, TAPPI 78(8):165–169.

Yilmaz, Y.; 1995 a, Lime-oxygen pulping of wheat straw, Paperi Ja Puu, 77(1–2):51–53.

Yilmaz, Y.; 1995 b, Lime-soda-oxygen (LSO) pulping of wheat straw, part 1 - pulping, Paperi Ja Puu, 77(4) 206–208.

Yilmaz, Y.; 1995 c, Lime-soda-oxygen (LSO) pulping of wheat straw, part 2 - effect of cooking parameters on paper properties, Paperi Ja Puu, 77(8):498–501

Zomers, F. H. A., Richard J. A. Gosselink, Jan E. G. Van Dam, and Boke F. Tjeerdsma; 1995, Organosolv pulping and test paper characterization of fiber hemp, TAPPI 78(5): 149–155.

www.iti-america.com/nonwood-pulping.

CHAPTER

11

Raw Material Preparation

11.1 INTRODUCTION

Handling of wood for pulp, paper, and board manufacturing processes has experienced many significant changes in recent decades due to stricter environmental regulations, increased production capacities, and the use of wood from plantations. Consequently, the research and development work has been focused on finding new solutions that best meet changing needs. Significant savings and pulp quality improvements can be obtained when using the latest wood handling technology. The question is how to process this raw material to make it perfect for further processing so that a high quality end product will result, while at the same time optimizing the yield of valuable commodities. Recent efforts have focused on developing ways to maximize process uptime, while optimizing process parameters during debarking and chipping. The main targets for the optimization of the debarking process are listed as follows:

- Increase uptime and capacity
- Improve chip quality
- Minimize energy consumption
- Maximize raw material yield

The raw material preparation is the first stage in pulp manufacturing. This stage includes debarking (when wood is used as raw material), chipping, chip screening, chip handling, and storage and other processes such as depithing (for example, when bagasse is used as the raw material).

11.2 WOOD HANDLING

The trees are cut in the forest into logs of pulpwood. The length of the logs varies depending on the type of wood and also between countries. Log debarking is usually done in the forest. It is also done as the first process step at the mill. The debarked logs are cut into chips about 20–30 mm long. The chips are then screened to remove fines and oversize particles. The accepted chips are transported to the chip storage at the pulp mill from where the chips are taken to the digester for cooking. Fig. 11.1 shows the wood handling process for pulpwood. In those mills, where mechanical pulp is also used, the wood handling line is common for both pulping types. Chips are also brought to the mills mainly from sawmills, where the chips are made from sawmill residues. In the United States, about 40% of the raw material for fiber production comes from saw mills. In Finland, the proportion is about 20%. Fig. 11.2A shows a typical pulp mill wood handling process arrangement consisting of a conveyor feeding the pulpwood to the debarking drum, debarking

Biermann's Handbook of Pulp and Paper: Raw Material and Pulp Making
https://doi.org/10.1016/B978-0-12-814240-0.00011-2

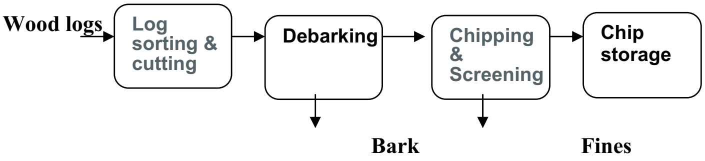


FIGURE 11.1 Flow diagram for wood preparation.

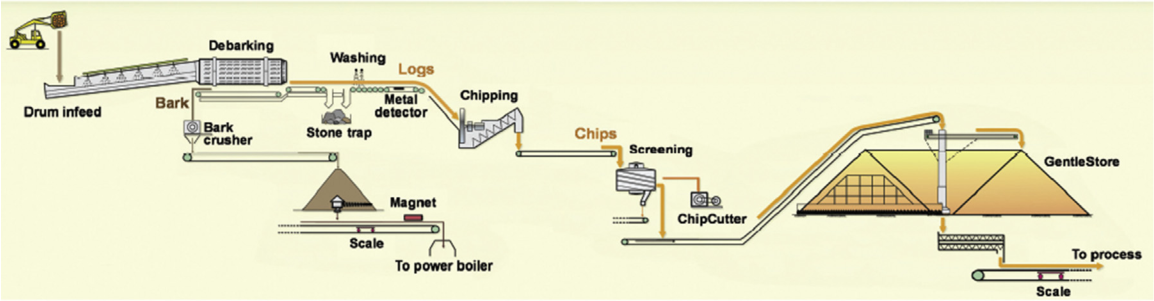


FIGURE 11.2A A typical pulp mill wood handling process arrangement. *Courtesy of Valmet.*

drum, chippers, bark presses, bark storage, chip piles, and chip screening. Fig. 11.2B shows Andritz debarking process.

11.3 DEBARKING

Wood is debarked before chipping and cooking. Bark can cause problems in the fiber lines as it does not contain proper fibers. Bark contains extractives, which cause deposit on the machinery and lead to dirt particles in the final pulp. Particularly, hardwood bark results in dirt particles in the pulp, and a high degree of debarking is required for most hardwoods. When bark is cooked along with the wood, much of the bark material is dissolved during cooking and can be found in the black liquor going to evaporation and combustion. The dissolved organic material will cause an extra load on the recovery boiler, and the bark will have extra requirement of cooking chemicals. A more efficient method to burn bark is in a separate bark boiler after pressing of bark, where the water content in bark is reduced. There are differences in debarking methods depending on the type of wood. Some tropical hardwoods are debarked in the forest in cases where the bark is easily removed from the fresh wood. Most of the pulpwood is debarked in debarking drums at the mills in Scandinavia before chipping. The major objective of debarking is to remove bark to the necessary extent for the final product quality. The debarking degree is a measure of the bark removal efficiency. This gives the percentage of debarked surface or bark content in chips, which expresses the share of bark in the weight of the chips. A debarking degree of 95% in pulpwood generally corresponds to a bark content of about 0.5%.

The pulp industry usually debarks all round wood that is received at the pulp mill. Log debarking is required to ensure that the pulp is free of bark and dirt. Both mechanical and hydraulic bark removal methods are commonly used. The barking drum is the most common

FIGURE 11.2B Andritz debarking process. *Courtesy of Andritz.*

form of mechanical debarking. Bark is removed from the logs by friction created from the rotating drum action as the logs get rubbed against each other. In wet drum barkers, water is added to the early solid steel portion of the drum. This will help loosen the bark. The remaining portion of the drum has slots to allow the removed bark to fall out while the log continues on through. In case of dry drum barkers, the entire length of the drum has slots for bark removal. Dry drum barkers are longer in length and rotate much faster than wet-type drum barkers. The bark from dry drum barking can be fired directly into bark-burning furnaces, while bark from a wet system must be collected in a water flume, dewatered, and pressed before burning. Drum barkers usually generate about 4%–5% wood waste and cause broomed ends on the logs that produce inferior wood chips for pulping. They have high power consumption and are relatively low-cost devices.

Dry debarking is used in areas where thawing or deicing of logs is not necessary. Both wet and dry debarking are in use in areas where thawing of logs is necessary. Dry debarking is today the preferred method for new installations. There are two types of debarking drums (Fig. 11.3):

- Tumbling debarking drums—In these drums, the log length is smaller than the diameter of the drum. The logs can tumble freely in the tumble debarking drum. The drum diameter is 4–6 m and the length is 20–40 m. The peripheral speed of the drum is 1.5 m/s–2 m/s corresponding to a rotating speed of 5.7–7.6 rpm with a 5m drum. In the tumble debarking drum, the logs move randomly through the drum, which rotates around its axis in a straight or a slightly inclined position. The logs become debarked by rubbing against each other.

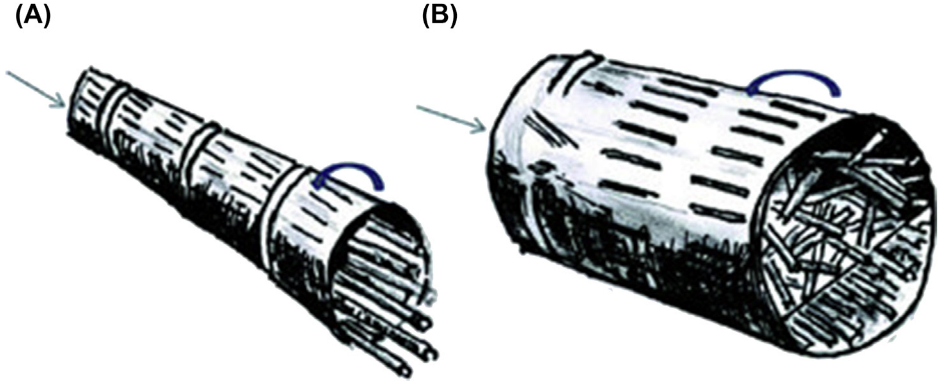


FIGURE 11.3 Debarking drum: (A) parallel debarking drum and (B) tumble debarking drum. *Reproduced with permission Ragnar et al. (2000).*

- Parallel debarking drums—These drums are used for full-length trees but is not as common as tumble debarking in Scandinavia. In parallel debarking drums, the log length is greater than the drum diameter. The debarking forces are weaker as compared with tumble debarking, and the drums are longer and have a smaller diameter.

Fig. 11.4 shows debarking drum and Fig. 11.5 shows rotary debarker from Andritz.

Valmet has developed the GentleBarking process, which involves debarking the logs in a relatively short drum, and bark is removed afterward in a roller section (Fig. 11.6). The debarking takes place in the drum, but the drum is shorter as compared to those made earlier by the major suppliers in the industry. There are no bark slots in the drum because the bark is separated in a special roll conveyor after the drum. In addition to a shorter debarking drum, there is less equipment and less civil and electrical work needed with GentleBarking. The significant advantage of the new method is a shorter debarking drum, allowing a shorter retention time, which means less wood losses and wood breakage. Another improvement is the even discharge rate from the debarking

FIGURE 11.5 Andritz Rotary debarker RotaBarker. *Courtesy of Andritz.*

FIGURE 11.4 Andritz debarking drum. *Courtesy of Andritz.*

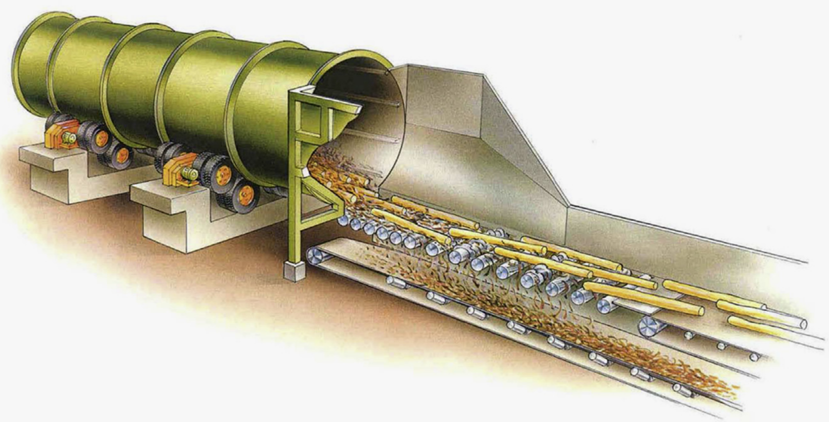


FIGURE 11.6 Gentle debarking process. *Courtesy of Valmet.*

drum obtained with a fundamental change in the discharge gate operating principle. Valmet's new debarking method results in lesser loss of wood, better chip quality, reduced operating and maintenance costs, and higher uptime. Furthermore, the total investment cost of the system is much lower as compared with present conventional methods. The Valmet debarking drum product range also includes the EasyTyre, EasyFloat, and EasyRoll debarking drums, as well as a steel roller–supported debarking drum, all with special features to meet different customer requirements.

Ring debarkers are being used by several mills for producing a high value of both hardwood and softwood lumber products. Ring debarkers are widely used in pulp mills, chip plants, log processing plants, and sawmills. This debarker features a ring of cutting heads or knives which are mounted in a circular position (Fig. 11.7). The log is fed into the machine in a continuous mode, and the bark of the log gets peeled down to the cambium layer as it rotates. The first ring debarker was developed in Sweden and called the Cambio. Now the ring debarkers are available in various configurations. For example, the tool pressure can be adjusted to match the thickness and bark characteristics of different wood species. The machines also rely on a centering feed conveyor system, which is monitored by a weight-sensing mechanism that steers logs into the center of the ring.

FIGURE 11.7 Ring debarker (USNR). *Courtesy of Logging and Sawmilling Journal, www.forestnet.com.*

The rosser head debarker is used for debarking hardwoods. It functions similarly to a lathe in the way it cuts bark from trees and is better adapted for handling crooked logs. Logs are placed into the debarker from an infeed conveyor and dispersed from the machine via an outfeed conveyor. Inside the debarker, the log rests upon a cradle driven by rollers that rotate the log while a rotating cutterhead travels over the length of the log and removes the bark. A manual operator controls the movement of the cutterhead. This method of debarking is slow. However, the machines cost less and can be managed easily.

Different types of wood species have different debarking characteristics. The thickness and structure of the bark have a significant effect on debarking. Table 11.1 shows the effect of bark-to-wood adhesion on debarking of some selected wood species. The cutting season greatly affects the debarking degree. In the dormant season, spruce bark may attach to wood 100% tighter and poplar 250% tighter as compared with the growing season. In the northern regions, debarking becomes increasingly difficult as log temperatures fall and the logs become frozen. The bark may adhere to frozen logs with a force 2.5–5 times greater than that of thawed logs. In Table 11.2, debarking times for some wood species is presented. The cleanliness requirement for bleached sulfate pulp is high. The debarking degree requirements for softwoods are usually 85%–92%. This leaves less than 1% by weight of bark on the log. Bark extractives are a problem, particularly in the manufacture of bleached hardwood sulfate pulp. The debarking degree for pulpwood should be higher with bleached hardwood pulps than with bleached softwood kraft pulps.

Some wood is always lost during debarking. The amount varies significantly depending on the following factors:

- Quality of wood to be debarked
- Required degree of wood cleanliness after debarking
- Debarking equipment
- Local conditions.

Typically, wood losses, as percentage of wood feed, are small when large-diameter and uniform pulpwood logs are debarked (see Fig. 11.8). It is possible to reach a wood loss of about 1%–1.5% in wood weight with appropriate debarking

TABLE 11.1 Effect of Bark-to-Wood Adhesion on Debarking of Few Selected Wood Species

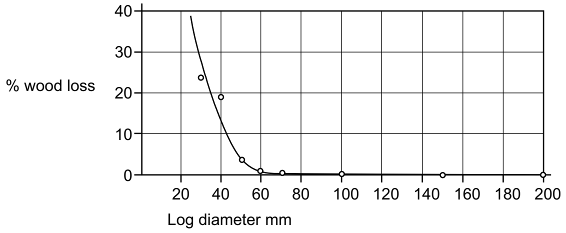
Bark-to-Wood Adhesion		
kg/cm^3	**lb./sq.in**	**Effect on Debarking**
…3–4	40…55	Can be debarked easily maple, southern pines
5…6	70…110	Can be debarked normally Hemlock, white pine, spruce, beech
8–10	140	Can be debarked with difficulty elm, birch
12…14	170…200	Can be debarked with great difficulty ironwood, black poplar
>20	~300	Cannot be debarked basswood, hickory

Based on Gullichsen (2000).

TABLE 11.2 Debarking Time for Some Wood Species

Wood Species	**Debarking Time (min)**
Oak, maple, southern pine, most tropical hardwood species (trees easy to debark, for pulpwood)	10–15
Spruce, most northern pine species (normal to debark, softwood for pulpwood)	20–25
Birch (normal to debark, hardwood for pulping)	30
Spruce (Fresh groundwood)	30–40
Aspen, birch (dry hardwood for pulping)	40–60
Aspen, spruce (dry groundwood)	60

Based on Gullichsen (2000).



Based on docshare01.docshare.tips/files/23393/233934272.pdf

Log diameter (mm)	% Wood loss
30	24.0
40	19.5
50	4.2
60	2.0
70	0.5

FIGURE 11.8 Wood losses during debarking (effect of log diameter). *Based on docshare01.docshare.tips/files/23393/233934272.pdf.*

conditions. Fresh and short pulpwoods that debark easily have wood losses of about 1%–2%. Debarking dry hardwood or mixed wood, which consists mainly of thin logs and some big logs, leads to large wood losses, which can be up to 4%–5% of the wood weight.

11.4 CHIPPING

After debarking, the logs or portions of logs are reduced to chip fragments suitable for the subsequent pulping operations. Several designs of chippers are in use. The most commonly used chippers are the flywheel-type disc with a series of blades mounted radially along the face. The logs are generally fed to one side of the rotating disc at an optimum angle, which is about 45 Degrees, through a vertical directing chute. The logs can also be fed horizontally to a disc mounted at the proper angle. Generally, the horizontal feed provides better control but is not much suitable for scrap wood pieces. Off-size chips have an adverse effect on the processing and quality of pulp.

Acceptable size chips are generally isolated from fines and oversized pieces by passing the chips over multistage vibratory screens. The oversized chips are rejected to a conveyor, which carries them to a "rechipper." The fines are usually burned with the bark (unless special pulping facilities are available).

Conventional screening segregates chips only on the basis of chip length. More recently, the greater importance of chip thickness has been recognized, and a few recently designed screens now segregate according to this parameter. Also, new design "rechippers" that slice the chip lengthwise to reduce thickness cause far less damage to the fibers than the old-style crushers.

Within mill areas, most chips are transported on belts or in pipes using an airveying system. Chips are readily handled by air over distances of 300–400 m, but power consumption is high and chip damage can be significant. By contrast, a belt conveyor system has a much higher initial cost. Other systems such as chain and screw conveyors are also used to move chips but usually for relatively short distances. Bucket elevators are used for vertical movement.

Chip storage is widely utilized primarily because chips are more economical to handle than logs. Some disadvantages are apparent, e.g., blowing of fines, airborne contamination, but it has been only recently that the significant loss of wood substance from respiration, chemical reactions, and microorganism activity has been quantified. It is now recognized that losses of 1% wood substance per month are typical. Considerable research has already been carried out to find a suitable chip preservative treatment, but so far, a totally effective, economical, and environmentally safe method has not been identified. In the meantime, it makes good sense to provide a ground barrier of concrete or asphalt before building a chip pile to reduce dirt contamination and inhibit the mobility of ground organisms. Chips should be stored on a first-in/first-out basis to avoid infection of fresh chips by old chips; the ring-shaped pile facilitates the complete separation of "old" and "new" chips. Windblown concentrations of fines should be avoided because they reduce the dissipation of heat that builds up in the pile from various causes. Thermal degradation and even spontaneous combustion can result from localized heat buildup. Optimum chip handling depends partly on pulping requirements. As loss of extractives is high for the first 2 months of outside storage, all chips for sulfite pulping should go to storage (to reduce resin problems). If by-product recovery is important (as for some kraft pulping operations), fresh chips should bypass storage wherever possible to maximize yield. Valmet has developed the latest cutting-edge technology for woodchip storage and reclamation. GentleStore—chip storage system—(Fig. 11.9) operates on the first-in first-out principle, meaning the chip pile is built up at the front and reclaimed from the back. The chips are reclaimed gently from the whole cross section of the pile, which ensures excellent blending and homogenization of the chips while minimizing chip damage. GentleStore includes several unique features and allows low operation and maintenance costs, making it a beneficial total investment.

FIGURE 11.9 GentleStore chip storage system. *Courtesy of Valmet.*

A number of reclaiming methods are in use. Older installations employ a belt or chain conveyor along the side of the pile, which is fed by a bulldozer that pushes chips down the side of the pile onto the conveyor. This arrangement is labor-intensive (necessitating a full-time bulldozer operator) and inevitably results in damage to the chips. Modern installations work automatically, some employing augers or chain conveyors on rotating platforms at the base of the pile.

With respect to a given wood source, the quality of chips is measured by uniformity of size (i.e., length and thickness) and by the relative absence of "contaminants." All chips 10–30 mm long and 2–5 mm thick are usually considered to be of good quality. Contaminants are considered to be: oversized chips (either length or thickness), pin chips (passing 3/8″ screen), fines (passing 3/16″ screen), bark, rotten wood (including burnt wood), dirt and extraneous.

Oversize chips represent a handling problem and are the main cause of screen rejects in chemical pulping (Smook, 1992a). Size reduction of the oversize fraction is difficult to accomplish without generation of fines. Pin chips and (especially) fines and rotten wood cause lower yields and strengths in the resultant pulps and contribute to liquor circulation problems during cooking of chemical pulps. Bark mainly represents a dirt problem, especially in mechanical and sulfite pulping. The kraft pulping process is much more tolerant of bark because most bark particles are soluble in the alkaline liquor.

The wood is cut into chips to make mass and heat transport possible during cooking. The chips have to be small enough so that chemicals and heat can penetrate and diffuse into the wood material so that the whole chip is cooked in a homogeneous way. In case of very large wood pieces, the center of the chip will be at least partly uncooked. On the other hand, the chips have to be large enough so that liquids can circulate in the digester during cooking around the chips without causing too much flow resistance and pressure gradients. The size and shape of the chips is determined by the raw material used and the geometry when cutting the chips.

The complementary angle affects the chip's length-to-thickness ratio and can be used to control the chip geometry at least to some extent. Another important parameter is the speed of cutting that influences the formation of oversize chips and fines. Other parameters influencing the result when producing chips are wood species, size of the logs, cutting conditions, and condition of cutting edge.

The size of the chip affects how the cooking liquor penetrates and diffuses into the wood material. The size of the chip has to be small enough to ensure good impregnation of cooking chemicals. The most critical dimension is the thickness of the chip. During chipping, physical damage to the fibers has to be minimized. The longer the chips are, the fewer number of fibers are cut by the knife. Fig. 11.10 shows the relationship between average fiber length in the chip and wood and the chip length. When choosing the length of the chip, a balance has to be found between the number of fibers cut in the chipper and the length and thickness of chips. A longer chip will also mean a thicker chip, and a long and thick chip will be more difficult to

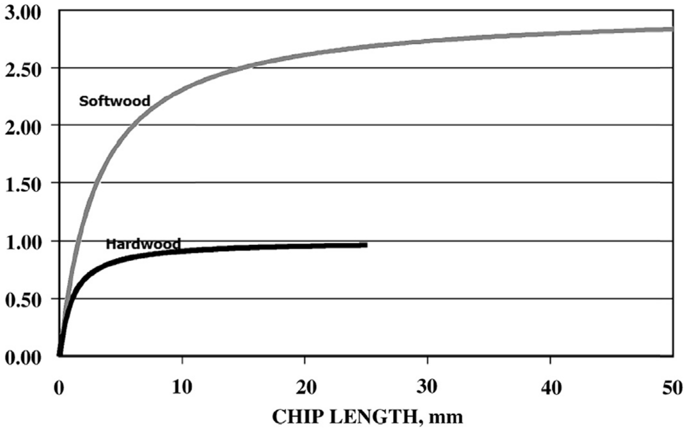


FIGURE 11.10 Relationship between average fiber length in the chip, the fiber length in wood, and chip length. Fiber length of softwood—3 mm. Fiber length of hardwood—1 mm. Fiber length in chips—L*I (L + I) L = chip length mm I = original fiber length in wood, mm. *Adapted from Gullichsen (2000).*

impregnate. Fibers are also damaged because of the compression forces when the chipper knife hits the log. The compression damage depends on the design of the chipper, condition of the knife, as well as knife angle. In a chipper, the log is fed at a controlled angle toward the rotor with the cutting knives. Industrial chippers are generally equipped with multiple motors for balancing the momentum with which the rotor rotates while cutting the log into chips. Figs. 11.11–11.15 show industrial chipper.

FIGURE 11.11A Whole log chippers. *Courtesy of Acrowood.*

11.5 CHIP SCREENING

The chip is characterized by length. Industrial chips are typically 20 –30 mm long and have a thickness typically below 8 mm. Width is as such not critical for cooking. Heat and mass transfer in the thickness and width directions will be mostly controlled by diffusion and, as thickness is smaller than the width of the chip, the thickness will be the dimension controlling the time required by impregnation. The chips are usually screened after chipping and before transfer to the chip storage to remove oversize particles and fines. Oversize particles are particles which are not able to pass through a hole of a certain size, usually a hole with a diameter of 45 mm. Fines are particles which are able to pass through a hole of a certain size, usually a hole having a diameter of 3 mm. These fines and oversize particles are not considered good for cooking and can also cause mechanical problems in the digester. The other objective of chip screening is to remove bark, sand, and grit, which are small size contaminants.

In some mills, chips are also screened after the chip storage and before the transfer of chips to the digester. Generally, the chips are screened with respect to thickness in this position. A chip thicker than 8 mm is often considered overthick and can remain partly uncooked in the digester, causing reject after cooking. Screens are used in the thickness screening of chips. Today, several kinds of chip screen designs are being used in the industry. The most common screen is the gyratory screen (Fig. 11.16) used after chipping. The gyratory screen is a vibrating screen plate, usually having round holes of certain size, either for oversize or fines separation. The disc screen is composed of discs, which are mounted on parallel rotating shafts (Fig. 11.17). These screens are designed to pass or retain chips based on thickness only. The discs are arranged in a

FIGURE 11.11B Whole tree chipper. *Courtesy Peterson Pacific Corp. and Michael Spreadbury (photographer).*

FIGURE 11.12 Drum chippers 4310B from Peterson. *Courtesy Peterson Pacific Corp. and Michael Spreadbury (photographer).*

staggered pattern and leave slot openings with a width of 5 –13 mm, usually about 8 mm between the discs. All shafts rotate in the same direction. Oversize particles separated during chip screening are cut into smaller size or crushed and returned to the chip screens for rescreening. There are many technical alternatives for doing this. The objective is to avoid cutting or crushing the oversize chips into very small particles.

Fines can be taken to the bark boiler and used for energy production. Fines can also be taken to a digester to be cooked into pulp. Some mills have digesters which are suitable for cooking small material, where the fines can be cooked into pulp.

Chips are also screened in laboratories for classifying the chips. Fig. 11.18 shows chip classifier. The amount of chips being retained on each screen gives the size distribution of the chip sample.

FIGURE 11.13 Drum chipper P1020314 from Peterson. *Courtesy Peterson Pacific Corp. and Michael Spreadbury (photographer).*

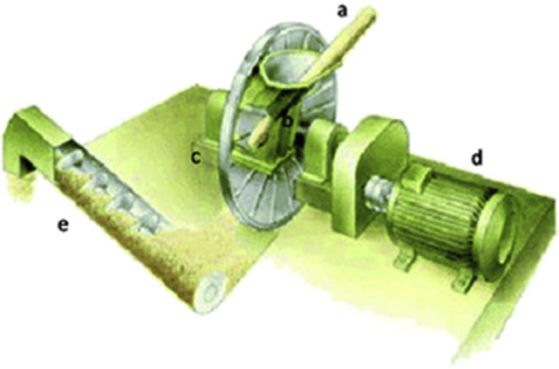


FIGURE 11.14 Disc chipper: (A) log; (B) axle; (C) disc with knives; (D) motor; and (E) screw for chip for transport. *Reproduced with permission Ragnar et al. (2000).*

Sawmill Chips

Sawmill chips and sawmill residue wood is used in the form of sawdust for fiber production and are usually screened at the pulp mill before cooking. The sawdust must be free of large wood particles before being fed into a sawdust digester. The sawmill chips should be screened to remove fines and oversize wood particles before cooking in a digester for chips. The sawmills use logs with a large diameter to produce sawn goods, and much of the residual wood from sawmills is from the outer part of the logs containing long mature fibers. Sawmill chips are treated and stored separately at many mills and added to the chip stream going to the digester in a controlled way and are a source of raw material for pulps with good strength properties. The portion of sawmill chips added to the chip flow will affect the properties of the pulp produced particularly in the case of softwoods.

11.6 CHIP STORAGE

Pulp mills generally store and process enormous volumes of wood chips before the pulping process. Storage volumes of 120,000 BDt (750,000 m^3) are common. The mills have specific requirements for storing wood chips to reduce fiber losses and maximize fiber recovery because the value of these chips is in the tens of millions of dollars. When designing chip storage piles, the following things should be taken into consideration:

- Material being handled
- Total required storage volume
- Practical live-storage volume

FIGURE 11.15 Disc Chipper from Peterson. *Courtesy Peterson Pacific Corp. and Michael Spreadbury (photographer).*

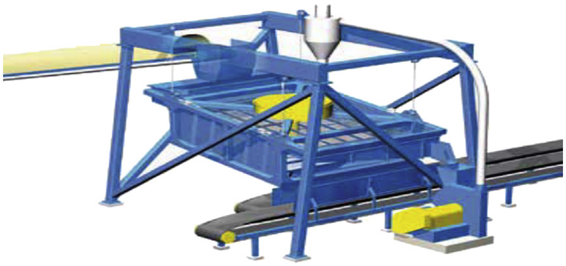


FIGURE 11.16 Gyratory chip screen 3-D view. *Courtesy ANDRITZ.*

- Fiber aging
- Pile turnover
- Dry fiber loss
- Chip degradation and breakage
- Dust and fire control
- Inventory management
- The methods of pile-building and reclaiming

Chips are stored in the pulp mills in piles or silos. The chip storage is actually a buffer area between wood handling and cooking. The amount of chips stored usually varies but can correspond to a few weeks of pulp production. Different types of chips are generally stored in separate piles or silos. The chip storage is used to homogenize the flow of wood material to the digester. It is also used to control the portion of various chip types being fed to the digester. This way, the quality of the pulp produced can be kept stable and controlled with respect to the type of raw material used. The wood material in the chip storage is affected by bacterial and fungal activities. This will result in an increase in the temperature in the chip storage, and there will be some wood losses.

Wood losses can be reduced by cooling and covering the chip piles. The mills should store enough chips not to inhibit pulp production. But as the inventory is costly, the mill will not unnecessarily want to store excessive volumes.

The extractive content of the wood reduces during chip storage. This phenomenon is used by pulp mills to reduce the extractive content of hardwoods particularly. Mills are storing hardwoods for a minimum time of few weeks to get the content of extractives low enough to enable easier processing. On the other hand, the loss of extractives from softwoods will result in reduced production of turpentine and tall oil.

Chips are transported in the chip handling area with pneumatic systems or belt conveyors (Fig. 11.19). In pneumatic systems, the chips

FIGURE 11.17 Disc screens. *Courtesy of Advanced Biomass Consulting Inc., Canada; http://www.advancedbiomass.com/2014/10/disc-screen-fundamentals/.*

are transported inside pipes by air blowing. The chip piles and silos are equipped with screws or conveyors, which take the chips out of the lower part of the storage in a controlled manner.

11.7 ANNOTATED BIBLIOGRAPHY

Acrowood Corporation, (2007). Case Studies in Improving Your Chip Supply Primary Thickness Screening, Efficiency and Chip Size Distribution. Website acrowood.com/downloads/WCH-Article%202.pdf

Case studies on the use of chip thickness screening (CTS) for improving pulp mill operations, reducing costs, improving productivity, yield, and overall operational efficiency are presented. By separating chips that exceed the pulping system's processing ability and treating them while they are still chips, CTS allows the digester to process more chips, make more pulp, and produce higher pulp yield, saving time, energy, and money.

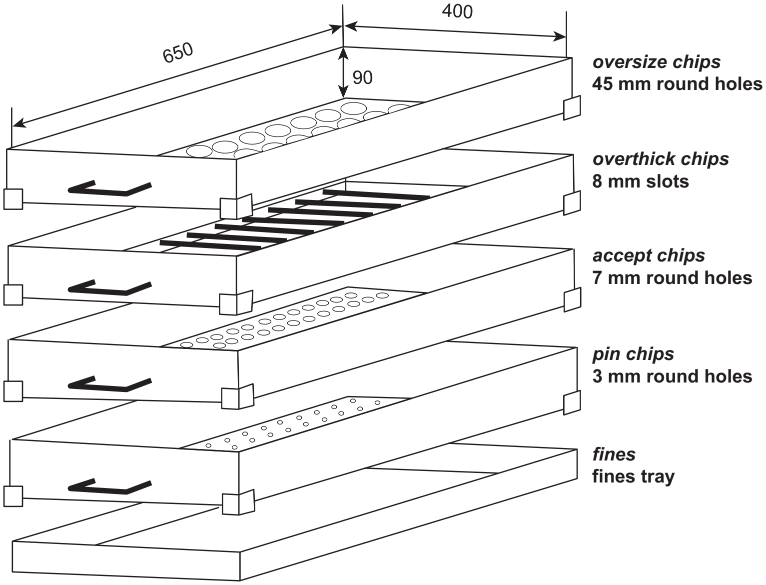


FIGURE 11.18 Chip classifier SCAN-CM. *Reproduced with permission Gullichsen (2000).*

FIGURE 11.19 Belt conveyer. *Courtesy FEECO International, Inc. — Process Development & Equipment Manufacturing — Green Bay, WI USA.*

Anonymous, May 1 (1995). Woodhandling Focus. Pulp and Paper International. Miller Freeman Publications, San Francisco, CA, Available from: http://www.pponline.com/db_area/archive/ppi_mag/1995/9504/95040109.htm.

Woodhandling technology to improve the quality and profitability of the total paper-making process is presented.

Anonymous (2008). Ring debarkers lift fiber recovery profits. Timberline Magazine. Available from: http://www.timberlinemag.com/articledatabase/view.asp?articleID=279.

Ring debarkers are discussed in this paper. These debarkers improve chip quality because ring systems remove more bark from the wood. With less bark residue, sawmills get higher prices for their chips and experience a lower level of rejects.

Bajpai P (2010). Environmentally Friendly Production of Pulp and Paper. John Wiley & Sons, Hoboken, NJ.

This book on Environmentally Friendly Production of Pulp and Paper provides information to implement the internationally recognized process of cleaner production (CP). It provides updated information on CP measures in different areas of pulp and paper making.

Gullichsen J (2000). Fiber line operations. In: Gullichsen, J., Fogelholm, C.-J. (Eds.), Chemical Pulping —Papermaking Science and Technology: Book 6A. Fapet Oy, Helsinki, Finland.

This book deals step by step, why and how things are done to obtain fibers from wood by chemical pulping. This book combines science and technology in a way that allows both students and mill engineers to benefit from learning about modern fiber lines, while increasing their awareness of the challenges and opportunities involved in research and in the design and operation of new pulp mills.

Sixta, H. (Ed.) (2006). Handbook of Pulp. WILEY-VCH Verlag GmbH & Co. KgaA, Weinheim Germany, pp. 69—107 (Chapter 3).

This is a comprehensive handbook dealing with the traditional aspects of pulping processes. It describes all pulping processes used for paper and board manufacturing as well as waste liquor treatment, pulp bleaching and environmental aspects, while also covering pulp properties and applications.

Smook GA (2003). Handbook for Pulp and Paper Technologists. Joint Textbook Committee of the Paper Industry of the United States and Canada, 425 p.

This book provides an introduction to the entire technology of pulp and paper manufacture, covering all aspects of pulping and papermaking.

Strakes G (1995). Mills enhanced chip quality with modern woodyard options. Pulp and Paper Magazine. July. Available from: http://www.risiinfo.com/db_area/archive/p_p_mag/1995/9507/95070118.htm.

This paper outlines key components of CTS systems used by pulp and paper mills to maximize wood fiber utilization.

Strakes G, Bielagus, J (1992). New chip thickness screening system boosts efficiency, extends wear life. Pulp Paper, 105.

New CTS system which boosts efficiency and extends wear life is described in this paper.

Valmet (2000). The total woodyard. Valmet, Technical Paper series. www.valmet.com/globalassets/media/downloads/white-papers/.../wpo_woodyard.pdf

This white paper, prepared by Valmet, offers information on the total woodyard.

CHAPTER

12

Pulping Fundamentals

12.1 INTRODUCTION TO PULPING

Pulp

Pulp consists of wood or other lignocellulosic materials that have been broken down physically and/or chemically such that (more or less) discrete fibers are liberated and can be dispersed in water and reformed into a web. Fig. 12.1 shows a brown paper (no bleaching) kraft mill process.

Pulp is also commonly manufactured using recovered wastepaper as a raw material. Less commonly, pulp can also be manufactured from other types of fibrous materials such as linters, used or recycled rags, scrap paper, and straw. Pulp mills produce "market pulp," which is the pulp sold in the open market for the production of paper at separate facilities. Major North American producers of market pulp include as follows:

- Weyerhaeuser
- Tembec
- Canfor
- AbitibiBowater
- Daishowa-Marubeni

Paper mills are engaged in the manufacture of paper products from pulp. An integrated paper mill is one that manufactures its own pulp in house; however, paper mills may also purchase market pulp. Some paper mills may also convert the paper that they make into final products (e.g., boxes or bags).

The prices of pulps currently are as follows:

Bleached softwood kraft: $735–760
Bleached hardwood kraft: $685–730
Unbleached softwood kraft: $670–700
Dissolving pulp: $800–810
Bleached chemithermomechanical pulping (CTMP): $625

Pulping

There are four broad categories of pulping processes: *chemical*, *semichemical*, *chemimechanical*, and *mechanical pulping*. These are in order of increasing mechanical energy required to separate fibers (fiberation) and decreasing reliance on chemical action. Thus, chemical pulping methods rely on the effect of chemicals to separate fibers, whereas mechanical pulping methods rely completely on physical action. The more the chemicals are involved, the lower the yield and lignin content because chemical action degrades and solubilizes components of the wood, especially lignin and hemicelluloses. On the other hand, chemical pulping yields individual fibers that are not cut and give strong papers because the lignin, which interferes with hydrogen bonding of fibers, is largely removed. Fig. 12.2 shows electron micrographs of several pulp types that demonstrate this

Biermann's Handbook of Pulp and Paper: Raw Material and Pulp Making
https://doi.org/10.1016/B978-0-12-814240-0.00012-4

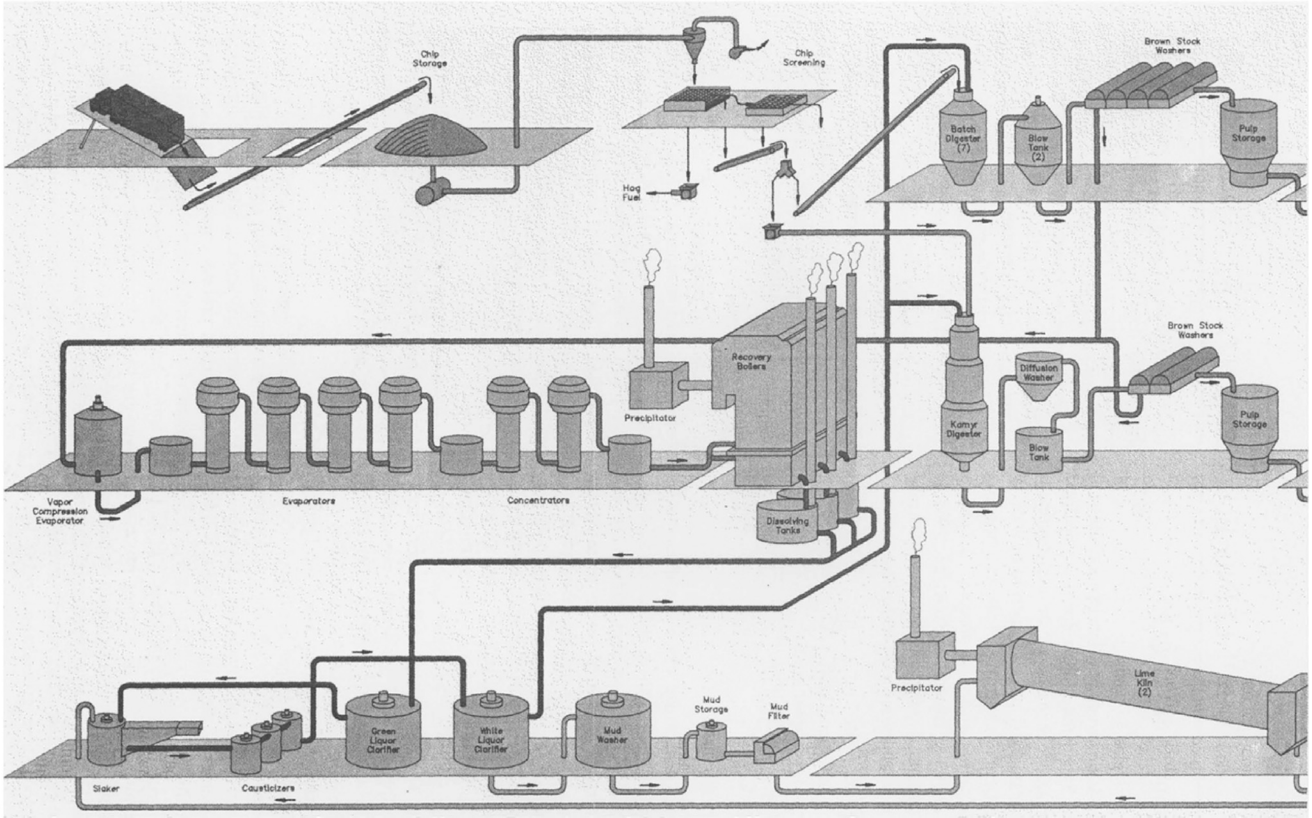


FIGURE 12.1 Mill layout of a kraft linerboard mill (no bleaching). *Courtesy of Weyerhaeuser Paper Co.*

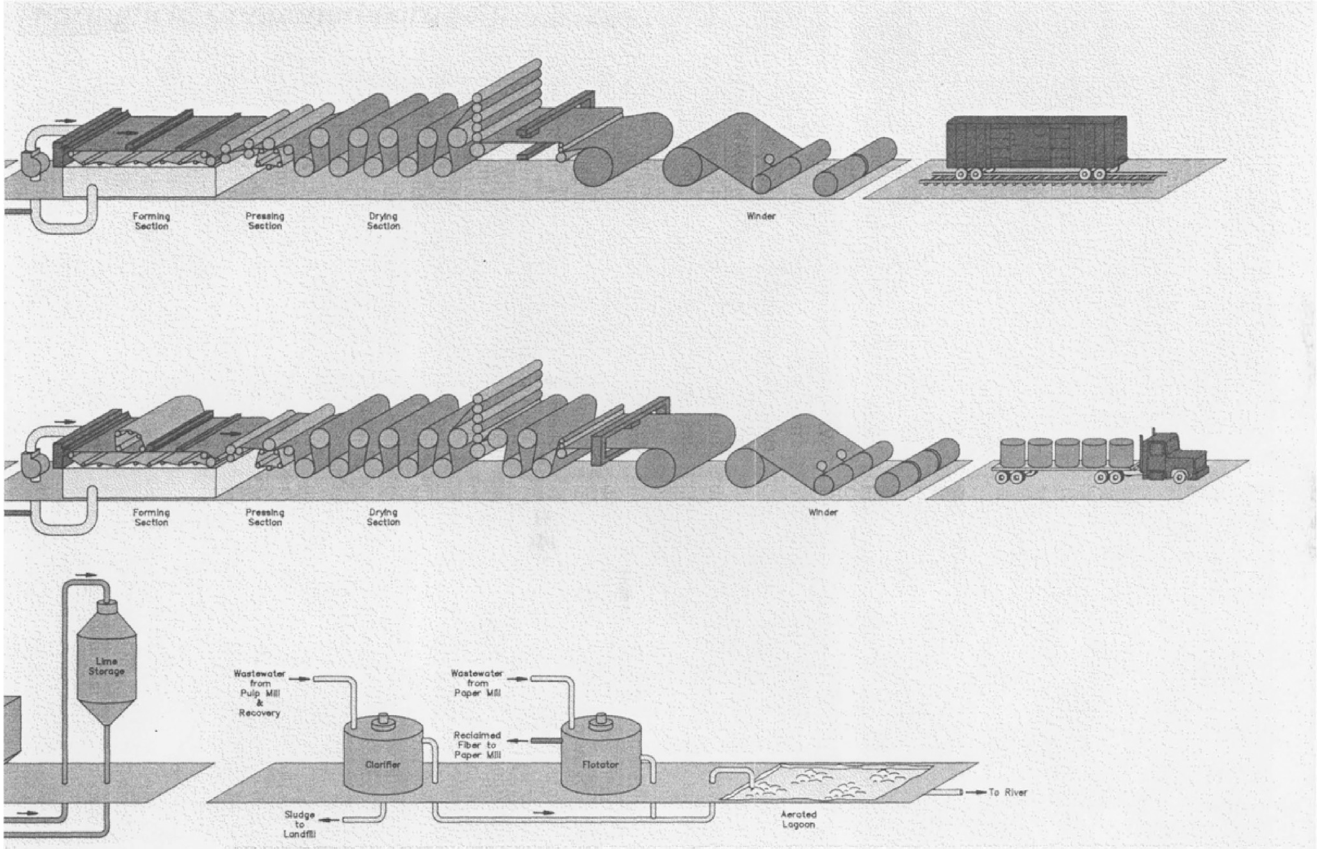


FIGURE 12.1 cont'd.

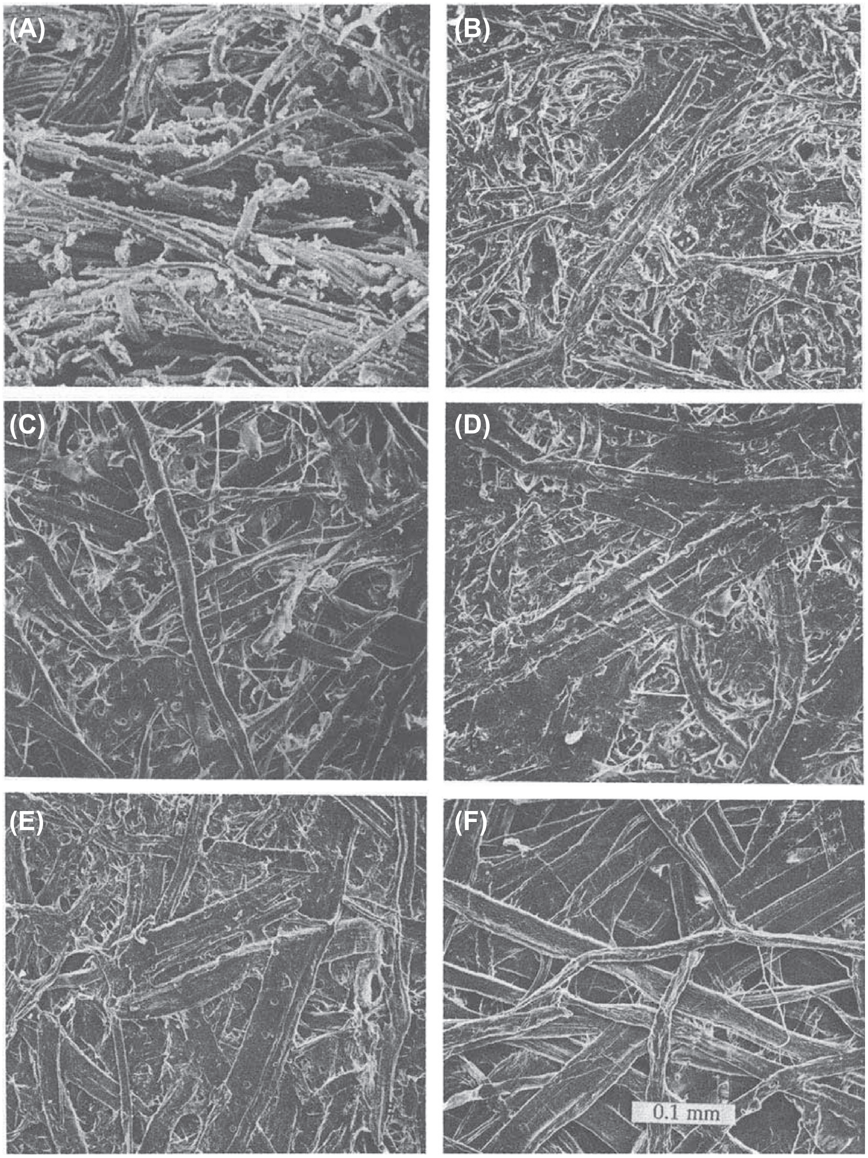


FIGURE 12.2 (A) Steam exploded hardwood. Papers of (B) SGW hardwood, (C) TMP softwood, (D) newsprint, (E) NSSC hardwood/OCC medium, and (F) bleached kraft softwood fibers. *NSSC*, neutral sulfite semichemical; *OCC*, old corrugated container; *SGW*, stone groundwood; *TMP*, thermomechanical pulp.

point. Details of these types of pulps will be considered below.

Table 12.1 summarizes important aspects of the most common classes of pulping processes. Table 12.2 shows production of paper grade wood pulp (1000 tons) in 2012. The relative strength of kraft:sulfite:soda:stone groundwood (SGW) pulps for a given species of wood is

TABLE 12.1 Summary of Pulping Processes

Process	Chemicals	Species	Pulp Properties	Uses	Yield
Mechanical pulping	None; grindstones for logs; disc refiners for chips	Hardwoods such as poplar or light-colored softwoods such as spruce, balsam fir, hemlock, true firs	High opacity, softness, bulk; low strength and brightness	Newsprint, books, magazines	92%–96%
Chemimechanical pulping	Chemithermomechanical pulp; mild action; NaOH or $NaHSO_3$		Moderate strength		88%–95%
Kraft process, pH 13–14	$NaOH + Na_2S$ (15%–25% on wood); unlined digester, high recovery of pulping chemicals, sulfur odor	All woods	High strength, brown pulps unless bleached	Bag, wrapping, linerboard, bleached pulps for white papers	65%–70% for brown papers; 47%–50% for bleachable pulp; 43%–45% after bleaching
Sulfite, acid, or bisulfite pH 1.5–5	$H_2SO_3 + HSO_3^-$ with Ca^{2+}, Mg^{2+}, Na^+, or NH_4^+ base; Ca^{2+} is traditional but outdated because no recovery process; lined digesters	Hardwoods such as poplar and birch and nonresinous softwoods; Douglas fir is unsuitable	Light brown pulp if unbleached, easily bleached to high brightness, weaker than kraft pulp but higher yield	Fine paper, tissue, glassine, strength reinforcement in newsprint	48%–51% for bleachable pulp; 46%–48% after bleaching
	Mg^{2+} base	Almost all species, spruce and true firs, preferred	Same as above but lighter color and slightly stronger	Newsprint, fine papers, etc.	50%–51% for bleachable pulp; 48%–50% after bleaching
Neutral sulfite semichemical pH 7–10	$Na_2SO_3 + Na_2CO_3$; about 50% of the chemical recovered as Na_2SO_4	Hardwoods (preferred): aspen, oak, alder, elm, birch; softwoods: Douglas fir sawdust, and chips	Good stiffness and moldability	Corrugating medium	70%–80%

Reprinted from Krahmer, R.L. and A.C. VanVliet, Ed., Wood Technology and Utilization, *O.S.U. Bookstore, Corvallis, Ore., 1983 with permission.*

TABLE 12.2 Production of Paper Grade Wood Pulp (1000 tons) in 2012

Total paper grade	167,001
Bleached softwood kraft	34,825
Bleached hardwood kraft	60,131
Sulfite	3,010
Unbleached kraft	33,629
Semichemical	5,246
Mechanical	30,160

From www.risiinfo.com/Marketing/ahd/Excerpts/world_pulp.pdf.

roughly 100:70:40:30, although this depends on the species of wood, strength property, and pulping conditions. Table 12.3 gives some mechanical and physical properties of representative commercial pulps. Although this may not mean much on the first reading through the book, it is useful information for understanding the reason why particular pulps are used in particular grades of paper.

Wood-Free (Free-Sheet)

Wood-free pulp or free-sheet paper contains no mechanical pulp or pulp subjected to a minimum of refining; consequently, during its manufacture the water drains very quickly from the pulp on the fourdrinier wire.

Screening

Screening of pulp after pulping is a process whereby the pulp is separated from large shives, knots, dirt, and other debris. *Accepts* consist of the pulp that has passed through the screens. The *accept yield* is the *yield* of accepts. *Rejects* or *screenings* are the larger shives, knots, large dirt particles, and other debris removed by the screens after the pulping process.

Shives

Shives are small fiber bundles of fibers that have not been separated into individual fibers during the pulping process. They appear as "splinters" that are darker than the pulp.

Yield

Yield is a general term used in any phase of pulping, papermaking, chip screening, bleaching, etc. indicating the amount of material recovered after a certain process compared with the starting amount of material before the process. To have meaning, both samples must be compared on an ovendry basis. In pulping operations the yield is the ovendry pulp mass expressed as a percentage of the ovendry wood mass. Mechanical pulp yields are typically 92%–96%, and bleached chemical pulp yields are typically 40%–45%. For example, 100 lb of dry wood yields about 40–45 lb of pulp for bleached printing paper.

$$\text{yield, \%} = \frac{\text{dry product mass out}}{\text{dry material mass in}} \times 100\%$$

Total Yield, %

The total yield is equal to the amount of pulp removed during screening and the yield of pulp after the screens when all three are expressed as a percentage of the original wood put in the digester. When one speaks of pulp yield it is necessary to state whether it is the total yield or screened yield.

$$\begin{aligned}\text{Total yield}(\%) &= \text{Screenings}(\%)\\ &\quad + \text{Screened yield}(\%)\end{aligned}$$

Consistency

Consistency is a measure of the *solids content* as a percentage in a pulp slurry.

$$\text{consistency} = \frac{\text{dry solids mass}}{\text{slurry mass}} \times 100\%$$

TABLE 12.3 Properties of Commercial Pulp Samples c.1975 From Manufacturer's Specifications[a]

Beating Time (min)	CSF (mL)	Breaking Length (km)	Tear Factor (metric)	Double Folds	Bulk (cc/g)	Air Resistance (s)	Opacity
IA. Softwood kraft pulp (Kamyr dig.) of long-fibered western hemlock, red cedar, and Douglas fir. The alpha cellulose content is 82%, the pentosans content is 5.6%, and the lignin content is 2.7%.							
0	662	4.7	222	70	1.88	4	
20	508	9.1	121	780	1.60	50	
45	205	11.3	104	1720	1.44	802	
IB. The same fiber mix as IA after fully bleaching by CEDED to 88+ brightness is 86.5% alpha cellulose and 4.5% pentosans. The cellulose viscosity is C_p 22, and the stretch is 3.2%–3.5%.							
0	661	5.0	242	120	1.83	3	73
15	494	9.9	122	900	1.56	34	67
30	249	11.0	114	1600	1.48	513	63
II. Sulfite softwood pulp of 94% brightness, 88% alpha cellulose, and 350 cps viscosity.							
0	705	1.9	136	3	1.78	1	75
31	550	5.9	102	130	1.45	15	70
75	250	7.5	83	650	1.33	250	65
III. Hardwood kraft pulp of 91% brightness, 87.5% alpha cellulose, and 65 cps viscosity.							
0	585	2.6	106	5	1.85	2	82
13	550	4.5	101	30	1.75	5	79
81	250	8.3	87	350	1.45	80	74
IV. Hardwood sulfite of 93% brightness, 88.5% alpha cellulose, and 160 cps viscosity.							
0	625	1.5	54	0	1.85	1	82
15	550	2.8	67	5	1.67	5	80
74	250	5.5	68	40	1.35	65	86
V. Softwood thermomechanical pulp of 50% brightness (determined in OSU lab. in 1991).							
0	396	1.3	5.4	1	3.49		97
120 (PFI)	123	3.4	7.8	8	2.65		97
240 (PFI)	102	3.8	6.7	9	2.53		96

CSF, Canadian standard freeness; *PFI*, papperindustriens forsknings intitutet; *TMP*, thermomechanical pulp.

[a] *Note that testing conditions of 60 g/m^2 handsheets at 73°F at 50% relative humidity with refining by the valley beater (except TMP as noted). The relative mullen burst values are similar to those of the tensile breaking length. All tests are TAPPI Standard methods.*

12.2 MECHANICAL PULPING

Mechanical Pulp

Mechanical pulp is pulp produced by using only mechanical attrition to pulp lignocellulosic materials; no chemicals (other than water or steam) are used. Light-colored, nonresinous softwoods and some hardwoods are often the fiber source. The total yield is about 90%–98%. Lignin is retained in the pulp; therefore, high yields of pulp are obtained from wood. Mechanical pulps are characterized by high yield, high bulk, high stiffness, and low cost. They have low strength because the lignin interferes with hydrogen bonding between fibers when paper is made. The lignin also causes the pulp to turn yellow with exposure to air and light.

The main subdivisions of mechanical pulping method are SGW pulping, refiner mechanical pulping (RMP), thermomechanical pulping (TMP), CTMP, and pressure groundwood (PGW) pulping. Mechanical pulping processes are electricity intensive and account for the majority of power consumption. The specific energy consumption in mechanical pulping is 1000–4300 kWh/ADt pulp for different mechanical pulping methods (SGW, RMP, TMP, or CTMP) (European Commission, 2013). The specific energy consumption in mechanical pulping is dependent on the particular pulping process, the properties of the raw material (wood species), and, to a large extent, the quality requirements (freeness) of the pulp set by the end product. Typical ranges of energy consumption are shown in Table 12.4.

The use of mechanical pulps is confined mainly to nonpermanent papers such as newsprint and catalog paper. Mechanical pulps constitute 20%–25% of the world production, and this is increasing due to the high yield of the process and increasing competition for fiber resources. Furthermore, technological advances have made mechanical pulps increasingly desirable.

TABLE 12.4 Energy Consumption and Recovery of Energy in Mechanical Pulping

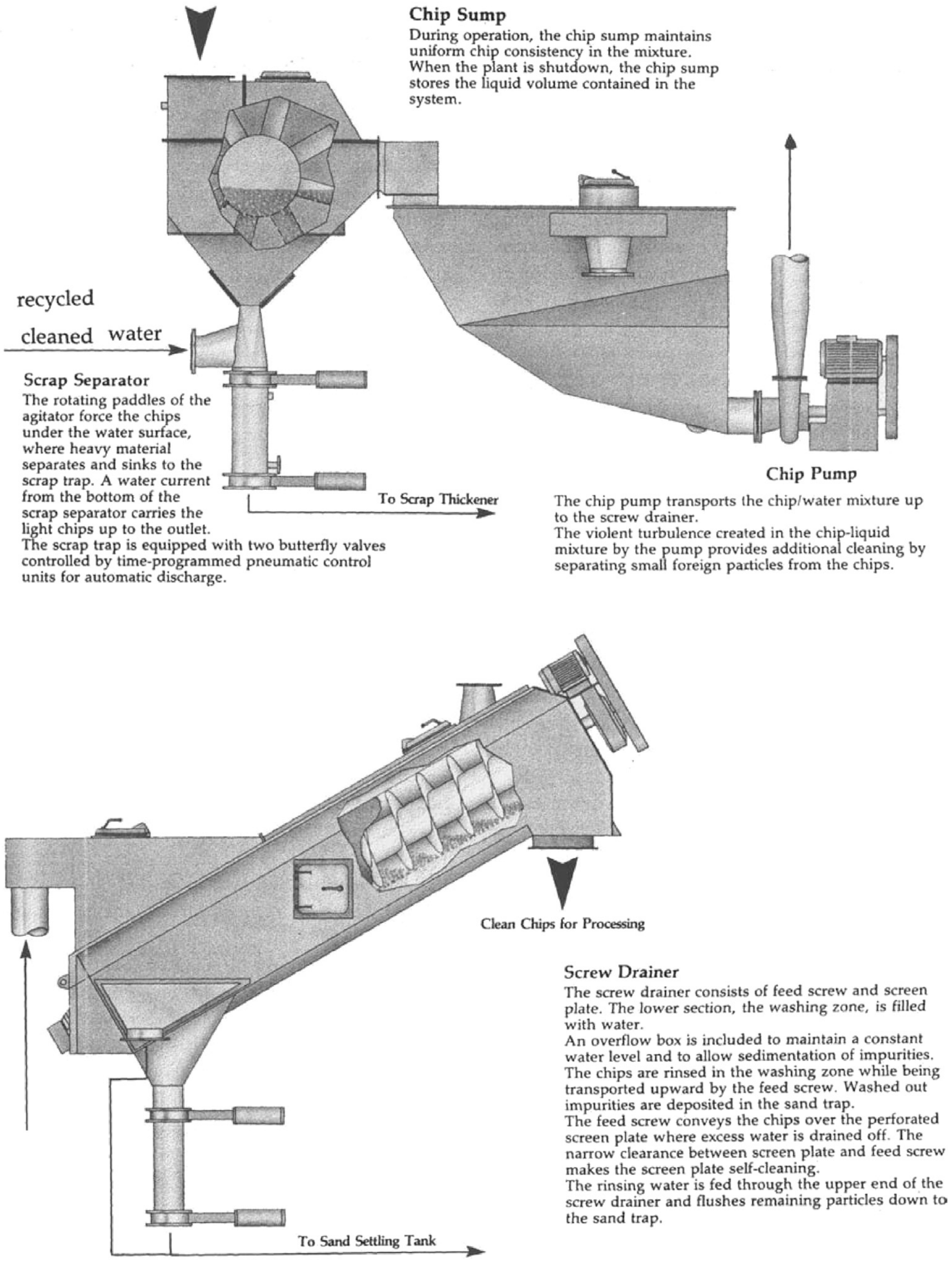
Mechanical Pulp and Freeness (mL CSF)	Energy Consumption (kWh/t of Pulp)
GW 350–30	1100–2200
PGW 350–30	1100–2200
PGW-S 350–30	1110–2300
RMP 350–30	1600–3000
TMP 400–30	800–3600
CTMP 700–30	1000–4300

CSF, Canadian standard freeness; *CTMP*, chemithermomechanical pulp; *GW*, groundwood; *PGW*, pressure groundwood; *PGW-S*, super pressure groundwood; *RMP*, refiner mechanical pulping; *TMP*, thermomechanical pulp.
Based on European Commission (2001).

In the last two decades, TMP processes have largely replaced SGW. CTMP and bleached CTMP (BCTMP) are displacing small amounts of chemical pulps in certain grades of paper. Most CTMP is produced in Canada. PGW is important in Scandinavia but has limited production outside this region.

Chip Quality and Cleanliness

Some aspects of chip quality are very important in mechanical pulping. Because mechanical pulps cannot be brightened very much by chemicals, chip quality (except for SGW, which uses wood logs) is of extreme importance. Generally chips less than 2 weeks old are used with stringent bark and dirt tolerances. Chips older than 2 weeks tend to be discolored too much by decay and air oxidation. Washing the chips (Fig. 12.3 shows one type of chip washing system) before pulping is a necessity, just as in any mechanical or semichemical pulping operation where disc refining is ultimately required to break apart the wood chips. Sand, pebbles, tramp metal, and other gritty materials would otherwise cause undue damage to the refiners.



Chip Sump

During operation, the chip sump maintains uniform chip consistency in the mixture. When the plant is shutdown, the chip sump stores the liquid volume contained in the system.

Scrap Separator

The rotating paddles of the agitator force the chips under the water surface, where heavy material separates and sinks to the scrap trap. A water current from the bottom of the scrap separator carries the light chips up to the outlet.
The scrap trap is equipped with two butterfly valves controlled by time-programmed pneumatic control units for automatic discharge.

Chip Pump

The chip pump transports the chip/water mixture up to the screw drainer.
The violent turbulence created in the chip-liquid mixture by the pump provides additional cleaning by separating small foreign particles from the chips.

Screw Drainer

The screw drainer consists of feed screw and screen plate. The lower section, the washing zone, is filled with water.
An overflow box is included to maintain a constant water level and to allow sedimentation of impurities.
The chips are rinsed in the washing zone while being transported upward by the feed screw. Washed out impurities are deposited in the sand trap.
The feed screw conveys the chips over the perforated screen plate where excess water is drained off. The narrow clearance between screen plate and feed screw makes the screen plate self-cleaning.
The rinsing water is fed through the upper end of the screw drainer and flushes remaining particles down to the sand trap.

FIGURE 12.3 Chip washing system that incorporates water reuse. *Courtesy of Sunds Defibrator.*

Stone Groundwood

Groundwood mechanical pulp is produced by grinding short logs, called *bolts*, with grindstones on the tangential and radial surfaces. Original grindstones were sandstone, but segmented stones with embedded silicon carbide or aluminum oxide are used now. The sandstone grindstones had to be treated carefully to prevent them from bursting due to thermal shocks; they were phased out in the early 1940s. SGW was first produced in the 1840s as a wood meal using technology from grain mills; the French naturalist de Reamur realized that paper could be made from wood when his study of wasp nests in 1719 showed that they were made from wood particles held together with proteins from wasp saliva. Early mechanical pulps were merely fillers to extend the supply of cotton and other fibers. However, advances in the process gave stronger pulps. The large amount of fines makes this pulp useful for increasing the opacity of some printing papers although hardwood CTMP (discussed later) is a suitable substitute for this purpose. The energy use is about 1300 kWh/ton (50−80 hp-day/ton) with the higher amounts for high-grade papers; yields are 93%−98%. The mechanism of grinding is not a cutting action, and stones with sharp edges are not desired. Instead, reasonably selective fiber−fiber separation is achieved by peeling caused by repeated shear stresses. The shear stresses begin when the fibers are about 3−5 fiber diameters away from the stone's surface. These are obtained by repeated compression and decompression of the wood generated by the groove pattern on the stone's surface. Woods of low density are particularly suited to groundwood production because they allow the most deformation due to large lumens that accommodate expansion and contraction of the fibers caused by impact with the grits on the surface of the stone. If the wood is not able to distribute the load by flexing, fibers tend to be cut rather than separated from each other, leading to pulp of high fines content and low strength.

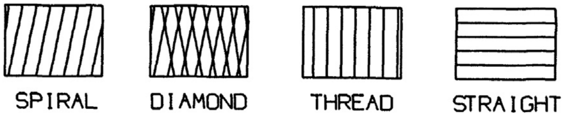


FIGURE 12.4 Burr patterns used for sharpening pulp stones for stone groundwood production.

The burr pattern is very important. The commonly used patterns are shown in Fig. 12.4. They include *spiral*, which is the most commonly used pattern type because it produces a high-quality pulp; *diamond*, which is usually used to erase old patterns and resurface the stone; *thread*, which is not often used because it tends to generate both chunky fibers and fines (actually flour); and *straight*, which makes long, coarse pulp fibers suitable for building and insulation boards. A No. 9, 1 in. lead, spiral burr has 9 threads per inch with the thread rising 1 in. from the left to the right hand side. Burr patterns are cut by the metal burr that makes several passes over the stone until the burr pattern depth on the stone is about 1.6 mm. This is called stone sharpening and must be done every 50−150 h. Pulp strength properties are considerably lower right after sharpening of the stone, so stone sharpening must be staggered from grinder to grinder in a mill. Pulp burst and strength properties increase between stone sharpenings by 25%−50% (advantageous). However, pulping specific energy increases 25%−50%, production rate decreases 25%−100%, and freeness decreases by a factor of 1−3, all three of which are disadvantages. Water is used in the grinding process before and after the grinding area to control the temperature of the grindstone and to wash the pulp from the grindstone. The pulp leaves at 2%−5% consistency. A 3000−5000 hp motor spinning a 1.5-m (typically 54−70 in.) diameter grindstone at 240−300 rpm (18−24 m/s or 3400−4500 ft/min at the grinding surface) will grind about 50 ton/day, corresponding to 30–40 hp/ft^2 grinding area. The grinding pressure is 40–80 psi. The water temperature in the pit is 140–180°F. Newsprint requires 55–70 hp-day/ton, whereas book paper uses 60–85 hp-day/ton. The important grinding variables are as follows:

1. Wood species and other wood variables.
2. Type of pulp stone.
3. The use (or not) of a water-filled grinding pit.
4. Type of burr pattern on the stone.
5. Stone surface speed.
6. Hours on the stone since last burring.
7. Pressure of wood against the stone.
8. Temperature of grinding surface, 130–180°C (265–355°F).
9. Amount of water used (and, therefore, the final pulp consistency).

An example of SGW paper from hardwoods is shown in Fig. 12.2. This paper was from an experimental press run of the March 26, 1959 *Savannah Evening News* where a mixture of seven southern US hardwoods were used. Although relatively intact fibers and vessel elements are observed in this figure, there are numerous fiber fragments as well. The overall process and grinding action are shown in Fig. 12.5. Fig. 12.6 shows some of the many types of grinder configurations that have been used. Pocket grinders were once popular but have been largely replaced by the various magazine grinders that have continuous feeding of wood, which greatly reduced the manpower required to load wood. The three pocket hydraulic grinder was introduced around 1900. When the wood in one of the pockets is consumed the door is opened after the pressure foot is retracted, wood is added manually, the door is closed, and the pressure foot is engaged with water pressure. The magazine grinder was introduced by Voith of Germany in 1908. The Great Northern Grinder (and modifications such as that of Koehring-Waterous Ltd.) was installed at many mills making newsprint in the 1950s. Large units grind wood 1.6 m (5 ft) long at the rate of 80 tons/day using 5500 hp. The chain grinder is the most common of the continuous grinders introduced in the 1920s. Large units pulp wood 2 m (6.5 ft) long at the rate of 100 tons/day using 7000 hp. The continuous Roberts ring grinder was introduced in the 1940s.

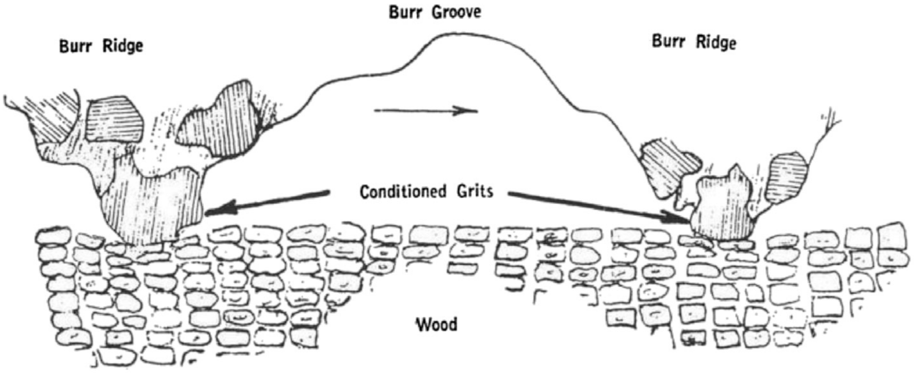
Pressure Groundwood

By pressurizing the grinder with steam at temperatures of 105–125°C (220–255°F), the wood is heated and softened before the grinding process. This gives better separation of fibers with less cutting action and lower fines generation. This process yields a pulp that has higher tear strength and freeness and is brighter than SGW, yet has lower power requirements. About one-half of the world's PGW is produced in the Scandinavian countries. As one reads through this section it will become apparent that PGW is to SGW as TMP is to RMP.

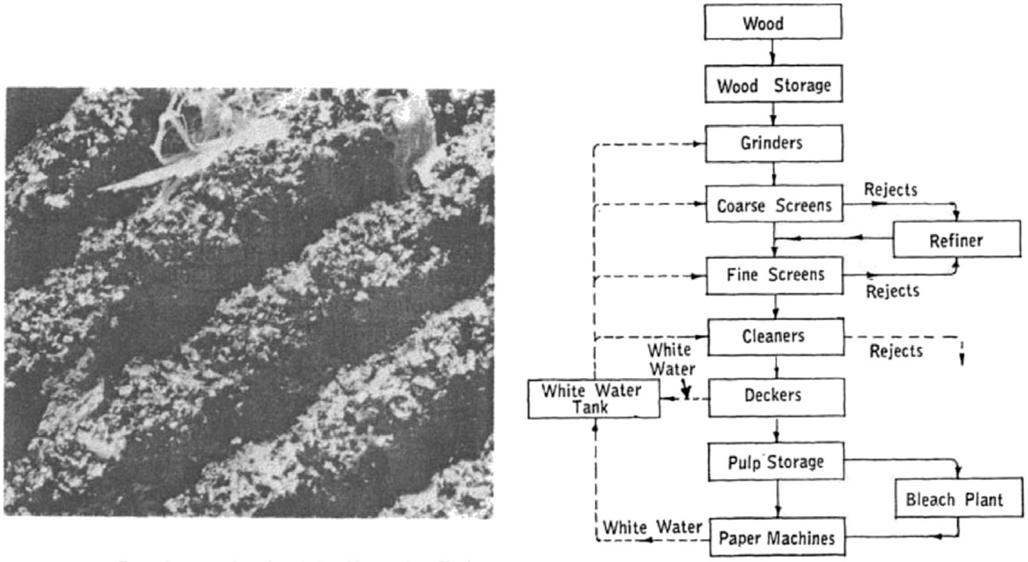
Refiner Mechanical Pulp

RMP is produced by disintegrating chips between revolving metal discs or plates with raised bars (Plate 12.1) at atmospheric pressure.

This process was developed during 1948–56 by Bauer Bros and is patented by Eberhardt. Some of the steam generated in the process softens the incoming chips, resulting in fibers that maintain more of their original integrity compared with SGW because there is less cutting action and increased separation of fibers at the middle lamella. Because of this action, there are less fines formed, and RMP is bulkier and stronger than SGW. Power requirements are 1600–1800 kWh/ton (90–100 hp-day/ton). Disc refiners are up to 1.5 m (60 in.) in diameter and rotate at 1800 rpm with 60 Hz power; this gives a velocity at the periphery of up to 140 m/s. The plates containing the metal bars must be replaced every 300–700 h or low-quality pulp is produced and energy use increases. Refining is usually carried out in two



Fiberizing by Compression of the Wood by Conditioned Grits



Burr Pattern Imprinted by Sharpening Tool (Stone Surface 9x)

Stone Groundwood Process—Flow Diagram

FIGURE 12.5 Grinding action and overall stone groundwood process. *Reprinted from Making Pulp and Paper, ©1967 Crown Zellerbach Corp., with permission.*

stages. The first is at 20%–30% consistency to separate the fibers, whereas the second is at 10%–20% consistency to alter the surface of the fibers for improved fiber bonding in the final paper. The pulping variables are as follows:

1. Wood species and other wood variables.
2. Pulp consistency.
3. Sharpness and pattern of refiner plates.
4. Temperature of refining.
5. The gap between the refiner plates (0.005–0.1 in.; 0.035 in. typically).
6. Rate of feed through the refiner.
7. Speed of the refiner plates.

The RMP process was an important development in the history of mechanical pulping. Now, however, TMP, a modification of the RMP process, and other mechanical pulping processes have made the RMP process almost obsolete.

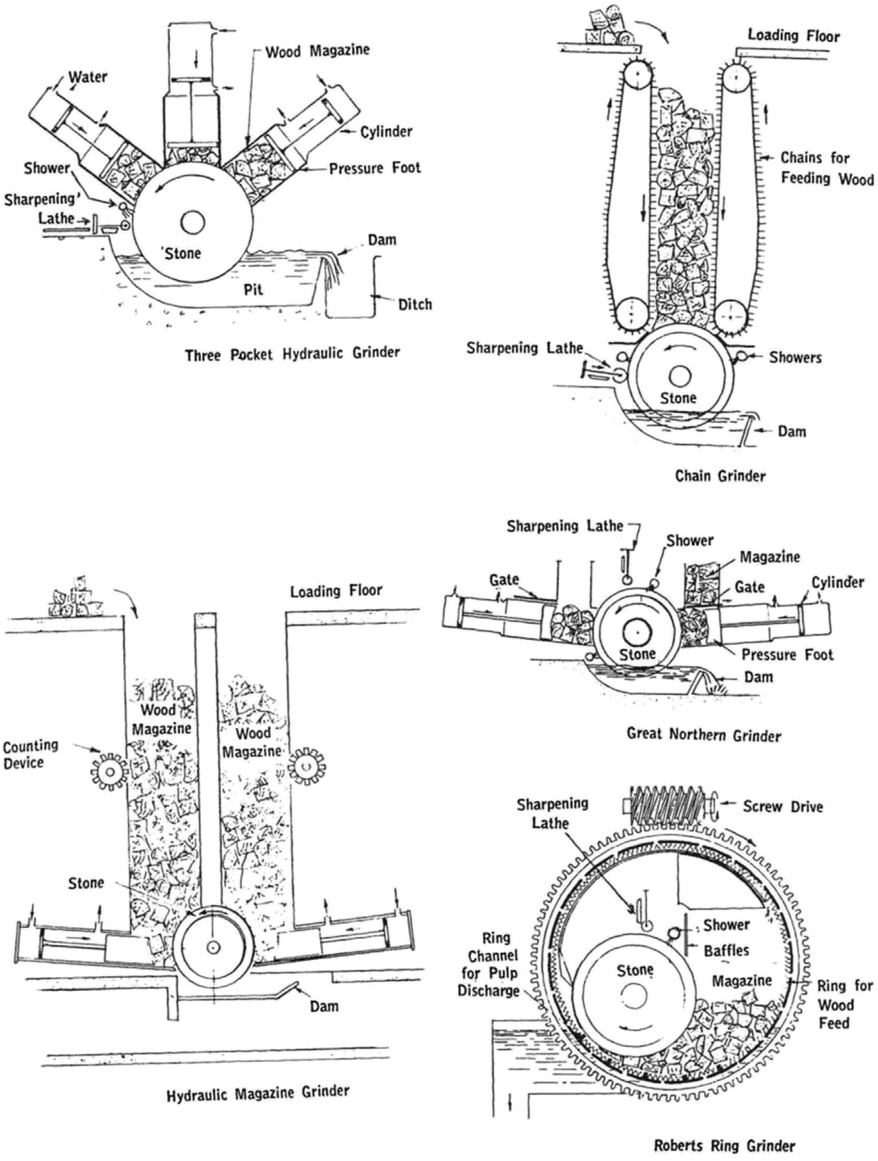


FIGURE 12.6 Grinder configurations used in the stone groundwood process. *Reprinted from Making Pulp and Paper, ©1967 Crown Zellerbach Corp., with permission.*

Thermomechanical Pulp

TMP was developed about 10 years after RMP and has become the most important mechanical pulping method. For example, in 1975, less than 200,000 metric tons of TMP were produced in North America. In 1989, the US capacity was less than 3 million metric tons, whereas Canada was just less than 6 million metric tons. The

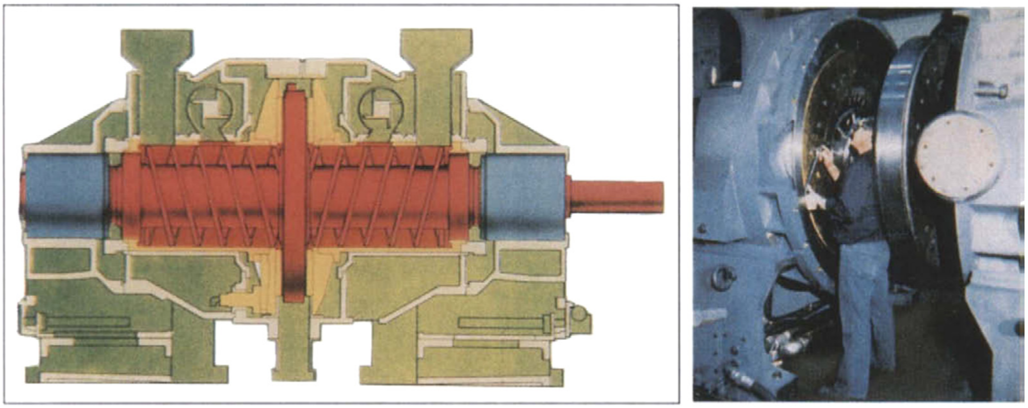


PLATE 12.1 Twin refiner. The rotating double-sided inner disc with ribbon feed (red) and axle is between two stationary discs (yellow). The insert shows the refiner open in the center for easy plate changing. *Courtesy of Andritz Sprout-Bauer.*

TMP process is very similar to the RMP process, except that pulp is made in special refiners that are pressurized with steam in the first stage of refining. Fig. 12.7 shows a typical flow diagram for a TMP plant. TMP is usually carried out in two stages of refining. In the first stage, the refiners are at elevated temperature and pressure to promote fiber liberation; in the second stage, the refiners are at ambient temperature to treat the fibers for papermaking. The higher temperature during refining in the first step, 110−130°C (230−265°F), softens the fibers and allows their recovery with minimal cutting and fines compared with SGW or even RMP. The refining is just below the glass transition temperature of lignin, which is approximately 140°C (285°F), so that separation of fibers occurs at the S1 cell wall layer. This improves fibrillation (surface area) and access to hydroxyl groups for hydrogen bonding. A laboratory pressurized refiner for making TMP pulp is shown in Fig. 12.8.

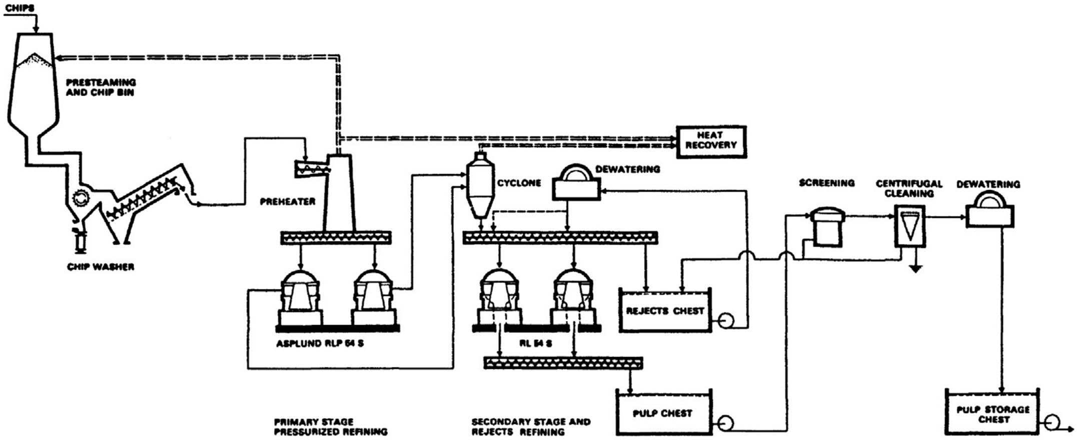


FIGURE 12.7 Representative layout of a newsprint thermomechanical pulp plant. *Courtesy of Sunds Defibrator.*

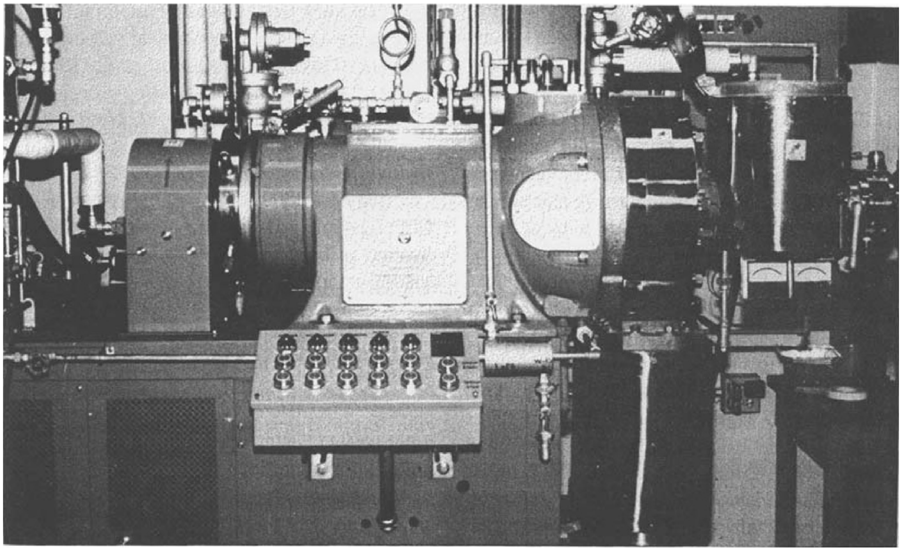


FIGURE 12.8 Pressurized laboratory refiner for making thermomechanical pulp.

The high strength of this pulp relative to the other mechanical pulps has made it the most important mechanical pulp. Energy requirements are 1900–2900 kWh/ton (100–150 hp-day/ton), slightly more than RMP and significantly more than SGW. Over two-thirds of this is used in the primary pressurized refining step, and less than one-third is used in the secondary atmospheric pressure refining step. An even consistency of 20%–30% is ideal for primary refining and is the most important operating variable; lower consistencies cause fiber damage from the refiner plate bars, whereas higher consistencies cause the refiner to plug. TMP tends to be darker than SGW because of chemical reactions at the elevated temperatures, and wood chip supplies often contain more bark, dirt, and other impurities than bolts used in SGW. The pulp yield is 91%–95%. Solubilization of wood components makes Biological Oxygen Demand (BOD) levels relatively high in mill effluents. If the steaming temperature is too high then the process has the problems of the Asplund process (Section 12.4), that is, the surface of the fibers becomes coated with lignin that interferes with hydrogen bonding. This results in weak, dark paper. Fig. 12.2 shows two samples of TMP. The first is softwood TMP from the refiner chest of a newsprint mill. The second is a sample of 1990 newsprint. These samples show much less fiber fragmentation than the SGW sample, but there are still more fiber fragments and fiber delamination than in the bleached kraft softwood fibers.

12.3 CHEMIMECHANICAL PULPING

General Aspects

What are now called chemimechanical processes were originally called chemigroundwood processes because these chemical pretreatments were developed and used commercially at a time (early 1950s) when SGW was the predominant mechanical process. (The original laboratory work on chemimechanical pulping and cold soda pulping of straw had been done much earlier.) However, these chemical pretreatments have application to all of the mechanical pulping processes. ESPRA (Empire State Paper Research Associates), whose laboratories are in Syracuse, New York, applied the neutral sulfite semichemical (NSSC) process (Section 12.5) in a mild form before groundwood pulping. In one operation, four-foot long hardwood logs were treated in large digesters (60 ft high by 10 ft in diameter). A vacuum was first applied to remove much of the air from the logs and allow better liquor penetration. The liquor, containing aqueous Na_2SO_3 and Na_2CO_3, was then introduced and kept at 130−155°C (265−310°F), depending on the species of wood. The pressure was maintained at 150 psi. The pretreated logs were then pulped by the SGW method. All of the advantages of the CTMP process (over TMP) were observed long before CTMP was thought of with the original chemigroundwood method. The grinding requirements were about half that required without pretreatment, and the Canadian standard freeness (CSF) was 300−350 mL. At around the same time, the cold soda method was developed, although it has only had limited use. The chemimechanical pulping process consists of two stages with yields of 85%−95%. A particularly mild chemical treatment is followed by a drastic mechanical action but not as drastic as without chemical pretreatment. The original lignin structure and content is preserved, but extractives and small amounts of hemicellulose are lost. When higher temperatures are used in the various steps, a darker pulp is usually obtained. One of several chemical pretreatments can be applied before SGW, PGW, RMP, or TMP. The most common chemimechanical process is now CTMP. The pretreatments are hot sulfite or cold soda and are particularly applicable to hardwoods that otherwise do not give mechanical pulps of high quality. Several mills have also begun to use an alkaline peroxide chip pretreatment.

Chemical Pretreatments

In the *hot sulfite* process, pressurized hot sulfite liquor is used to treat chips before fibration. This results in a pulp brighter than the cold soda process that is usable in book papers, catalogs, and newspapers. The pulp is usable in papers by itself in the case of softwood pulp, but 10%−15% chemical pulp must be added to the hardwood pulp to achieve adequate strength. With hydrogen peroxide bleaching, brightness levels up to 82% may be obtained.

The *cold soda* process was first investigated by the US Forest Products Laboratory in Madison in the early 1950s as a pretreatment before making RMP or SGW. By 1960, about 10 mills used the process; however, by 1970, only a few mills used the process, as other processes for pulping hardwoods had been developed. The yield of the cold process is 80%−95%. Chips are first soaked in 5%−15% cold caustic soda (sodium hydroxide solution) as a swelling agent. Lignin is retained, but some hemicelluloses and all resins are lost, resulting in a pulp with good drainage. Softwoods resist this treatment, producing coarse fibers with unusually high power demands. When used before SGW (CSGW), this method results in a pulp that drains faster than groundwood pulp, meaning that faster paper machines can be used. Refining energy is 500−700 kWh/ton (28−40 hp-day/ton). The *alkaline peroxide* pretreatment for mechanical pulping (APMP) was introduced by Sprout-Bauer in 1989. This process (McCready, 1992) is used to make 600 t/day of aspen pulp at the Millar Western mill in Saskatchewan, Canada, using a modification of Scott Paper's patented process. Four stages of chip compression (using a Hymac screw press with a 4:1 ratio) and chemical impregnation are used before refining. Much, if not all, of the bleaching is claimed to occur here, often saving the cost of a separate bleach plant. The refiners are reported to require about 30%−40% less energy than with sulfite pretreatment for BCTMP pulp. This pulp mill used a closed water loop by concentrating certain effluents to 70% solids for combustion. APMP does not require pressurized refiners. Increasing the amount of caustic in the pretreatment increases the strength of the pulp. Increasing the amount of peroxide increases the pulp brightness. This method is particularly profound because effluents with high BOD and inorganic chemical levels have prevented the use of CTMP in many locations.

Chemithermomechanical Pulp

CTMP is a chemimechanical process that is similar to the TMP process, except the chips are first pretreated with relatively small amounts (about 2% on dry wood) of sodium sulfite or sodium hydroxide (with hydrogen peroxide in the new alkaline peroxide method) below elevated temperature and pressure before refining. Liquor penetration is often achieved by a system that compresses the wood chips into a liquid tight plug that is then fed into the impregnator vessel where the chips expand and absorb the liquor (Fig. 12.9). Unlike TMP, CTMP is effective with most hardwoods, particularly with the cold soda process. CTMP processes produce effluents of high color and BOD, which may be difficult to treat; environmental considerations have kept this process from being used in many locations.

12.4 RELATED PULPING METHODS

Asplund Process

Interestingly, the Asplund process was developed about 30 years before TMP. It involves presteaming wood chips at temperatures above the glass transition temperature of lignin, 550–950 kPa (80–140 psi) steam pressure at 150–170°C (300–340°F), before refining between revolving metal discs or plates. The lignin is sufficiently soft that separation occurs at the middle lamella, and fibers are left with a hard lignin surface that is not amenable to fibrillation by refining or bonding by hydrogen bonding. Such fibers are very useful for hardboard materials where adhesives are used, which react with the lignin and pressing at high temperatures will allow the lignin-coated fibers to adhere to each other.

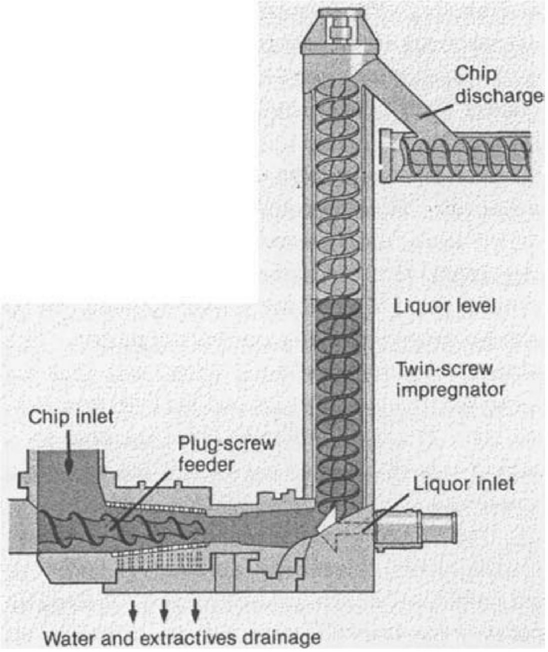


FIGURE 12.9 Liquor impregnation using the pressure-expansion technique. *Courtesy of Sunds Defibrator.*

Masonite Process (Steam Explosion)

This process was invented by Mason and patented in 1926 as an attempt to make pulp for paper. Chips are steamed at 180–250°C (355–480°F), well above the glass transition temperature of lignin, for 1–2 min until the final pressure is on the order of 4–7 MPa (600–1000 psi). The contents of the reactor are suddenly blown to atmospheric pressure through a slotted plate and to a cyclone where the fibers are collected. The glassy lignin surface and dark color of the fibers preclude their use in paper although they make a very useful, high-density fiberboard product. In fiberboard the fibers are held together by resins such as phenol-formaldehyde, not by hydrogen bonding as in paper. The yield is 80%–90%. However, a mild explosion pulping process is being used at one mill to process recycled paper.

Fig. 12.2 shows TMP fibers from mixed hardwoods of the southern United States. Notice the fibers exist in fiber bundles. The color (not observable in the SEM photograph) is dark brown. The fibers have glassy surfaces high in lignin that prevent hydrogen bonding. This pulp is unsuitable for use in paper.

12.5 SEMICHEMICAL PULPING

Vapor-Phase Pulping

Vapor-phase pulping is a process where chips are impregnated with cooking liquor (Fig. 12.9), the free liquor is drained or otherwise removed, and cooking occurs in an atmosphere of steam.

Semichemical Process

Also called high-yield chemical pulping, semichemical pulping processes involve two steps with pulp yields of 60%–80%. In the first step, a mild chemical treatment is used, which is followed by moderate mechanical refining. There is partial removal of both lignin and hemicellulose. The first step of the semichemical process may be similar to any of the commercial chemical pulping methods (to be described), except that the temperature, cooking time, or chemical charge is reduced. The NSSC and the kraft semichemical methods are the most common of this category. For yields below 65%, the pulp is washed and chemical recovery continues as outlined in the sulfite or kraft section, except the pulp can be cleaned by dewatering presses to limit dilution of the liquor. Up to 75% of the liquor can be removed without dilution. Because the liquor is not easy to recover in small operations, the majority of semichemical mills is integrated with chemical mills, so that the dilute spent liquors may be used as a source of makeup chemicals in the associated chemical process. This *cross recovery*, however, limits the size of the semichemical plant because a large plant would produce excess chemical beyond that required for makeup in the kraft mill.

Neutral Sulfite Semichemical

The NSSC process is most frequently used (and is the most common method) for production of corrugating medium. This process was developed in the early 1940s by the US Forest Products Laboratory in Madison as a means of using hardwood in the paper industry, especially the chestnut of the Appalachian region, which was being devastated by the chestnut blight. In this process, high pulp yields are obtained (75%–85%). NSSC cooking liquors contain Na_2SO_3 plus Na_2CO_3 (10%–15% of the chemical charge to act as a buffer); the liquor pH is 7–10. Cooking time is 0.5–2 h at 160–185°C (320–365°F). The residual lignin (15%–20%) makes paper from this pulp very stiff, an important property for corrugating medium. Hardwood is usually the fiber source, and NSSC hardwood pulp is approximately as strong as NSSC softwood pulp and even stronger than kraft hardwood pulp. The low lignin removal makes chemical recovery difficult. Anthraquinone (AQ) additives may be used to improve the pulp properties or yield, particularly from softwoods. The degree of cooking is controlled by the temperature, the chemical concentration, and the residence time in the digester. Subsequent refining energy of the pulp is 200–400 kWh/ton (10–20 hp-day/ton). Fig. 12.2 includes an electron micrograph of paper made with 50% hardwood NSSC pulp and 50% fiber recycled from old corrugated containers.

Kraft Green Liquor Semichemical Process

The green liquor semichemical pulping process for corrugating medium uses green liquor as the pulping liquor. The green liquor can be obtained from an associated kraft mill or from a recovery boiler specifically for the green liquor mill. In either case, the lime cycle is not required for liquor regeneration.

Defiberator or Hot Stock Refiner

The defiberator, also called the hot stock refiner, is an attrition mill designed to break apart the hard semichemical chips into pulp.

Cross Recovery

Cross recovery is the use of the waste liquor of a semichemical mill as the makeup chemical in the kraft recovery plant. For example, the Na_2SO_3 in the waste liquor of an NSSC mill, when added to the kraft recovery boiler, is converted to Na_2S during burning of the liquor and furnishes the kraft mill with its makeup sulfur and sodium. Fresh makeup chemicals are used to generate the pulping liquor for the NSSC mill. Obviously, the size of the NSSC mill is limited by the makeup chemical requirements of the kraft mill. In a green liquor semichemical mill, fresh chemical is taken from the kraft green liquor storage, while the spent pulping liquor is simply returned to the kraft recovery cycle.

12.6 GENERAL CHEMICAL PULPING

Delignification

Delignification is the process of breaking down the chemical structure of lignin and rendering it soluble in a liquid; the liquid is water, except for organosolv pulping.

Kappa Number, Permanganate Number

The Kappa number is a measure of the lignin content of pulp; higher Kappa numbers indicate higher lignin content. A similar test is the permanganate number (or K number). The Kappa number is used to monitor the amount of delignification of chemical pulps after pulping and between bleaching stages. For more detail on pulp tests, how they are carried out, and their significance, see Chapter 1, Volume 2.

Pulp Viscosity

The pulp viscosity (see Chapter 1, Volume 2) is a measure of the average chain length (degree of polymerization, DP) of cellulose. It is determined after dissolving the pulp in a suitable solvent such as cupriethylenediamine solution. Higher viscosity indicates a higher average cellulose DP that, in turn, usually indicates stronger pulp and paper. Decreases in viscosity result from chemical pulping and bleaching operations and to a certain extent are unavoidable but must be minimized by proper attention to important process parameters. Cellulose viscosity has little importance in mechanical pulping because the cellulose chains are not appreciably degraded by this operation.

Fiber Liberation Point

The fiber liberation point occurs when sufficient lignin has been removed during pulping so that wood chips will be soft enough to break apart into fibers with little or no mechanical action.

Full Chemical Pulps, Unbleached and Bleached

A pulp produced by chemical methods only is known as a full chemical pulp. Most chips are at the fiber liberation point after cooking at 130–180°C (265–355 F) with appropriate pulping liquors. The total pulp yield is about 50%, and the pulp contains about 3%–5% lignin. These pulps have high strength and high cost. The common methods are the kraft process (also called alkaline or sulfate process with a cooking pH above 12) and the various sulfite processes with a wide range of pH cooking conditions. An older method, enjoying only limited use these days on hardwoods and nonwood fiber such as straw, is the soda process that uses sodium hydroxide as the only active pulping ingredient. *Unbleached pulp* is a full chemical pulp, as it comes from the pulping process. It is light to dark brown in color. *Bleached pulp* is a white pulp produced by bleaching full chemical pulps.

Dissolving Pulp

Dissolving pulp is a low yield (30%–35%) bleached chemical pulp that has a high cellulose content (95% or higher) suitable for use in cellulose derivatives such as rayon, cellulose acetate, and cellophane (see the end of Section 2.6 for a description of these materials). Dissolving pulp is manufactured by the kraft process using an acid prehydrolysis step to remove hemicelluloses or by an acid sulfite process. Improved cellulose purity is achieved by a cold alkali extraction of the pulp.

Digester

The digester is a pressure vessel used for cooking chips into pulp. Digesters are designed to operate in either a continuous mode, if in a long, narrow tube shape, or a batch mode.

Batch Digester

Batch digesters are large digesters, typically 70–350 m^3 (2500–12,500 ft^3), that are filled with wood chips and cooking liquor. The top of a batch digester is shown in Fig. 12.10.

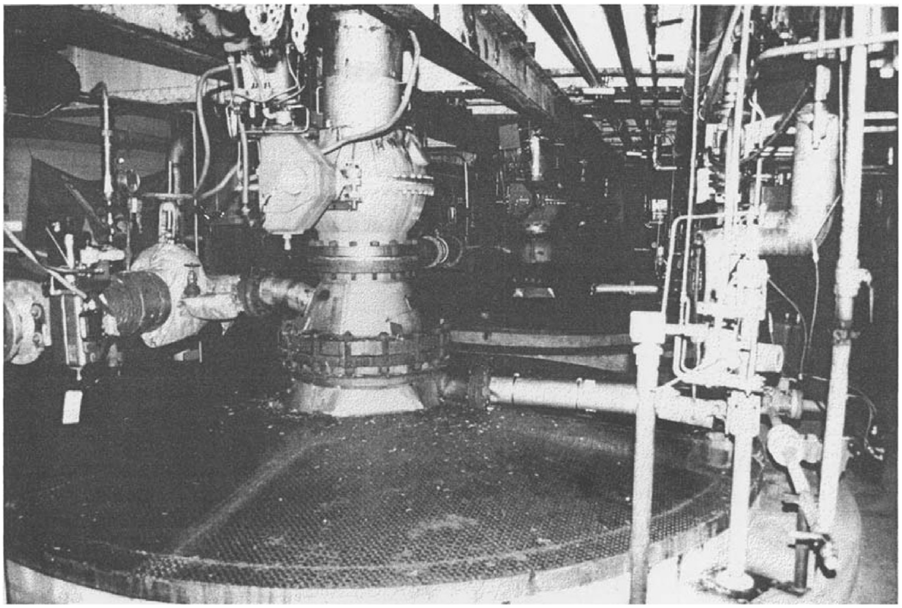


FIGURE 12.10 The top of a batch digester where digester loading occurs. In the background, several additional digester tops are visible.

A diagram of a batch digester is shown in Fig. 12.11. A laboratory batch digester is shown in Fig. 12.12. Typically a mill has a bank of six to eight digesters so that while several are cooking, one is filling, one is blowing, one might be under repair, etc. Heating with steam may be *direct*, where steam is added directly to the digester, which dilutes the cooking liquor, or *indirect*, where steam is passed through the inside of tubes within the digester, which allows reuse of expensive steam condensate and gives more uniform heating. The *cooking time* is the length of time from initial steaming of chips to the start of digester blowing; the *time to temperature* is the length of time from initial steaming to the point where the desired cooking temperature is reached; and the *time at temperature* is the length of time from when the cooking temperature is reached until the digester blow starts.

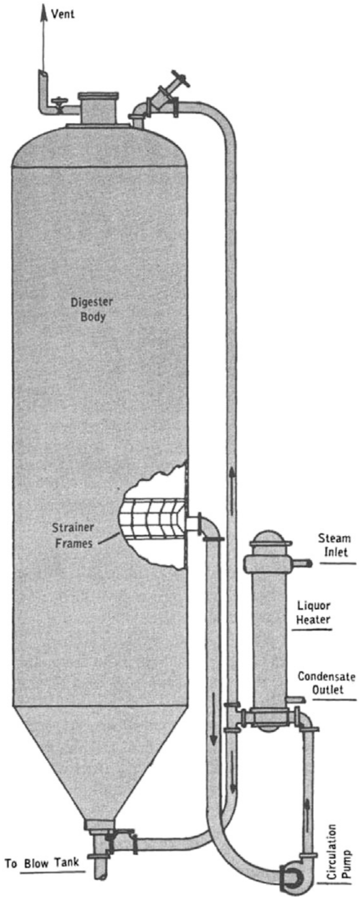


FIGURE 12.11 A stationary batch digester with indirect heating of the liquor. *Reprinted from* Making Pulp and Paper, *©1967 Crown Zellerbach Corp., with permission.*

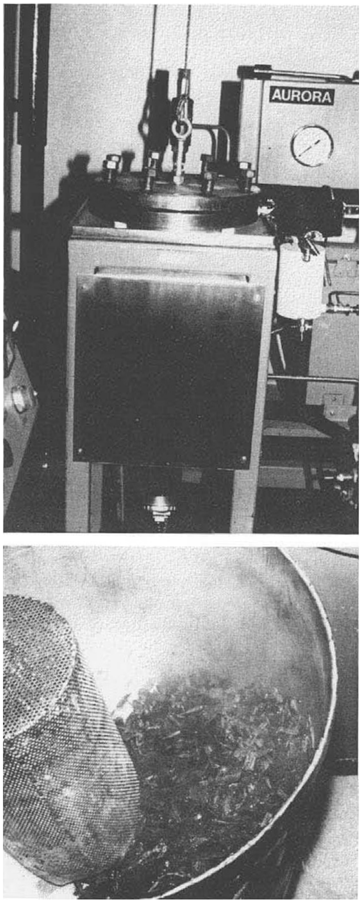


FIGURE 12.12 A laboratory batch digester with product.

A typical sequence of events for an entire cook is as follows:

1. The digester is first opened and filled with chips, white liquor, and black liquor.
2. After initial circulation of the liquor, additional chips are added as the contents settle.

3. The digester is then sealed, and heating with steam begins. The temperature rises for about 90 min until the cooking temperature is achieved.

4. The cooking temperature is maintained for about 20—45 min for the kraft process. During the heating time, air and other noncondensable gases from the digester are vented.

5. When the cook is completed, as determined by the kappa of pulp from the digester, the contents of the digester are discharged to the blow tank.

6. The digester is opened, and the sequence is repeated.

Continuous Digester

A continuous digester is a tube-shaped digester where chips are moved through a course that may contain elements of presteaming, liquor impregnation, heating, cooking, and washing. Chips enter and exit the digester continuously. Continuous digesters tend to be more space efficient, easier to control giving increased yields and reduced chemical demand, laborsaving, and more energy efficient than batch digesters. Because continuous digesters are always pressurized, special feeders must be used to allow chips at atmospheric pressure to enter the pressurized digester without allowing the contents of the digester to be lost. *Screw feeders* are used for materials such as sawdust and straw. A moving plug of fiber is used to make the seal. *Rotary valves* (Fig. 12.16) work like revolving doors. A pocket is filled with wood chips or other fiber source at atmospheric pressure. When the valve is rotated it is sealed from the atmosphere and then opened into the digester where the contents are deposited. *Kamyr* digesters (Figs. 12.13—12.15) are large, vertical digesters, where chips enter the top and exit the bottom continuously in a plug flow. The Kamyr continuous digester was developed in the 1950s and soon established itself as the dominant high production continuous digester. A single unit can produce over 2100 ton/day of pulp. There are several hundred Kamyr digesters operational worldwide. The chips are exposed to various areas of the digester where they are impregnated with liquor, heated to the cooking temperature, held at the cooking temperature to effect pulping, and partially washed. The pulp is then sent to the blow tank. In the typical process, chips from the bin are introduced to a low pressure presteaming chamber where the chips are transported by a screw feed. Here flash steam at atmospheric pressure preheats the chips and drives off air, so that liquor penetration will be enhanced. The chips pass through the high pressure feeder where cooking liquor carries them to the digester. Most of the liquor is returned to the high pressure feeder. Impregnation occurs for about 45 min at 130°C, so cooking will be much more uniform. Liquor heating occurs in the zone formed by two external liquor heaters. The cooking zone merely supplies the appropriate retention time for cooking to take place. The pulping reaction is terminated with the addition of cold, wash liquor from the brown stock washers that displaces the hot, cooking liquor. The M&D digester (Messing and Durkee) is a long digester inclined at a 45 degrees angle. A diagram of this is shown in Fig. 12.16, and an actual digester is shown in Fig. 12.17. This digester is often used for kraft pulping of sawdust or semichemical pulping methods. It has some use for kraft pulping of wood chips. The chips or sawdust enter the top, go down one side of the digester, return back up the other side being propelled by a conveyer belt, and exit out the top. The cooking time is about 30 min. A midfeather plate separates the two sides of the digester. Because the size of these shop-fabricated digesters is limited to about 2.4 m (8 ft) diameter, they are used for relatively small production levels.

Another continuous digester is the *Pandia* digester (Figs. 12.18 and 12.19), which is

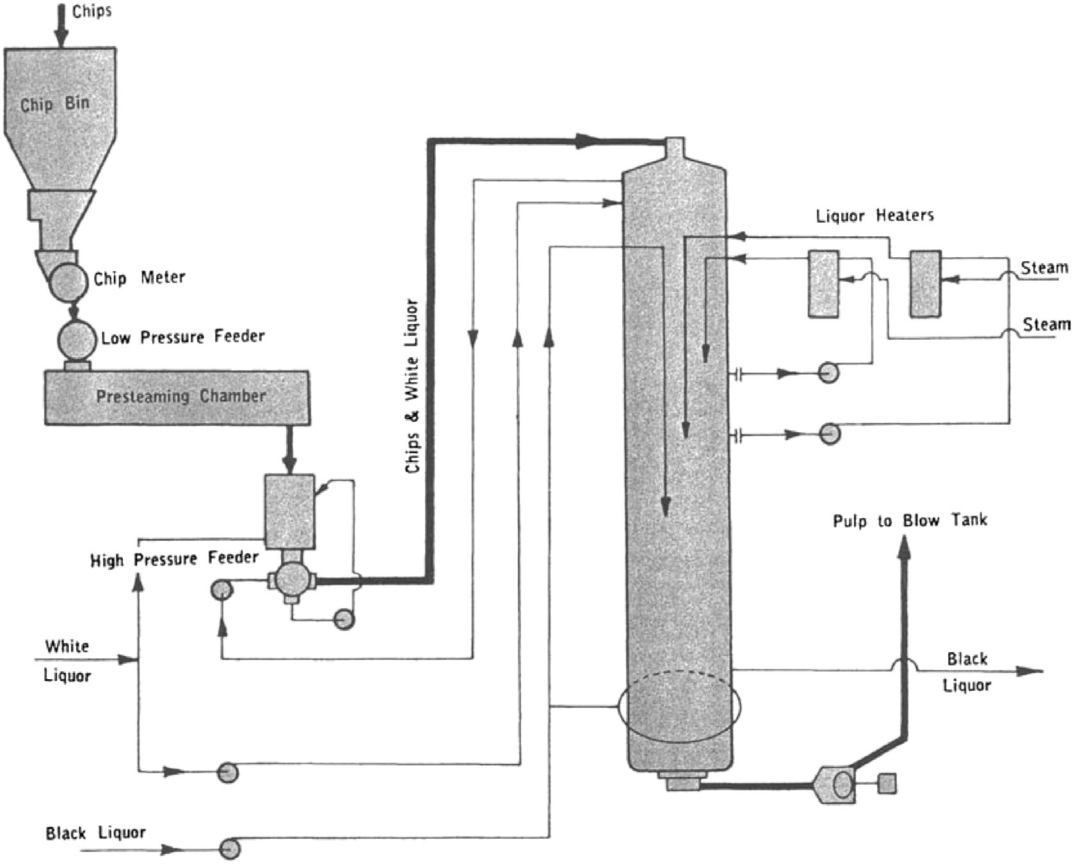


FIGURE 12.13 The Kamyr continuous digester. *Reprinted from Making Pulp and Paper, ©1967 Crown Zellerbach Corp., with permission.*

horizontal, uses a screw feed, and is often used in kraft pulping of sawdust, semichemical pulping of chips with short cooking times, and pulping of nonwood fiber such as straw.

Digester Charge, Relief, and Blowing

The *digester charge* includes the wood chips and cooking liquor in a digester. *Digester relief* occurs while the chips are heated to temperature and during the cooking process to relieve the pressure caused by the formation of volatile gases. These gases are released and condensed to improve the pulping process. This removes air from within and around the chips; increases the liquor circulation and evenness of cooking; reduces the digester pressure, which reduces fiber damage during the blow; and allows collection of turpentine, if desired.

Digester blowing occurs at the end of a cook when the contents of a digester are cooled to about 100°C (212°F) and allowed to escape to atmospheric pressure. There is usually sufficient force in a full chemical pulp to cause fiber separation. If the contents are blown from temperatures near that of cooking, 170°C (340°F) for

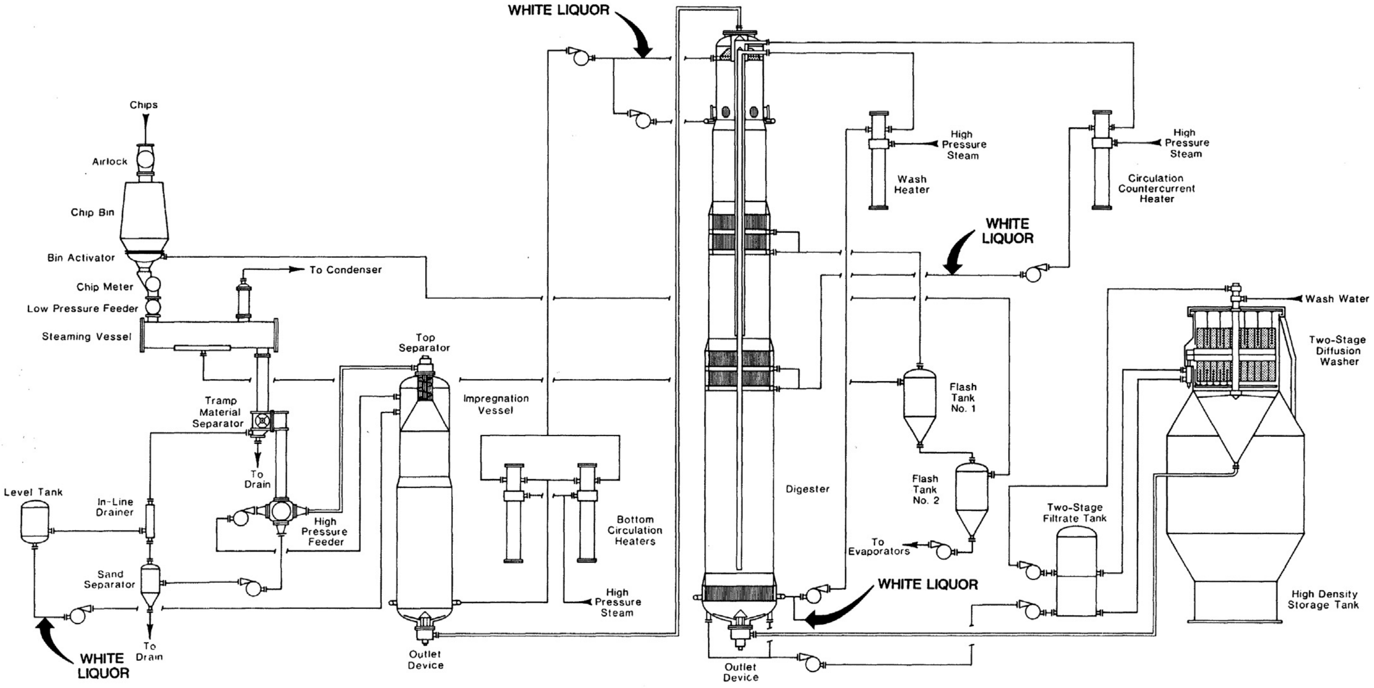


FIGURE 12.14 Two-vessel hydraulic digester with extended modified continuous cooking (MCC) and two-stage diffuser washer. *Courtesy of Kamyr, Inc.*

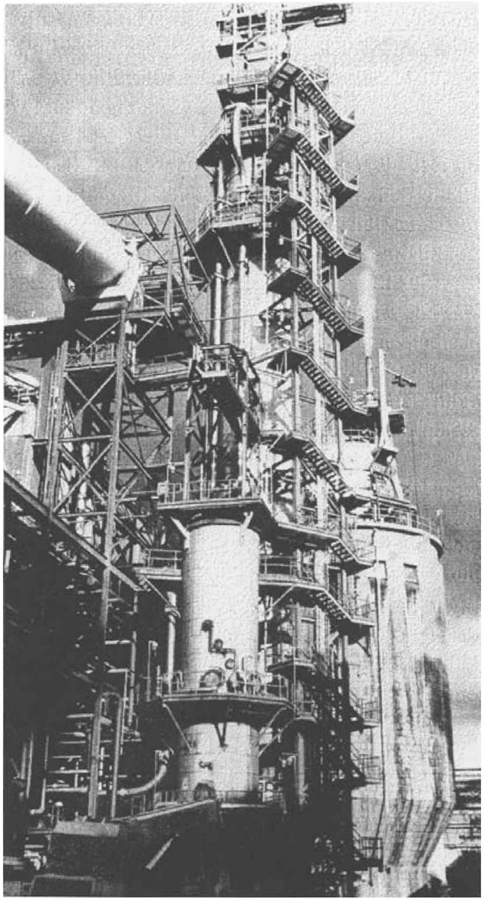


FIGURE 12.15 A two-vessel Kamyr digester.

kraft cooking, the pulp often loses a significant (10%−15%) amount of its strength.

Blow Tank

Blow tanks are large, cylindrical vessels that receive the hot pulp from the digesters (Fig. 12.20). Agitators mix the pulp from the digester with dilute black liquor so that the pulp slurry can be pumped and metered for the correct consistency. The heat of the hot gases from the blow tank is recovered by the *blow heat accumulator*, a large heat exchanger. Up to 1000 kg (2000 lb) of steam per ton of pulp is generated by batch digesters and some continuous digesters and must be condensed. Continuous digesters such as the Kamyr are able to recover the heat more efficiently by liquor displacement methods although this technology is being applied to batch digesters in the rapid displacement heating (RDH) method. Condensation of the blow gases also decreases pollution by recovering most of the volatile reduced sulfur compounds, organic compounds such as methanol, and related materials known together as *foul condensate*. The condensate is sometimes used for dilution water in applications such as lime mud dilution and brown stock washing where the foul compounds will be trapped before a combustion process. Noncondensable gases are often diverted to the limekiln for combustion. The pulp is then sent to be screened and cleaned in the brown stock washers.

Liquor

Cooking or pulping liquors are aqueous solutions of chemicals used for delignification of wood by pulping.

Chemical Concentration

The chemical concentration is a measure of the concentration of the pulping chemical in the liquor. For example, in sulfite pulping the liquor may be 6% SO_2, indicating 6 g of sulfite chemical (SO_2 basis) per 100 mL of liquor. In this case if the liquor:wood ratio is 4:1, the percent chemical on wood is 24% as SO_2. The following is an important relationship, not the definition of chemical concentration.

$$\text{chemical concentration in liquor} = \frac{\text{percent chemical on wood}}{\text{liquor to wood ratio}}$$

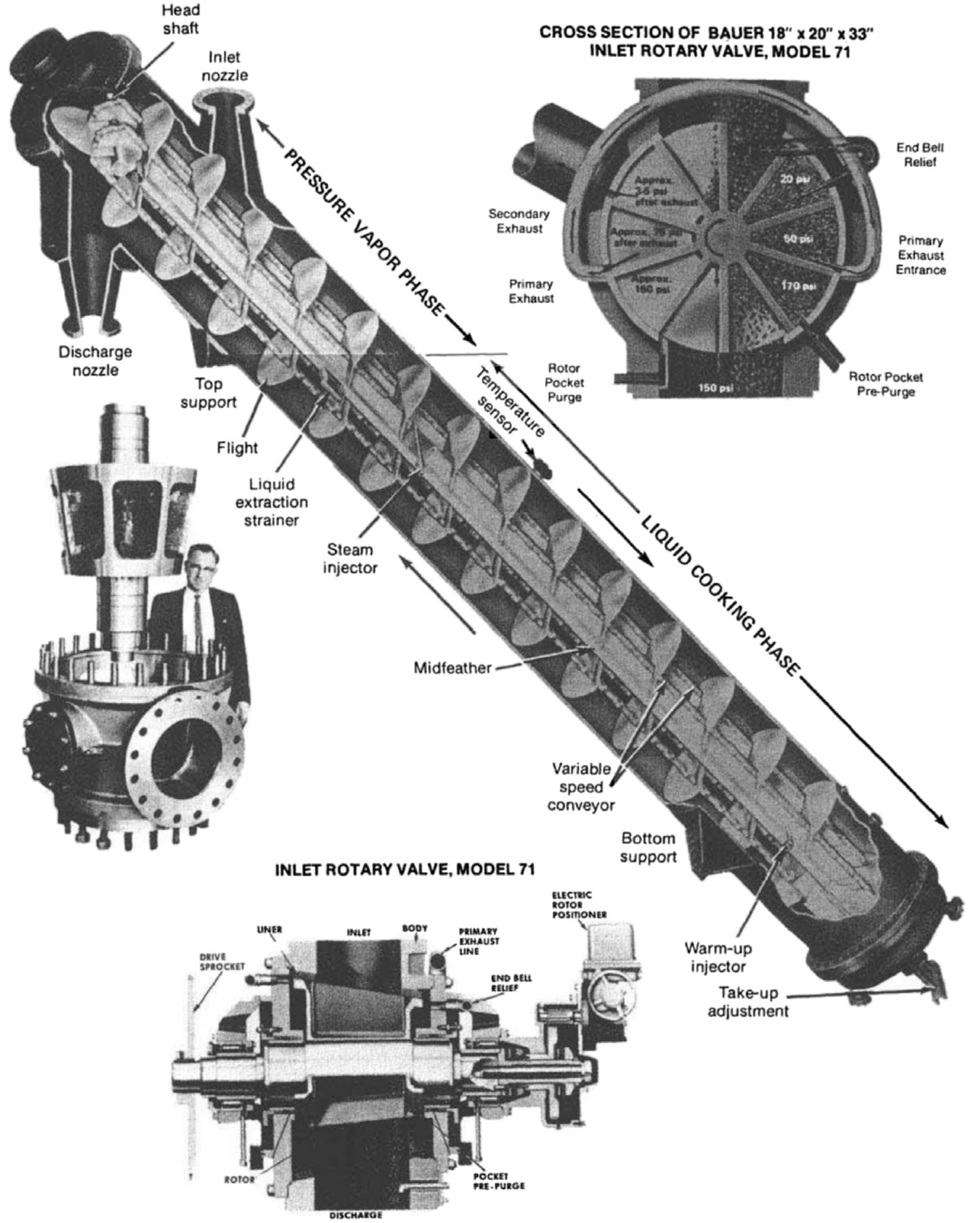


FIGURE 12.16 The M&D continuous digester. The inserts show various aspects of the rotary valve. *Courtesy of Andritz Sprout-Bauer, Inc.*

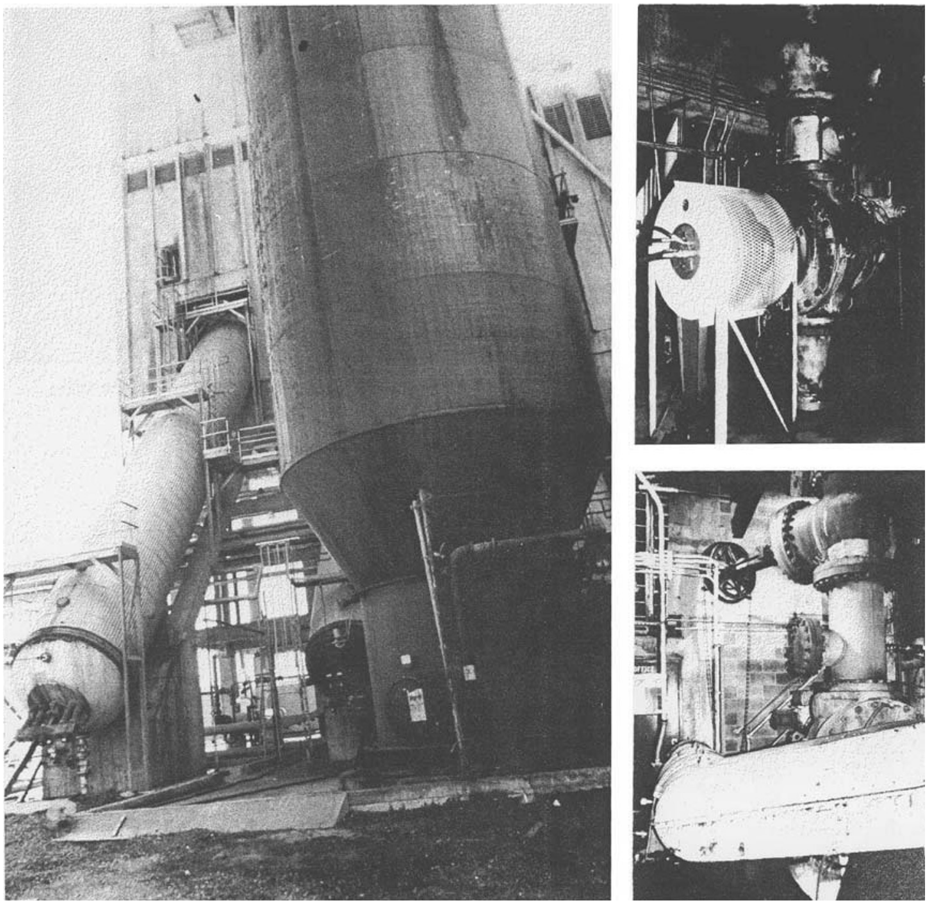


FIGURE 12.17 The M&D continuous digester (left). To the right is the blow tank: the top insert shows a hydraulically driven exit valve, and the bottom insert shows an electric-motor driven exit valve.

Chemical Charge (to a Process), Percent Chemical on Wood (or Pulp for Bleaching)

The chemical charge or chemical on wood is another fundamental parameter of chemical pulping processes. It is the measure of the weight of chemical used to process a material relative to the weight of the material itself. This applies to any chemical process, such as pulping and bleaching. For example, typically, kraft pulping is carried out with 25% total alkali (TA) on wood. This would indicate 500 lb of alkali as sodium oxide (in the United States, sodium-based chemicals are reported in terms of sodium oxide) for 2000 lb of dry wood. Chemicals in sulfite pulping are expressed on an SO_2 basis. Also, when bleaching mechanical pulp, one might use "0.5% sodium peroxide on pulp." This means that for every 1 ton of ovendry pulp, 10 lb of sodium peroxide is used.

$$\text{chemical charge} = \frac{\text{mass dry chemical used}}{\text{mass dry material treated}} \times 100\%$$

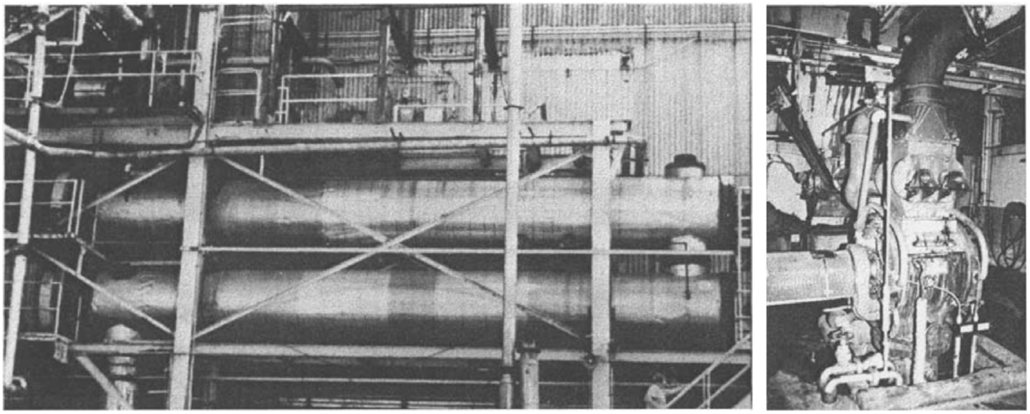


FIGURE 12.18 A Pandia continuous digester with two tubes. The insert shows the feed valve.

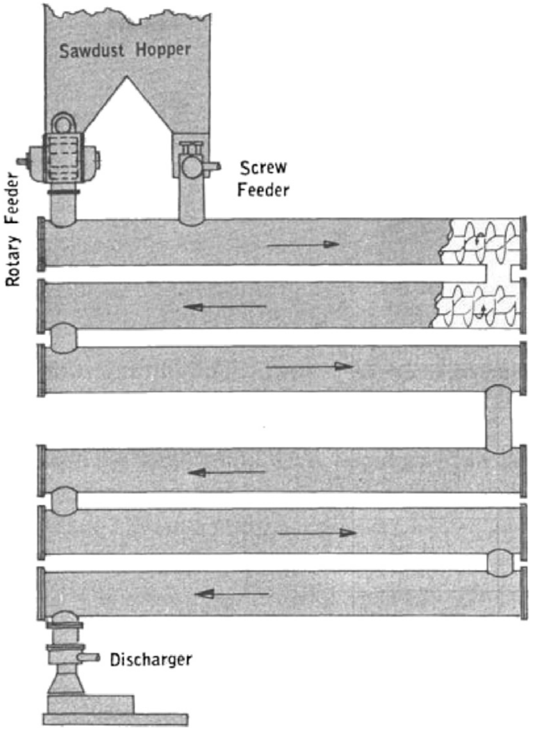


FIGURE 12.19 Pandia digester. *Reprinted from Making Pulp and Paper, ©1967 Crown Zellerbach Corp., with permission.*

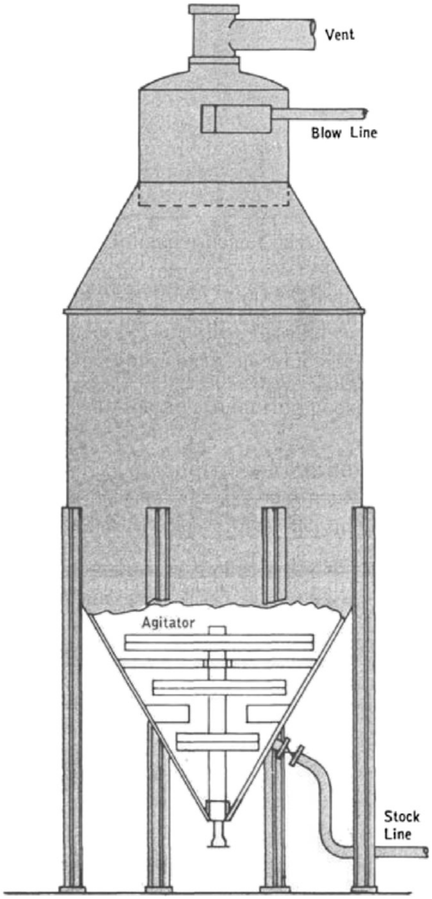


FIGURE 12.20 Blow tank. *Reprinted from Making Pulp and Paper, J ©1967 Crown Zellerbach Corp., with permission.*

Liquor-to-Wood Ratio

The liquor-to-wood ratio, liquor:wood, is normally expressed as a ratio; typically, it has a value of 3:1 to 4:1 in full chemical pulping. Rarely it is expressed as a percent. The numerator may or may not include the weight of water coming in with the chips but either way it must be specified to avoid ambiguity. The liquor-to-wood ratio is kept as small as possible while maintaining good digester operation, including good liquor circulation for even cooking.

$$\frac{\text{liquor}}{\text{wood}} = \frac{\text{total pulping liquor mass}}{\text{dry wood mass}}$$

Delignification Selectivity

Delignification selectivity is an important concept during pulping and bleaching operations where it is desired to remove lignin while retaining as much holocellulose as possible. Delignification selectivity is the ratio of lignin removal to carbohydrate removal during the delignification process. Although this ratio is seldom measured directly, it is measured in a relative manner by yield versus kappa plots as shown in Fig. 12.21. Here condition "A" is more selective than condition "B" because for a given Kappa number the yield is higher for "A" than for "B." A high selectivity alone does not mean that pulp "A" is better than "B" because the plot does indicate the condition, such as the viscosity, of the pulp. For example, acid sulfite pulping is more selective than kraft pulping; however, acid sulfite form pulp by coarse screening equipment (3/8 in. holes) before pulp washing. Coarse screenings from sulfite pulping are not reused in bleached grades of pulp. Coarse screening from kraft pulping is repulped. Suggested screen terminology is shown in Fig. 12.22. If pulps are undercooked, the screened yield may actually decrease because much of the (potential) pulp is removed in the screens, as shown in Fig. 12.23. After washing, pulps are screened to remove shives, dirt, and other contaminants to protect processing equipment and the product's integrity. Shorter fibers screen more easily, thus hardwoods are easier to screen than softwoods. Redwood pulps (long fibers) require about twice the screen capacity as spruce pulps. Similarly, mechanical pulps screen more easily than chemical pulps. Recently, pulp is screened before washing for improved washing efficiency. See Chapter 3, Volume 2, for information on pressure screens.

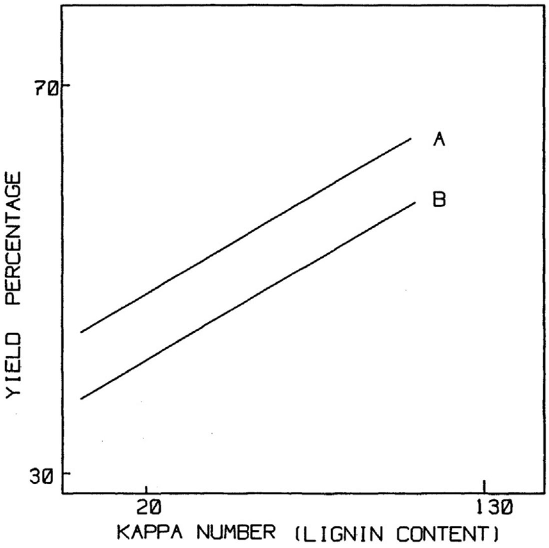


FIGURE 12.21 Pulping selectivity curve.

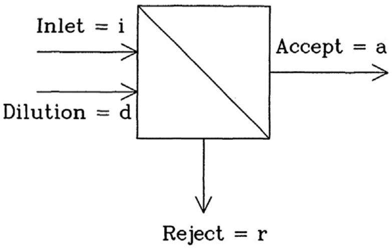


FIGURE 12.22 Screening symbols, terminology, and equations in TIS 0605-04.

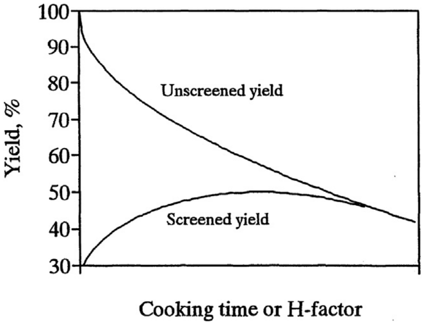


FIGURE 12.23 Hypothetical relationship of total and screened yields to cooking time or H-factor.

Brown Stock Washers

Chemical pulps require more washing than mechanical pulps to recover process chemicals, but mechanical pulps require more screening to remove shives, knots, and so forth. If chemical pulps are not properly washed, foaming will be a problem, additional makeup chemicals will be needed, more bleaching chemicals will be required, and additional pollutants will result. There are several types of brown stock washers available: (1) *diffuser washing systems*, which are slow, lead to high liquor dilution, and are therefore being phased out; (2) *press type washers*; (3) *countercurrent flow stock washers*; (4) *rotary vacuum drum washer* with a drop length of pipe to supply a vacuum with two to four stages (Plate 12.2); (5) *double-wire press washers* (Plates 12.3–12.5); (6) *diffusion washers*.

Rotary Vacuum Washers

Rotary vacuum drum washers are, by far, the most common type used. These consist of a wire-mesh covered cylinder that rotates in a tub of the pulp slurry with valve arrangements to apply vacuum as is suitable. As the drum contacts the slurry, a vacuum is applied to thicken the stock. The drum rotates past wash showers where the pulp layer is washed with relatively clean water to (more or less) displace black liquor. The vacuum is cut off beyond the wash showers, and the pulp mat is dislodged into a pulper. Most of the washing actually occurs at the pulpers between washing stages. Daily loadings for brown stock washers are about 8 t/m^2 (0.8 dry tons/ft^2) for softwood, 6 t/m^2 (0.6 dry tons/ft^2) for hardwood, and 1–2 t/m^2 (0.1–0.2 dry tons/ft^2) for straw pulps. Hardwoods are more difficult to wash than softwoods and have higher chemical losses partly because of the higher ion-exchange capacity of hardwoods from the carboxylic groups of their hemicelluloses. Typically, about 80% of the contaminants are removed at each stage, so at least three stages are required to thoroughly wash the pulp. Use of additional stages results in lower water consumption,

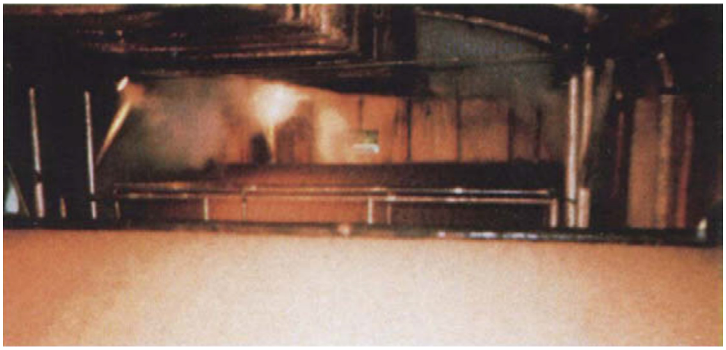


PLATE 12.2 Two brown stock washers in series.

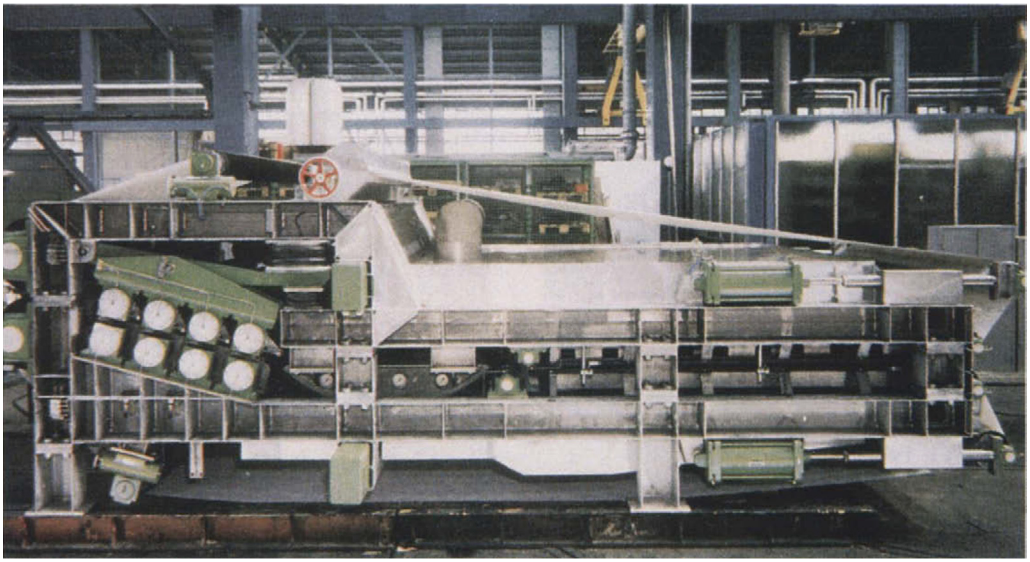


PLATE 12.3 Double-wire press suitable for market pulp production, pulp washing, bleaching, or stock thickening. *Courtesy of Andritz Sprout-Bauer.*

higher recovery of chemicals, and lower pulp dilution. Fig. 12.24 shows a typical configuration of vacuum drum washers for pulp washing. Fig. 12.25 shows an individual vacuum drum washer. Air is constantly sucked into the pulp sheet and must be separated from the spent cooking liquor to prevent foaming as it is further processed. This causes much foam to form in the seal tanks. Chemical and mechanical defoamers are often used here. The method of applying the wash water influences foam formation.

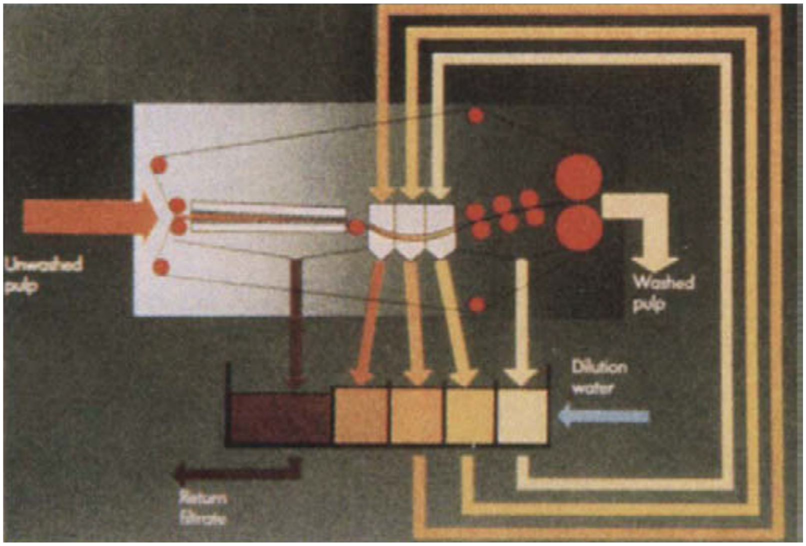


PLATE 12.4 Diagram of double-wire press for brown stock washing. *Courtesy of Andritz Sprout-Bauer.*

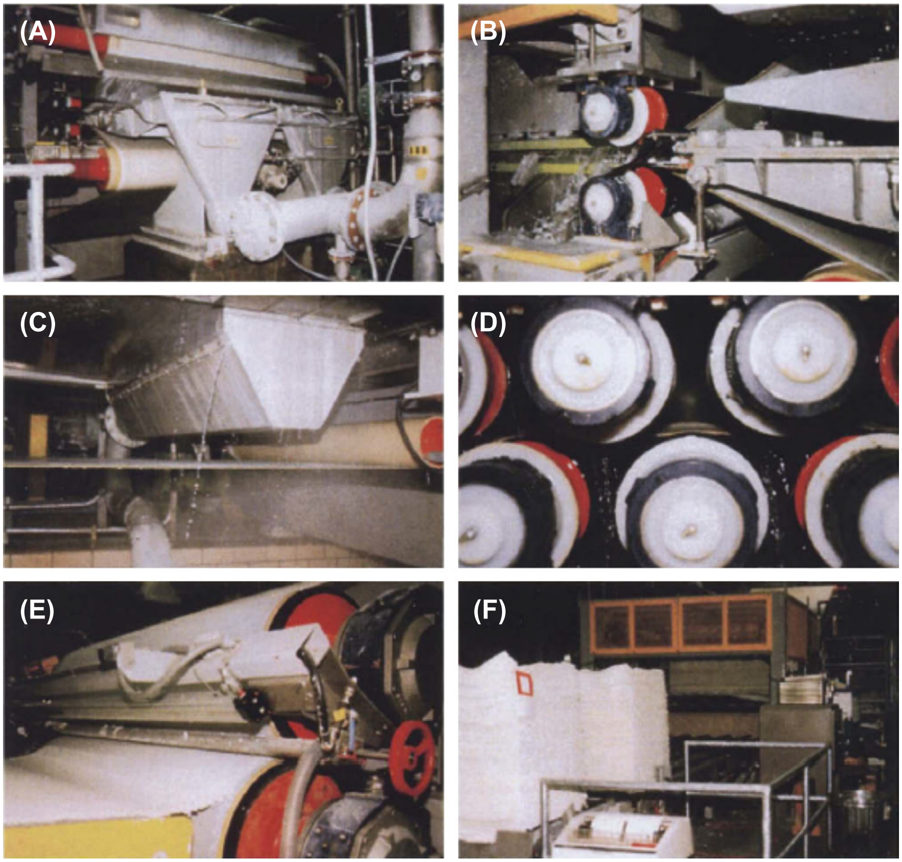


PLATE 12.5 Selected views of a double-wire press used for wet lap market pulp: (A) headbox approach, (B) headbox and slice, (C) dewatering with a drop leg, (D) presses, (E) wet lap, and (F) cut and stacked wet lap.

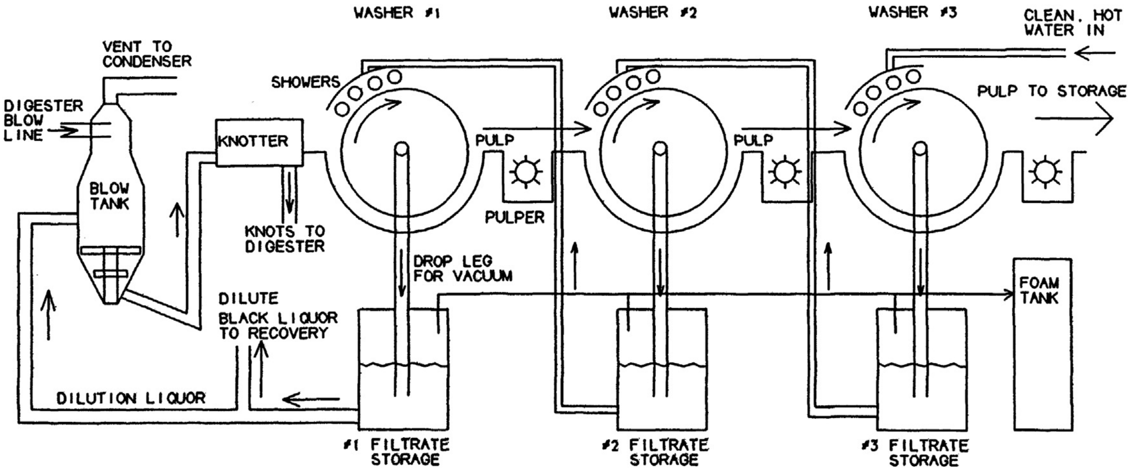


FIGURE 12.24 Brown stock washers showing countercurrent flow.

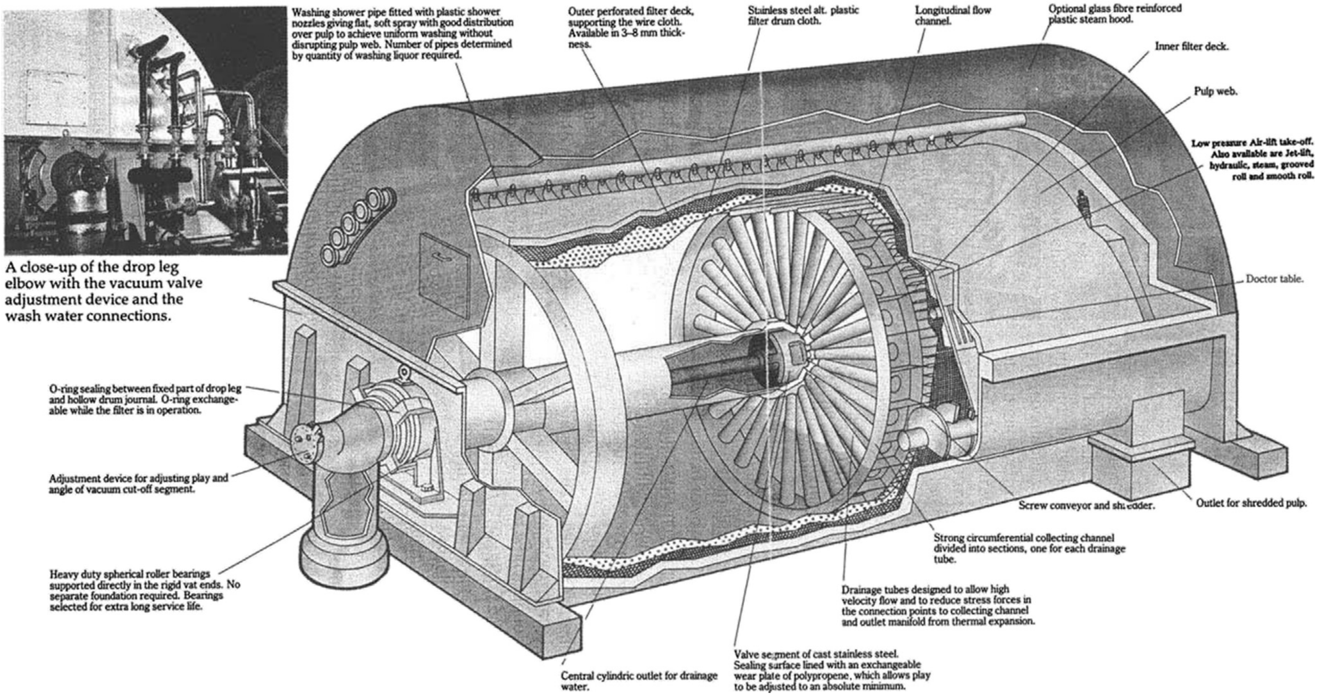


FIGURE 12.25 Vacuum drum washer suitable for brown stock washing, bleaching, or pulp thickening. *Courtesy of Sunds Defibrator.*

Diffusion Washing

Diffusion washing (Fig. 12.26) was first used by Kamyr for washing chips at the bottom of their digesters. The technique was extended for brown stock washing and washing of pulp between bleaching stages.

Double-Wire Press

Plate 12.3 shows a double-wire press suitable for market pulp production, brown stock washing, pulp washing between bleaching stages, and stock thickening. Plate 12.4 shows a double-wire press designed for brown stock washing. Notice this configuration incorporates the countercurrent washing technique.

Brown Stock

The washed, screened pulp is called *brown stock*. See Chapter 17, Volume 1, for more information on pulp washing from a chemical recovery point of view where dilution is considered.

Anthraquinone, Soluble Anthraquinone

AQ (whose structure is shown in Fig. 12.27) is a pulping additive used in kraft, soda, or alkaline sulfite processes to increase delignification and decrease carbohydrate degradation. It works by going through a cycle that leads to the reduction of lignin and the oxidation of the reducing end group of cellulose from an aldehyde to a carboxylic acid as shown in Fig. 12.28. In the latter case the carbohydrates are stabilized against the alkaline peeling reaction, leading to an increase in pulp yield. Because AQ goes through a cyclic process, it is typically used at about 0.1% on wood and results in a 1%–3% increase in pulp yield. The use of AQ was first reported in 1977. Modifications of AQ, such as soluble anthraquinone (SAQ, Fig. 12.27), properly called 1,4-dihydro-9,10-dihydroxyanthracene, have been shown to be even more effective. Although not used extensively in North America, AQ and SAQ are widely used in Japan and other countries where fiber supplies are quite limited and expensive.

Prehydrolysis

Prehydrolysis is a dilute acid hydrolysis with 0.5% sulfuric acid for 30 min at 100°C and is used to partially depolymerize the hemicelluloses of wood with little effect on the cellulose. Chips pretreated in this fashion followed by kraft pulping give a pulp with very high cellulose content, but low yield suitable for dissolving pulp.

12.7 SODA PULPING

Soda pulping, invented in England by Burgess and Watts in 1851, uses sodium hydroxide as the cooking chemical. Finding little enthusiasm in England for this new process, Burgess brought the method to the United States in 1854, and the first mill was started in 1866. Many of the early soda mills converted to the kraft process once it was discovered. The soda process still has limited use for easily pulped materials such as straws and some hardwoods but is not a major process. AQ may be used as a pulping additive to decrease carbohydrate degradation. A recent development is the use of oxygen in soda pulping. Although oxygen bleaching is not very specific to delignification compared with other bleaching methods, it is fairly specific to delignification relative to other pulping methods.

12.8 KRAFT PULPING

Kraft Pulping

In 1879, Dahl, a German chemist, used sodium sulfate as a makeup chemical for soda pulping to regenerate NaOH; actually Na_2S

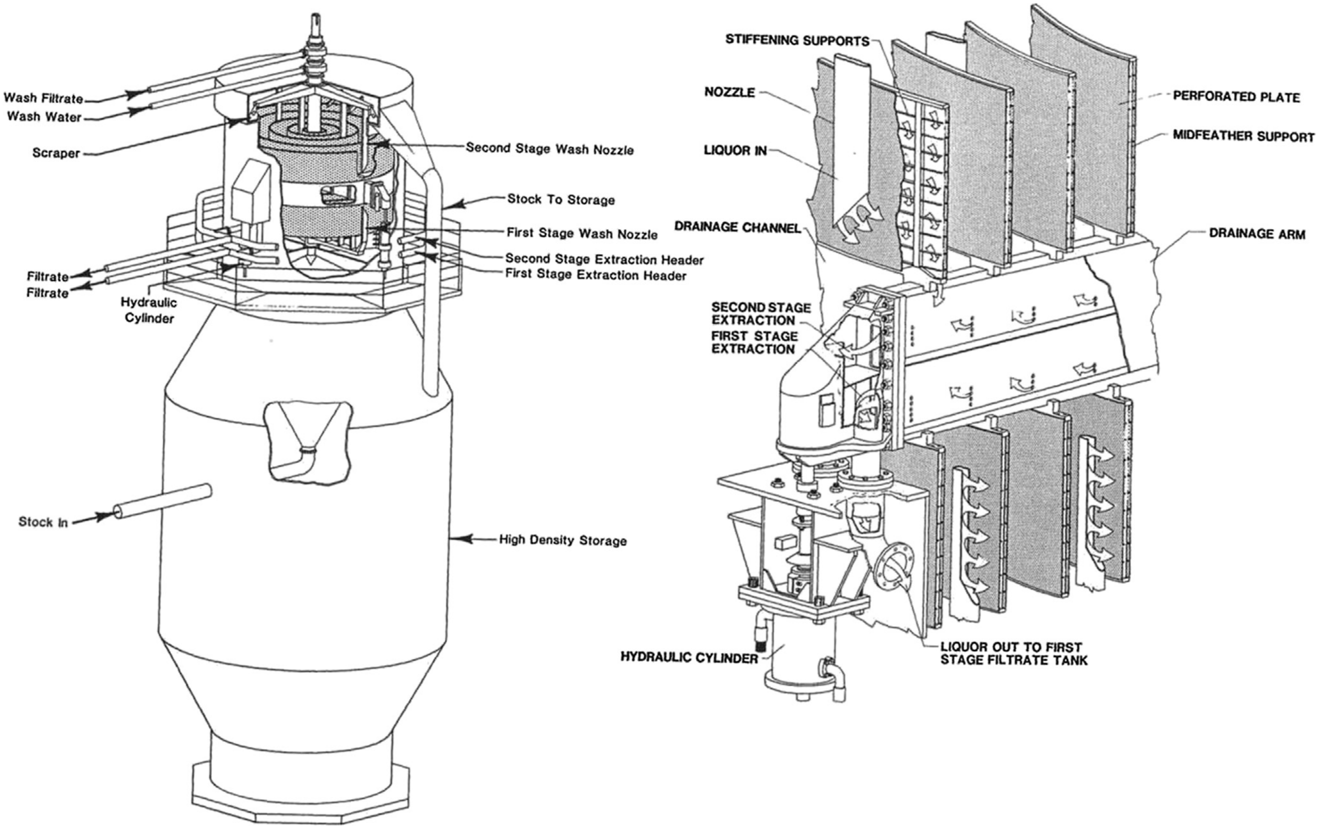


FIGURE 12.26 Two-stage diffusion washer. *Courtesy of Kamyr, Inc.*

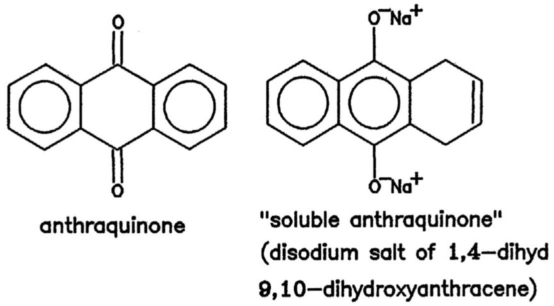


FIGURE 12.27 Structures of anthraquinone and soluble anthraquinone.

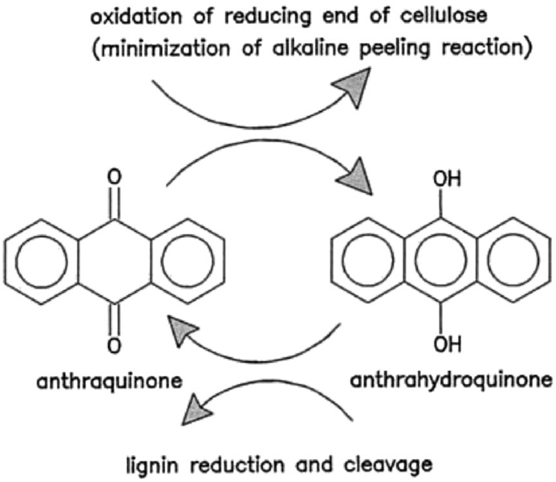


FIGURE 12.28 Cyclic action of anthraquinone.

was formed and, unexpectedly, gave much faster delignification and stronger pulps because shorter cooking times are used, resulting in less carbohydrate degradation. This led to the kraft (or sulfate) process, which is now the dominant process. Although related work on the process had been done earlier, Dahl discovered the kraft chemical recovery process, which is perhaps more important than the kraft cooking process. The first kraft mill went into operation in 1890 in Sweden because the German papermaking industry did not accept this new process. The process developed and grew quickly from 1915 to 1930, especially in the southern United States where the resinous pine species did not pulp well by the sulfite process with calcium base. Kraft pulping is a full chemical pulping method using sodium hydroxide and sodium sulfide at pH above 12, at 160–180°C (320–356°F), corresponding to about 800 kPa (120 psi) steam pressure, for 0.5–3 h to dissolve much of the lignin of wood fibers. It is useful for any wood species, gives a high strength pulp (kraft means strong in German and Swedish), is tolerant to bark, and has an efficient energy and chemical recovery cycle. The disadvantages are the difficulties with which the pulps are bleached compared with sulfite pulps, low yields due to carbohydrate losses, and sulfur in its reduced form provides emissions that are extremely odiferous (they can be detected by the olfactory sense at 10 parts per billion). Another consideration is that a green field (starting in an empty field) mill of 1000 tons/day production, including bleaching and paper machines, costs about $1 billion. About 75%–80% of the US virgin pulp is produced by this process. Important variables during kraft cooking are as follows:

1. Wood species (although all species can be pulped) and chip geometry.
2. Ratio of effective alkali (EA) to wood weight.
3. Concentration of EA and liquor:wood.
4. Sulfidity.
5. H-factor (which, in turn, is a function of cooking time and temperature).

For example, all other factors being equal in kraft pulping, a higher concentration of cooking chemical shifts the cooking selectivity (Fig. 12.21) from “A” toward “B” (unfavorable), but decreasing the liquor-to-wood ratio shifts the curve from “B” to “A” (useful but more evaporation costs). The importance of uniform wood chips in regard to species, chip thickness, and chip geometry cannot be overstressed. Even with careful screening of wood chips, variability in wood means that some of the pulp will be overcooked and some of it will be undercooked. Fig. 12.29 and Plate 12.6 demonstrate this point. Electron microscopy shows that overthick chips have incomplete fiber liberation (Kappa number of 94.7). Fine chips overcook (Kappa number of 36.9), leading to lignin condensation and dark, rigid fiber clusters. The pulp from the accept chips has a Kappa number of 42.4. The penetration of liquors at pH above 13 in wood is about the same in all three directions (Fig. 12.30). This is why chips for kraft cooking are separated on the basis of their thickness. The degree of a kraft cook is often indicated as *soft*, *medium*, or *hard* based on the pulp texture. Soft cooks, for bleachable grades of pulp, have a lignin content of 3.0% −5.2% (20−35 Kappa number) for softwoods or 1.8%−2.4% (12−18 Kappa number) for hardwoods. Medium softwood cooks for bag and saturating papers have a lignin content of 5.2% −7.5% (35−50 Kappa number). Hard softwood cooks are 9%−11% lignin (60−75 Kappa number) for top linerboards and 12%−16.5% lignin (80−110 Kappa number) for bottom liners.

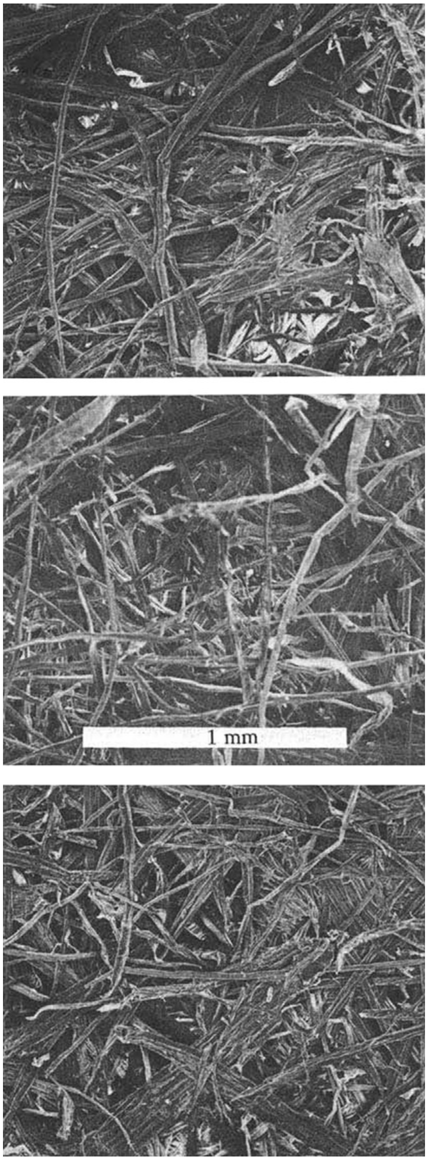


FIGURE 12.29 Overthick (top), accept (middle), and fine chips (bottom) cooked under identical conditions by kraft pulping.

H-Factor

The H-factor is a pulping variable that combines cooking temperature and time into a single variable that indicates the extent of reaction. Although different temperatures might be used, the degree of cook can be accurately estimated by this method provided that other variables such as active alkali (AA), sulfidity, and the liquor-to-wood ratio remain constant. There is no analogous variable for sulfite or soda pulping. The rate of delignification approximately doubles for an increase in reaction temperature of 8°C. To obtain a bleachable kraft softwood pulp of about 5% lignin, one typically cooks for about 1.5 h at 170°C. This corresponds to 0.75 h at 178°C or 3 h at 162°C. The integral of the reaction rate with respect to time combines these two parameters into the single parameter, the H-factor. By using the H-factor, cooks of varying reaction times and temperatures can be compared in a meaningful manner. This important process control variable is discussed in Chapter 13, Volume 1.

PLATE 12.6 Pulp and handsheets of overthick (left) chips, accept chips (center), and fine chips (right) after kraft pulping.

White Liquor

White liquor is fresh pulping liquor for the kraft process, consisting of the active pulping species NaOH and Na_2S, small amounts of Na_2CO_3 left over from the recovery process, oxidized sulfur compounds, and other chemical impurities from wood, salt water, corrosion, etc.

Black Liquor

Black liquor is the waste liquor from the kraft pulping process after pulping is completed. It contains most of the original cooking inorganic elements and the degraded, dissolved wood substance. The latter includes acetic acid, formic acid, saccharinic acids, numerous other carboxylic acids (all as the sodium salts), dissolved hemicelluloses (especially xylans), methanol, and hundreds of other components. It is an extremely complex mixture. About 7 tons of black liquor at 15% solids (about 10% organic chemicals and 5% inorganic chemicals with a total heat content of 13.5−14.5 MJ/kg solid [5500−6500 Btu/lb solid]) is produced per ton of pulp. The black liquor must be concentrated to as high a solids content as possible before being burned in the recovery boiler to maximize the heat recovery. The viscosity rises rapidly with concentration above 50%, with softwood black liquors being more viscous than hardwood black liquors. Black liquor is usually fired at 65%−70% solids content. More information on black liquor is in Chapter 17, Volume 1.

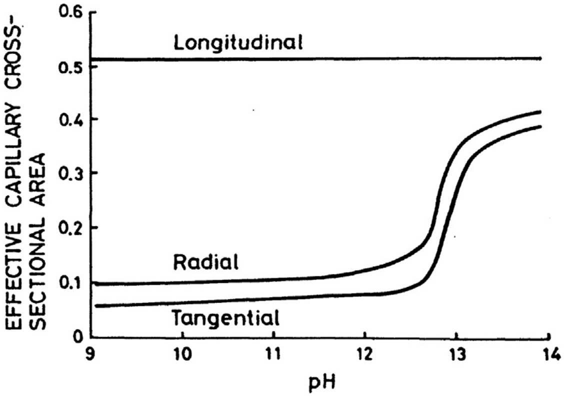


FIGURE 12.30 The effect of pH on wood permeability. *©1957 TAPPI. Reprinted from Stone, J.E.,* Tappi J. *40(7): 539−541(1957) with permission.*

Green Liquor, Chemical Recovery

Green liquor is the partially recovered form of kraft liquor. It is obtained after combustion of the black liquor in the recovery boiler. Green liquor is produced by dissolving the smelt from the recovery boiler (Na_2S, Na_2CO_3, and any impurities) in water. Further processing of the green liquor converts it to white liquor. The kraft chemical recovery cycle is fairly complex and detailed. It is considered in detail in Chapter 17, Volume 1.

Pulping Chemicals

The active chemicals in the kraft liquor are Na_2S and NaOH. Other chemicals in kraft liquors are important because they are involved in the recovery process; these include Na_2CO_3 and Na_2SO_4. Still other chemicals such as NaCl are important as contaminants that may build up in the system. The amounts of chemicals are reported on an Na_2O basis in North America. Various combinations of these chemicals are given special names because these combinations can predict how the liquor will behave better than considering the amount of chemicals themselves. Pulping chemicals are reported as concentrations in liquor or as a charge on dry wood. Cooking chemicals and calculations of the liquor properties described in the paragraphs below are reported in detail in Chapter 13, Volume 1.

Total Chemical or Total Alkali

TA is the sum of all sodium salts in the liquors (as Na_2O) that contribute to AA (i.e., NaOH or Na_2S) or are capable of being converted to AA in the kraft cycle. Specifically NaOH, Na_2S, Na_2CO_3, and $Na_2S_xO_y$ (as Na_2O) are included. All chemical amounts may be reported as concentrations of g/L or lb/gal or as a percent relative to ovendry wood.

$$\text{TA} = \text{NaOH} + Na_2S + Na_2CO_3 + Na_2S_xO_y$$

Total Titratable Alkali

Total titratable alkali (TTA) is the sum of all of the bases in the white liquor that can be titrated with strong acid. Generally this includes NaOH, Na_2S, and Na_2CO_3 (as Na_2O), although small amounts of Na_2SO_3 and other acids might be present. A typical value for TTA is 120 g/L (7.5 lb/ft^3).

$$\text{TTA} = \text{NaOH} + Na_2S + Na_2CO_3 \quad (\text{as } Na_2O)$$

Active Alkali

AA includes the active ingredients in the pulping process, i.e., NaOH + Na_2S (both as Na_2O). A typical value for AA is 100 g/L (6.4 lb/ft^3). Research clearly demonstrates that the AA should be kept constant during cooking by adding alkali during the cooking process as it is consumed, but this is difficult to carry out commercially and not practiced.

$$\text{AA} = \text{NaOH} + Na_2S \quad (\text{as } Na_2O)$$

Effective Alkali

EA is the ingredient that will actually produce alkali under pulping conditions. The EA is about 12%–18% on wood for the production of unbleached kraft and 18%–24% on wood for the production of bleached grades, with hardwoods using the lower amounts because of their lower lignin contents. Above 55 g/L EA, cellulose decomposition relative to lignin removal increases dramatically; consequently a liquor:wood ratio above 3:1 should be used.

$$\text{EA} = \text{NaOH} + \tfrac{1}{2}Na_2S \quad (\text{as } Na_2O)$$

Sulfidity

Sulfidity (of white liquor) is the ratio of Na_2S to the AA, expressed as percent. Typically a mill runs in the vicinity of 24%–28% sulfidity, depending largely on the wood species pulped. Sulfidity increases the rate of delignification that occurs by nucleophilic action of the hydrosulfide anion (HS). The net effect is cleavage of β-arylether linkages of lignin and the methoxy groups, the latter leading to the production of mercaptans. Sulfidity may protect against carbohydrate degradation directly, but the decreased cooking times also result in less carbohydrate degradation. All chemicals are as Na_2O.

$$\text{sulfidity} = \frac{Na_2S}{NaOH + Na_2S} \times 100\%$$

If the sulfidity is too low, the lignin content of the pulp may be relatively high and carbohydrate degradation may be severe, leading to low pulp strength. If the sulfidity is too high, emissions of reduced sulfur compounds may increase, and corrosion rates in the recovery process may be high.

Causticity

Causticity is the ratio of NaOH to AA (as always both chemicals are on an Na_2O basis), expressed as a percentage. Obviously, causticity + sulfidity = 100%; the term sulfidity is used much more commonly than causticity. All chemicals are as Na_2O.

$$\text{causticity} = \frac{NaOH}{NaOH + Na_2S} \times 100\%$$

Causticizing Efficiency

The causticizing efficiency is the ratio of NaOH to NaOH and Na_2CO_3 (as Na_2O). This is a measure of how efficient causticizing is; it represents the percentage of the Na_2CO_3 from the recovery boiler that is converted back into useful NaOH cooking chemical. A value of 78%−80% is typical commercially.

$$\text{causticizing eff.} = \frac{NaOH}{NaOH + Na_2CO_3} \times 100\%$$

Reduction Efficiency

The ratio of Na_2S to Na_2S and Na_2SO_4 in green liquor is known as the reduction efficiency. This is a measure of reduction efficiency of sulfur in the recovery boiler; preferably, this value is high. Typically it is 95% and not routinely measured in the mill. In addition to sodium sulfate, other oxidized forms of sulfur are present such as sodium sulfite and sodium thiosulfate.

$$\text{reduction eff.} = \frac{Na_2S}{Na_2S + Na_2SO_4} \times 100\%$$

Dead Load

Inorganic materials, principally NaCl, present in kraft liquor but cannot be regenerated in the recovery process to AA, contribute to the dead load. Dead load merely circulates through the system thereby decreasing energy recovery and throughput during chemical recovery, increases corrosion, and may interfere with pulping.

Residual Alkali

The EA remaining in a cook at its completion is termed residual alkali. The level of residual alkali determines the final pH of the liquor. At a pH of about 12, some hemicelluloses in the liquor may be deposited on the fibers with a slight increase in yield. If the pH drops much below 12, lignin may deposit on the pulp, increasing the Kappa number and bleaching requirements or decreasing the bonding of unbleached pulps. Scaling and lignin precipitation will occur during black liquor concentration if the pH is low.

Polysulfide Cooking

Polysulfide is another additive that has been examined by several researchers (Kleppe and Kringstad, 1963; Teder, 1968). The polysulfide has a positive effect both on the delignification rate (Lindström and Teder, 1995) and on the carbohydrate stability, as it oxidizes the carbohydrates, reducing the end groups to alkali-stable aldonic acid end groups. The positive effect of polysulfide on the delignification rate is evident at concentrations of 0.02 mol/dm^3 and higher (Berthold and Lindström, 1997). Even though polysulfide is formed during the kraft cook, most of it rapidly decomposes at temperatures higher than 110°C. Without polysulfide addition, the concentration of polysulfide is lower than required to achieve the positive effect on the delignification rate (Gellerstedt, 2003). Because of this, polysulfide has to be added to the cooking liquor. The drawback of polysulfide addition is that the amount of sulfur in the system is increased, and this disturbs the sodium—sulfur balance in the mill, thereby generating higher emissions to the atmosphere. Polysulfide pulping is a variant of kraft pulping in which half or more of the sodium sulfide of kraft white liquor is first oxidized. This orange liquor has the ability to preferentially oxidize end groups of hemicelluloses, making them more stable to alkaline attack and resulting in higher yields of pulp from wood. Laboratory studies have shown that the addition of polysulfide to modified cooking makes it possible to produce a fully bleached pulp from softwood brown stock in the 15—18 kappa range with final yield and strength properties comparable with those from conventional.

Modifications/Developments of Kraft Pulping

Extended delignification addresses environmental issues, improves mill energy efficiency, and has received wide use in the pulp and paper industry. Extended delignification is performed before the bleach plant for reducing the lignin content in the pulp entering the bleach plant for reducing the use of the bleaching chemicals. Reduction in the use of bleaching chemicals reduces the amount of pollutants discharged and increases the amount of organic substances going to the recovery boiler. New cooking methods have been developed, which allow more selective delignification and provide mills with new pulping options. Mills are able to cook to lower Kappa numbers, allowing less bleach chemical usage or permitting alternative bleaching methods. Mills can also maintain Kappa numbers, while improving yield and physical strength properties. There are different types of batch extended delignification systems available:

- RDH
- SuperBatch
- Enerbatch

RDH for batch digesters and modified continuous cooking (MCC) for continuous digesters such as the Kamyr (for which it was developed) improve kraft pulping by increasing uniformity although by slightly different mechanisms. One aspect of the improvements is that alkali is of more constant concentration during cooking. Furthermore, it is important to have adequate sulfide present at the beginning of the cook to improve the selectivity of delignification.

RDH is a recent modification of kraft cooking in batch digester that promises high strength pulps and decreased steam consumption. The first installation was at the Nekoosa Packaging mill in Valdosta, Georgia. The process was developed by the Rader Division of Beloit and involves preimpregnation of steam packed chips with weak black liquors (usually three) of increasing temperatures. The final hot black liquor is then displaced with a mixture of hot white and black liquors at the cooking temperature. Because the liquor is preheated, the heating time is minimal and production is increased. The original purpose of this method was to recover the energy of the warm black liquor and decrease digester heating time; however, many other benefits have been obtained. Cooking is achieved using direct steaming until the desired H-factor is achieved. Wash water then displaces the hot, black liquor that passes through a heat exchanger to warm incoming white liquor. Because blowing is at a lower temperature, pulp strength is increased. Good process control is important with RDH. It is known that the NaOH is depleted to a high extent in black liquor, but large amounts of the sulfide remain.

Wood is able to absorb sulfide from black liquor (Tormund and Teder, 1989). This means (hypothetically) the RDH process allows one to cook at high effective sulfidities without the problems of recovering liquor containing high sulfidities. In short, the RDH process allows some direct recovery of sulfide, allowing substantially lower concentrations of sulfide in the prepared cooking liquor. It is also known that the effective concentration of sulfide is low at the initial stage of conventional kraft cooks. Thus, sulfide depletion is less likely to occur during cooking with the RDH process (where extra sulfide is obtained from the black liquor), so that pulping selectivity is improved. Decreased sulfide in black liquor has numerous advantages, including decreased foaming, corrosion, and total reduced sulphur (TRS) emissions. Residual alkali in the black liquor is able to cleave acetyl groups from the hemicelluloses and form salts of the phenolic groups of lignin, thereby decreasing the alkali consumption in white liquor that is later introduced. This has a leveling effect on the concentration of alkali during the cook. Better diffusion of cooking chemicals, especially sulfide, before cooking would lead to more selective delignification so that lower Kappa numbers may be achieved. Holding black liquor at elevated temperature before concentration also lowers its viscosity, so that it can be fired at slightly higher solids content. Another advantage is that the washing action inside the digester from the wash water before blowing the digesters helps keep dilution minimal and improves the washing efficiency. If excess recovery boiler capacity is available, *this technique could be modified by using some green liquor to wash the chips*. This lowers chemical demand during pulping, and the green liquor goes back to the recovery boiler.

In the RDH and SuperBatch processes, impregnation with black liquor is performed for decreasing the heat consumption and at the same time increasing the initial sulfide concentration and decreasing the EA charge. Developments in SuperBatch cooking have focused on the cooking technology and chemistry that yield the highest possible strength. The SuperBatch system allows the extension of cooking to very low lignin contents without any process modifications and without losing pulp strength. Today, we are able to produce pulps that not only meet stringent pulp requirements but also because of effective impregnation stages and high chip quality improve the operation of the following stage, i.e., the knotting and screening process. SuperBatch cooked pulps can also improve profitability in papermaking process by enabling higher machine speeds. There are several installations of SuperBatch cooking plant worldwide. In the Enerbatch process, a pretreatment with white liquor followed by a pretreatment with black liquor is performed. All these displacement cooking processes show significant energy saving and an improved pulp quality. The lignin content is usually measured as the Kappa number with a standardized method. In all these modified batch cooking methods, chips are impregnated in the digester before the bulk delignification that is proceeded by an alkali concentration profile. In displacement batch cooking, the heat in the spent cooking liquor is recovered by displacing it from the digester with a washing liquid and using it to preheat chips in the next cooking batch (impregnation).

There are limitations in case of conventional cooking regarding how low the Kappa number can be brought without affecting the pulp quality. This Kappa number is around 30–32 for softwood and 18–20 for hardwood. By use of several cooking modifications, the kappa from the cooking of softwood can be reduced to a level of 18–22 for softwood and 14–16 for hardwood, while maintaining the yield and strength properties. The kappa reduction depends beside others on the modified cooking technology applied and whether a retrofitted or new installation is used. Several mills in the world with conventional batch cooking installations have rebuilt their conventional batch cooking plants to modified batch cooking systems. Modified batch cooking includes liquor displacement stages in the cooking cycle. Most new batch cooking installations are modified batch cooking installations. The advantages of the modified systems are better heat economy, improved pulp quality, and less rejects. The modified batch cooking system consists of several batch digesters and a tank farm. The production rate determines the number and size of digesters. The tank farm consists of hot liquor (black and white) accumulators, tanks for impregnation and displacement liquors and soap separation, and a pulp discharge tank. Intermediate black and white liquor accumulators are essential for balancing the flows between different cooking stages. Several heat exchangers recover heat from the hot liquors.

In the modified system, after cooking, the digester is cooled by displacement with cold wash liquor. The hot displaced liquor is taken to a pressurized tank. After cooling, the pulp suspension is pumped out of the digester at a low consistency. The hot liquor is reused in the cooking cycle to heat up the digester after impregnation liquor fill. White liquor can be added both to the impregnation fill and the hot liquor fill. Compared with conventional batch cooking, a tank farm is needed in the modified system to store the different liquors between the digesters. Depending on the displacement batch process (RDH, SuperBatch, Cold Blow, or Enerbatch), there are some differences in the cooking cycles, displacement liquors, and tank farm configurations, but the principles are similar. The digesters are heated at the beginning after filling by using hot displacement liquors, and the cook is ended with a cold displacement before discharging by pumping. In a conventional cooking system, more time is needed to heat the digester than in modified cooking. In displacement cooking, the cook is brought to a high temperature in the relatively short hot liquor fill or displacement stage. The digester is at a high temperature for a longer period, and a lower cooking temperature can be used. Furthermore, the alkali profile can be adjusted and controlled in the different stages of cooking in the modified system. A higher residual alkali can be used at the end of the cook, as the displaced cooking liquor containing considerable amounts of alkali is reused in the next cook as hot liquor fill. The longer cooking time at a lower temperature and the higher residual alkali level at the end of the cook give several advantages with respect to pulp quality. The chips are cooked more homogenously, the Kappa number deviations inside the digester are reduced, and less reject is produced. The strength properties of pulp produced by displacement batch cooking as compared with conventional batch cooking are improved. There are several reasons for this improvement in pulp quality, the main reasons being gentler blowing after cooking, more uniform cooking, high residual alkali at the end of cook, and lower cooking temperature. There is sufficient automation in the modern displacement cooking plants, and a computer system controls the entire operation. The control system includes controls at basic (distributed control system) and supervisory levels.

Continuous digesters are being used in modern kraft pulping. Continuous kraft cooking was the standard until the 1980s, but in the middle of the 1980s, the breakthrough of modified continuous kraft cooking occurred and the technology has since been developed further. The major principles of modified kraft cooking that distinguish it from conventional kraft cooking are the split white liquor charge, prolonged delignification by using the washing zone for delignification, and the use of countercurrent cooking at the later part of the cook because it was thought at that time that the concentration of dissolved lignin and sodium ions in the liquor should be as low as possible, particularly in the final phase of the kraft cook. The introduction of split alkali charge actually reduces the hydroxide ion concentration at the beginning of the cooking process, which reduces the carbohydrate loss and increases the hydroxide ion concentration at the end of the kraft cooking process. This in turn enables the transformation of the slowly reacting residual-phase lignin to react like the faster bulk-phase lignin (Lindgren and Lindström, 1996). The use of the modified kraft cooking principles made it possible to reduce the temperature of both continuous kraft cooking and batch cooking systems. The major benefits of modified kraft cooking are improved yield and selectivity (drop in limiting viscosity number vs. reduction in Kappa number) (Andbacka and Svanberg, 1997). The first continuous cooking application on the market that adapted split white liquor charge and countercurrent cooking was named MCC and developed by Kamyr. Later, similar industrial continuous cooking concepts were established, such as Extended Modified Continuous Cooking (EMCC) by Alström, Iso Thermal Cooking (ITC) by Kvaerner Pulping, and Lo-Solids by (Alström/Andritz) (Andbacka, 1991). Modified continuous kraft cooking was later improved by black liquor impregnation, where black liquor was withdrawn from a later part of the digester and charged into the impregnation phase at the start of the cooking process. The idea of using black liquor recirculation during continuous cooking was adapted from the batch cooking systems. The initial sulfide ion concentration thus increased significantly, which led to faster degradation of the initial-, bulk-, and residual-phase lignin. Although high sulfidity is advantageous from a chemical delignification point of view, the sulfidity charge is also regulated in practice by discharge limits. Black liquor contains organic matter, which when present during the impregnation phase has been shown to have a rate-increasing effect on bulk-phase delignification but a rate-decreasing effect when the final residual delignification phase dominates (Wedin, 2012). To avoid severe carbohydrate loss, the kraft cook should thus be terminated before the even slower residual phase begins to dominate, for example, by terminating the cook at a higher Kappa number. The positive effect on the bulk phase has been related to lignin structures having free phenolic groups (Sjödahl et al., 2006).

At the end of the 1990s, a new application called Compact Cooking was marketed and supplied by Kvaerner. Compact Cooking used black liquor recirculation in a continuous cooking system. It was carried out using a significantly simplified digester compared with that used in ITC, consisting of two cooking zones used concurrently and two sieves for black liquor extraction. A separate impregnation vessel also became a standard in the Compact Cooking concept. This made it easier to decrease the temperature during impregnation. The alkali charge was split between two positions as black liquor (adjusted with white liquor to the right concentration) to the impregnation vessel and as white liquor to the first cooking zone of the digester. After the first cooking zone, the black liquor was extracted and transferred to the impregnation. The recirculation of the black liquor made it possible to reduce the cooking temperature (without increasing the size of the digester) because it allowed for a higher hydroxide ion concentration through the entire cooking process. This resulted in an increased delignification rate and reduced amount of residual-phase lignin (Lindgren and Lindström, 1996). The implementation of black liquor recirculation allowed for a decrease in temperature of approximately 10°C for softwood and 5°C for hardwood, which improved the yield and selectivity in comparison with ITC cooking. Another improvement in the Compact Cooking was the use of a higher liquor-to-wood ratio during impregnation. This was able to remove one of the most harmful alkali peaks for hemicellulose dissolution and degradation during kraft cooking.

MCC (Fig. 12.14) is a countercurrent process where the concentration of alkali is lower than normal at the beginning of the cook and higher toward the end of the cook. The addition of alkali throughout the cook is an old concept that has been attempted in many ways in the past but has been difficult to implement. The

TABLE 12.5 Comparison of Organosolv Process With Kraft Pulping Process

Pulping Process	Raw Materials	Cooking Chemicals	Cooking Process Parameters	Kappa Before Bleaching
ALCELL	Northern hardwood	Denatured ethanol/ water mixture	190–200°C	N/A
ASAM	Softwood Hardwood Annual plants	Sodium sulfite (alkaline) Anthraquinone Methanol	175–185°C 11–14 bar	13–20
FORMACELL	Softwood Hardwood Annual plants	Acetic acid Formic acid	160–180°C	2–10
MILOX	Hardwood Annual plants	Formic acid Hydrogen peroxide	60–80°C 90–110°C	30–35
Modified kraft	Softwood Hardwood Annual plants	Sodium hydroxide Sodium sulfide	155–175°C 8 bar	10–20

Based on data from Ministry of Food, Agriculture and Forestry (1997) and Young (1998).

concentration of dissolved lignin toward the end of the cook is decreased by the countercurrent operation. (One wonders what happens to hemicelluloses that are sometimes redeposited on the fibers toward the end of the cook because of the decreased pH as much of the alkali has been consumed.) Proponents of the process claim higher pulp viscosity, brighter pulps, lower Kappa numbers, easier bleaching, etc. The pulp is said to be suitable for oxygen delignification down to a Kappa number of 12. The first commercial demonstration of the process was carried out in Varkaus, Finland. Another modification of the kraft process is to replace about 20% of the sodium sulfide with sodium sulfite in the *sulfide–sulfite process*. The sulfite presumably is able to effectively cleave some lignin linkages to improve the pulping process, to give higher yields, increased brightness and strength, and increased fiber flexibility. Table 12.6 shows MCC systems.

EMCC was a further development in extended cooking. The EMCC process further decreases the initial hydroxide concentration and increases the amount of cooking in the countercurrent zone. A fourth white liquor addition point is added to the high heat circulation, and the temperature in the high heat zone is increased from approximately 290–300°F. ITC (developed by Kvaerner) expands on EMCC with an additional circulation loop and fifth white liquor addition point (Engstrom, 1996). The ITC circulation is a very high volume (2100 gal/b.d.st) and requires a special type of screen to handle the flow. The screens are equipped with backflushing valves, which reduce blinding. The high circulation rates result in

TABLE 12.6 Modified Continuous Cooking Systems

MCC—Modified continuous cooking (Kamyr)
EMCC—Extended modified continuous cooking (Kamyr Inc./Ahlstrom)
ITC—Isothermal cooking (Kvaerner Pulping)
BLI—Black liquor impregnation (Kvaerner Pulping)
Lo-Solids—Lo-solids cooking (Ahlstrom/Andritz)
CC—Compact cooking

Based on Bajpai (2015).

even more cooking in the countercurrent zone. As compared with EMCC, the initial hydroxide concentration is reduced. The temperature in the digester is lower and nearly uniform throughout the digester. The amount of cooking in the countercurrent zone is increased. Existing digesters can be retrofitted to ITC, provided an upflow exists in the digester. The downtime required is 10−14 days. The cost of a retrofit is approximately $3 million. To date, several digesters in Europe and Japan have been converted to ITC. One retrofit has been installed in North America in a southern kraft mill.

Black liquor impregnation, also developed by Kvaerner, takes extraction liquor from the digester back to the impregnation vessel. This liquor has a relatively low hydroxide concentration and comparatively high hydrogen sulfide concentration. Black liquor impregnation is only applicable for new digester installations or when replacing the impregnation vessel because of corrosion or other problems. Existing impregnation vessels cannot be converted to black liquor impregnation unless operated well below design capacity. The retention time required is approximately 40 min compared with 30 min for a conventional impregnation vessel. The major benefit observed with black liquor impregnation is a 10% increase in tear.

12.9 SULFITE PULPING

Introduction

The first known patent on work related to sulfite pulping was granted to Julius Roth in 1857 for treatment of wood with sulfurous acid. Benjamin Tilghman is credited with the development of the sulfite pulping process and was granted a US patent in 1867. Numerous difficulties (mainly from sulfuric acid impurities that led to loss of wood strength and darkening of the pulp) prevented commercialization of the sulfite process initially. The first mill using the process was in Sweden in 1874 and used magnesium based on the work of the Swedish chemist C. D. Eckman, although calcium became the dominant metal base in the sulfite pulping industry until 1950. The sulfite pulping process is a full chemical pulping process, using mixtures of sulfurous acid and/or its alkali salts (Na^+, NH^{3+}, Mg^{2+}, K^+, or Ca^{2+}) to solubilize lignin through the formation of sulfonate functionalities and cleavage of lignin bonds. By 1900 it had become the most important pulping process but was surpassed by kraft pulping in the 1940s. It now accounts for less than 10% of pulp production. Woods with high pitch contents or certain extractives (such as the flavones dihydroquercitin in Douglas fir) are not easily pulped at the lower pHs. Once the dominant pulping process, now less than 10% of pulp is produced by the sulfite method in this country partly because of environmental considerations. Some advantages of sulfite pulping are bright, easily bleached pulps, relatively easily refined pulps, pulp that forms a less porous sheet that holds more water than kraft pulps (for use in grease-resistant papers), and pulps with higher yield than kraft. Disadvantages include a pulp that is weaker than kraft, not all species of wood can be pulped easily, cooking cycles are long, and chemical recovery is fairly complicated or, in the case of calcium, impractical. (In the case of ammonia, the sulfur is recovered, but the ammonia must be replaced as it is burned in the recovery process.) The process involves treating wood chips with the cooking liquor at 120−150°C (250−300°F) from 500 to 700 kPa (75−100 psig).

Liquor Preparation

The liquor is ordinarily made at the mill by burning sulfur to form SO_2 and dissolving this in water to produce sulfurous acid (H_2SO_3). Before sulfur is oxidized to form SO_2, it is handled above 160°C (320°F) because it is then a liquid and easy to convey. During combustion of sulfur at 1000°C (1830°F), the amount of oxygen must be carefully regulated to insure complete oxidation but not over oxidation that would result in the formation of sulfur trioxide (which forms sulfuric acid when added to water). The SO_2 gas is cooled fairly rapidly (if cooled too slowly, an undesired equilibrium reaction is favored with sulfur trioxide) before reaction with water. The sulfurous acid is then treated with alkaline earth element (as the hydroxide or carbonate salt) in an acid–base reaction. The reactions are summarized as follows (where $M = Na$, K, NH_4, $^1/_2$ Ca or $^1/_2$ Mg and are in solutions as their ions):

$$S + O_2 \rightarrow SO_2$$
$$SO_2 + H_2O \rightleftarrows H_2SO_3$$
$$H_2SO_3 + MOH \rightleftarrows MHSO_3 + H_2O$$
$$MHSO_3 + MOH \rightleftarrows M_2SO_3 + H_2O$$

For example,

$$2H_2SO_3 + CaCO_3 \rightleftarrows Ca(HSO_3)_2 + H_2O + CO_2$$

The highly deleterious reactions that produce sulfuric acid that quickly degrades the cellulose and delayed the first commercial use of sulfite pulping are as follows:

$$SO_2 + {}^1\!/\!{}_2O_2 \rightarrow SO_3$$
$$SO_3 + H_2O \rightarrow H_2SO_4$$

One can easily check for sulfuric acid in cooking liquor using TAPPI UM 600 to see if this is a problem at one's mill. It is accomplished by filtering the liquor, adding formaldehyde, adding $BaCl_2$ to precipitate sulfate as $BaSO_4$, settling overnight, filtering the precipitate, igniting the precipitate, and weighing the precipitate. UM 657 is analysis of sulfur burner gases for SO_2 and SO_3 by the Orsat apparatus.

Sulfite Pulping

The sulfite cooking liquor is heated only part way to the desired temperature and held with the wood chips until uniform liquor penetration is achieved, particularly in acid sulfite processes. This is very important, even more important than uniform liquor penetration in the kraft process. Without uniform liquor penetration, the chips will char because there may not be enough base to supply the necessary buffering action. In short, the sulfurous acid is able to penetrate the wood chip very quickly in the vapor form of SO_2, leading to high concentrations of sulfurous acid in the center of the chip. Long impregnation times allow the metal bases to "catch up" and buffer the system. The temperature is then raised quickly to the desired cooking temperature. After the proper cooking time, the digester pressure is reduced from 90 to 40 psig before blowing the chips. Sudden decompression during blowing effectively separates the wood fibers. Pressure is reduced before blowing to prevent damage to the fibers. Important variables are wood species, base ion, maximum cooking temperature, cooking time (8–14 h), acid concentration, and liquor-to-wood ratio (3.25–4:1). (The magnefite process uses a pH of about 3.5 and cooking time of about $4^1/_2$ h at 130–135°C. This method has a higher retention of hemicellulose.) In general, the sulfite process produces a medium strength pulp with soft, flexible fibers. The lignin content is low and the pulps are easily bleached using about one-half the amount of bleaching chemicals that kraft pulps require. Yields are from 40% to 52%. Spruce, balsam fir, and hemlock are the preferred species. Resinous species such as southern pine and Douglas fir (which contains a compound that inhibits pulping) are not suitable to acid sulfite cooking. Aspen, poplar, birch, beach maple, and red alder are hardwoods suited to sulfite pulping because of uniformity of structure and low extractive contents. These pulps impart softness and bulk in the final sheet.

Sulfite Pulping Base Metals

Calcium is the traditional base used in sulfite pulping. Limestone ($CaCO_3$) reacts with H_2SO_3

in pressurized towers to produce the pulping liquor. The liquor is used at a pH of 1–2 (maintained with excess SO_2); at higher pH values, calcium sulfite precipitates. The cooking temperature is 140°C. Pulping is characterized relative to the other bases by intermediate pulping rate, moderate amount of screenings, high scaling tendencies, and no chemical recovery. Developments in sulfite pulping since 1950, including the use of the bases mentioned below, which are soluble in much wider pH ranges and have chemical recovery cycles, have greatly increased the versatility of the sulfite process. *Magnesium*-based sulfite pulping is carried out at a pH below 5 and is characterized relative to the other bases by intermediate pulping rate, moderate scaling and screenings, and relatively simple chemical recovery. There are two major processes: acid sulfite at pH below 2 and bisulfate pulping at pH 4.5 (the magnefite process). Because of limited solubility of magnesium sulfite, magnesium-based sulfite pulping must be carried out below pH 5. See the *Magnefite Process* section below for more information. The magnesium-based sulfite pulping system has a relatively simple recovery process, for example, as shown in Fig. 12.31. *Sodium*-based sulfite pulping can be carried out at any pH. NaOH or Na_2CO_3 may be used to form the cooking liquor from H_2SO_3. The process is characterized by a slow pulping rate, low amounts of screenings, and low scaling and complex chemical recovery. *Ammonium*-based sulfite pulping is very similar to sodium-based pulping (because the ammonium ion is very similar to the sodium ion), except for two important differences. The cooking rate is faster than the other three bases mentioned, and the ammonium ion is lost in chemical recovery by combustion; however, the use of fresh ammonia (which reacts as ammonium hydroxide) allows the sulfur to be recovered in a relatively simple process. The upper practical pH limit is about 9; above this pH, free ammonia begins to be significant. At pH 9.24 at 25°C, half of the ammonium appears as free NH_3.

$$NH_4{}^{+} \rightleftharpoons H^{+} + NH_3 \quad pK_a = 9.24 \text{ at } 25°C$$

Potassium-based sulfite pulping has been studied in the laboratory and gives pulping results similar to those of sodium. It has the advantage that the spent liquor makes a good fertilizer if liquor recovery is not to be practiced as in the case of small mills that may be used for nonwood fibers (Wong and Derdall, 1991).

Cooking Liquor

The cooking liquor is the fresh pulping liquor for the sulfite process, consisting of a mixture of SO_2 together with one of the bases (alkali ions).

Brown (or Red) Liquor

Brown or red liquor is the waste liquor from the sulfite pulping process.

Actual Forms of Sulfite-Based Cooking Chemicals

The cooking chemicals all start out with SO_2. This is in turn dissolved in water to give H_2SO_3 or alkali solution to give HSO_3^- *or* SO_3^{2-}. *Sulfur dioxide* is SO_2, a gas formed by burning sulfur; it has an acrid, suffocating odor and limited solubility in water. *Sulfurous acid* is H_2SO_3, the reaction product of SO_2 and water. *Monosulfite salt or sulfite* is the completely "neutralized" form (salt) of H_2SO_3:M_2SO_3, where M = monovalent cation (Na^+, K^+, $NH4^+$, $^1/_2$ Ca^{2+}, or $^1/_2$ Mg^{2+}). For example, Na_2SO_3 is sodium monosulfite or, simply, sodium sulfite. *Bisulfite salt* is the "half-neutralized" salt of H_2SO_3:$MHSO_3$. Although not used by the industry, the preferred term is *hydrogen sulfite*. For example, $NaHSO_3$ is sodium bisulfite or, preferably, sodium hydrogen sulfite.

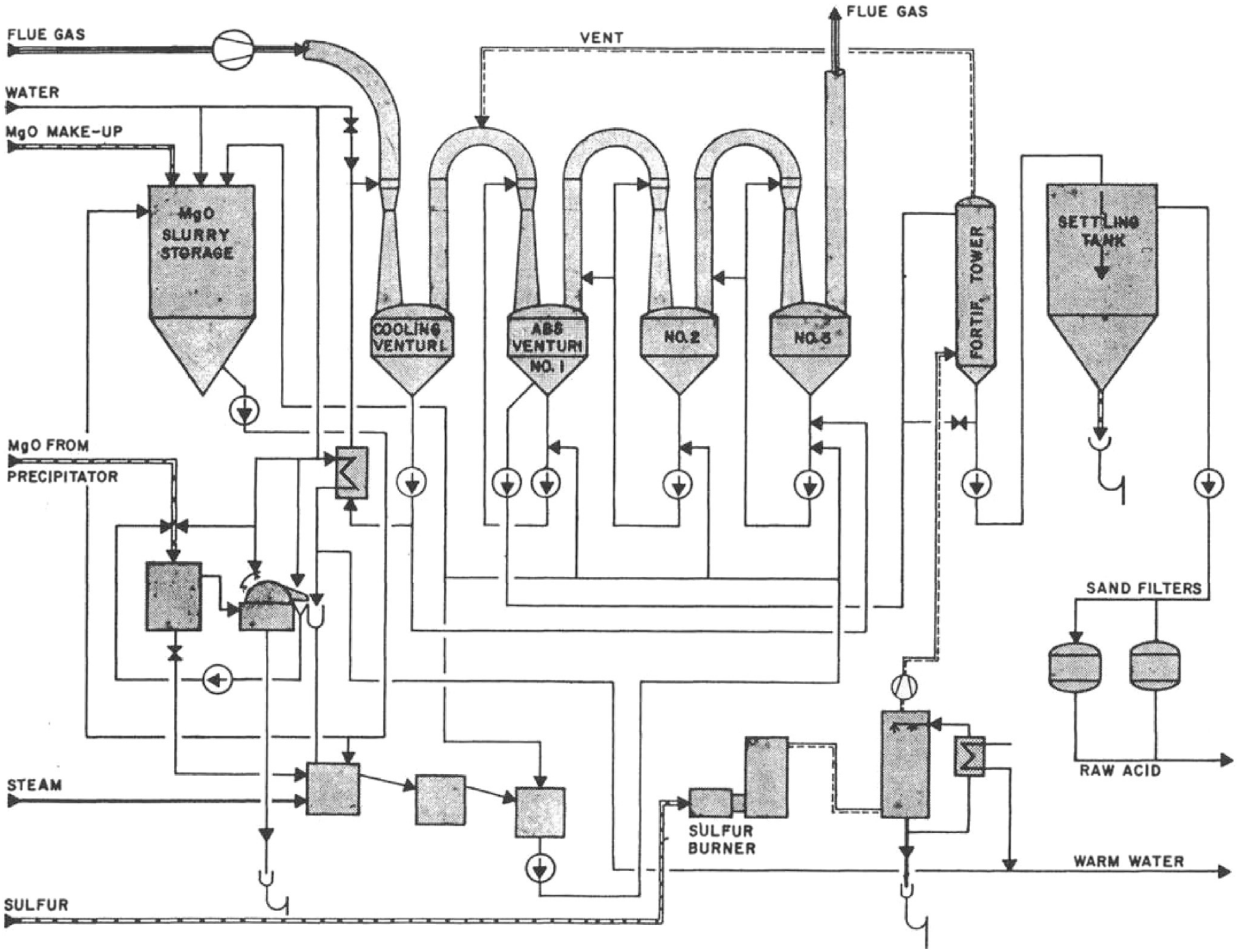


FIGURE 12.31 Babcock and Wilcox process for magnesium-based sulfite chemical recovery. *Reprinted from EPA-625/7-76-001.*

Cooking Chemical Terminology

All sulfite-based cooking chemicals are expressed on a molar-equivalent-to-SO_2 basis but expressed as a weight percent SO_2. (This is rather confusing and explained in detail in Chapter 13, Vol. 1 with examples.) For example, the formula weights for Na_2SO_3 and SO_2 are 126 and 64 g/mol, respectively. Therefore, a solution containing 126 g/L of Na_2SO_3 is equal to 64 g/L on an SO_2 and would be expressed as 6.4% SO_2. The cooking chemicals are expressed as *total, free, or combined* SO_2. The term *true free* SO_2 is also used. *Total* SO_2 is, for sulfite cooking liquors, the ratio of the total weight of SO_2 to the total weight of the solution containing the SO_2, usually expressed as a percent. Total SO_2 is determined by the Palmrose method, titration with potassium iodate (TAPPI Standard T 604).

$$\text{total } SO_2 = \text{free } SO_2 + \text{combined } SO_2.$$

Free SO_2 is the amount of sulfite chemical, based on SO_2, present in the form of the free acid, H_2SO_3, in addition to that which can be converted to free acid (i.e., 1/2 of the HSO_3^-, see reaction below the next definition), as a percent of total liquor weight. It is determined by titration with NaOH. *Combined* SO_2 is the difference between the total and free SO_2 expressed as percent of total liquor weight; it is the SO_2 existing in the form of the monosulfite salt, in addition to that which can be converted to the monosulfite salt (1/2 of the HSO_3). 2 mol of bisulfite form 1 mol of sulfurous acid and 1 mol of monosulfite by the reaction below; the equilibrium is very, very far to the left.

$$2HSO_3{}^- \rightleftharpoons H_2SO_3 + SO_3{}^{2-}$$

True free SO_2: In liquors where the free SO_2 exceeds the combined SO_2, the difference is equal to the true free SO_2 and represents the actual amount of sulfurous acid in the pulping liquor.

Square Liquor

A square sulfite cooking liquor has equal amounts of *free* SO_2 and *combined* SO_2. Because the actual species is all HSO_3^-, there is very little buffering capacity unless a buffer such as sodium carbonate is added.

Acid Sulfite Process

The acid sulfite process uses a cooking liquor that is strongly acidic (pH 1.5–2, and, therefore, has a preponderance of free SO_2 in solution), with a pulping temperature of 125–145°C (260–290°F) and a cooking time up to 7 h. A long heating time (3 h) is necessary to prevent diffusion of SO_2 ahead of the base that causes lignin to condense at high temperature in the center of the chip causing a "black cook." The base is usually calcium. Because of acid hydrolysis, the result is a weak pulp, with low hemicelluloses content suitable for dissolving pulp, tissue paper, and glassine.

Bisulfite Process

A full chemical pulping process with higher liquor pH (3–4) and nearly equal amounts of free and combined SO_2 in the liquor ("square" liquor) is known as the bisulfite process. The temperature is 160–180°C with a cooking time of 0.25–3 h giving yields of 55%–75%. The Arbisco process uses sodium as the base; the magnefite process uses magnesium as the base. Ammonia is also a suitable base, but, more recently, potassium is being used as the base. This pulp is suited for medium grades of paper such as newsprint and writing papers.

Alkaline Sulfite

The alkaline sulfite, a full chemical pulping process, uses a chemical charge containing approximately equal amounts of NaOH and Na_2SO_3 at temperatures of 160–180°C

(320−356°F) and 3−5 h at the maximum temperature. This process produces pulps fairly similar in quality to kraft pulps in terms of yield, brightness, bleachability, and strength.

Magnefite Process

The magnefite process is used at pH 4.5 and 160°C (320°F) with Mg^{2+} as the base. The process is often used to produce reinforcing pulps for newsprint. Chemical recovery is necessary because of the high cost of the base. One recovery process is summarized in Fig. 12.31. Spent sulfite liquor is concentrated to 55% solids and burned at 1350°C (2460°F). MgO and SO_2 are recovered. The MgO is slurried in water to give a slurry containing 50%−60% $Mg(OH)_2$, which is used to scrub SO_2 from the flue gases using a bubble cap tower or venturi scrubber.

$$MgO + HOH \rightarrow Mg(OH)_2$$
$$Mg(OH)_2 + 2SO_2 \rightarrow Mg(HSO_3)_2 + H_2O$$

Stora Process

The Stora process is a two-stage sulfite process with a mild neutral sulfite stage followed by an acid sulfite stage to give a pulp with high yield and low kappa compared with kraft cooking.

Sivola Process

The Sivola process is a three-stage sulfite process for producing dissolving pulps. The neutral sulfite stage provides sulfonation of lignin for easy removal, the second stage of acid sulfite is then used to lower the molecular weight of cellulose for viscosity control and hemicelluloses for their subsequent removal, and the final stage of basic sulfite removes the hemicelluloses.

Chemical Recovery

Chemical recovery in the sulfite process involves six steps:

1. Washing of the spent sulfite liquor from the pulp.
2. Concentration of the spent sulfite liquor.
3. Burning of the concentrated liquor.
4. Heat recovery during liquor combustion.
5. Pulping chemical regeneration.
6. By-product recovery (mostly in Ca^{2+}-based system).

If ammonia is used as the base, it cannot be recovered in the burning process because it is converted to H_2O and N_2; consequently, fresh ammonia must be used for each batch of pulp. Mg^{2+} and Na^+ bases must be recovered because of their high costs. Magnesium has a well-developed, proven recovery system whereby it and sulfur are recovered in their original forms, MgO and SO_2. In this process, the spent sulfite liquor is concentrated to 55% solids before burning at 1370°C (2500°F) in special furnaces. The magnesium is recovered from the gases as MgO, which is slurried in water to form $Mg(OH)_2$. The $Mg(OH)_2$ is then used in the scrubbers to trap SO_2, generating $Mg(HSO_3)_2$. The reactions are summarized as follows:

$$MgCO_3 + 2H_2SO_3 \rightarrow Mg(HSO_3)_2 + CO_2 + H_2O$$
$$MgO + HOH \rightarrow Mg(OH)_2$$
$$Mg(OH)_2 + 2SO_2 \rightarrow Mg(HSO_3)_2 + HOH$$

Sulfite By-products

There are several important by-products to sulfite cooking. The hexoses, produced by acid hydrolysis of hemicellulose and cellulose, are sometimes fermented to ethanol, leaving lignosulfonates (salts of sulfonated lignin) that are water soluble at useful pHs. The lignosulfonates are used in leather tanning, drilling mud dispersants, ore flotation, and resins. Alkaline oxidation of lignosulfonates leads to the production of vanillin, that is, artificial vanilla. It takes only a few mills to meet the world's demand for artificial vanilla.

12.10 OTHER PULPING METHODS

Extended Delignification

Chemical pulping and bleaching of chemical pulps are both delignification reactions. Of course, bleaching reactions are much more specific for lignin removal than pulping but are much more expensive. Improvements in pulping that allow cooking to lower lignin contents and new processes before conventional bleaching are referred to as extended delignification. A variety of pretreatment processes (many of which are experimental) applied to pulp lower the amount of bleaching chemicals required, leading to lower levels of chlorinated organic materials.

Organosolv Pulping

Pulping processes under development are based on organic solvents such as methanol, ethanol, acetic acid, acetone, etc. to remove lignin (Muurinen, 2000). For some of these processes it can be expected that the gaseous emissions of sulfur dioxide and odorous gases are reduced because of the use of sulfur-free technology. All new pulping processes intend to achieve a closed mill by direct recovery of the solvent after the cooking step by distillation and combustion of the dissolved wood components or its alternative use as chemical feedstock for different products. The principal aims of Organosolv pulping are reduced environmental impact and improved economy of the pulping process.

The Organosolv pulping processes can be classified in organic acid-based, alcohol/water-based, and mixed processes, which use inorganic and organic pulping chemicals. None of the proposed Organosolv processes have been implemented successfully on a mill scale. A full-scale Organocell plant in Kelheim, Germany, had to be shut down because of insolvable problems. The Repap Enterprises Alcell mill at Newcastle, New Brunswick, Canada, had a similar fate. It is too early to make a conclusive judgment on the alternatives, but it is clear that Organosolv pulping is not accepted modern technology. Information on the environmental impact of the Organosolv pulping processes is scarce and is mainly derived from pilot-scale trials. Whether the advantages can be achieved in full-scale plants is to a certain extent doubtful or at least not proven. Table 12.5 compares Organosolv pulping processes with modified kraft pulping (Ministry of Food, Agriculture and Forestry, 1997; Young, 1998).

Klason was the first to try to remove lignin from wood by dissolving it in acidified alcohol solutions in solutions of 5% HCl in ethanol in 1893. Cooking dry spruce chips for 6–10 h led to dissolution of 28%–32% of the wood. The AlCell (alcohol cellulose) process of Repap enterprises using 50% ethanol and 50% water at 195°C for approximately 1 h has been demonstrated at 15 t/day. One advantage of the system is a relatively simple recovery system (evaporation of the liquor to recover the alcohol) that allows small mills to be economically feasible. The pulp has tensile and burst strengths and brightness equal to kraft pulp and a higher tear strength by 6%–7% (at 400 CSF). For an unknown reason, the pulp appears to be particularly amenable to oxygen delignification without significant strength loss. Also DED (D: Chlorine dioxide, E: Extraction, D: Chlorine dioxide) bleaching gives a brightness of 90 ISO. Lignin, furfural, and hemicelluloses are obtained as by-products.

Young (1992) describes a 450 ton/day mill in Germany using the organocell solvent pulping process. The mill uses a single-stage process with 25%–30% methanol as the solvent to pulp spruce. The alkali charge is 125 g/L with a liquor-to-wood ratio of 4.2:1. AQ, 0.1% on wood, is also used. The cooking temperature is about 160°C (320°F). Bleaching is carried out with an $O_{E/P}PP$ process. The use of oxygen with methanol, ethanol, and propanol has also been investigated as a pulping technique (Deinko et al., 1992).

Biological Pulping

Biological pulping is an experimental process whereby chips are pretreated with white rot fungi or lignin degradation enzymes. Although researchers (promoting additional research funding) sometimes paint a very favorable picture for this process, the high costs of growth media, biological reactors, and other factors are not mentioned. It appears that this is modestly effective as a treatment before mechanical pulping. When reading publications in this area, see if cellulose viscosities are measured as an indicator of selectivity of lignin attack. Many of the strength improvements and yields observed with these methods do not consider the effect of fungal hyphae (see Chapter 24, Volume 1, for more details).

Other, Novel Pulping Methods

Fengel and Wegener in *Wood* (p. 464) list other, unconventional pulping processes with references. They include nitric acid pulping, Organosolv pulping, pulping with a variety of organic solvents, and formaldehyde pulping.

12.11 MARKET PULP

Many mills sell their pulp on the open market. The pulp must be prepared in thick sheets of 50% moisture content if shipping costs are not high (for example, for short distances) or dry lap of 80%−86% solids. Plate 12.3 shows a double-wire press suitable for making wet lap, washing pulps, or thickening stock. Plate 12.5 shows a double-wire press used for making wet lap. The machine acts like a slow paper machine, having a notable similarity in purpose. Some mills make wet lap for their own use to keep paper machines running when the pulp mill is shut down.

12.12 ANNOTATED BIBLIOGRAPHY

General Mechanical Pulping

Pearson, *A J, A Unified Theory of Refining,* No. 6 of Pulp and Pap. Technol. Ser., Joint Textbook Comm., 1990, 128 p., 20 ref.
This book is a very useful comparison of SGW, RMP, and TMP processes. A small portion of the book (pp 65−85) covers beating and refining of chemical pulps. Mechanical pulping is defined as "pulping brought about by the absorption of energy by the repeated compression and decompression of the fiber." This work mentions much of the early, fundamental work accomplished by the key investigators in this area with few, unfortunately, references.

Kayserberg, S. A., High yield pulping-recent trends, *1989 Wood and Pulping Chemistry,* pp 81−84, TAPPI Press, 1989.
This is an interesting reference on the production of various grades of mechanical pulps (TMP, CTMP, PGW) by region of the world from 1976 to 1988. Included are new developments in mechanical pulping and areas where mechanical pulps are competing against other pulps such as in tissue, fluff, paperboard, and writing paper.

European Commission (2001) Reference document on best available techniques in the pulp and paper industry, Institute for prospective technological studies. Integrated Pollution Prevention and Control (IPPC), Seville.

Stone Groundwood

White, J.H., Manufacture of mechanical pulp, in *Pulp and Paper Manufacture,* Vol. 1, 2nd ed., MacDonald, R.G., Ed., McGraw-Hill, New York, 1969, pp 148–190.
This is a fairly detailed review.

Pressurized Groundwood

Burkett, K. and Tapio, M., Super pressurized groundwood (PGW) from southern pine, *Tappi J.* 73(6): 117–120(1990).
Lucander, M., Pressurized grinding of chemically treated wood, *Tappi* J. 71(1): 118–124(1988), no references.

Alkaline Peroxide Chemithermomechanical Pulp

McCready, M., Millar Western – Meadow Lake making quality APP/BCTMP that's environmentally correct, *PaperAge* 108(1): 10–12(1992).

Cold Soda Process

McGovem, J.N. and E.L. Springer, History of FPL cold soda CMP process: 1950-present, *Tappi Proceedings, 1988 Pulping Conference,* pp 641–648.

Kraft Pulping

Kleppe, P.J., Kraft pulping, *Tappi J.* 53(1): 35–47(1970).
This is a useful summary article with 115 references on the kraft pulping process.

Modifications/Developments of Kraft Pulping

Tormund, D. and A. Teder, New findings on sulfide chemistry in kraft pulping, *TAPPI 1989 International Symposium on Wood and Pulping Chemistry Proceedings* pp 247–254.
This article studied the selective absorption of sulfide by wood. Lignin in wood can absorb large amounts of sulfide from cooking liquors so that the concentration of free HS^- is very low. This causes the pulping process to be less selective (like soda cooking) but is the basis of MCC and RDH improvements.
Vikstrom, B., M.S. Lindblad, A.-M. Panning, and D. Tormund., Apparent sulfidity and sulfide profiles in the RDH cooking process, *Tappi Proceedings, 1988 Pulping Conference,* pp 669–676.
This article looks at sulfidity in the RDH process and concludes that free hydrosulfide is four times higher in RDH versus conventional kraft pulping (both at 32% sulfidity), and RDH pulping at 32% sulfidity is equal to 46% sulfidity in conventional kraft.
Scheldorf, J.J., L.L Edwards, P. Lidskog, and R.R. Johnson, Using on-line computer simulation for rapid displacement heating control system checkout, *Tappi J.* 74(3) 109–112 (1991).
Evans, J.W.C., Batch digester heat displacement system reduces steam consumption, *Pulp & Paper* 63(7) 132–135(1989).
Installation of rapid displacement heating system also cuts pulping chemical use and improves pulp strength at several mills.
Swift, L.K. and J.S. Dayton, Rapid displacement heating in batch digesters. *Pulp Pap, Can.* 89(8)T264–T270(1988).
Mera, F.E. and J.L. Chamberlin, Extended delignification, an alternative to conventional kraft pulping, *Tappi J,* 71(1): 132–136(1988).
Johansson, B., J. Mjoberg, P. Sandstrom, and A. Teder, Modified continuous kraft pulping, *SvenskPapperstidn,* 10:30–35(1984).
The first commercial demonstration of the process was carried out in Varkaus, Finland, and reported here.

Sjödahl RG, Axelsson P, Lindström ME (2006) Addition of dissolved wood components to improve the delignification rate and pulp yield in hardwood kraft pulping. Appita J 59(4):317–320.
Lindgren CT, Lindström ME (1996) The kinetics of residual delignification and factors affecting the amount of residual lignin during kraft pulping. J Pulp Pap Sci 22(8):J290–J295.
Engstrom JH (1996) Black liquor impregnation and iso thermal cooking. Pap Asia 12(2):18–21.
Andbacka S (1991) Experiences of modified continuous cooking. Presentation at the Kamyr Symposium in Portugal, April 1991.
Andbacka S, Svanberg J (1997) Isothermal cooking and pulp washing in a modern fiber line. In: 51st Appita general conference, proceedings 1, Melbourne, Australia.
Wedin H (2012) Aspects of extended impregnation kraft cooking for high-yield pulping of hardwood. Ph.D. thesis, KTH Royal Institute of Technology, Stockholm, Sweden.
Bajpai P (2015). Green Chemistry and Sustainability in Pulp and Paper Industry Springer International Publishing AG Switzerland (part of Springer Science + Business Media).

Poly Sulfide Pulping

Green, R.P., Polysulfide liquor generation and white liquor oxidation, in Hough, G, Ed., *Chemical Recovery in the Alkaline Pulping Process,* TAPPI Press, Atlanta, 1985, pp 257–268.
Details on the MOXY and descriptions of other methods for generating polysulfide in the white liquor are given here.
Teder A (1968) Redox potential of polysulphide solutions and carbohydrate stabilisations. Sven Pap 71(5):149.
Lindström ME, Teder A (1995) The effect of polysulfide pretreatment when kraft pulping to very low kappa numbers. Nord Pulp Pap Res J 10(1):8.
Kleppe PJ, Kringstad K (1963) Sulfate pulping by the polysulfide process. II. Birch. Norsk Skogind 18(1):13.
Berthold F, Lindström ME (1997) Polysulfide addition as a means to increase delignification in kraft pulping. Nord Pulp Pap Res J 12(4):230.
Gellerstedt G (2003) Condensation in kraft pulping. A reality? In: 12th International Symposium on Wood and Pulping Chemistry (ISWPC) Madison, USA, June 9–12, 2004, Vol I, 1.

Sulfite Process

Kocurek, M.J., O.V. Ingruber, and A. Wong, Ed., *Sulfite Science and Technology,* Joint Textbook Committee, 1986, 352 p.
McGregor, G.H., Manufacture of sulfite pulp, in Stephenson, J.N., Ed., *Pulp and Paper Manufacture,* McGraw-Hill, New York, 1950, pp 252–362.
This chapter is cited primarily for the extensive information on preparation of SO_2 (43 pages of the chapter).
Wong, A. and G. Derdall, *Pulp Pap. Can.* 92(7): T184–T187(1991).

Magnesium Sulfite Chemical Recovery

Powers, W.E., M.W. Short, J.A. Evensen, and B.A. Dennison, Retrofit options for controlling particulate emissions from a magnesium sulfite recovery furnace, *Tappi J.* 75(5): 113–119(1992).
Nine North American mills are using the magnesium sulfite process. The emission of submicron particulates is detailed.

Anthraquinone Catalyst

Holton, H.H., Soda additive softwood pulping: a major new process, *Pulp Paper Can.*, 78(10):T218–T223(1977).

This was the first published work describing the effect of AQ on pulping.

Dutta, T. and C. J. Biermann, Kraft pulping of Douglas-fir with l,4-dihydro-9,10-dihydroxy anthracene (DDA), *Tappi J.* 72(2): 175–177(1989).

Wandelt, P., The effect of 1,4-dihydro-9,10-dihydroxy anthracene on soda and kraft cooking of pine, *Paperija Puu-Papper och Trd,* (11):673–681(1984).

Organosolv Pulping

European Commission, 2013. Best Available Techniques (BAT) Reference Document for the Production of Pulp,Paper and Board. Industrial Emissions Directive 2010/75/EU.

Hagglund, E., *Chemistry of Wood,* Academic Press, New York, 1951, pp 237–252.

A very good account of the early work on organosolv lignin is given in this work.

Black, N.P., *Tappi J.* 74(4):87(1991). The alkaline sulfite anthraquinone methanol (ASAM) organosolv process claims higher pulp yield and strength than the kraft process.

Aziz, S. and K. Sarkanen, Organosolv pulping-a review, *Tappi J.* 72(3): 169–175 (1989).

Jamison, S. Alcell pulping: world class research right here in Canada, *Pulp Paper Can.* 93(3): 16–19(1991).

This interesting article summarizes progress in the process.

Pyle, E.K. and J.H. Lora, The Alcell™ process: A proven alternative to kraft pulping, *Tappi J.* 74(3): 113–118(1991).

This article summarizes the process.

Goyal, G.C., J.H. Lora, and E.K. Pyle, Autocatalyzed organosolv pulping of hardwoods: effect of pulping conditions on pulp properties and characteristics of soluble and residual lignin, *Tappi J.* 75(2): 110–116(1992).

Process variables of the title process were studied in this work.

Young, J., Commercial organocell process comes online at Kelheim Mill, *Pulp & Paper* 66(9):99–102(1992).

Deinko, LP, O.V. Makarova, and M.Ya. Zarubin, Delignification of wood by oxygen in low-molecular-weight alcoholic media, *Tappi J.* 75(9): 136–140(1992).

Muurinen E (2000). Organosolv pulping. Academic Dissertation, Faculty of Technology, University of Oulu, Linnanmaa.

Ministry of Food, Agriculture and Forestry (1997). Environmentally compatible pulping processes (in German: Umweltverträgliche Holzaufschlußverfahren), on behalf of Ministry of Food, Agriculture and Forestry, Project. No. 95 NR076-S, Landwirtschaftsverlag GmbH, Münster, 1997, ISBN 3-7843-2877-6.

Young RA, Akhtar M (Ed.) (1998). Environmentally Friendly Technologies for the Pulp and Paper Industry, John Wiley & Sons, Inc., New York, ISBN 0-471-15770-8

Novel Pulping Methods

Dahlbom, J., L. Olm, and A. Teder, The characteristics of MSS-AQ pulping—a new pulping method, *Tappi J.* 73(3) 257–261(1990).

The mini-sulfide-sulfite-anthraquinone process uses low amounts of sulfide (about 10% of the sulfur cooking chemical) in an alkaline sulfite process. The authors claim an 8% increase in yield over the kraft process with the possibility of achieving a Kappa number of 8 if the process is followed by oxygen bleaching with strength properties at least as high as pulp produced by the kraft process.

Pollution Aspects

U.S. Env. Prot. Agency, Environmental pollution control. Pulp and Paper Industry, Part I, air, EPA-625/7-76-001 (1976).

EXERCISES

General Aspects of Pulping

1. What are the two principal mechanisms whereby fibers are separated from the woody substrate?
2. What are the four broad categories of pulping processes?
3. Check the appropriate column for the pulp type exhibiting the higher value for each of the following properties:

	Chemical	Mechanical
a. Yield	—	—
b. Tensile strength of paper	—	—
c. Unbleached brightness	—	—
d. Sheet density	—	—
e. Opacity of paper	—	—

Mechanical Pulping

4. What happens if steaming temperatures of 145°C or higher are used during the production of TMP pulp?
5. Chemical pulp has been traditionally used to strengthen newsprint made with stone groundwood pulp. More recently lower amounts of chemical pulp or no chemical pulp has been used with newsprint made from TMP or CTMP. Why is this the case?

Chemimechanical Pulping

6. Describe the pretreatment processes of wood in the chemimechanical pulping methods?

Chemical Pulping

7. What are the two major categories of pulping digesters?
8. The yield versus Kappa number is the most fundamental relationship for chemical pulping methods. What does this information tell us about the selectivity of a process for lignin removal relative to carbohydrate removal?
9. If an inexpensive pulping process is highly selective for lignin removal, is it necessarily good for making paper?
10. Explain how AQ (a pulping additive) stabilizes cellulose and hemicelluloses during alkaline pulping. (From what does it stabilize the carbohydrates?)

Kraft Pulping

11. What are the two active chemicals in the kraft pulping process? Is sulfate an active pulping chemical? Why is the kraft process also called the sulfate process?
12. The H-factor combines what two kraft pulping variables? Does the H-factor alone tell you the degree of cook?

Sulfite Pulping

13. Why has calcium-based sulfite pulping, once the dominant pulping process, been replaced by other pulping processes?
14. What are the two forms of SO_2 in sulfite cooking liquors? Give these by their common names and the corresponding chemical forms.
15. Briefly describe how chemical recovery occurs in magnesium-based sulfite pulping.

Market Pulp

16. What is market pulp?

CHAPTER

13

Pulping Calculations

13.1 GENERAL CHEMICAL PULPING DEFINITIONS

Introduction

Brief definitions are given for the various pulp liquor terms in this chapter. The significance and other information about these terms are found in Chapter 12 (Vol. 1). Here the terms are presented as mathematical variables to be manipulated algebraically.

Chemical Concentration

Chemical concentration is a measure of the concentration of the pulping chemical in the liquor. For example, in sulfite pulping the liquor may be 6% SO_2, indicating 6 g of sulfite chemical (SO_2 basis) per 100 mL of liquor. If the liquor: wood ratio is 4:1, the percent chemical on wood is 24% as SO_2. The following is an important relationship, not the definition of chemical concentration.

$$\text{chemical concentration in liquor} = \frac{\text{percent chemical on wood}}{\text{liquor : wood ratio}} \tag{13.1}$$

Chemical Charge (to a Process), Percent Chemical (on Wood or Pulp)

The chemical charge is a measure of the weight of chemical used to process (i.e., pulp or bleach) a material. For example, kraft pulping is carried out with about 25% total alkali on wood. This would indicate 500 pounds of alkali for 2000 pounds of dry wood. Chemicals in sulfite pulping are expressed on an SO_2 basis. When bleaching mechanical pulp, one might use "0.5% sodium peroxide on pulp." This means that 10 pounds of sodium peroxide are used per ton of dry pulp.

$$\text{chemical charge, \%} = \frac{\text{dry weight of chemical used}}{\text{dry weight of material treated}} \times 100\% \tag{13.2}$$

Liquor to Wood Ratio

The liquor to wood ratio is normally expressed as a ratio, not as a percent. It is typically 3:1 or 4:1 in full chemical pulping. The numerator may or may not include the weight

Biermann's Handbook of Pulp and Paper: Raw Material and Pulp Making
https://doi.org/10.1016/B978-0-12-814240-0.00013-6

of water coming in with the chips, and it must be specified to avoid ambiguity.

$$\frac{\text{liquor}}{\text{wood}} = \frac{\text{total weight of pulping liquor}}{\text{dry weight of wood}} \qquad (13.3)$$

13.2 KRAFT LIQUOR—CHEMICAL CALCULATIONS

Total Chemical or Total Alkali or Total Titratable Alkali

The total alkali is the sum of all of the sodium salts in the liquors (as Na_2O) that contribute to active alkali (AA) or are capable of being converted to AA in the kraft cycle, specifically NaOH, Na_2S, Na_2CO_3, and $Na_2S_xO_y$ (as Na_2O). All chemical amounts may be reported as concentrations of g/L or lb/gal or as a percent relative to ovendry wood. Chemicals are reported on a Na_2O basis in North America.

$$\text{TA} = \text{NaOH} + \text{Na}_2\text{S} + \text{Na}_2\text{CO}_3 + \text{Na}_2\text{S}_x\text{O}_y \quad (\text{as Na}_2\text{O}) \qquad (13.4)$$

Total Titratable Alkali

Total titratable alkali (TTA) is the sum of all of the bases in the white liquor that can be titrated with strong acid. Generally, it is considered as NaOH, Na_2S, and Na_2CO_3 (as Na_2O) although small amounts of Na_2SO_3 and other acids might be present.

$$\text{TTA} = \text{NaOH} + \text{Na}_2\text{S} + \text{Na}_2\text{CO}_3 \quad (\text{as Na}_2\text{O}) \qquad (13.5)$$

Active Alkali

The sum of the active ingredients in the pulping process is known as AA.

$$\text{AA} = \text{NaOH} + \text{Na}_2\text{S} \quad (\text{as Na}_2\text{O}) \qquad (13.6)$$

Effective Alkali

Effective alkali (EA) is the sum of sodium chemicals that will produce OH^- during kraft pulping. NaOH is completely ionized, and for every two sodium atoms of Na_2S, there will be one OH^- produced.

$$\text{EA} = \text{NaOH} + 1/2\text{Na}_2\text{S} \quad (\text{as Na}_2\text{O}) \qquad (13.7)$$

Often AA and EA are given, and one needs to determine the concentration of individual species. A very useful relationship to remember is that: $Na_2S = 2$ (AA−EA); all species are expressed as Na_2O in this formula.

$$\text{Na}_2\text{S} = 2(\text{AA} - \text{EA}) \quad (\text{as Na}_2\text{O}) \qquad (13.8)$$

Sulfidity

In the white liquor, sulfidity is the ratio of Na_2S to the AA, expressed as a percent. Typically, a mill runs in the vicinity of 25%—30% sulfidity, depending largely on the wood species pulped. Sulfidity increases the rate of delignification, which occurs by nucleophilic action of the hydrosulfide anion (HS^-) and appears to protect cellulose against degradation.

$$\text{sulfidity} = \frac{\text{Na}_2\text{S}}{\text{NaOH} + \text{Na}_2\text{S}} \times 100\% \quad (\text{as Na}_2\text{O}) \qquad (13.9)$$

Causticity

The causticity is the ratio of NaOH to AA, expressed as a percentage; therefore, causticity + sulfidity = 100%. The term sulfidity is used much more than the term causticity, and both give the same information. It will not be considered further in this text.

$$\text{causticity} = \frac{\text{NaOH}}{\text{NaOH} + \text{Na}_2\text{S}} \times 100\% \quad (\text{as Na}_2\text{O}) \qquad (13.10)$$

Causticizing Efficiency

The causticizing efficiency is the ratio of NaOH to NaOH and Na_2CO_3. This is a measure of how efficient causticizing is; it represents the percentage of the Na_2CO_3 from the recovery boiler that is converted back into useful NaOH cooking chemical. A value of 77%–80% is typical.

$$\text{causticizing efficiency} = \frac{\text{NaOH}}{\text{NaOH} + \text{Na}_2\text{CO}_3} \times 100\% \quad (\text{Na}_2\text{O basis}) \tag{13.11}$$

Reduction Efficiency

The reduction efficiency is the ratio of Na_2S to the sum of Na_2S and Na_2SO_4 in green liquor expressed as a percentage. This is a measure of the reduction efficiency in the recovery boiler. This value should be high, is usually 95%, and is not routinely measured in the mill. In addition to sodium sulfate, other oxidized forms of sulfur are present, such as sodium sulfite and sodium thiosulfate, which should be considered.

$$\text{Reduction efficiency} = \frac{\text{Na}_2\text{S}}{\text{Na}_2\text{S} + \text{Na}_2\text{SO}_4} \times 100\% \quad (\text{Na}_2\text{O basis}) \tag{13.12}$$

It is convenient to set up a table of conversion factors of use to solve some of the values just given. Table 13.1 gives many of these conversion

TABLE 13.1 Sodium Oxide Equivalents and Other Gravimetric Factors for Kraft Pulping Chemicals

Convert From	Name	Formula Weight	Equivalent Weight	Convert From Na_2O by Multiplication	Convert to Na_2O by Multiplication	NaOH	Na_2S	Na_2CO_3
WHITE LIQUOR COMPONENTS								
Na_2O	Sodium oxide	61.98	31.0	1	1	1.291	1.259	1.710
NaOH	Sodium hydroxide	40.00	40.0	1.291	0.775	1	NA[a]	2.650
Na_2S	Sodium sulfide	78.04	39.0	1.259	0.794	NA	1	NA
Na_2CO_3	Sodium carbonate	105.99	53.0	1.710	0.585	0.377	NA	1
Na_2SO_4	Sodium sulfate	142.04	71.0	2.291	0.436	NA	0.549	NA
Na^+	Sodium ion[b]	22.99	23.0	0.742	1.348	1.740	NA	2.305
NaHS	Sodium hydrogen sulfide	56.06	56.1	1.808	0.553	NA	NA	NA
$Na_2S_2O_3$	Sodium thiosulfate	158.10	79.0	2.551	0.392	NA	NA	NA
Na_2SO_3	Sodium sulfite	126.04	63.0	2.034	0.492	NA	0.619	NA
$NaHSO_3$	Sodium bisulfite	104.06	104.1	3.358	0.298	NA	NA	NA
RECOVERY CHEMICALS[c]								
CaO	Calcium oxide	56.08	28.0	0.905	1.105	1.427	NA	1.890
$Ca(OH)_2$	Calcium hydroxide	74.10	37.0	1.196	0.836	1.080	NA	1.430
$CaCO_3$	Calcium carbonate	100.09	50.0	1.615	0.619	0.799	NA	1.059

1 g/L = 0.008345 lb/(US gal) = 0.06243 lb/ft^3.

[a] *NA indicates these chemicals are not directly interconvertible in the kraft process. Although this is true of the conversion of all sulfur containing compounds to Na_2O, here the weight containing (or reacting with) 1 mol of sodium ion is used because it is the standard of the industry.*

[b] *Sodium is associated with organic chemicals such as sodium carboxylates or phenolates but not associated with halides such as sodium chloride.*

[c] *These values can be used to calculate recovery chemical demands; however, recausticizing is typically less than 83%, so recovery demand is actually about 20% higher.*

factors for kraft cooking and chemical recovery. The cooking chemicals of the NSSC process, Na_2SO_3 and Na_2CO_3, are often expressed on an Na_2O basis as well.

Several examples are presented to demonstrate kraft liquor calculations. Example 1 shows the conversion factor for gravimetrically converting NaOH to Na_2O. Although Na_2O is a hypothetical species in aqueous solutions and does not occur in aqueous solutions, it is a convenient way of expressing cooking chemicals on a weight basis but at the same time on an equal molar basis. Example 1 demonstrates how the conversion factors in Table 13.1 are derived.

Example 2 shows how to calculate the actual concentration of chemical species based on cooking liquor parameters. Example 3 is a detailed pulping problem. Example 4 demonstrates the calculation and use of causticizing efficiency values.

There are additional exercises on which to practice these calculations.

EXAMPLE 1

Derive the conversion factor of 0.775 used to express the weight of NaOH on an Na_2O basis.

Solution

First, the molar relationship between these two species is expressed.

$$2NaOH + \rightleftarrows Na_2O + H_2O$$

From this relationship the gravimetric factor is determined as follows:

$$1\text{ g NaOH} \times \frac{1\text{ mol NaOH}}{40\text{g NaOH}} \times \frac{1\text{ mol } Na_2O}{2\text{ mol NaOH}} \times \frac{62\text{ g } Na_2O}{1\text{ mol } Na_2O} = 0.775\text{g } Na_2O$$

EXAMPLE 2

Given the following information for TTA, AA, EA, and TA (all as Na_2O), determine the sulfidity as a percentage and concentration of the actual species NaOH, Na_2S, Na_2CO_3, and Na_2SO_4 in grams per liter. Assume these are the only sodium-containing species present.

TTA = 120 g/L; AA = 104 g/L; EA = 88 g/L; and TA = 128 g/L

Solution

Using Eq. (13.8), $Na_2S = 2(AA-EA)$, the following is obtained:

$$\begin{aligned}\text{sulfidity} &= \frac{Na_2S}{NaOH + Na_2S} \times 100\% \\ &= \frac{2(AA - EA)}{AA} \times 100\% \\ &= \frac{100 \times 2(104 - 88)}{104} = 30.8\%\end{aligned}$$

chemical composition:

$$\begin{aligned}Na_2S &= 2(AA - EA) = 2(104 - 88) \\ &= 32\text{ g/L (as } Na_2O);\end{aligned}$$

$$32\text{ g/L } Na_2S \times 1.259 = 40.3\text{ g/L } Na_2S$$

$$\begin{aligned}NaOH &= AA - Na_2S = 104 - 32 \\ &= 72\text{ g/L (as } Na_2O);\end{aligned}$$

$$72\text{ g/L NaOH} \times 1.291 = 93\text{ g/L NaOH}$$

$$\begin{aligned}Na_2CO_3 &= TTA - AA = 120 - 104 \\ &= 16\text{ g/L (as } Na_2O);\end{aligned}$$

$$16\text{ g/L} \times 1.710 = 27.4\text{ g/L } Na_2CO_3$$

$$\begin{aligned}Na_2SO_4 &= TA - TTA = 128 - 120 \\ &= 8\text{ g/L (as } Na_2O);\end{aligned}$$

$$8\text{ g/L} \times 2.294 = 18.3\text{ g/L } Na_2SO_4$$

$$\text{Total active chemical} = 40.3 + 93 = 133.3\text{ g/L}$$

$$\text{Total inactive chemical} = 27.4 + 18.3 = 45.7\text{ g/L}$$

Problem

What is the causticizing efficiency of this liquor? Answer: 85.3%.

EXAMPLE 3

Given: 1 metric ton of wood (ovendry basis). The moisture content of the chips is 50% on the green weight basis. The AA of the white liquor is 20% on ovendry wood, and the sulfidity is 25%. The liquor:wood ratio is 4:1 (ovendry wood), not including the water in the chips. Assume the specific gravities of all liquors are 1.00; in fact, they are closer to 1.05 g/mL. In this problem, consider only the active chemical species NaOH and Na_2S, ignoring the presence of Na_2CO_3, Na_2SO_4, and other chemicals normally present. Calculate:

1. NaOH per ton as Na_2O and NaOH
2. Na_2S per ton as Na_2O and Na_2S
3. Total white liquor mass per ton (do not include the mass of water in the chips here)
4. (A) Mass of water in the original liquor; (B) mass of water in chips; (C) total mass of water in digester
5. (A) Concentration of NaOH and Na_2S in the white liquor (as Na_2O); (B) in the diluted liquor

Solution

Wood mass × chemical charge = mass of chemical (AA). 1000 kg × 20% = 200 kg AA (as Na_2O).

1. AA × sulfidity = Na_2S.
200 kg AA × 25% = 50 kg Na_2S (as Na_2O);
50 kg Na_2S × 1.259 = 63.0 kg Na_2S (as Na_2S).

2. AA − Na_2S = NaOH (all of these can be on a mass basis, as Na_2O).
200 kg AA−50 kg Na_2S = 150 kg NaOH;
150 kg NaOH × 1.291 = 193.5 kg NaOH (as NaOH).

3. Ovendry wood mass × L:W ratio = total mass of added liquor.
1000 kg × 4 (kg liquor)/(kg wood) = 4000 kg of liquor.

4A. Total liquor mass − mass of chemicals = mass of water in the liquor.
4000 kg − (63 kg + 193.5 kg) = 3743.6 kg of water in the added white liquor.

4B. MC_{GR} = mass of water in chips/(mass of water in chips + ovendry mass of chips).
$0.500 = x/(x + 1000 \text{ kg dry wood})$;
x = mass of water per 1000 kg dry chips = 1000 kg.

4C. Water in liquor + water in chips = total water in cook. 3743.6 + 1000 = 4743.6 g (or kg) of total water.

5. Mass of dry chemical/volume of solution = concentration.
(A) 150 kg/4000 L = 37.5 g/L NaOH (as Na_2O).
50 kg/4000 L = 12.5 g/L Na_2S (as Na_2O).
Therefore, AA = 50 g/L.
(B) 150 kg/5000 L = 30.0 g/L NaOH (as Na_2O).
50 kg/4000 L = 10.0 g/L Na_2S (as Na_2O).
Therefore, AA = 40 g/L.

EXAMPLE 4

Your boss tells you that the white liquor fresh from the recovery cycle contains 85 g/L NaOH (as NaOH) and 35 g/L Na_2CO_3 (as Na_2CO_3). He asks you if everything is all right. Use the definition of causticity and (knowing typical mill values for this) indicate whether or not you think there is a problem.

Solution

85 g/L NaOH × (62 g Na_2O/80 g NaOH) = 65.9 g/L NaOH (as Na_2O). 35 g/L Na_2CO_3 × (62 g Na_2O/106 g Na_2CO_3) = 20.5 g/L Na_2O_3 (as Na_2O). Causticity = 100% × 65.9/(65.9 + 20.5) = 76.3%; this indicates that only 76.3% of the sodium carbonate is being converted to the active species sodium hydroxide. The conversion should be 77%–80%, so you tell your boss there is a problem.

13.3 KRAFT LIQUOR—CHEMICAL ANALYSIS

The relative proportions of NaOH, Na_2S, and Na_2CO_3 are determined by titration with HCl in so-called "ABC titrations." The procedures are detailed in TAPPI Standard T 624 for kraft and soda white and green liquors and in T 625 for kraft and soda black liquors. The pH versus the forms of Na_2S and Na_2CO_3 are very useful to examine to understand the titration method. The titration curve for NaOH was presented in Fig. 21.1, Volume 1. Fig. 13.1 shows the pH as a function of the species Na_2S, HS^-, and H_2S. Fig. 13.2 shows this for Na_2CO_3. These graphs are valid for dilute solutions at 25°C. There is appreciable variation in the acid dissociation constants from various sources, which may alter the pH from 0.1 to 0.5 or more units. Titration curves are approximately accurate but not exact. For acids such as H_2CO_3 and H_2SO_3, which exist in equilibrium with gases, CO_2 and SO_2, respectively, the total concentration of both the acid and the gas is included in the equilibrium constant.

The titration curve of Na_2S (sodium sulfide) represents the titration of a weak base in the presence of a strong base. Na_2S reacts in water essentially to completion to give NaHS (sodium hydrogen sulfide) and NaOH. NaHS, however, is a weak base with a pK_b of 6.96. The titration curve is that of a strong base—strong acid titration until all of the initially formed NaOH is neutralized, then it is a weak base—strong acid titration until all of the NaHS is H_2S (hydrogen sulfide).

For the titration curve of H_2CO_3, it is assumed that CO_2 is kept in the solution, even

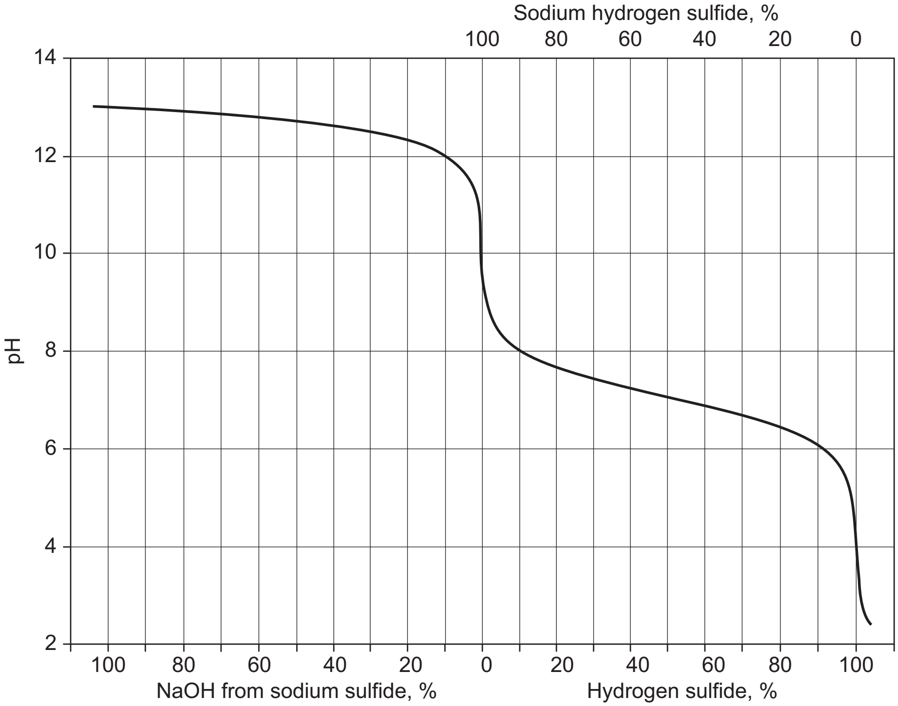


FIGURE 13.1 Titration curve of 0.1 *M* Na_2S with 2 mol of HCl.

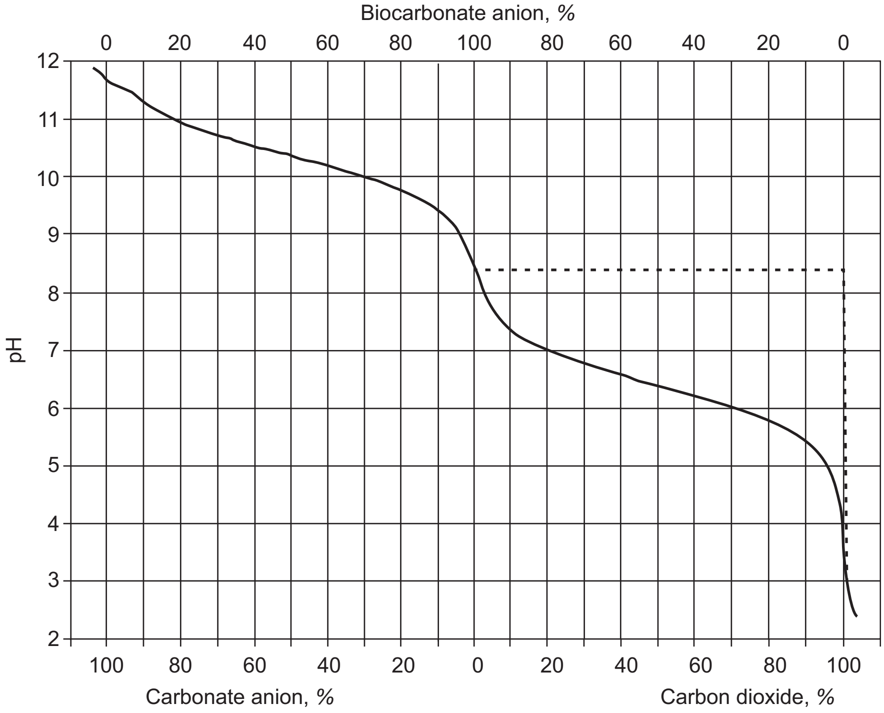


FIGURE 13.2 Titration curve of 0.1 *M* Na_2CO_3 with 2 mol of HCl.

though it is not very soluble. The dashed line shows the titration curve if CO_2 is removed from solution; this is commonly done by boiling the CO_2 off (as it is not soluble in water at elevated temperatures) to sharpen the endpoint. As CO_2 is boiled off, all that remains is $NaHCO_3$ so the pH is approximately constant at $(pK_1 \cdot pK_2)^{0.5} = (6.37 \cdot 10.32)^{0.5} = 8.345$. A similar method involves titrating beyond the endpoint with HCl, swirling the solution to drive off the CO_2, and then back titrating to the endpoint with standardized NaOH solution. The *x*-axis represents the addition of 2 mol of HCl. As the first mole is added, the carbonate anion decreases from 100% to 0%, whereas the bicarbonate anion increases from 0% to 100%. As the second mole of HCl is added, the bicarbonate anion decreases from 100% to 0%, whereas the carbon dioxide increases from 0% to 100%. The first endpoint is titrated to a phenolphthalein endpoint, and the second endpoint is titrated to a methyl orange endpoint. A graph in this form gives the relative concentration of two species at any pH.

An ABC titration (shown in Fig. 13.3) is carried out with three titrations. Before the first titration, excess $BaCl_2$ is added to the liquor to precipitate carbonate anion according to the reaction:

$$Ba^{2+} + CO_3{}^{2-} \rightleftarrows BaCO_3 \downarrow K_{sp} = 8.1 \times 10^{-9}$$

The sample is then titrated with acid to the endpoint at 10.5 (phenolphthalein), the "A" titration. This corresponds to all of the NaOH and half of the Na_2S because all of the Na_2S is converted to NaHS in water with the liberation of NaOH. The amount of acid corresponds to the effective alkali.

The titration curve up to this point is identical to that of Na_2S with HCl (Fig. 13.1). In the second

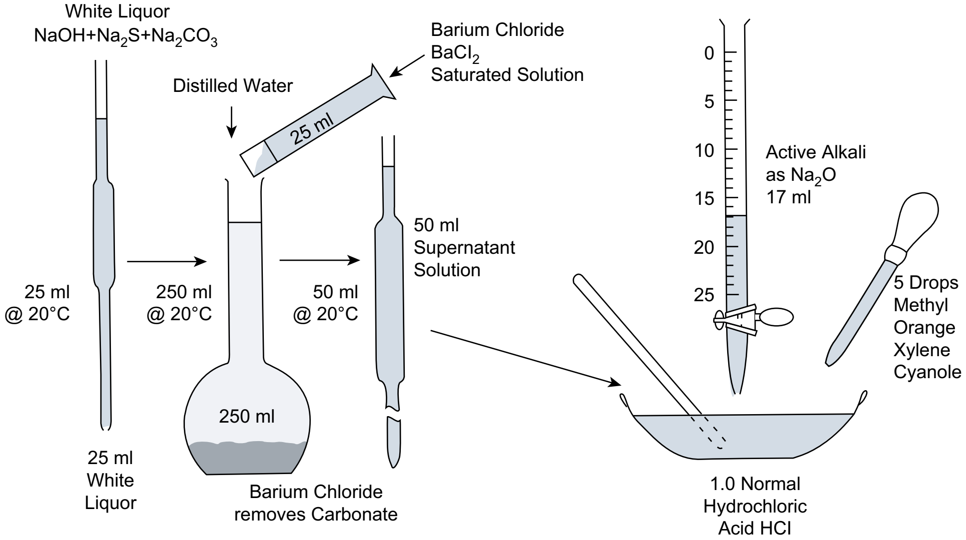


FIGURE 13.3 Titration of white liquor. *Redrawn from J. Ainsworth,* Papermaking, *© 1957 Thilmany Paper Co., with permission.*

titration, excess formaldehyde is added to the same sample to convert the NaHS to NaOH by the reaction:

$$HS^- + CH_2O + H_2O \rightleftarrows CH_2(OH)SH + OH^-$$

The pH rises as NaOH is liberated on addition of formaldehyde, and the solution is titrated again to the phenolphthalein endpoint in the "B" titration. This corresponds to half of the original Na_2S, as all of the NaHS is converted to the complex (avoiding H_2S fumes that would be emitted without formaldehyde addition). The acid consumed from A to B corresponds to AA − EA. The solution is then titrated with HCl to a methyl orange endpoint of pH 4, the "C" titration. The acid consumed from B to C corresponds to Na_2CO_3. At this endpoint the carbonate has redissolved and has been converted to CO_2 according to the reaction:

$$BaCO_3(s) + 2HCl \rightleftarrows BaCl_2 + H_2O + CO_2\uparrow$$

To summarize, the significance of A, B, and C are as follows:

EA = A	NaOH = 2A−B
AA = B	H_2S = 2 (B−A)
TTA = C	Na_2CO_3 = C−B

Black liquor is titrated in a similar fashion if one is interested in residual concentrations of these species after the pulping process. One important difference is that after the $BaCl_2$ is added, the sample is centrifuged to collect the precipitate at the bottom of a test tube. An aliquot is taken from the supernatant for titration. Otherwise, the $BaCO_3$ interferes with the first two endpoints as it does not precipitate well. The "C" endpoint must then be determined on a separate aliquot that has not been treated with $BaCl_2$. This brings up the important point that during an ABC titration of white liquor, it is important to avoid high concentrations of acid that might redissolve the $BaCO_3$; it would probably be better to handle it like black liquor.

EXAMPLE 5

Given: 0.500 N H_2SO_4 is used to titrate 5.00 mL of a white liquor sample. The titration values were A = 30.6 mL, B = 34.2 mL, and C = 38.7 mL. Calculate AA, EA, and TTA.

Solution

Each milliliter of H_2SO_4 is equivalent to 0.500 meq/mL × 31 mg Na_2O/meq = 15.5 mg Na_2O. 15.5 mg Na_2O/5 mL liquor = 3.1 mg Na_2O/(mL white liquor)/(mL titrant) = 3.1 g/L Na_2O. Therefore,

$$\begin{aligned}\text{EA} &= 30.6 \times 3.1 = 94.9\ \text{g/L}\\ \text{AA} &= 34.2 \times 3.1 = 106\ \text{g/L}\\ \text{TTA} &= 38.7 \times 3.1 = 120\ \text{g/L}\end{aligned}$$

13.4 SPECIFIC GRAVITY AND VISCOSITY OF KRAFT LIQUORS

The specific gravity of white liquor at room temperature may be *estimated* as follows:

$$\text{specific gravity} = 1.0 + (\%\ \text{solids}/100\%)$$

The specific gravities and Baumé values as a function of southern pine kraft black liquor solids content are given in CPPA data sheet C-5 (issued in 1943, reissued in 1952, but now apparently abandoned; it was at one time TAPPI DATA SHEET 58A). It should be used with care with other species; however, it is a good approximation lacking any other information. Fig. 13.4 is a graphical presentation of the specific gravity versus solids content. The data sheet gives Baumé values for black liquor at 80–210°F in 10° intervals. Work in my laboratory with commercial kraft black liquor of Douglas fir (from a brown paper mill) at 72°F

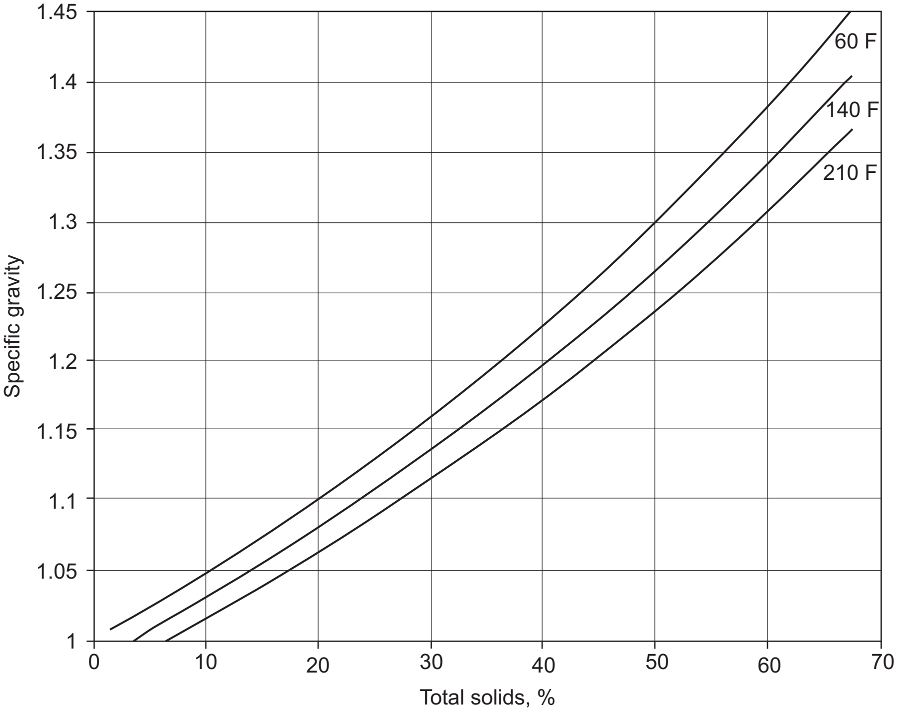


FIGURE 13.4 Specific gravity of black liquor from southern pine versus solids content at 60–210°F.

gave a specific gravity of 1.300 for 51.0% solids, which agrees well with the earlier results. Equations are easily determined from this table to calculate °Bé (which can be converted to specific gravity) as a function of solids content for various temperatures.

$$^{\circ}\text{Bé} = 2/3 \times (\text{solids}, \%) \quad \text{at } 60^{\circ}\text{F}$$

$$^{\circ}\text{Bé} = -2.296 + 0.6524 \times (\text{solids}, \%) \quad 140^{\circ}\text{F}$$

$$^{\circ}\text{Bé} = -4.288 + 0.6384 \times (\text{solids}, \%) \quad 210^{\circ}\text{F}$$

$$\text{specific gravity} = 145/(145 - {}^{\circ}\text{Bé}); \quad \text{sp gr} > 1.0$$

The viscosity of black liquors depends on several factors, particularly the temperature and solids content, as shown in Fig. 13.5. The source of the black liquor is also important, with hardwood black liquors generally having lower viscosities than softwood black liquors.

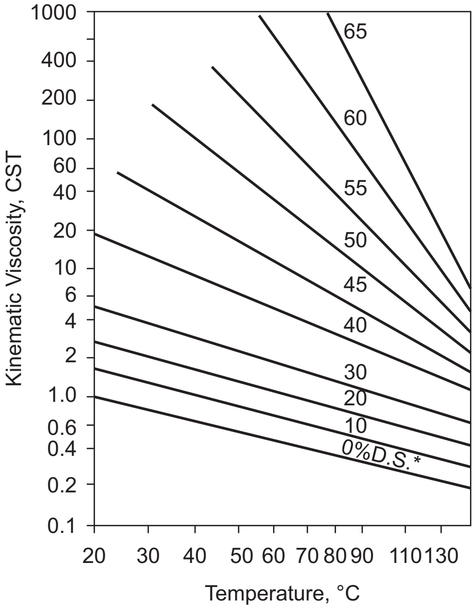


FIGURE 13.5 The viscosity of black liquor. *DS, dissolved solids, CST, centistokes. *From U.S. EPA.*

13.5 IMPORTANCE OF BLACK LIQUOR PH

If the black liquor pH decreases below 12, lignin begins to precipitate. This is due to conversion of phenolate anions to phenol. The salt form is much more polar and water soluble. The pK_a values of phenols representing structures of lignin (model compounds) are shown in Table 13.2.

13.6 KRAFT H-FACTOR AND OTHER PROCESS CONTROL EQUATIONS

The H-factor is a single variable used in the kraft cooking process to combine the variables of temperature and time into a single variable representing the extent of the cook. It is the integral of the *relative reaction rate* with respect to time. It is an extremely important operating parameter in modern process control. The H factor combines only time and temperature, not AA, sulfidity, and other variables assumed to be held constant. The original publication on the H-factor is Vroom (1957).

The H-factor is based on the assumption that delignification is a single reaction. Although this model holds well, lignin is not actually a "pure" compound undergoing a single chemical reaction to achieve delignification. Rather, lignin is a complex molecule with many types of reactions occurring during the delignification process.

TABLE 13.2 The pK_a Values for Various Phenols

Compound	pK_1	pK_2
Phenol	9.99	
4-Methylphenol	10.26	
2-Methoxyphenol	9.99	
1,2-Dihydroxybenzene	9.36	12.98

In 1889, Arrhenius observed that the rate of reaction, k, for most chemical reactions fits Eq. (13.13), where E_a is the *Arrhenius activation energy*, A is the *preexponential factor*, T is the temperature in Kelvin, and R is the gas constant. E_a can be determined within about 1 kcal/mol, and A within a factor of 3. Most chemical reactions increase by a factor of 2–3 with a 10°C increase in temperature; this is attributed to the increased number of collisions of reactants with sufficient energy to achieve the activation energy of the transition species in order for the reaction to proceed. The rate of delignification during kraft pulping increases by a factor of about 2 for an increase in temperature of 8°C. Taking the natural log, ln, of both sides of Eq. (13.13) leads to Eq. (13.14). For a *relative reaction rate*, which is what the H-factor is, Eq. (13.14) is simplified to Eq. (13.15), where B and C are constants.

$$k = Ae^{-Ea/RT} \tag{13.13}$$

$$\ln k = \ln A - E_a/(RT) \tag{13.14}$$

$$\ln k = B - C/T \tag{13.15}$$

Eq. (13.15) was solved by Vroom using $C = 16{,}113$ (based on data in the literature) and arbitrarily setting a relative reaction rate = 1 at 100°C (373.15 K). This leads to Eq. (13.16), which gives the relative reaction rate (which I will call the relative *H-factor rate*) as a function of temperature. The H-factor is determined by the area under a cooking curve corresponding to the H-factor rate at a given temperature and the time (in hours) at each temperature. The H-factor is therefore the integral of the H-factor rate with respect to time expressed in hours. The relative H-factor rate is shown as a function of temperature in Fig. 13.6. Fig 13.7 shows the H-factor rate for a linear heating temperature ramp from 80 to 170°C. In this case the H-factor may be estimated by using a suitable approximation method, such

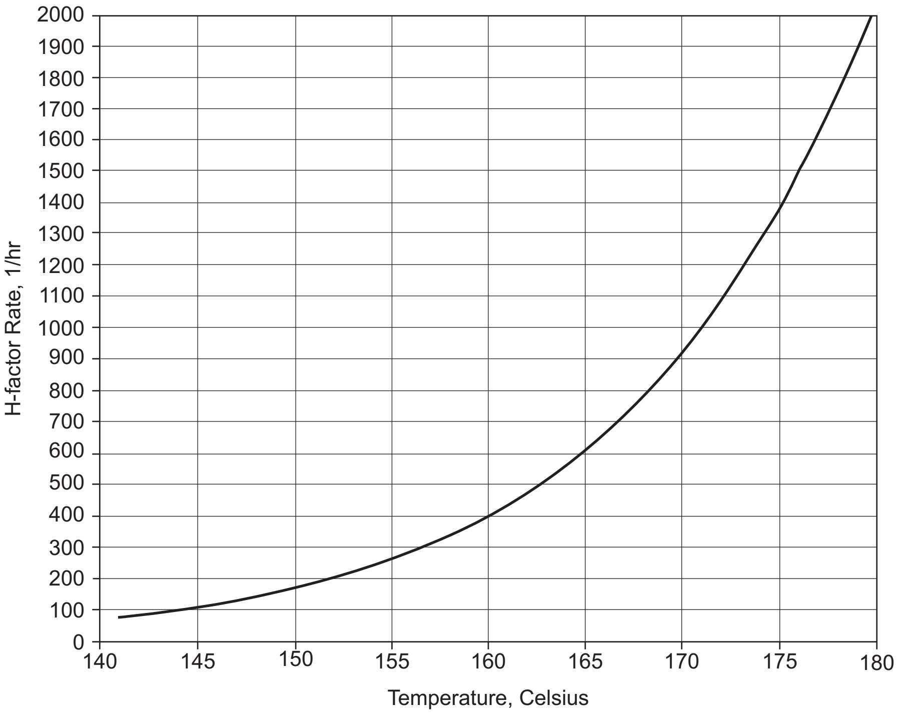


FIGURE 13.6 The relative H-factor rate/h as a function of temperature.

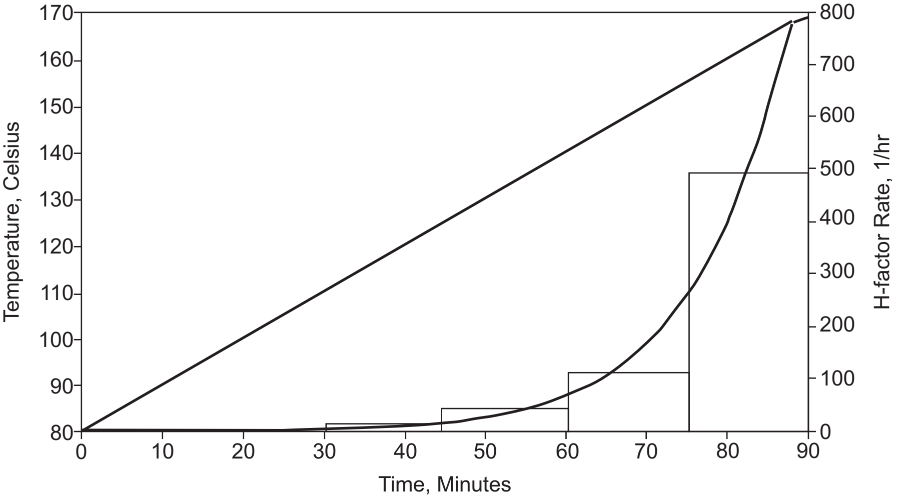


FIGURE 13.7 A linear heating ramp from 80 to 170°C with an approximation of H-Factor by the area under the curve as rectangles.

as the one explained below. Temperatures below 130°C (265°F) contribute very little to the overall extent of the cook.

$$\ln k = 43.181 - 16113/T \qquad (13.16)$$

There are slight discrepancies between calculated values and values given in Vroom's paper, but this is due to the available calculation methods of the time that Vroom did his work. Also, Vroom used 100°C = 373 K (obtaining a B of 43.20) instead of 373.15 K. For 180°C and using $B = 43.20$, the H-factor is 2060/h at 453 K and 2084/h at 453.15 K (a 1.2% difference) although Vroom reported it as 2042/h. I suggest using Eq. (13.16) and adding 273.15 to the temperature in Celsius for reasonable agreement with Vroom's published values and to promote a consistent theoretical basis. At 170°C, this modification gives 917/h, Vroom's equation gives 923/h, and Vroom reported 927/h. At 160°C, this gives 396/h, Vroom's equation gives 398/h, and Vroom reported 401/h. These differences are insignificant and presented only to alleviate concern an individual might have when calculating values that differ from published values.

The H-factor alone cannot be used to predict the yield or other properties of the pulp. However, once the H-factor versus yield relationship (or other pulping parameter relating to lignin content such as Kappa number) is determined for a particular set of pulping conditions, the yield for a given H-factor will be known (presumably) for any time—temperature combination used to achieve that H-factor.

EXAMPLE 6

Sawdust is pulped in a continuous digester at a constant temperature (zero heat-up time) of 180°C for 45 min to a Kappa number of 30. If the digester temperature is increased by 5°C and the other pulping conditions are held constant, solve the following:

1. What pulping time is required to reach the same Kappa number?
2. What is the percent increase in digester output?

Note: the H-factor rate at 180°C = 2042/h and at 185°C = 3054/h.

Solution

1. The H-factor of the cook at 180°C is 2042/h × 0.75 h = 1532. To cook to the same H-factor at 185°C, solve for time as: $t = 1532/3054\ \text{h}^{-1} = 0.50\ \text{h} = 30\ \text{min}$. Cooking at the higher temperature gives 3 batches/90 min or a 50% increase in production.

Although Eq. (13.16) enjoys widespread use in industry, there is no reason to assume that the activation energy of the Arrhenius equation is the same for hardwoods and softwoods or even among species of either group. Furthermore, the composition of cooking chemical may influence the activation energy somewhat. Taking the derivative of the Arrhenius equation and solving for the activation energy gives Eq. (13.17).

$$\begin{aligned} E_a &= RT^2 d \ln k/dT \\ &\approx RT_1T_2(\Delta T)^{-1} \ln(k_{T2}/k_{T1}) \end{aligned} \tag{13.17}$$

EXAMPLE 7

Solve for E_a based on the H-factor relative reaction rates at 165°C and 175°C.

Solution

$(0.001987\ \text{kcal mol}^{-1}\ \text{K}^{-1}) \times (438\ \text{K})\ (448\ \text{K})\ (10\ \text{K})^{-1} \times \ln(1387/610) = 32.0\ \text{kcal}$. Also, comparison of Eqs. (13.14)–(13.16) shows that $16{,}113 = E_a/R$; therefore, $E_a = 32.0\ \text{kcal/mol}$ and is independent of temperature.

Often linear temperature ramps are used or assumed during digester heating. It would be ideal to integrate Eq. (13.16) with respect to time using a linear temperature ramp to solve for the H-factor during the heat-up time. By integrating from absolute zero the form of the equation could be written as follows, where T_r is the rate of temperature increase:

$$\begin{aligned} \text{H-factor} &= \int k(t)dt \\ &= -e^{43.181} \int e^{-16113/(Tr \cdot t)} t^2 t^{-2} dt \end{aligned}$$

Let $a = -16{,}113/T_r$ and $x = 1/t$, so $dx = -t^2\ dt$; the integral is now in the following form:

$$\text{H-factor} = C \int e^{ax}/x^2 dx$$

Unfortunately this integral leads to a series that requires several hundred terms before diverging because of the large value of a, involving numbers on the order of 100! (factorial), making it more difficult to solve than "manual" methods. Below is a short program listed in BASIC, which can be used to solve the H-factor for linear temperature ramps (or any ramp with suitable modification). The program is setup for a temperature ramp of 80–170°C during 90 min. Running the program as is with six time intervals of 15 min gives an H-factor of approximately 165.4 for the time period. Fig. 13.7 is a graphic depiction of what the program accomplishes. The program works by dividing the temperature interval defined by the final temperature, TF, and initial temperature, TI, into rectangles of time. The reaction rate is determined at the temperature corresponding to the center of the time interval and applied to the entire time interval to give an H-factor for that rectangle, TOTAL. The more rectangles used, the closer the approximation. Using 10 time intervals gives an H-factor of 171.6, whereas using 900 time intervals gives 175.2; obviously only a few intervals are needed for sufficient accuracy.

```
10   TI = 80
20   TF = 170
25   TIME = 90
30   REM REMARK STP IS THE WIDTH OF THE
     RECTANGLES IN DEGREES (WHICH IS
     CONVERTED TO TIME), AND INCR IS THE AREA
     OF EACH RECTANGLE. BE SURE TO THAT THE
     NUMBER OF DEGREES IN THE TEMPERATURE
     RAMP IS EVENLY DIVISIBLE BY STP.
40   STP = 15
50   FOR I = TI TO (TF-STP) STEP STP
60   INCR = EXP(43.181-(16113/(273.15 + I +0.5 * STP)))
70   TOTAL = TOTAL + (INCR*(STP/((TF-TI)/(TIME/
     60))))
80   NEXT I
90   PRINT TOTAL
```

Empirical equations have been published, which have found uses in process control. Hatton (1973, 1976) discusses many of these and presents his own model for pulp yield and Kappa number. His equation of pulp yield is in the form of the equation: Yield $= A - B[(\log H)(\mathrm{EA})^n]$, where EA is the effective alkali and H is the H-factor.

The coefficients were solved for a variety of different species of both hardwoods and softwoods. Generally, the softwoods had much higher correlation coefficients.

Edwards and Norberg (1973) developed an extension of the H-factor called the τ (tau) factor, which is a single variable combining the effects of time, temperature, initial EA, and liquor to wood ratio. Earlier work had established the τ factor concept for hypochlorite and chlorine dioxide bleaching data. At constant sulfidity, $\tau = (\mathrm{EA}/L{:}W)^2H$. Lin et al. (1978) calculated the Kappa number as a function of H-factor, liquor to wood ratio, and alkali to wood ratio, obtaining a single equation for hardwoods of Taiwan and the Ivory Coast. Tasman (1981) calculated the yield as a function of the liquor sulfidity, effective alkali, and the H-factor for several species of hardwoods and softwoods in his equations. Recently, Paulonis and Krishnagopalan (1991) discussed a sophisticated process control system for kraft batch digester that uses liquid density, electrical conductivity, and other techniques in addition to the usual parameters to predict Kappa number despite variations in wood chip supply and digester operation.

Kubes et al. (1983) have developed a G-factor that is analogous to the H-factor, except that remaining cellulose viscosity is correlated to cooking temperature and time under constant conditions for any alkaline cooking process. The method works for any alkaline method because cellulose viscosity loss is due to random alkaline cleavage, and there are no known additives that decrease this reaction. Although one may not expect viscosity to be correlated to extent of reaction, the authors' model fits the data fairly well. The authors obtain the value of 175–180 kJ/mol for this reaction.

Table 13.3 lists the H-factor rate, G-factor rate, and ratio of H-factor to G-factor rates at various temperatures. The higher this ratio, the less cellulose viscosity decrease is predicted when cooking to a specified Kappa number. Table 13.3 indicates that cooking at 160°C would give pulp with twice the viscosity as pulp cooked at 180°C.

TABLE 13.3 The H-Factor Rate, G-Factor Rate, and Ratio of H-Factor to G-Factor Rates at Various Temperatures

Temperature (°C)	H-Factor	G-Factor	*H*/*G* Ratio
160	400	2960	0.135
165	610	5220	0.117
170	927	9100	0.102
175	1387	15,600	0.089
180	2042	29,600	0.069

13.7 SULFITE LIQUOR CALCULATIONS

The concentrations of chemicals in sulfite pulping are reported on an SO_2 basis. This allows the various forms of sulfurous acid and its salts to be compared on an equal molar basis although the concentrations are reported on a weight basis. (This is the same principle as using Na_2O as the basis for kraft pulping and recovery chemicals.) The concentration is reported as % or g/100 mL, both of which are identical units if the specific gravity is unity. Full chemical sulfite methods, all use approximately 20% chemical (SO_2 basis) on a dry wood basis. Table 13.4 gives conversion factors to and from the *actual* chemical concentrations and the SO_2 basis. See Example 8 to see how these conversion factors are derived.

The various salts of sulfurous acid are of central importance to the various sulfite-based processes. The chemistry of sulfurous acid as a function of pH is very important. For the titration curve of H_2SO_3, the first proton is a moderately strong acid and titrates along with any strong acids present. Therefore no initial "endpoint" below 0 mL base (corresponding to excess acid) is present as there is for a weaker acid such as acetic acid. The Henderson—Hasselbalch equation cannot be used for this part of the titration curve because the H_2SO_3 ionizes appreciably, thereby reducing the concentration of H_2SO_3 and changing the ratio of acid to conjugate base significantly. The quadratic equation must be used to solve $[H^+]$ for the initial part of the titration curve. After about 40 mL of NaOH is added, the pH is calculated accurately by this equation.

It is assumed that SO_2 is kept in the solution, even though it is only partially soluble at room temperature. The *x*-axis represents the addition of 2 mol of NaOH. As the first mole is added,

TABLE 13.4 Gravimetric Factors for Chemicals Involved in Sulfite Pulping

Convert From	Name	Formula Weight	Convert to SO_2 by Multiplication	Convert From SO_2 by Multiplication
SO_2	Sulfur dioxide	64.06	1	1
SO_3	Sulfite ion	80.06	0.800	1.250
HSO_3^-	Bisulfite ion	81.07	0.790	1.266
H_2SO_3	Sulfurous acid	82.07	0.780	1.282
Na_2SO_3	Sodium sulfite	126.04	0.508	1.968
$NaHSO_3$	Sodium bisulfite	104.06	0.616	1.624
$MgSO_3$	Magnesium sulfite	104.36	0.614	1.629
$Mg(HSO_3)_2$	Magnesium bisulfite	186.43	0.687	1.455
$CaSO_3$	Calcium sulfite	120.14	0.533	1.875
$Ca(HSO_3)_2$	Calcium bisulfite	202.21	0.634	1.578
$(NH_4)_2SO_3$	Ammonium sulfite	116.13	0.552	1.813
$(NH_4)HSO_3$	Ammonium bisulfite	99.10	0.646	1.547

the SO_2 decreases from 100% to 0%, whereas the bisulfite anion increases from 0% to 100%. As the second mole of NaOH is added, the bisulfite anion decreases from 100% to 0%, whereas the sulfite ion increases from 0% to 100%.

The ionization of sulfurous acid is temperature dependent. Rydholm, in *Pulping Processes*, p. 456, gives the pK_a as 1.8 at 25°C, 2.3 at 70°C, 2.6 at 100°C, 3.0 at 120°C, and 3.3 at 140°C.

Sulfurous acid is a moderately strong acid. It will react completely with any of the five common hydroxides used in sulfite cooking. The form of the reaction is independent of the base and occurs in two steps if enough base is present.

$$\mathrm{MOH} + \mathrm{H_2SO_3} \rightleftarrows \mathrm{MHSO_3} + \mathrm{H_2O}$$

$$\mathrm{MOH} + \mathrm{MHSO_3} \rightleftarrows \mathrm{M_2SO_3} + \mathrm{H_2O}$$

$$\text{M is } 1/2\mathrm{Mg}^{2+}, 1/2\mathrm{Ca}^{2+}, \mathrm{Na}^+, \mathrm{NH}_4^+, \text{or } \mathrm{K}^+$$

Because $CaSO_3$ has limited solubility ($K_{sp} = 6.8 \times 10^{-8}$ at 25°C), calcium based sulfite cooking has to be carried out at a pH of 1–2 to maintain SO_2 as the soluble HSO_3^-. Similarly, because $MgSO_3$ has a limited solubility ($K_{sp} = 3.2 \times 10^{-3}$ at 25°C), magnesium based sulfite cooking is carried out at a pH below 5. At the lower pH values the sulfite exists as HSO_3^-.

Fig. 13.8 shows clearly that H_2SO_3 and SO_3^{2-} do not exist in solution together in any appreciable amount. Because the standard terminology of free and combined SO_2 is used, the following equation is important.

$$2\mathrm{HSO_3}^- \rightleftarrows \mathrm{SO_3}^{2-} + \mathrm{H_2SO_3} \qquad (13.18)$$

Again, the equilibrium for the above reaction lies far to the left. When free and combined forms of SO_2 are added in solution, they will react together until one of them is exhausted as the

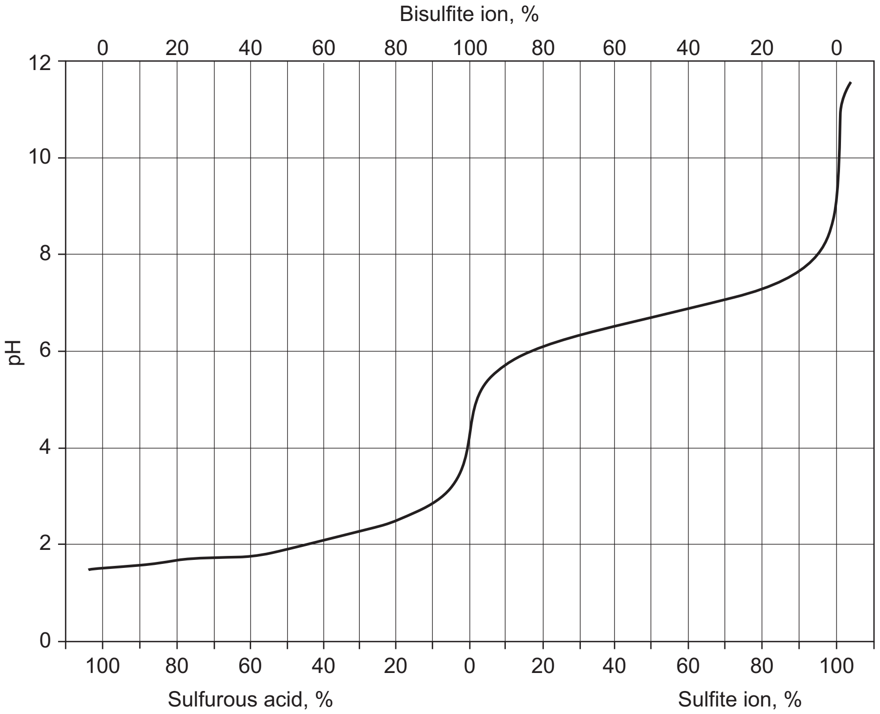


FIGURE 13.8 Titration curve of 0.1 *M* SO_2 with 2 mol of NaOH.

reaction proceeds to the left. On the other hand, if the solution is of known composition and the free and combined equivalents are to be determined, one imagines the reaction to proceed to the right until all the bisulfite is exhausted.

EXAMPLE 8

Derive the gravimetric factor for converting $Ca(HSO_3)_2$ to SO_2.

Solution

1 mol of $Ca(HSO_3)_2$ gives 2 mol of SO_2: $Ca(HSO_3)_2 \rightarrow 2SO_2 + Ca(OH)_2$

Therefore,

$$1\ \text{g}\ Ca(HSO_3)_2 \times \frac{2\ \text{mol}\ SO_2}{1\ \text{mol}\ Ca(HSO_3)_2} \times \frac{1\ \text{mol}\ Ca(HSO_3)_2}{202.21\ \text{g}\ Ca(HSO_3)_2} \times \frac{64.06\text{g}\ SO_2}{1\ \text{mol}\ SO_2} = 0.634\ \text{g}\ SO_2$$

EXAMPLE 9

Case 1: A cooking liquor consists of 6% free SO_2. What is the form of SO_2? Answer: All of the SO_2 is in the form of H_2SO_3, and the pH is about 1.2 at 25°C. This is only a hypothetical cooking liquor.

Case 2: A cooking liquor consists of 4.2% free SO_2 and 1.8% combined SO_2. What is the form of the SO_2? Answer: The limiting chemical is combined SO_2, so 1.8% combined SO_2 reacts with 1.8% free SO_2 (leaving 2.4% free SO_2 as H_2SO_3) to produce 3.6% $MHSO_3$, pH ≈ 1.85.

Case 3: A cooking liquor contains 2.5% free SO_2 and 2.5% combined SO_2. What is the form of the SO_2? Answer: All of the free SO_2 reacts with all of the combined SO_2 to give 5% $MHSO_3$. The pH is 4.3, but there is little buffering capacity. This is a *square* liquor.

Case 4: A cooking liquor contains 1% free SO_2 and 5% combined SO_2. What is its actual composition? Answer: 1% free SO_2 reacts with 1% combined SO_2 (leaving 4% M_2SO_3) to produce 2% $MHSO_3$. The pH is about 5.8.

Case 5: NSSC is carried out with sulfite at pH 8–9. Fig. 13.8 shows that all of the SO_2 is in the combined form. Notice also there is no buffer capacity in this region. NSSC cooking is carried out with 10%–15% carbonate to supply some buffering action.

EXAMPLE 10

A solution is 3% Na_2SO_3 (as SO_2) and 2% $NaHSO_3$ (as SO_2). What is the free and combined SO_2? What is the actual concentration of $NaHSO_3$?

Solution

2% $NaHSO_3 \rightarrow$ 1% H_2SO_3 + 1% Na_2SO_3. Therefore, this corresponds to 4% combined SO_2 and 1% free SO_2. From Table 13.4 the gravimetric factor of 1.624 is obtained to convert SO_2 to $NaHSO_3$. 2% $NaHSO_3$ (SO_2 basis) × 1.624 = 3.25% $NaHSO_3$ = 32.5 g/L $NaHSO_3$.

EXAMPLE 11

Given: A digest charge with 1 kg of dry wood, a calcium liquor containing 5% free SO_2 and 1% combined SO_2, and a liquor:wood ratio of 4:1 (including the water in the wood).

Calculate the concentrations and amounts of the actual chemical species. Assume the specific gravity of the liquor is 1.00.

Solution

The total SO_2 is equal to the concentration in the liquor times the liquor to wood ratio, or 24% on wood, which is 240 g SO_2 for the charge. The 1% combined SO_2 reacts with 1% free SO_2 to give 2% (60 g on wood) as bisulfite leaving 4%

(160 g on wood) as sulfurous acid. From Table 13.4, 80 g bisulfite (SO_2 basis) corresponds to 80 × 1.578 = 126.4 g $Ca(HSO_3)_2$ on wood or 31.6 g/L. In a similar fashion, 160 g free SO_2 corresponds to 205.2 g H_2SO_3 on wood or 51.3 g/L.

Problem

For this problem, what would the concentrations be for Mg based cooking? Answer: 29.1 g/L $Mg(HSO_3)_2$.

13.8 SULFITE LIQUOR ANALYSIS

Sulfite pulping liquors could be titrated with NaOH to each endpoint to determine the free SO_2 and combined SO_2. However, the first endpoint is not very sharp, and even the second endpoint may not be very sharp in sulfite liquors. Palmrose (1935) developed a method where, under acidic conditions, all of the SO_2 is converted to SO_4^{2-} by periodate ion, as shown in the following two chemical equations. Periodate thus measures the *total* SO_2.

$$KIO_3 + 3H_2SO_3 \rightarrow KI + 3H_2SO_4$$

$$2KIO_3 + 3\left(HSO_3^-\right)_2 \rightarrow 2KI + 3H_2SO_4 + 3SO_4^{2-}$$

I of KIO_3 is reduced from +5 to −1, whereas each sulfur of $\left(SO_3^{2-}\right)$ is oxidized from +4 to +6. The equivalent weight of KIO_3 is one-sixth the molecular weight, and the equivalent weight of H_2SO_3 is one-half the molecular weight. These reactions are actually fairly slow, and the endpoint would easily be overrun. Small amounts of KI (from the indicator solution), however, allow the following two reactions, which are rapid, to occur:

$$IO_3^- + 3H_2SO_3 + 5I^- \rightarrow 3SO_4^{2-} + 3I_2 + 3H_2O$$

$$3SO_4^{2-} + 3I_2 + 3H_2O + 3H_2SO_3 \rightarrow 6I^- + 6H_2SO_4$$

The titration is carried out with 0.1 *N* potassium iodate to blue endpoint using KI/starch indicator. The excess I_2 at the end of the reaction reacts with starch to give a characteristic blue color, a well-known reaction used as an indicator for starch. The slight excess of KIO_3 at the end of the reaction is reacted with thiosulfate.

The liberated acid is then titrated with 0.1 *M* NaOH to a methyl red endpoint and represents the *free* SO_2. Notice that the latter titration is a strong acid–strong base titration with a well-resolved endpoint. When this method was first developed, calcium was the only base used for sulfite pulping, and the liquors were necessarily acidic. With other bases where the cooking liquor is above pH of 4–5, a known amount of sulfuric acid is added before the iodate titration. The liberated acid is then titrated, but the additional amount of sulfuric acid added is subtracted from the free SO_2 value obtained in the second titration. This procedure is described in TAPPI Standard T 604.

EXAMPLE 12

A sulfite liquor was diluted 1:10. A 10.00 mL aliquot of the diluted solution was titrated by the Palmrose method. Calculate the total and combined SO_2 in the original solution based on the following amounts of titrants: 12.18 mL of 0.2060 *N* KIO_3 and 10.78 mL of 0.0946 *N* NaOH.

Solution

The total SO_2 in $N = 10 \times (12.18\text{ mL} \times 0.2060\ N)/10\text{ mL} = 2.51\ N$.

The total $SO_2 = 2.51\ N \times 32$ g/eq

$SO_2 = 80.32$ g/L total SO_2 or 8.03% total SO_2.

The free $SO_2 = 10 \times (10.78\text{ mL} \times 0.0946\ N)/10\text{ mL} = 1.020\ N$.

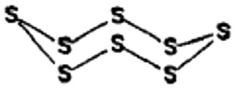
The free $SO_2 = 1.02\ N \times 32$ g/eq

$SO_2 = 32.64$ g/L free SO_2 or 3.26% free SO_2.

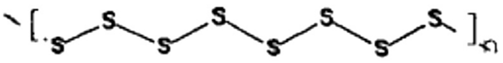
13.9 THE CHEMISTRY OF SULFUR

Elemental Sulfur

Elemental sulfur occurs in many complex forms. The chemistry of elemental sulfur presented here is a simplification of its complex chemistry but will be useful to explain its properties. Crystalline sulfur contains sulfur rings with 6—20 sulfur atoms or chains of sulfur atoms called catenasulfur, S_∞. The most common form is cyclooctasulfur, S_8, which has two common allotropes: orthorhombic sulfur, S_α, and monoclinic sulfur, S_β. S_α is, thermodynamically, the most stable of the S_8 forms. The structures are:



Cyclooctasulfur



Catenasulfur

Above 95°C, S_α slowly converts to S_β. With rapid heating, the melting point of S_α (113°C) is obtained. S_β melts at 119°C. S_β crystallizes from sulfur melts and, over the course of months, converts to S_α. Liquid S_8 sulfur becomes increasingly viscous above 160°C, as it is converted to catenasulfur. Above 200°C the viscosity of the catenasulfur decreases, as its maximum degree of polymerization is at 200°C, where the formula weight is above 200,000. The boiling point of sulfur is 445°C. If catenasulfur of high viscosity is quenched by pouring into ice water, a plastic solid results. The solid catenasulfur slowly reverts to S_8 over time. S_8 is soluble in CS_2, whereas S_∞ is not soluble.

Sulfur is recovered in large amounts from H_2S in natural gas by the reaction:

$$2H_2S + SO_2 \rightarrow 3S + H_2O$$

In Europe, large amounts of sulfur are used from iron pyrite, FeS (the substance called fool's gold because of its similarity to real gold), which is a solid. Sulfur is also a by-product of copper production from CuS. Sulfur is also mined in large amounts in its elemental form from volcanic deposits by the *Frasch* process, where steam is injected into the ground to heat the sulfur, and the molten sulfur is pumped from the ground.

Sulfur combustion to produce SO_2, i.e., elemental sulfur is burned to produce sulfur dioxide.

$$S + O_2 \rightarrow SO_2(\text{gas})$$

Above 1000°C (1830°F), no sulfur trioxide is produced; however, some might be produced in the process of cooling the gases. Sulfur trioxide, which produces sulfuric acid on reaction with water, is very undesirable in pulping reactions and is removed during the cooling/scrubbing process (by countercurrent flow of water and sulfur dioxide).

$$SO_3 + H_2O \rightarrow H_2SO_4$$

The SO_2 forms H_2SO_3 in water, which in turn is reacted with metal bases to produce sulfite pulping liquors, as described in other sections. Because H_2SO_3 is much more acidic than H_2CO_3, salts of carbonate can be used to form salts of sulfite. For example, wet SO_2 is traditionally formed into calcium bisulfite by calcium carbonate (limestone) by the following equation:

$$CaCO_3 + 2H_2SO_3 \rightarrow Ca(HSO_3)_2 + CO_2 + H_2O$$

Total Sulfur by Gravimetric Analysis

Often the total content of organically bound and inorganic sulfur is desired. This is accomplished by treating the sample with a strong oxidant under alkaline conditions to convert the sulfur to sulfate. For example, when sodium peroxide is used, sodium sulfate is formed, and the organic chemicals are largely converted to carbon dioxide and water. After the sample is acidified with HCl, the SO_4^{2-} is precipitated with excess $BaCl_2$. The precipitate is washed with small amounts of water and then dried in a muffle furnace. The precipitate is weighed and converted to a sulfur equivalent with the appropriate gravimetric factor.

13.10 CALCINING EQUATIONS

Two equations are used to characterize calcining of lime mud to produce fresh lime. The *specific energy consumption* is an indication of how much fuel is required to process the lime mud and is often reported as Btu per ton of lime.

$$\text{specific energy consumption} = \frac{\text{fuel to kiln}}{\text{CaO output}}$$

The *lime availability* is an indication of the purity of the lime in terms of available CaO divided by the amount of lime product.

$$\text{lime availability} = \frac{\text{CaO}}{\text{lime}} \quad \text{as mass ratio}$$

13.11 ANNOTATED BIBLIOGRAPHY

H-Factor and Process Control Equations

Edwards, L. and S.-E. Norberg, Alkaline delignification kinetics: A general model applied to oxygen bleaching and kraft pulping, *Tappi J.* 56(11):108–111(1973).

Kubes, GJ., BI. Fleming, JM. MacLeod, and HI. Bolker, Viscosities of unbleached alkaline pulps. II. The G-factor, *J. Wood Chem. Tech.* 3(3):313–333(1983).

Hatton, JV., Development of yield prediction equations in kraft pulping, *Tappi J.* 56(7): 97–100(1973).

Hatton, JV., The potential of process control in kraft pulping of hardwoods relative to softwoods, *Tappi J.* 59(8):48–50(1973).

Lin, CP., WY. Mao, and CY. Jane, Development of a kappa number predictive equation in kraft pulping for all types of hardwood, *Tappi J.* 61(2)72(1978).

Paulonis, MA. and A. Krishnagopalan, Adaptive inferential control of kraft batch digesters as based on pulping liquor analysis, *Tappi J.* 74(6):169–175(1991).

Tasman, JE., Kraft delignification models, *Tappi J.* 64(3):175–176(1981).

Vroom, KE., The “H” factor: A means of expressing cooking times and temperatures as a single variable, *Pulp Paper Mag. Can.* 58(3):228–231(1957).

Sulfite Liquor Analysis

Palmrose, GV., A mill test for the exact determination of combined sulphur dioxide, *Tech. Assn. Papers.* XVIII:309–310(1935); the same article is reprinted as ibid., *Paper Trade J.* 100(3):38–39(1935).

Chemistry of Sulfur

Cotton, FA. and G. Wilkinson, *Advanced Inorganic Chemistry*, 4th ed., Wiley and Sons, New York, 1980. 1396 p.

EXERCISES

Kraft Liquor—Chemical Calculations

1. Derive the gravimetric conversion factor to express Na_2CO_3 as Na_2O.
2. White liquor has the following composition of the *actual* chemical species. Calculate TTA,

AA, EA, TA, causticizing efficiency, and sulfidity.

NaOH = 145 g/L; Na_2S = 55 g/L
Na_2CO_3 = 17 g/L; Na_2SO_4 = 14 g/L

Kraft Liquor—Chemical Analysis

3. The effective alkali concentration of white liquor is 93.7 g Na_2O/L. The sulfidity is 37.5%, and the causticizing efficiency is 77.9%. Calculate the following:
  a. The A, B, C values in mL for a 10 mL aliquot of liquor titrated with 1.017 *N* HCl.
  b. The molar concentrations of the chemical species NaOH, Na_2S, and Na_2CO_3 in this liquor.
  c. The active and effective alkali charges on wood (as a percent) if 200 mL of this liquor is used to pulp 200 g Douglas fir chips at 50% MC_{gr} (with some additional dilution water).

H-Factor

4. What is the H-factor for a cook that is held at 165°C for 1.43 h? If this H-factor is satisfactory, how long should one cook if the temperature is increased to 170°C for a different cook?

Sulfite Liquor Calculations

5. By comparing sulfite cooking chemicals all on a SO_2 basis, one is really comparing them on an equal (molar or weight) basis. Circle the correct choice.

6. Analysis of a sulfite cooking liquor indicates a total SO_2 of 7% and 4% free SO_2.

The combined SO_2 is _____%.
The SO_2 as sulfurous acid is _____%.
The SO_2 in the form of the bisulfite ion $\left(HSO_3^-\right)$ is _____%, and the SO_2 in the form of sulfite ion $\left(SO_3^{2-}\right)$ is _____%.

Analysis of a sulfite cooking liquor indicates a total SO_2 of 8% and a combined SO_2 of 2%. Solve for unknown free SO_2, as well as the concentration of the sulfurous acid, bisulfite ion, and sulfite ion species (all as % SO_2 that equals g/100 mL), and the pH of the liquor.

7. A solution is made by weighing 1.1 g sulfurous acid (as sulfurous acid) and 10.3 g sodium sulfite (as sodium sulfite) to make 0.193 L of solution. Solve for unknown free SO_2, combined SO_2, total SO_2, as well as the concentration of the sulfurous acid, bisulfite ion, and sulfite ion species (all as % SO_2 that equals g/100 mL), and the pH of the liquor.

Sulfite Liquor Analysis

8. Analysis of a pulping liquor with iodometric titration gives a SO_2 value of 10%. Titration with NaOH gives 6.5% SO_2. Solve for unknown free SO_2, combined SO_2, total SO_2, as well as the concentration of the sulfurous acid, bisulfite ion, and sulfite ion species (all as % SO_2 that equals g/100 mL), and the pH of the liquor. If sodium is the base, how many grams of sulfurous acid, sodium bisulfite, and/or sodium sulfite are needed to make 1 L of cooking liquor?

CHAPTER

14

Production of Dissolving Grade Pulp

14.1 INTRODUCTION

Dissolving pulps require a high degree of purity (Table 14.1). They are used for production of cellulose derivatives such as cellulose acetate, cellulose nitrate, viscose, rayon, methylcellulose, and carboxymethylcellulose, among many others (Fig. 14.1). The overall yield of dissolving pulp is in the range of 30%–35%. Their production costs are quite high compared with regular paper pulp. These pulps have a high α-cellulose content (95%–98%) and relatively low hemicellulose (1%–4%) and lignin (<0.05%) contents. Worldwide, over 70% of dissolving pulp is utilized in the production of viscose staple alone. The global production of dissolving pulp was 5.6 million tons in 2013 and 7.5 million tons in 2015. Demand is expected to grow fastest in China and the rest of Asia. One of the largest consumers of viscose fiber is China. Its output is expected to keep a growth rate of 10% per year. This will result in an increase in dissolving pulp demand. China is the second largest producer of dissolving pulp and the world's biggest buyer with the past decade's development.

TABLE 14.1 Dissolving Grade Pulp

HIGH CELLULOSE CONTENT
Controlled, adjusted viscosity (DP)
Viscosity adjustment over the whole fiberline → viscosity control stages (cooking, oxygen delignification stage, hypo, hydrogen peroxide, ozone)
HIGH PURITY
High brightness
Low hemicellulose content
Low extractives content
Low metal ion profile
Low brightness reversion

Sappi Specialised Cellulose, a division of Sappi, is the world's largest manufacturer and seller of dissolving wood pulp (DWP). With a total global DWP capacity of over 1.3 million tons, they are currently supplying 17% of global demand from their three mills located in South Africa and North America. DWP is being used in textiles, pharmaceuticals, and food applications.

Dissolving pulp is also called dissolving cellulose, having a high cellulose content. It has special properties including uniform molecular weight distribution and a high level of brightness. This pulp is manufactured for uses requiring low hemicellulose content and high chemical purity, as the chemically similar hemicellulose may interfere with subsequent processes. Dissolving pulp is actually not made into paper but dissolved either in a solvent or by derivatization into a homogeneous solution, which makes it completely chemically accessible and removes any remaining fibrous structure.

Biermann's Handbook of Pulp and Paper: Raw Material and Pulp Making
https://doi.org/10.1016/B978-0-12-814240-0.00014-8

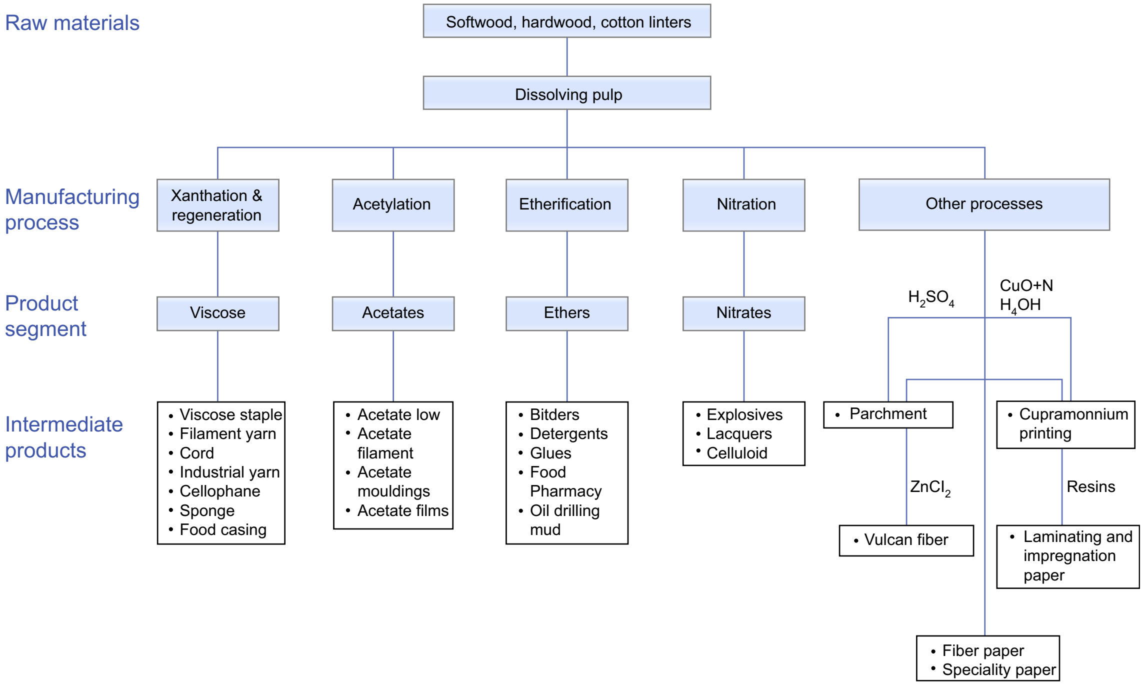


FIGURE 14.1 Dissolving pulp intermediates and end products. *Reproduced with permission Välimaa (2015).*

After it is dissolved, it can be converted into viscose or lyocell or be chemically reacted to produce derivatized celluloses, such as cellulose triacetate, which is a plastic-like material formed into fibers or films, or cellulose ethers such as methyl cellulose, used as a thickener. As a result, production of dissolving pulp has increased globally. About 70% of the global dissolving pulp production is used for commodity applications, e.g., rayon, whereas the remaining is converted to cellulose derivatives. Several existing pulp and paper mills in North America and Europe have completed the conversion of their production lines to dissolving pulp, and several new dissolving pulp mills were recently built in Asia.

Dissolving pulp producing mills these days are considered as the prototypes of the future forest biorefineries. This is due to the fact that the dissolving pulp process requires production of high-purity cellulose with low content of hemicellulose and traces of other components. Therefore, opportunities exist for the on-site separation and use of the other major wood components. This is in alignment with the integrated dissolving pulp biorefinery concept (Fig. 14.2). Furthermore, as dissolving pulp is the raw material for production of a range of abovementioned cellulose derivatives, opportunities exist for their upgradation with dissolving pulp conversion facilities.

Cotton as the alternative feedstock for production of dissolving pulp is to compete with food for fertile land and needs a large amount of water and prime land to grow in comparison with woody biomass. The increasing demand for

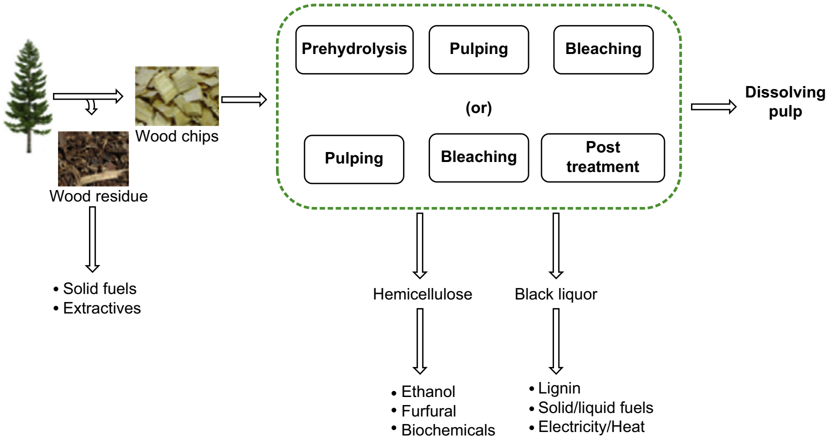


FIGURE 14.2 Integrated dissolving pulp biorefinery. *Reproduced with permission Kumar and Christopher (2017).*

cellulose derivatives and recent price increases in dissolving pulp prices have led to the conversion of several kraft mills to dissolving pulp mills, facilitating the development of additional biorefinery applications. The production cost of dissolving pulps is higher in comparison with the commonly used paper pulps. The cost difference is due to the following factors:

- Lower dissolving pulp yields
- Higher capital and chemical costs as more extensive pulping and bleaching is required
- Higher inventory and storage space requirements

For this reason, several lower-cost alternatives for conversion of paper pulps to dissolving pulps have been studied.

Dissolving pulps typically are produced from cotton linters (soda pulping) and wood via the prehydrolysis kraft (PHK) and acid sulfite (AS) pulping processes. Wood pulps, particularly those obtained using the sulfite process, require a subsequent hemicellulose removal step; this is mostly done by using cold caustic extraction (CCE), which is performed during the bleaching operation. In the United States, the sulfate process is important, especially for the production of higher purity cellulose. Sulfite hardwood pulp is mainly used for the production of viscose; softwood pulp, both sulfite and sulfate, is used in viscose textile yarn, whereas high-purity sulfate pulps are used for viscose industrial yarn. The viscose staple application is characterized by a high degree of backward integration into pulp supply. The current high costs of wood and cotton linters, combined with environmental regulation against traditional bleaching (chlorine and hypochlorite), have resulted in a significant increase in the cost of dissolving pulp obtained from these raw materials.

14.2 DISSOLVING PULP MANUFACTURE

Currently, DWP is produced by the AS and the vapor-phase PHK processes, which were both developed in the 1950s. Whereas the former remained technically largely unchanged, a modern displacement cooking procedure was adopted to the steam PHK process. These dissolving pulp technologies, Visbatch and VisCBC, combine the advantages of displacement technology and steam prehydrolysis. They are characterized by their low energy requirements, short cover-to-cover times, and homogeneous and high product quality. Andritz recently developed cooking system upgrades for retrofit to DWP operation in continuous digesters, including a prehydrolysis reactor vessel for water prehydrolysis.

Table 14.2 shows major processes for production of paper-grade pulp and dissolving grade pulp. Paper pulp is mainly produced from the kraft pulping process (Fig. 14.3), whereas dissolving pulp is produced by the AS method and the PHK process (Fig. 14.4) and from cotton linters. Hemicelluloses are undesirable impurities in dissolving pulps and affect the cellulose filterability, xanthation reaction in the viscose process, and viscose strength of the cellulose end products. During the PHK process, large amounts of hemicelluloses are dissolved in the prehydrolysis liquor (PHL) before pulping. The prehydrolysate contains the following which can potentially be converted to valuable products:

- Short-chain carbohydrates (arabinose, xylose, mannose, galactose, glucose)
- Polysaccharides (galactomannan, glucuronoxylan)
- Other chemical compounds (acetic acid, furfural, phenolic compounds)

As a dissolving pulp production method, the PHK process is typically characterized with a lower pulp yield and higher capital and chemical costs. So, it is very important to optimize each step of the PHK process that affects dissolving pulp purity, process integration, and energy

TABLE 14.2 Major Processes for Production of Paper-Grade Pulp and Dissolving Grade Pulp

PAPER PULP
More than 90% from the kraft pulping process
DISSOLVING PULP
65% by acid sulfite method
5% by the prehydrolysis kraft process
10% from cotton linters

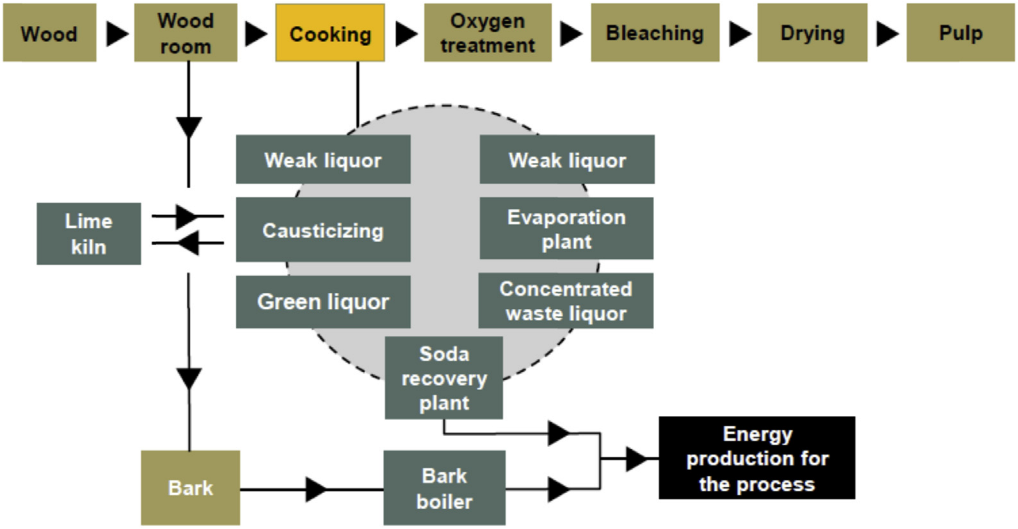


FIGURE 14.3 Kraft process (paper-grade pulp). *Reproduced with permission Välimaa (2015); Courtesy Stora Enso; https://mycourses.aalto.fi/.../Dissolving%20pulp%20and%20viscose%20manufacturing_.*

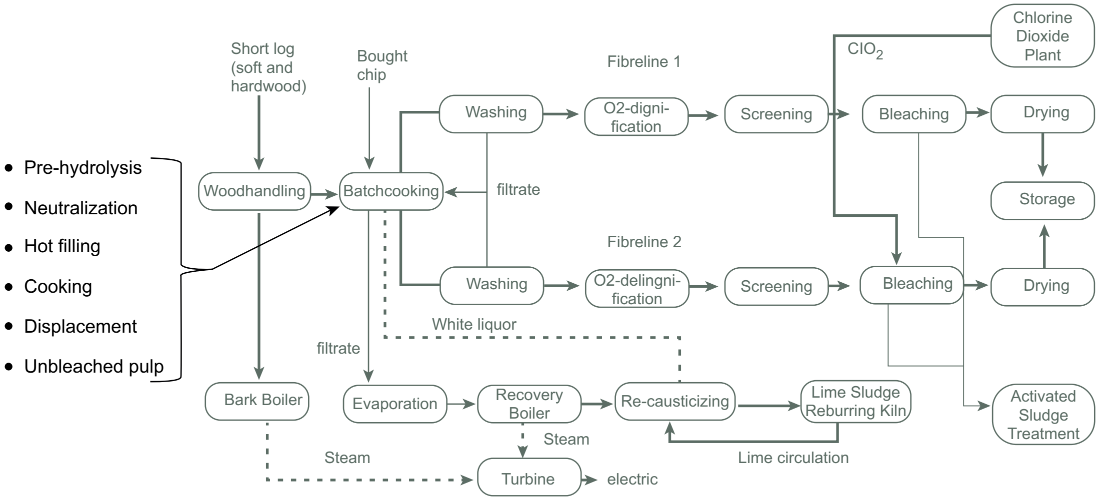


FIGURE 14.4 Prehydrolysis kraft process. *Courtesy Stora Enso; Reproduced with permission Välimaa (2015); https://mycourses.aalto.fi/.../Dissolving%20pulp%20and%20viscose%20manufacturing_.*

efficiency without compromising cellulose accessibility and reactivity.

DWP is a chemically refined bleached pulp composed of more than 90% pure cellulose. When producing dissolving pulp for making products such as carboxymethyl cellulose, viscose, cellulose film, and sausage skin, determining the pulp quality is essential. The dissolving pulp quality depends both on properties of the raw wood material and the pulp processing. The reactivity of cellulose pulp shows its capacity to participate in diverse chemical reactions. The two secondary hydroxyl groups on carbons two and three are more reactive than the primary hydroxyl group on carbon six. For derivatization reactions, it is important to note that reactions with the hydroxyl groups on carbons two and three are kinetically favorable, whereas substitution on carbon six is thermodynamically more stable. Both celluloses I and II have been found in pulp. Cellulose II is more thermodynamically stable than cellulose I, which may make the dissolving pulps with large proportions of cellulose II more resistant to heating than pulps with large proportions of cellulose I. In the recent years, various innovative pulping methods have been developed, mainly in response to environmental considerations.

Raw materials used for the production of dissolving pulp are shown in Table 14.3. Cotton linters are commonly used for the production of dissolving pulps because of very high cellulose content (>86%). Softwoods and hardwoods have been used because of increased demand and advancements in pulping technologies.

TABLE 14.3 Raw Material Used for Manufacturing Dissolving Pulps

Cotton linters
Softwoods
Hardwoods
NONWOOD RAW MATERIALS
Bamboo
Reed
Bagasse
Corn stalk

TABLE 14.4 Global Dissolving Pulp Production

Softwoods (e.g., pine and spruce) and hardwoods (e.g., beech and eucalyptus)—85%
Cotton linters—10%
Bamboo and other lignocellulosic materials— ∼5%

Based on Chen et al., (2016).

Nonwood raw materials, such as bamboo, reed, bagasse, corn stalk, have also been used for producing dissolving pulps. About 85% of the global dissolving pulp is produced from softwoods and hardwoods, whereas about 10% is produced from cotton linters, and approximately 5% is produced from bamboo and other lignocellulosic materials (Table 14.4). In China, some bamboo dissolving projects have been completed and put into production.

Different raw materials have unique characteristics that are dependent on the morphological structure and chemical composition of the lignocellulose. Qualities of the raw material used and the species affect the manufacturing process and the final product quality of dissolving pulp. In the case of cotton linters, impurities constitute less than 20% of the total content, and 60% of these impurities (i.e., seed hulls, sand, foreign matter, etc.) are easily removed by chemical and mild physical methods that cause minimal damage to the native cellulose. Very high quality cellulose products are required to have a 99% α-cellulose content and a molecular weight of 7000. Cotton linters are considered as the best raw material, as they have the advantage of greater Mw homogeneity in comparison with other raw materials.

Wood is the main raw material for dissolving pulp production, but not all types of wood species can be used. Chemistry of wood and composition must be considered to select the most appropriate pulping process. Some wood species are not suitable for AS pulping. In the AS process, phenolics, such as pinosylvin in pine heartwood or taxifolin in Douglas fir, react with lignin to form condensed structures that impede delignification. Also, taxifolin decreases the stability of the sulfite cooking liquor by converting sulfite to thiosulfate. Therefore, wood species that are rich in resin, such as pine and larch, are not suitable for AS pulping.

Bamboo is an important raw material for the pulp and paper industry not only for paper-grade pulp production but also for dissolving pulp production. Bamboo belongs to the grass family, and it contains 45%–55% cellulose, 23%–30% lignin, 20%–25% hemicelluloses, 10%–18% total extractives, and 1.5% ash. Its fibers are 1.5–2.5 mm in length. Its structure and composition (cellulose, hemicelluloses, and lignin) are similar to those found in some hardwood species; however, the minor substances, such as extractives (organic and water-extractable compounds) and ash, are more abundant in bamboo than in hardwood. These factors present challenges during pulping, bleaching, and chemical recovery process. The fiber cell volume of bamboo is less than that of wood, for example, 40%–70% for bamboo versus 60%–80% for hardwoods and 90%–95% for softwoods. Bamboo has other disadvantages that include high impurities (ash and metal ions), cellulose with low-molecular weight and intrinsic viscosity, and poor uniformity. Bamboo fiber structures possess multiple layers with complex orientations and arrangements in the secondary cell wall. By contrast, wood fibers have a simple three-layer (outer, middle, and inner layers) secondary wall. The thicker cell wall, compact structure, and higher hybrid cell content of bamboo may result in negative effects during dissolving pulp manufacture. Therefore, harsh cooking and bleaching conditions may be required for making good quality dissolving pulp from bamboo.

Pulping is a crucial step in dissolving pulp manufacturing. The traditional pulping method uses AS process. This process is carried out under acidic conditions where most of the hemicelluloses and some of the cellulose with low-molecular weight are removed, which results in an unbleached pulp with a high cellulose content. During the past several decades, the PHK pulping process has been successfully commercialized for manufacturing dissolving pulps. Contrary to the acidic conditions of AS pulping, the PHK process is conducted with both acidic (prehydrolysis) and alkaline (kraft cooking) conditions. In the prehydrolysis stage, short-chain carbohydrates, mainly hemicelluloses, are hydrolyzed by the release of acetic acid from acetyl groups. Therefore, most hemicelluloses are extracted from the chips before kraft pulping.

The major properties of dissolving pulps from AS and PHK with respect to carbohydrate composition, molecular weight distribution (MWD), accessibility, and reactivity are different because different chemical reactions occur in acidic or alkaline environments. AS pulps have lower cellulose content, higher *S*10/*S*18 contents, wider MWDs, and higher reactivity as compared with PHK pulps.

Prehydrolysis of wood chips helps in loosening the pulp matrix and improves the accessibility of lignin to pulping and bleaching chemicals. Hemicelluloses are easier to hydrolyze than cellulose because of their branched structure and low degree of polymerization. The PHK process for production of dissolving pulp from hardwood is being used commercially. In this process, a prehydrolysis step is used to extract most of the hemicelluloses, followed by kraft pulping to remove most of the lignin, and a bleaching/purification step, which results in the production of dissolving pulp with a high cellulose content (90%). This process which fractionates the three major components of wood has been considered as a base for development of an integrated forest biorefinery (IFBR). The cost-effective recovery/value-added utilization of the dissolved organics in the PHL/black liquor would add extra revenues to the pulp mill. However, PHK also poses some limitations, such as increase in the total dissolving pulp production time because of the additional prehydrolysis steps (the total reaction time of 160−200 min and 240−270 min for conventional kraft pulping and PHK pulping, respectively) and reduction in the dissolving pulp yield (on average 38%) as compared with 48% for the conventional kraft pulping. Prehydrolysis of wood chips before kraft pulping can be performed using various methods such as hot water, autohydrolysis, acidic or alkaline medium. Acid prehydrolysis is usually carried out for hemicellulose removal by hydrolysis to monosugars. Hemicellulose sugars are nowadays considered an alternative source of value-added chemicals. Acid prehydrolysis, however, may lead to a number of undesirable corrosive effects, extensive lignin condensation, and poor yield because of partial but undesirable cellulose hydrolysis. For the above reason, aqueous autohydrolysis is most commonly practiced in the dissolving pulp industries. During autohydrolysis (carried out at 150−180°C), organic acid (acetic acid) is formed due to cleavage of the acetyl groups (from hemicellulose) that act as a catalyst to hydrolyze the glycosidic bonds in hemicellulose and reduce the pH of the PHL to about 4. The degraded hemicelluloses, mainly present in their oligomeric form, are solubilized in the PHL and can subsequently be extracted from the digester and used. A significant amount of wood materials is dissolved in the PHL, which contains up to 50% and 10% hemicelluloses and lignin, respectively. Hemicelluloses and lignin can be separated from the PHL; moreover, their efficient recovery and conversion to value-added products is a step toward building a dissolving pulp−based biorefinery. Numerous individual separation techniques or combined multistep processes, which include acidification, flocculation, adsorption, membrane filtration, extraction, and ion-exchange, have been studied for recovery of the PHL organics. Production of dissolving pulp requires higher recovery area in comparison with normal kraft pulp mill because of lower yield and high charging in cooking. The organic portion of the dry solids to the recovery boiler is slightly lower in production of dissolving pulp, resulting in lower heat value. Valmet has the experience and widest scope of technologies in supplying equipment and flexible processes for the production of dissolving pulps for various end products. Fig. 14.5 shows typical DP fiberline.

The hemicelluloses present in the PHL are a valuable source of hexose and pentose sugars, which can be converted to value-added products (Table 14.5).

PHK is popular in new dissolving pulp mills because of the advantages associated with the capital investment, operation, and environmental compatibility. The PHK process accounted for 56% of the world's dissolving pulp production (as of 2014), whereas the AS process accounted for 42%. For Canada's dissolving pulp sector, the AS process still accounted for 64% of dissolving pulp production capacity, although the PHK process has become increasingly important. In China, the PHK process accounts for 78% of the total production capacity.

TABLE 14.5 Conversion of Hemicelluloses From Prehydrolysis Liquor to Value-Added Products

Prehydrolysis Liquor
Hemicellulose
Xylitol
Ethanol
Paper additives
Furfural
Organic acids
Chemical intermediates

A novel dissolving pulp process providing the basis for an advanced biorefinery has been discussed. The SO_2—ethanol—water process has the

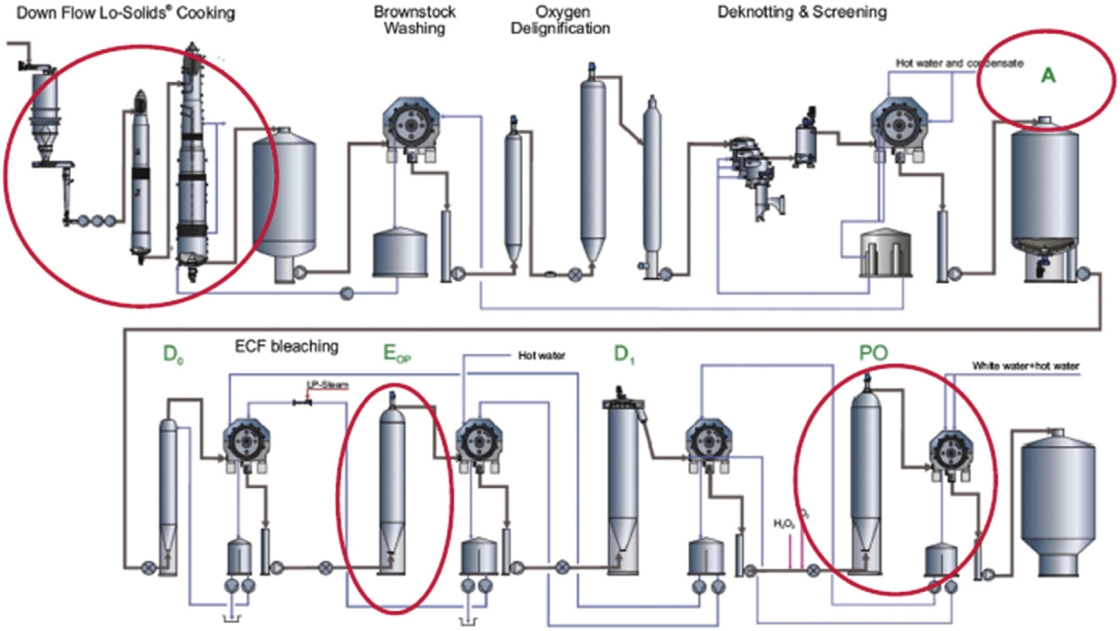


FIGURE 14.5 Typical DP fiberline. *Courtesy Andritz; Vehmaa J (2013). 6th International Colloquium on Eucalyptus Pulp, Nov 24—27 Colonia UY.*

potential to replace the acid sulfite process for the production of rayon-grade pulps, owing to a higher flexibility in the selection of the raw material source, substantially lower cooking times, and the near absence of sugar degradation products. Special attention is paid toward developments targeting selective and quantitative fractionation of paper-grade pulps into hemicelluloses and cellulose of highest purity. This target has been achieved by the IONCELL process, where the entire hemicellulose fraction is selectively dissolved in an ionic liquid in which the H-bond basicity and acidity are sufficiently adjusted by the addition of a cosolvent. At the same time, pure hemicellulose can be recovered by further addition of the cosolvent, which then acts as a nonsolvent. The residual pure cellulose fraction may then enter a lyocell process for the production of regenerated cellulose products.

The bleaching process not only increases the brightness of the dissolving pulp but also increases the purity, adjusts the viscosity and MWD of the cellulose, and modifies the reactivity of the dissolving pulp to meet the requirements of premium end-use products Therefore, bleaching is a critical process during dissolving pulp manufacturing. Currently, the main methods being used are the combination of oxygen delignification (O), chlorine dioxide delignification (D0) and brightening (D1 and D2), hypochlorite bleaching (H), and hydrogen peroxide bleaching (P). Although hypochlorite has been almost phased out from pulp bleaching for paper grades due to environmental reasons, it is still commonly used for dissolving pulp manufacture. Hypochlorite can oxidize and degrade cellulose in such a way that it can adjust its molecular weight and viscosity to improve the uniformity of pulp.

Figs. 14.6 and 14.7 show fiberline for dissolving pulp using totally chlorine free (TCF) and elemental chlorine free (ECF) bleaching, respectively.

Production of dissolving pulp from cotton linters involves the removal of the linters fibers, being attached to the cotton seeds. This process is termed delintering, producing fibers of different lengths. The second-cut linters or

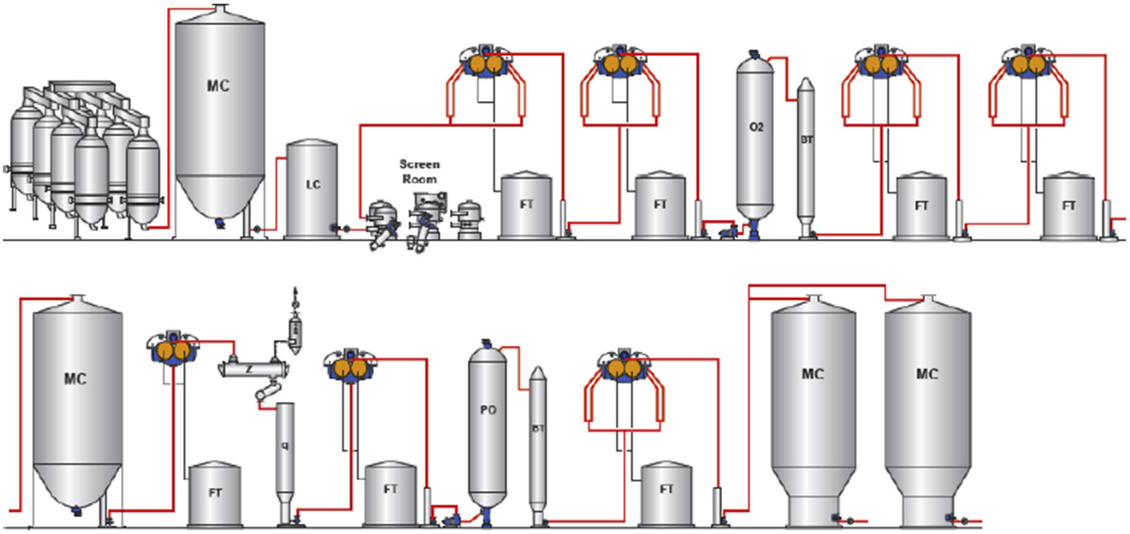


FIGURE 14.6 Fiberline for dissolving pulp, TCF bleaching. *Courtesy Metso; Paul Flickinger, Lari Lammi, Bertil Ernerfeldt (2011). Tappi Peers, Dissolving Pulp, October 2, 2011.*

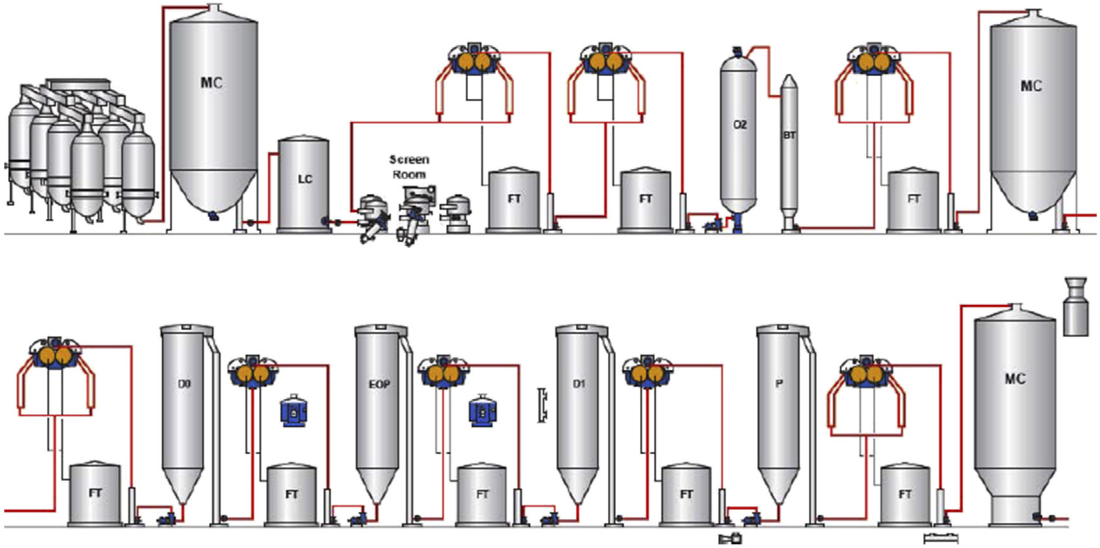


FIGURE 14.7 Fiberline for dissolving pulp, ECF bleaching. *Courtesy Metso; Paul Flickinger, Lari Lammi, Bertil Ernerfeldt (2011). Tappi Peers, Dissolving Pulp, October 2, 2011.*

shortest fibers are used as chemical feedstock. Purification is performed by a combination of mechanical and chemical treatments comprising mild alkali treatment at high temperature for removing proteins, waxes, pectins, and other polysaccharides and bleaching for obtaining the required brightness. Dissolving pulp of highest cellulose purity are manufactured from purified cotton linters and used for manufacturing of acetate plastics and high-viscosity cellulose ethers.

Some special types of treatments (posttreatments) have been used for improving the quality of pulp, especially its purity and reactivity. These treatments are as follows:

- Treatment with chemicals
- Treatment with enzymes
- Mechanical actions
- Microwave
- Combinations of above treatments

The methods of posttreatment can be used before and after bleaching. Many of these treatments have been used commercially. In addition, these posttreatments also play an important role in the process of converting paper-grade pulp to dissolving pulp.

Hemicelluloses are readily dissolved in alkali, thus caustic extraction is an effective way to remove hemicelluloses from pulp fibers, especially in AS pulps. Generally, alkaline purification is carried out as a CCE. The CCE process is conducted at 20–40°C and 8%–10% sodium hydroxide. In CCE, lower temperatures and higher alkali concentrations are used. The mechanism involves fiber swelling and the dissolution and removal of hemicelluloses from the inner fiber to the bulk phase. The alkali consumption in the CCE process is not much. The cellulose content of the pulp treated by CCE can reach 98% and higher.

Hot caustic extraction (HCE) uses higher temperatures and lower alkali concentrations. HCE is carried out at 95–135°C and 0.4%–1.5% sodium hydroxide. The fibers do not swell sufficiently because of the low alkali concentration, so the hemicellulose in the deep wall of fibers cannot be removed more completely, but the chemical reactions of carbohydrate degradation and further oxidations take place at the high temperatures, which has several disadvantages such as lower yields, lower pulp viscosities, and additional consumption of chemicals. It is more difficult to make high-purity dissolving pulps (α-cellulose content of 96% or higher) by HCE.

In contrast to alkaline extraction, acid extraction (A) allows for the dissolution of a fraction of alkali-resistant hemicelluloses. Acid extraction is carried out at pH 2.5 to 3.5 and 95—150°C for 1—2.5 h. The alkaline-resistant hemicelluloses get removed easily under these conditions, and so, they are suitable for treating PHK pulps. Both the hemicelluloses and metal cations are removed. The hemicelluloses in the pulp decreased from 16.27% to 11.08%, which represented a 31.9% decrease with acid treatment of an oxygen-delignified softwood kraft pulp at pH 3 and 150°C for 2 h.

Pulp fibers can be fractionated according to their size. The fractionation treatment has been used in traditional pulp manufacturing process for the purpose of improving bleached pulp brightness and mechanical strength properties. Fiber fractionation has been used for improving the purity of dissolving pulps. By fractionating a softwood sulfite pulp, the long-fiber fraction retained on a 30-mesh screen had lower hemicellulose levels (9.59%) than the short-fiber fraction that passed through a 30-mesh screen (11.65%). The α-cellulose content of the long-fiber fraction was about 2.5% higher than that in the short-fiber fraction (91.08% vs. 88.53%). The effects of fractionation on bamboo dissolving pulp showed that the cellulose purity can be improved by removing the fines. As more fines were removed, the purity of the resulting dissolving pulp was higher. For a bleached bamboo pulp with the removal of 14.7% (w/w) of original pulp, the α-cellulose content increased from 94.7% to 96.2%, lignin content decreased from 0.86% to 0.63%, and ash content decreased from 0.89% to 0.41%.

Treatment with cellulase and hemicellulase enzymes can be used to modify dissolving pulps, improving pulp properties such as purity, viscosity, and reactivity. Cellulase acts on the amorphous cellulose, which is located on the fiber surface and between the microfibrils. This enzymatic treatment increases the swelling and accessibility of cellulosic fiber, which increases its reactivity to derivatization. Treatment of a PHK hardwood dissolving pulp with cellulase opened up the structure and increased the porosity of the fibers, which improved the accessibility and reactivity of the treated pulp. The pore volume of fibers increased from 4.79 to 6.74 μm3/g, and the Fock reactivity improved from 47.67% to 66.02%. Compared with cellulases, hemicellulases (e.g., mannanase and xylanase) are mainly used for pulp purification.

Certain mechanical methods—refining, milling, and shredding—that open the fiber wall structure and improve the penetration of chemical into the fiber have been used. These positive changes in fiber morphologies significantly enhance the reactivity of the cellulosic fibers. Some mechanical treatments can be readily commercialized. Mechanical refining of a hardwood PHK pulp resulted in an increase in the surface area, pore size, and volume; these changes increased the Fock reactivity of the resultant pulp. Refining a PHK hardwood pulp sample with 25,000 revolutions in a PFI refiner increased specific surface area from 0.98 to 1.20 m^2/g, decreased crystalline ratio from 1.27 to 1.17, and increased Fock reactivity from 49.27% to 58.32%.

Metal complexes such as nitren and cuen have been applied in the conversion of paper-grade pulp to dissolving pulp. The nitren, a strongly alkaline solution consisting of tris (2-aminoethyl)-amine and nickel(II)-hydroxide in a molar ratio of 1:1, is effective in extracting hemicellulose from paper-grade pulps. It can dissolve both xylan and cellulose by coordinative binding of the hydroxyl groups at the C2 and C3 positions of the anhydro sugars. The complexation of xylan is more favored than cellulose, as xylan can be solubilized at lower nitren concentrations. Nitren is, however, ineffective against softwood pulps which are rich in glucomannan. Cuen (copper ethylenediamine complex) is known as a cellulose solvent and can also be used for purification of dissolving pulps. But, cuen is less selective in xylan removal because it also dissolves some of the cellulose, which affects the desired pulp purity.

Hydrogen bonding in dissolving pulps prevents the penetration and diffusion of chemicals into the inner fiber, which is important for cellulose derivatization of dissolving pulps. There are also few other methods in addition to the above methods which improve purity and/or cellulose reactivity in dissolving pulps. These methods include ionic liquid solvent treatment, microwave treatment, and electronic radiation treatment. But these treatments have not been put into commercial use yet. Recent research has demonstrated that new treatment methods, such as modified caustic extraction, acid extraction, mechanical treatment and, enzyme treatment, are very efficient in improving the quality of dissolving pulps.

The use of nontraditional, fast-growing wood and nonwood species for the production of dissolving pulp has significantly increased in the recent years. *Trema orientalis* was used for the production of PHK-based dissolving pulp. Jute sticks and corn stalks were also used. Nonwood paper-grade pulps from flax, hemp, and sisal were upgraded to dissolving pulp, using treatments with enzymes and alkali for selective removal of hemicellulose. Because of the low concentrations of hemicellulose and other organics (acetic acids, furfural, and lignin) in PHL, their recovery and use is found to be challenging. Laccase treatment was used for improving the membrane filterability during nanofiltration of PHL for product recovery. Recent research and development has also focused on improving the dissolving pulp properties.

14.3 PROPERTIES OF DISSOLVING PULP

There are several methods for evaluation of pulp quality, but they are not sufficient to provide a full picture of the dissolving pulp's properties. The relationships between structure, chemical composition, and behavior with regard to topochemical reactions are very complex. There is a problem in cellulose characterization. The processability of a dissolving pulp is most often characterized by its reactivity toward derivatizing chemicals or solvents. Reactivity is related to the accessibility of chemicals to the cellulose, which means the relative ease by which the hydroxyl groups can be reached by the reactants. The structure and morphology of cellulose is responsible for the homogeneity of the conversion process and the quality of the final product. A reliable analysis of the property profile of dissolving pulps involves the extensive characterization of the cellulose structure at the following different levels:

- The molecular level of the single macromolecule
- The supramolecular level of aggregation of macromolecules to highly ordered structural entities
- The morphological level comprising the architecture of well-organized fibrillar elements

Furthermore, the pore system providing access to the molecular structure is an important characteristic of dissolving pulps. Finally, the qualitative and quantitative determination of organic and inorganic impurities completes the analytical characterization of a dissolving pulp. Table 14.6 presents the parameters for characterizing dissolving pulp.

TABLE 14.6 Dissolving Pulp Characterization

CHEMICAL COMPOSITION
Organic compounds (carbohydrates, extractives, residual lignin)
Inorganic compounds
MACROMOLECULAR PROPERTIES
Molar mass and molar mass distribution
Mechanical properties: short-chain molecule (DP < 100) fraction corresponds strongly with weakened properties
Functional groups
SUPRAMOLECULAR STRUCTURE
Ratio of amorphous and crystalline regions
Cellulose polymorphism (e.g., Cellulose I → Cellulose II)
CELL WALL STRUCTURE
Removal of primary cell wall during acid sulfite (AS) pulping
Different arrangement of hemicelluloses across the cell wall in PHK and AS pulps
FIBER MORPHOLOGY
Different cell types and dimensions (hardwoods)
Pore structure, accessibility
Pore volume and distribution, water retention value (WRV), hornification
DEGRADATION OF DISSOLVING PULPS
Degradation experiments provide information about the supramolecular structure, functionalities, and changes in the molecular weight distribution
Thermal, chemical, mechanical, or radiation degradation
Pulp specification

Reproduced with permission Sixta (2006).

14.4 ANNOTATED BIBLIOGRAPHY

Chen C, Duan C, Li J, Liu Y, Ma X, Zheng L, Stavik J, Ni Y (2016) Cellulose (dissolving pulp) manufacturing processes and properties: a mini-review. Bioresour 11: 5553–5564.

In this review, the production and consumption of dissolving pulp are analyzed, with a focus on the Chinese market. The manufacturing processes, including raw materials, pulping methods, pulp bleaching, and posttreatments, are discussed.

Lundberg V, Bood J, Nilsson L, Axelsson E, Berntsson T, Svensson E (2014) Converting a kraft pulp mill into a multi-product biorefinery: techno-economic analysis of a case mill. Clean Technol Environ 16: 1411–1422.

In this case study, the researchers investigated the conversion of an existing Swedish kraft pulp mill to the production of dissolving pulp, with export of electricity, lignin, and a hemicellulose stream suitable for upgrading. By increasing the level of heat integration of the mill, it was possible to achieve self-sufficiency in terms of steam and to produce significant amounts of excess steam. The excess steam could facilitate the integration of a lignin separation plant or be used for power generation.

Sixta H, Iakovlev M, Testova L, Roselli A, Hummel M, Borrega M, van Heiningen A, Froschauer C, Schottenberger H (2013) Novel concepts of dissolving pulp production. Cellulose 20:1547–1561 (2013).

The existing and novel dissolving pulp processes providing the basis for an advanced biorefinery are presented.

Sixta, H. (2006). Handbook of Pulp, Wiley-VCH Verlag, Weinheim, Germany, Chaper 8, 933–965.

This handbook contains valuable information on properties and application of dissolving grade pulp.

Sixta H and Schild G (2011). Sulfur-free dissolving pulps and their application for viscose and lyocell, Cellulose 18(4), 1113–1128.

In this study, the concept of multifunctional alkaline pulping to produce high-purity and high-yield dissolving pulps has been discussed.

Sixta H, Iakovlev M, Testova L, Roselli A, Hummel M, Borrega M and Schottenberger H (2013). Novel concepts of dissolving pulp production, Cellulose, 20(4), 1547−1561.

The existing and novel dissolving pulp processes providing the basis for an advanced biorefinery are discussed in this paper.

Jackson LS, Heitmann J, Joyce TW (1998). Production of dissolving pulp from recovered paper using enzymes. Tappi J 81:171−178.

This study suggests that pulps with chemical properties similar to a dissolving pulp can be produced from once-dried, commercially available, bleached hardwood kraft fiber and from high-quality recovered paper rich in hardwood fiber. A sequence employing an initial cold alkali extraction, xylanase treatment, and a second cold alkali extraction can effectively remove hemicelluloses and produce pulps with high alpha-cellulose content and acceptable viscosity.

Jahan MS, Ahsan L, Noori A, Quaiyyum M (2008) Process for the production of dissolving pulp from trema orientalis (Nalita) by prehydrolysis kraft and soda-ethylenediamine (EDA) process. Bioresources 3:816−828.

Process for the production of dissolving pulp from *Trema orientalis* by PHK and soda-ethylenediamine process is presented.

Köpcke V (2010) Conversion of wood and non-wood paper-grade pulps to dissolving-grade pulps. Doctoral Thesis, KTH Royal Institute of Technology, Stockholm, Sweden.

The viability of converting paper-grade pulps into dissolving pulps with enzymes is examined in this study. It was demonstrated that pulps from birch, eucalypt, and sisal fulfill the requirements of a commercial dissolving pulp for the viscose process after being subjected to enzymatic treatments and alkali extraction steps.

Köpcke V, Ibarra D, Ek M (2008) Increasing accessibility and reactivity of paper grade pulp by enzymatic treatment for use as dissolving pulp. Nord Pulp Pap Res J 23: 363−368.

The feasibility of using different kraft pulps (bleached hardwood kraft pulps from eucalypt and birch) as dissolving pulps for the viscose process has been investigated in this paper. In both pulps, the endoglucanase enhanced the cellulose reactivity and reduced the viscosity.

Lundberg V, Bood J, Nilsson L, Axelsson E, Berntsson T, Svensson E (2014). Converting a kraft pulp mill into a multi-product biorefinery: techno-economic analysis of a case mill. Clean Technol Environ 16:1411−1422.

The authors investigated the conversion of an existing Swedish kraft pulp mill to the production of dissolving pulp, with export of electricity, lignin, and a hemicellulose stream suitable for upgrading. By increasing the level of heat integration of the mill, it was possible to achieve self-sufficiency in terms of steam and to produce significant amounts of excess steam. The excess steam could facilitate the integration of a lignin separation plant or be used for power generation.

Van Heiningen A (2006). Converting a kraft pulp mill into an integrated forest biorefinery. Pulp Pap Can 107:38−43.

Opportunities to convert economically marginal chemical pulp and paper mills into integrated forest biorefineries that produce new biomaterials beside traditional structural wood and paper products are discussed. This is due to the very strong alignment of the forest products industry need for added value with the societal, governmental, and global goals of rural development and jobs, energy self-sufficiency, and control of greenhouse gas emissions. Particularly attractive to improve the profitability of the forest products industry is the IFBR, which produces new structural products, diesel fuel, and pulp.

CHAPTER

15

Pulp Washing

15.1 INTRODUCTION

A challenge facing the pulp and paper industry is to develop technology that reduces impact on the environment and meets the high product quality standards of the marketplace while reducing capital and operating costs. As the replacement of existing equipment to meet these demands may not be a viable alternative for some mills, enhancing the existing system's performance by other means becomes increasingly important. Improving brown and bleached stock washing is an area that should be considered. The objective of pulp washing is to remove as much of the soluble impurities as possible with minimum levels of fresh water usage (Table 15.1). The better washing of pulp results in lesser use of bleach chemicals, which in turn generates lesser effluent. Poor washing can lead to resin buildup, which can manifest itself as pitch deposits, causing downtime and production problems. While large amounts of resin are removed in brown stock washing, substantial amounts can still remain with the pulp. Increasing washing efficiency will reduce resin content and total solids in the pulp. Reducing carryover of total dissolved solids to subsequent processes will enhance recovery and bleaching operations. Resin and chemical carryover can negatively affect surface and strength properties of unbleached paper and cause deposit problems on the papermaking equipment in bleached mills. Additionally, high carryover in brown stock and bleach plant areas can limit the functioning of bleach chemicals, destroying their bleaching capabilities and increasing chemical demand. Efficient washing would result in lower organic and inorganic carryover, increased mat consistency, and lower shower flows. Other mill objectives, such as reduction of mill bottlenecks, decreased deposition, lower bleach chemical cost, increased production, and reduced environmental discharge, can also be realized. Various benefits of pulp washing are shown in Table 15.2.

Washing of pulp can be done according to the following three different principals:

1. By dewatering
2. By displacement
3. By pressing

An industrial washer usually includes more than one of these principles. Bleach plant washing has become a factor of ever increasing importance as bleach plants are made more closed at the same time as more expensive chemicals are being utilized in the sequence. Washing efficiency with respect to chemical oxygen demand (COD) and metals are affected by temperature, pH, the type of washer used, and the volume and quality of wash water. The concentration of scaling substances increases as the degree of bleach plant closure increases. Therefore it is essential to use a washer, which establishes a barrier between stages and to open up the filtrate loop at the correct points.

Biermann's Handbook of Pulp and Paper: Raw Material and Pulp Making
https://doi.org/10.1016/B978-0-12-814240-0.00015-X

TABLE 15.1 Objectives of Pulp Washing

Recovery of inorganic chemicals is a primary reason for using pulp washing. Inorganic chemical recovery directly affects the cost associated with makeup chemical purchasing. In modern kraft mills, usually 96%–99% of the inorganic cooking chemicals are recovered back into the system.
Recovery of organic matter (dissolved lignin and carbohydrates) plays a role further downstream in the process. For mills having oxygen delignification and/or bleaching sequences, elimination of organic chemicals in the pulp entering these processes reduces operating costs. Because these stages are oxidative in nature, improved lignin removal through enhanced brown stock washing will result in reduced process chemical consumption and reduced load to the waste treatment plant.
Brown stock washing assists in the removal of undesirable material, such as metals, pitch, and wood extractives. Wood extractives that are not successfully removed from the pulp by washing tend to concentrate in downstream processes and form sticky deposits on equipment, which in turn can result in the production of off-quality paper through the formation of spots and holes.

TABLE 15.2 Benefits of Pulp Washing

Reducing the chemical loss from the cooking liquor cycle
Maximizing recovery of organic substances for further processing or incineration
Minimizing the environmental impact of fiberline operations
Limiting the carryover between process stages
Maximizing the reuse of chemicals and the energy conservation within a single bleaching stage
Obtaining a clean final pulp product

In the mill, pulp washing operations can be found in brown stock washing, in the bleach plant, and, as the case may be, also in digesting and on the dewatering machine. The pulp washing is done to remove unwanted soluble material from the pulp. In some cases, this can be performed by replacing the contaminated liquor accompanying the pulp fibers by clean water. In the modern pulp mill, washing operations also include displacement of one type of liquor by another type of liquor. Aside from its washing function, washing equipment must at times also allow the effective separation of chemical regimes or temperature levels between single fiberline process steps. Pulp washing results in several benefits. These are shown in Table 15.2.

Pulp washing should be carried out with the minimum amount of wash water for conserving freshwater resources and to take capacity burden from downstream areas, which process the wash filtrate. Most often, pulp washing is a compromise between the cleanness of the pulp and the amount of wash water to be used. Fig. 15.1 shows the washing system, and Fig. 15.2 shows examples of possible locations of washing, screening, and oxygen delignification.

15.2 TYPES OF PULP WASHING

Dilution/Extraction Washing

In dilution/extraction washing, the pulp slurry is diluted and mixed with weak wash liquor or clean water. The liquor is then extracted by thickening the pulp. This is done either by filtration or by pressing. This process should be repeated many times to wash the pulp sufficiently. The efficacy of dilution/extraction washing depends mainly on the consistencies to which the pulp is diluted and thickened. The efficiency of this operation is usually low and depends mainly on the consistencies to which the pulp is diluted and thickened and also on the extent to which solute is sorbed on the fibers

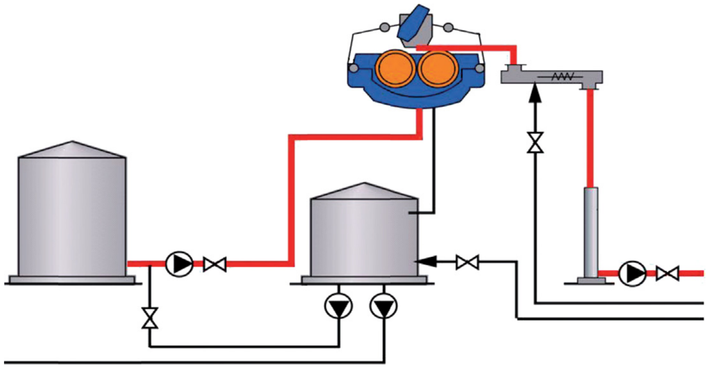


FIGURE 15.1 Washing system. *Courtesy Metso; http://valveproducts.metso.com/documents/neles/ApplicationReports/2611_Pulp/2611_04_02en.pdf.*

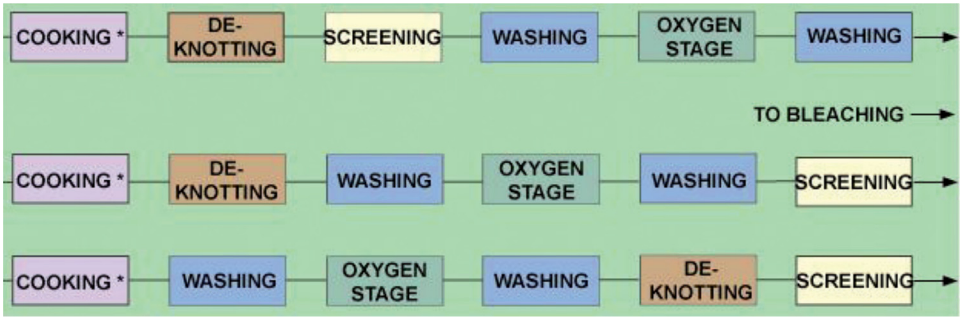


FIGURE 15.2 Examples of possible locations of washing, screening, and oxygen delignification. *Courtesy Metso; http://valveproducts.metso.com/documents/neles/ApplicationReports/2611_Pulp/2611_04_02en.pdf.*

and the time required for the solute to diffuse out of the fibers. Modern pulp mills do not have room for dilution/extraction as a separate washing process. Nonetheless, dilution/extraction phenomena occur when there is a need for dilution in the process for the following:

- Fiber separation during screening
- Even fiber distribution in the mat formation zone of a washer
- Homogeneous mixing of chemicals

Displacement Washing

In displacement washing, the liquor in the pulp is either displaced with weaker wash liquor or clean water. Ideally, no mixing takes place at the interface of the two liquors. However, in practice, it is impossible to avoid a certain degree of mixing. Some of the original liquor remains with the pulp, and some of the wash liquor channels through the pulp mass. The efficiency of displacement washing depends on this degree of mixing and also on the rate of desorption and diffusion of chemicals and dissolved solids from the pulp fibers. Apparently, one single stage of displacement washing is much more efficient than one single stage of dilution/extraction washing. Ideally, it would be possible to remove all the liquor in the pulp feed, together with all the soluble substances, by displacing it with the same volume of wash liquor. But the reality is far from ideal. Mixing occurs at the interface between the wash liquor and displaced liquor; diffusion limits the mass transfer from enclosed liquor; sorption plays its role; and homogeneities in the fiber web cause channeling of the wash liquor flow. Fig. 15.3 shows displacement washing.

Compressive Dewatering

Another method of reducing the amount of unwanted substances being carried along with the pulp is liquor removal by mechanical pressing. The pulp feed enters a device where it can be subjected to mechanical pressure. The pressure then drives the filtrate which is also called the pressate out of the pulp mat. The filtrate initially represents mainly free liquor from around the fibers. With the increase of pressure, an increasing amount of the liquor gets forced out from the fiber voids. Compressive dewatering reduces the amount of undesirable substances in the pulp discharge by reducing the volume of liquor, whereas displacement washing is based on a change in liquor concentrations. If sufficient time is allowed before pressing for intrafiber and extrafiber concentrations to even out, the concentrations in the liquor entering with the pulp in the filtrate and in the liquor leaving with the pulp are the same. In the real case, the liquor inside the fibers often has a higher concentration as compared with the free liquor around the fibers because of the sorption or due to a lack of diffusion time. The measured discharge concentration will then be higher than the measured feed concentration, as the highly concentrated liquor is set free from inside the fibers only in the final phase of pressing.

Multistage Washing

One washing stage alone is actually not sufficient to carry out the required washing. In such a case, multistage washing should be conducted either on a number of single washers in series or on one piece of multistage washing equipment. The number of stages depends mainly on the pulp furnish, necessary washing efficiency, equipment used, and liquor management. In a multistage system, the maximum solute removal could be obtained if the pulp were washed in each stage with fresh water. But this method of multistage washing generates a huge amount of very dilute filtrate. So, it is not acceptable in practice. Modern plants using multistage washing utilize the countercurrent principle, where the wash medium flows countercurrent to the pulp flow. The pulp is contacted with the cleanest available wash liquor before it leaves the last washing stage. The filtrate from the last stage is sent back in the opposite direction of the pulp flow to serve as wash liquor on the next to last stage and so on until it reaches the

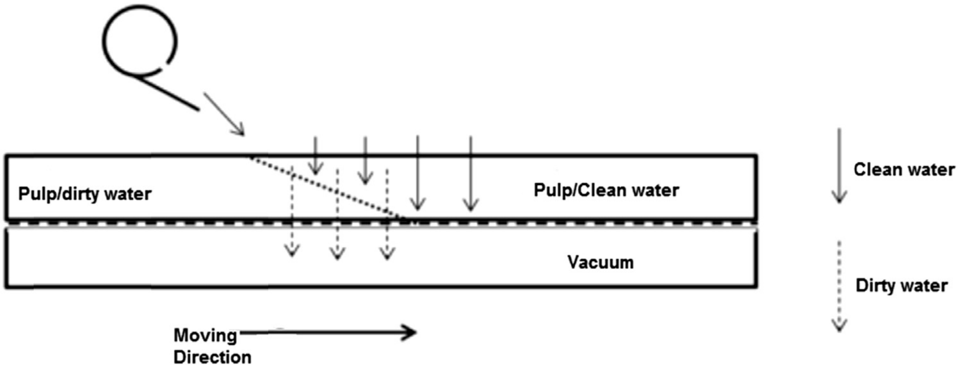


FIGURE 15.3 Displacement washing. *Reproduced with permission from Santos and Hart (2014).*

first washing stage. The filtrate from the first washing stage has the highest concentrations and is ready for processing elsewhere in the mill; for instance, in the evaporation plant. Countercurrent washing, besides the advantage of delivering a limited amount of filtrate at high concentrations, also features reasonable energy efficiency, as the amount of filtrate also limits the thermal energy leaving the system with this filtrate. The efficacy of multistage washing is affected by the method of pulp transport between stages at a given number of washing stages. Intermediate mixing of the pulp slurry, for instance, due to pump transfer to the next stage, reduces the washing efficiency as compared with the unaltered advancement of the pulp mat. In the latter case, a concentration gradient over the height of the mat is maintained between the stages. This eases the washing in the second stage.

Fractional Washing

Fractional washing is a specialty of countercurrent displacement washing. In fractional washing, the filtrates can be divided into two or three fractions having different chemical properties. It improves the washing efficiency over standard multistage washing. The concept of fractional washing includes the split application of wash liquor and/or the split collection of wash filtrate in a single washing stage. The principle of fractional washing is presented in Fig. 15.4. Following the idea of fractional washing, first the dirtier filtrate from the second stage 2/1 is used to displace the most contaminated fraction of the liquor coming with the feed into 1/1. Then, the cleaner filtrate from the second stage 2/2 is applied to stage 1/2. Filtrate from 2/2 is cleaner because it is more diluted with wash liquor.

15.3 WASHING EFFICIENCY CALCULATIONS

Researchers have developed several different ways to determine washing efficiency calculations. The most common methods are displacement ratio (DR), equivalent DR, Norden's method, and solids reduction ratio.

Displacement Ratio

The parameter DR is used to describe the efficiency of displacement. It compares the amount of dissolved solids removed from the pulp mat with the maximum amount of solids that could be removed from the pulp mat if the displacement of dirty water in the vat with cleaner shower water was 100% effective. The DR is a dimensionless number between 0 and 1. If the DR is zero, no displacement occurred. If the DR is 1, it means that perfect displacement occurred. The minimum amount of possible solids in the mat is the amount of

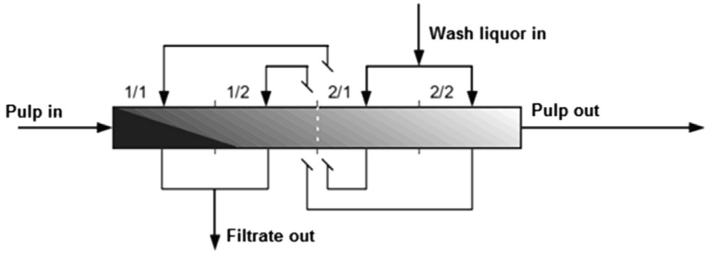


FIGURE 15.4 Principle of fractional washing (two-stage system without intermediate mixing). *Reproduced with permission from Sixta (2006).*

dissolved solids present in the shower water (cleanest water added). When shower water is added to the pulp mat, it displaces the dirty water washing out of the mat and replaces it with the cleaner shower water. DR is commonly used to compare the washing efficiency of similar types of equipment. DR is calculated according to the following equation:

$$\begin{aligned} DR &= [(\text{solids in vat}) \\ &\quad - (\text{solids in mat})]/[(\text{solids in vat}) \\ &\quad - (\text{solids in shower water})] \text{ or} \\ DR &= (Sv - Sm)/(Sv - Sw) \end{aligned}$$

where Sv = solids concentration in the vat; Sm = solids concentration in the mat leaving the washer; Sw = solids concentration in shower water.

The displacement of spent liquor out of the pulp pad is a time-dependent process, i.e., an unsteady state operation. The displacement washing taking place in the high-heat zone in a continuous digester is purely countercurrent washing. Most other displacement washing operations are crosscurrent in the radial direction through the pulp web. This is true for drum washers and drum presses of all types, and the resulting efficiency depends on the fact that the outer surface of the pulp web, where the wash liquid is added, is better washed than the inner surface adjacent to the wire. During periods with undisturbed production, high-heat washing is a real steady-state process, which is true also for multiple stage drum washers if the process is studied at a stationary point. Mathematical models for the specific operation taking place inside the continuous digester are available. Development work is going on for improving these models.

Equivalent Displacement Ratio

Equivalent displacement ratio (EDR) is a useful mathematical tool for comparing washers of different designs. The washer with the highest EDR value for the same dilution factor (DF) will be the most effective one. The term equivalent means that the hypothetical washer has the same DF as the actual one, the solid loss being the same in both cases.

The EDR is used to compare the actual washer with a hypothetical one, operating at a standard inlet consistency of 1% and outlet of 12%. For the hypothetical washer, EDR is calculated with the following formula:

$$(1 - EDR) = (1 - DR)(DCF)(ICF)$$

where DCF = discharge correction factor = Ld/7.333; ICF = inlet correction factor = 99.0(Li + DF)/[Li (99.0 + DF) − Ld (99.0−Li) (1−DR)]; Ld = Amount of liquor in the discharged pulp [(100 − discharge consistency)/discharge consistency] reported as mass of liquor/mass of pulp; Li = Amount of liquor inside the vat or inlet [(100 − inlet consistency)/inlet consistency] reported as mass of liquor/mass of pulp; DR = displacement ratio; DF = dilution factor.

Norden Method

The Norden number is an excellent method of comparing washing devices that discharge at different mat consistencies. The device with the higher Norden number has the better washing. The Norden method describes washer effectiveness, comparing the washer with a series of dilution extraction washers operating with an inlet consistency of 1% and a mat discharge consistency of 10% with no liquor displacement. Modified Norden numbers use different mat discharge consistencies and have a subscript after the N to let the reader know what the discharge consistency actually is. For instance, an N12 number would have a mat discharge consistency in the theoretical dilution/extraction washer of 12% instead of 10%. The method was developed by Norden et al. in 1966. It defines the number of dilution/extraction washing stages that will give the same washing efficiency as the washer in consideration. Equipment such as vacuum drums and single-stage diffusers present the lowest Norden numbers, indicating low washing efficiency. Properly operating Kamyr digesters with extended washing zones (up to 4 h) present the highest Norden numbers and consequently the highest washing efficiency. The Norden number may be calculated with the following formula:

$$Nn = \ln((V1\,(W1 - X0)/V0(W0 - X1))\,/\ln(Y1/V0)$$

where N = Norden number; V1 = flow of liquor to the vat; W1 = weight fraction of alkali in the vat; X0 = weight fraction of alkali in the filtrate to filtrate tank; V0 = flow of liquor out with the mat; W0 = weight fraction of alkali out with the mat; X1 = weight fraction of alkali in the shower water; Y1 = flow of liquor in the shower water; Ln = natural log.

Solids Reduction Ratio

Because of its calculation complexity, solids reduction ratio is impractical to use in operating systems. The method was developed to relate the solids content of the mat liquor leaving the final washer to the solids content of the liquor before any washing. The concept demonstrated solids content reduction as a function of the solids content of the liquor entering the stage, and reemphasized washing systems as fractionating devices.

15.4 WASHING SYSTEM VARIABLES

The major variables are DF, drum speed, stock consistency to the vat and sheet formation, entrained air in the pulp and liquor, wash liquor distribution and temperature, and pulp discharge consistency.

Dilution Factor

One of the first and most important variables to be considered during brown stock washing is the DF. It is defined as the amount of excess liquor added to a washing system. DF is important for determining the overall system material balance and performance. For reducing steam usage during black liquor evaporation, the DF should be minimized. DF can be defined as liquor added to pulp in terms of ovendried pulp or air-dried pulp. Typically, the DF varies from 2 to 4.5 m3/o.d. ton.

In theory, the DF should be maintained constant at each stage of washing; in reality, it rarely is. Extra water input into the washing system (e.g., seal water, freshwater hoses placed into the system, filtrate tank level control water, etc.) will result in changes in the DF between stages. A negative DF shows that less water than the amount present in the discharged sheet was added to the system. The following equation is used for calculating the DF:

DF = WS − C1 where,
WS = washing shower (ton liquor/ton pulp)
C1 = liquor discharged with pulp (ton liquor/ton pulp)

Drum Speed

Drum speed is another important variable when one is trying to obtain improved washing efficiency. Drum speed should vary as a function of vat level or sheet formation. It is always an improvement when the pulp mat is maintained to a certain thickness across the washer. If the mat is too thick, it will carry over more of the dirty liquor because the shower water will not be able to fully displace the dirty liquid retained in the mat when it was formed on the drum. On the other hand, a washer operating with an extremely thin pulp mat can be challenging to run. The thin mat will not provide good resistance to air penetration of the sheet into the liquor and the drum will tend to seal over, resulting in no drainage and no liquor displacement. Some washers use drum speed as the vat level control. In these types of washers, a higher drum speed maximizes water removal from the drum vat, which reduces the vat level. The opposite is also true. When considering the production rate, a 100% increase in cylinder speed from 2 to 4 rpm will result in a 42% increase in production. The combination of drum speed and vat consistency should be the best available option when one is looking for an increase in productivity.

Stock Consistency to the Vat and Sheet Formation

When operating a washing device which relies on dilution/extraction as one of its major washing principles (for example, rotary vacuum washers), the stock inlet consistency is of great importance. The inlet consistency for a rotary vacuum washer should be about 1.0%−1.5% in an ideal situation. These washers can be operated at much higher inlet consistencies, but the quality of washing suffers. When the inlet consistency is increased to a level of 2%−3% range, these devices tend to become more of a pulp conveyor, which moves pulp from one stage to another with very little washing. The highest washing efficiency is achieved when stock consistency to the vat is maintained as low as possible, preferably in the 1.5% range. Low vat consistency typically results in good, uniform sheet formation across the washer, which results in a uniform displacement of the dirty liquor. The low vat consistency and uniform mat formation allow each fiber to be exposed to its share of wash water, resulting in uniform and efficient pulp washing. The high amount of water in the stock also results in overall better solids removal. Improved sheet formation can also be a function of washer design. It is important to place stock pipes and dilution water in such a manner as to maximize mixing before the vat. Stock and dilution lines placed in a Y configuration often result in poor mixing. A 90° joint between the two results in a more turbulent flow with better mixing ability.

The disadvantage of operation in low consistency is the reduced production rate across the washer. Vat consistency is almost a square root of washing capacity. An increase of 100% in consistency (increase in consistency from 1% to 2%) implies that washer capacity increased by 52%. Nonetheless, one should be aware of the negative washing effects of running a washer at high inlet consistency.

Entrained Air in the Pulp and Liquor

For maximizing brown stock washing, it is important to prevent and eliminate the entrained air in the pulp and liquor. Formation of air/bubble can occur in the drum vat when the vat level is low, resulting in a more turbulent system. Filtrate tank design and level set point can contribute to air entrainment in the liquor used to dilute the pulp between stages. Dropleg seal pots inside the filtrate tanks should be designed for allowing air removal from the liquor. The filtrate level should not be above the top of the centerline of the horizontal run of the drop leg and definitely not above the standpipe or seal pot. Air which gets trapped in the pulp also increases the drum speed by decreasing stock drainability and reduces DR. Basically, entrained air bubbles in the pulp mat behave as solids and plug the drainage channels within the mat, resulting in a reduction in the DR. It is important to note that underwashing in one area of the mat cannot be compensated by overwashing in another area, making elimination of air entrainment and good sheet formation over the drum a requirement for optimum washing.

Wash Liquor Distribution and Temperature

In pulp washing, each fiber should get the same amount of washing liquor. Washing liquor should be gently and uniformly applied all the way across the washer. Design of shower header and setup determines the liquor distribution and flow rate. With fewer shower headers, liquor flow rates need to be increased to achieve the desired displacement. Also, an improper shower bar setup can result in pulp mat disruption (holes), which will reduce vacuum and washer efficiency. It is common to have five shower bars arranged in a symmetrical manner on top of the drum. Temperature of liquor plays an important role by affecting the viscosity of the washing liquor. Higher temperature results in reduced viscosity and consequently results in better diffusion of liquor into the mat. This results in better washing. Washing temperatures of 145°F and 155°F are the optimum point for vacuum drum washers running softwood and hardwood, respectively. Typically, operating a vacuum drum washer line with higher temperature of wash water on the last washing stage results in liquor flashing in the first washer drop leg. When flashing occurs, washing efficiency decreases and, in extreme cases, the resulting vapor bubble can mechanically damage the washer.

Pulp Discharge Consistency

A higher discharge consistency will provide the system with a better DR and, consequently, better washing. The impact of discharge consistency tends to be more important when the discharge consistency is low. Once the discharge consistency increases beyond about 14%, the effect of increasing discharge consistency on washing efficiency has been found to be less important. To better illustrate this example, Table 15.3 presents a summary of the variables influencing solids removal during washing. Table 15.4 shows the effect of discharge consistency on soda loss, assuming a constant dissolved soda concentration of 10 g/L and discharge consistency varying from 8% to 16%. Once the discharge consistency increases beyond 14%–16%, the effect of discharge consistency clearly diminishes.

TABLE 15.3 Variables Affecting Solids Removal

SHOWER LIQUOR
Arrangement
Temperature
Distribution
SHEET FORMATION
Vat consistency
Specific load
Drum speed
OPERATIONAL
Pulp temperature
Air entrainment
Dilution factor
Black liquor solids content
Wire mesh characteristics
Washer incrustations
Discharge consistency

Adapted from Santos and Hart (2014).

15.5 WASHING EQUIPMENT

There is a large variety of pulp washing equipment available these days. The rotary vacuum washer is still by far the most widely used washer equipment, but other methods of washing have been developed and are becoming more common. Among these are rotary pressure washers, diffusion washers, horizontal belt filters, and wash presses. The following equipment are described briefly.

TABLE 15.4 Effect of Discharge Consistency on Soda Loss

Discharge Consistency (%)	Mass Filtrate/Mass Fiber	Soda Loss/TP* (lb)
8	11.5	240
10	9.0	188
12	7.3	153
14	6.1	128
16	5.3	109

** o.d.*

Reproduced with permission from Santos and Hart (2014).

Vacuum Drum Washing

Vacuum drum washers are by far the most abundant washers in the industry. These washers usually consist of three to six counterflow stages. Each stage consists of a rotating screen drum having a partial vacuum applied to the interior. The drum is located in a tank where pulp is diluted with recirculated filtrate. The vacuum draws a pulp mat against the surface and wash water through the mat. The rotation of drum advances the washed pulp mat to the next stage. Wash water discharged from this wash stage is sent to the previous washing stage. Most of these washers are older and run far beyond their original design capacity and have a reputation of poor washers. But they are very easy to operate. The main negative point with vacuum drum washers is the space and building requirements. They require a large tank to deaerate the filtrate. The washer should be located about 30–35 feet above the filtrate tank to get sufficient vacuum in the drop leg. Another issue with vacuum washers is that they are not the best choice as the first stage out of the digester because it is generally too hot and this can cause flashing of the filtrate in the drop leg of the washer and cause it to shut down. Many mills have installed new vacuum drum washers and/or replaced existing drums with newer designs and greatly improved washing efficiency. Low operating vacuum with low differential pressure has also been known to cause problems, such as low discharge consistency.

Andritz has a vacuum washer system which incorporates several features from the many machines it has designed and manufactured over the years. Because the patented Maxton Deck has less pressure drop as compared with the conventional deck, the discharge consistency and the washing efficiency are higher. Improved washing efficiency results in reduced operating costs.

In one case, when the Andritz team replaced an 11.5′ × 14′ D100 washer, the discharge consistency increased more than 2%. The replacement was made for maintenance reasons; the increase in discharge consistency was a desirable benefit because it substantially reduced the caustic requirement in the following stage. This improvement can be expected from either bleached or brown stock drums.

GL&V has also developed a comprehensive line of washer drum technologies. Their selection ranges from the reliable Dorr-Oliver and Canron washers through to the advanced composites for severe corrosion environments of the GL&V/LaValley fiber reinforced polymer (FRP) composite washer drum. They are reputed to handle high freeness pulp with a high discharge consistency and are maintenance friendly and very efficient.

Pressure Washing

Pressure washing is similar to vacuum drum. It differs by spraying water under pressure through the pulp mat as the drum rotates. The popular washer compaction baffle (CB) filter is based on this concept. The CB filter is a very efficient washer and is the preferred choice for new washing equipment. As it is pressurized, high temperatures are not a problem and the filtrate tank does not need to be located below the washer, as in the case of vacuum washers. The only negative point with these washers is that they are more complex to run.

Diffusion Washing

Diffusion washing is a counterflow process that takes place in one or more stages. Pulp flow is upward and is conducted on a perforated plate; water flow is downward, through a series of baffles. This method offers a high degree of cleaning and the water use is low. Pressure diffusers are the preferred washer technology out of a continuous digester. They can be considered as an extension of the digester wash zone, and as several mills are cooking farther down the digester, they can recoup some lost washing capacity. Higher temperatures are usually not a problem. At higher temperatures, washing efficiency is greatly improved because of the greater diffusion rate of material from inside the fibers and also the greater solubility of soaps. Atmospheric diffusers are not as popular these days, mostly due to the high efficiency of the pressure diffusers. They are generally not a good choice as the last washer of a line because of their relatively low discharge consistency. The pressure diffuser from Andritz is a high efficiency, diffusion-type washer, which is fully enclosed and operates under pressure, pushing the pulp through the machine without the use of pumps, reducing energy and maintenance expenses. Also, with the pressurized wash, higher blow temperatures from the digester can be used. There are no gas emissions or pulp spills from the pressure diffuser as they are totally closed. The vertical pressure diffuser requires very little space for installation.

The atmospheric diffuser from Andritz is a compact washing system which maximizes washing efficiency while reducing energy consumption. It eliminates the requirement for intermediate dilution between washing stages and can use the pressure from a continuous digester to transport pulp through the diffuser. This eliminates the pumps required by other washing systems.

Belt Washing

Belt washing is a counterflow process where pulp enters the washer area on a wire belt and washing takes place under a series of showers. Clean water enters on the opposite end from the pulp and is sprayed on the pulp to displace the liquor in the pulp mat. The used wash water is then collected and reapplied to the dirtier pulp by the next washing head countercurrent to the direction that the pulp moves. This process is continued through several stages until the wash water is saturated with liquor after washing pulp enters this area. The wash water is then sent to the recovery process. Reduced dilution of the liquor recovered from washing would result in reduced energy consumption in the recovery process.

A Chemi or belt washer has the simplest washing system design, but these are found to be sensitive to feed consistency, production rate, and DF. Despite the reduced water usage, there are not many installed.

Wash Presses

Basically, wash presses are dilution/extraction washers. Some wash presses also have a displacement stage. Wash presses are frequently used for pulps which are difficult to permeate. For reaching sufficient efficiencies, a press must be able to reach a very high discharge consistency up to 40% or 50%. A wash press system consists of a number of presses arranged in a series with an agitated tank for dilution between them. A system's efficiency mostly depends on two factors: the degree of equilibrium reached in the agitation tank and the degree of extraction in the presses.

These are typically easy to operate and very efficient. When used in the last stage of washing, they work well because of their high discharge consistency. They create a good water barrier between the mill areas (i.e., between brown stock and the bleach plant), and fresh shower use is less compared with that for a washer which discharge at medium consistency.

For efficient washing, the wash presses rely on high discharge consistency. Therefore they are not as good in those areas where the liquor has a higher viscosity, such as at the start of brown stock washing. They are mostly used after oxygen delignification stages or even in bleach plants.

Valmet, the world's leading supplier, introduced the press wash technology. TwinRoll is the new generation of presses. It is based on only two roll diameters. Production rates of more than 3000 ATD/d can be obtained on a single machine with different roll lengths. Extensive modularization in the recent past has resulted in more efficient production, improved wear, and spare part economy.

Drum Displacer Washers

New demands being placed on washing performance are improved efficiency, reduced costs for installation, operation and maintenance, and environmental compliance. Drum Displacer (DD) washer of Andritz is environmentally friendly and cost-effective. It incorporates one to four washing stages in a single unit. This greatly simplifies the entire fiberline layout. The DD washer uses displacement washing and delivers high washing efficiency in any position in the fiberline and can produce several filtrates with different properties. Innovative connection of filtrates reduces the amount of chemicals required in the oxygen delignification and bleaching stages and also reduces heat and water consumption. This reduces operating costs and produces low effluents.

The washer family includes DDs with low consistency feed and medium consistency feed, with between one and four washing stages. The washing efficiency is very high because of the DD's fractioned countercurrent washing. These are fairly complex units but are appropriate for mills where space is a critical factor. There is generally no diffusion of liquor from within the fibers between washing stages.

The DD is a pressurized, mostly multistage washer, which can have as many as four washing stages in one single unit. A four-stage washer may be efficient enough to serve as the only brown stock washing equipment after cooking. The pulp fed to the formation section of the DD washer can be of either low consistency (3%−5%) or medium consistency (8%−10%). The circumference of the rotating drum is divided into compartments, which are filled with pulp in the formation section and proceed to the washing stages. At each washing stage, the pulp is washed countercurrently with the filtrates from the succeeding washing stage. In the discharge zone, the pulp is dewatered by means of vacuum and eventually removed from the compartments by pressurized air to drop into a shredding screw conveyor. The DD washer has the smallest footprint of all multistage washers. It features the specialty of fractional washing. Unlike other washers, where in one washing stage the liquor volume in the pulp is overdisplaced (DF larger than zero), the DD washer has two or three liquor cycles for each stage, each operating at a negative DF. As the overall washing efficiency of fractional washing is superior to the washing efficiency of other units with the same number of stages, DD washers generate rather high E factors. The E factors for two-stage, three-stage, and four-stage DD washers are 6−9, 9−12, and 11−14, respectively. The outlet consistency is usually in the range of 12%−16%. The handling of wash filtrate is very compact as it is brought from stage to stage by pumps mounted on the washer itself. In the simplest arrangement, the multistage unit requires just one filtrate tank. More tanks are required in case the filtrate from the first stage needs to be divided into fractions having different properties such as temperature, pH, chemical concentration. The DD washer's gas-free operation, enclosed design and mostly submerged, assure good tolerance for high-temperature pulp feed, reduced foaming and high standards with regard to air emissions.

The overall choice of equipment is sometimes governed by circumstances such as inlet consistency. For instance, vacuum drum washers needs a low vat consistency (∼1.5%) to form a good uniform mat on the washer. Wash presses and pressure drum washers require an inlet consistency of about 4%, whereas diffusers need an inlet consistency of about 9%–10%. Therefore for thickening after low consistency screening, vacuum drums are still preferred. However, if space and lower hydraulic recirculation are important, more modern washers may be required.

Efficiency-wise, modern vacuum drum washers can compete, but they should be properly designed for the production load. Modernizing an existing drum washer with anti-rewet drums, high efficiency end-valves, or possibly resizing the drop leg can only get you part of the way there if the washer is heavily overloaded. Focused engineering in this area could help a mill obtain uniform sheet formation and maximum chemical recovery during pulp production. Pictures of some commercial washers are shown (see Fig. 15.5–15.10).

15.6 USE OF ADDITIVES/PROCESSING AIDS

Antifoam additives play an important role in increasing the washing effectiveness. Antifoam materials help achieve washing effectiveness by preventing entrapped air from forming in the system, which allows for an easier, unrestricted flow of filtrate through the screens and washers. Earlier, the kraft industry used mineral oils or kerosene-based antifoams. At the time, these products allowed for substantial increases in production and reduction of chemical losses in the recovery cycle and reduced carryover to the bleach plant. The use of oil-based antifoam also resulted in some negative effects for the industry, particularly in the paper machine with pitch deposits of high molecular weight fractions of oil and waxes. Environmental impacts were also a concern because dioxin and furan precursors could be found in antifoam products. Also, oil-related sheen often could be found on the surface

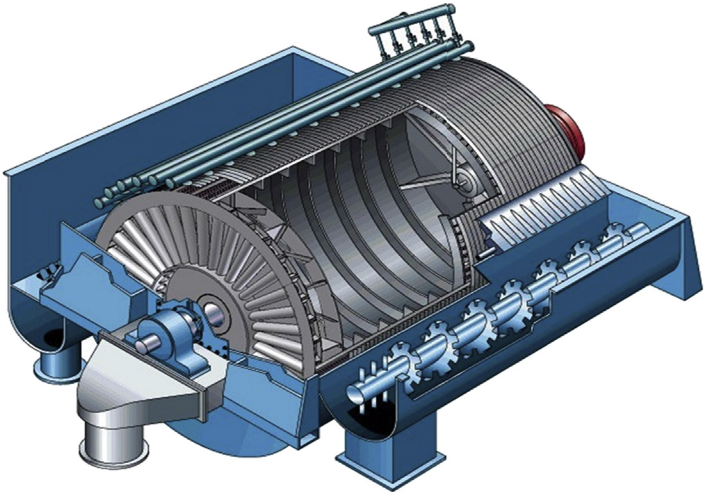


FIGURE 15.5 Vacuum washer. *Courtesy GLV; http://www.glv.com/pulp/Washing/VacuumWasher.*

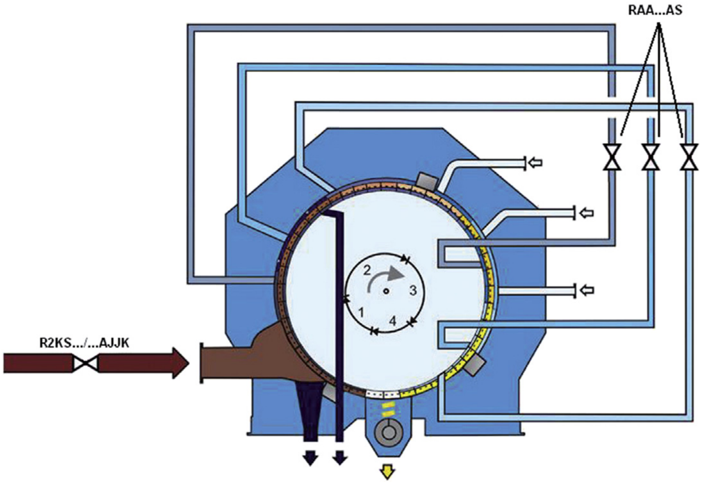


FIGURE 15.6 Drum displacer washer and its typical valves. *Courtesy Metso; http://valveproducts.metso.com/documents/neles/ApplicationReports/2611_Pulp/2611_04_02en.pdf.*

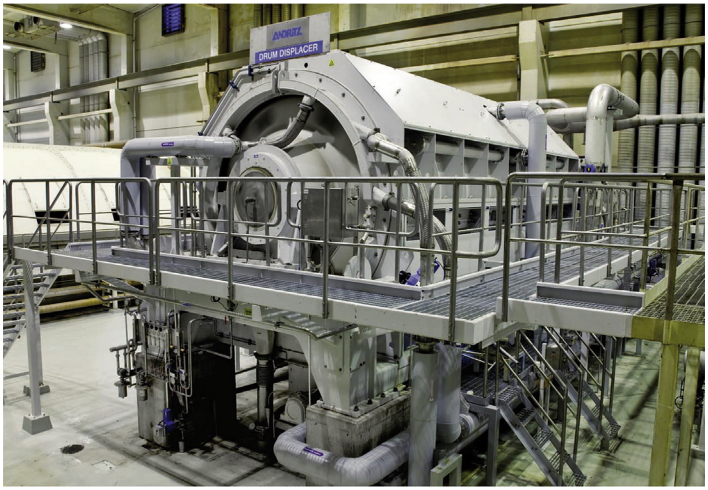


FIGURE 15.7 Drum displacer washer. *Courtesy Andritz.*

of receiving waters. Another negative point of its use was price volatility, as it depended on petroleum supply and demand. After 1940, the use of silicone increased steadily, and a vast array of products were developed and used. By the late 1980s, environmental concerns over antifoam additives provided greater motivation toward the use of silicone-based antifoam in brown stock washing. Silicone antifoam products were found to be effective at very low dosages, allowing for foam prevention and improvements in washer drainage, with substantial gains in chemicals for recovery and bleach plants. Silicones are the polymeric materials with Si—O— as the main repeated unit. Covalent bonds of inorganic/organic substituents also may be present in the molecule. Aqueous silicone emulsions are mostly preferred in the pulp and paper industry.

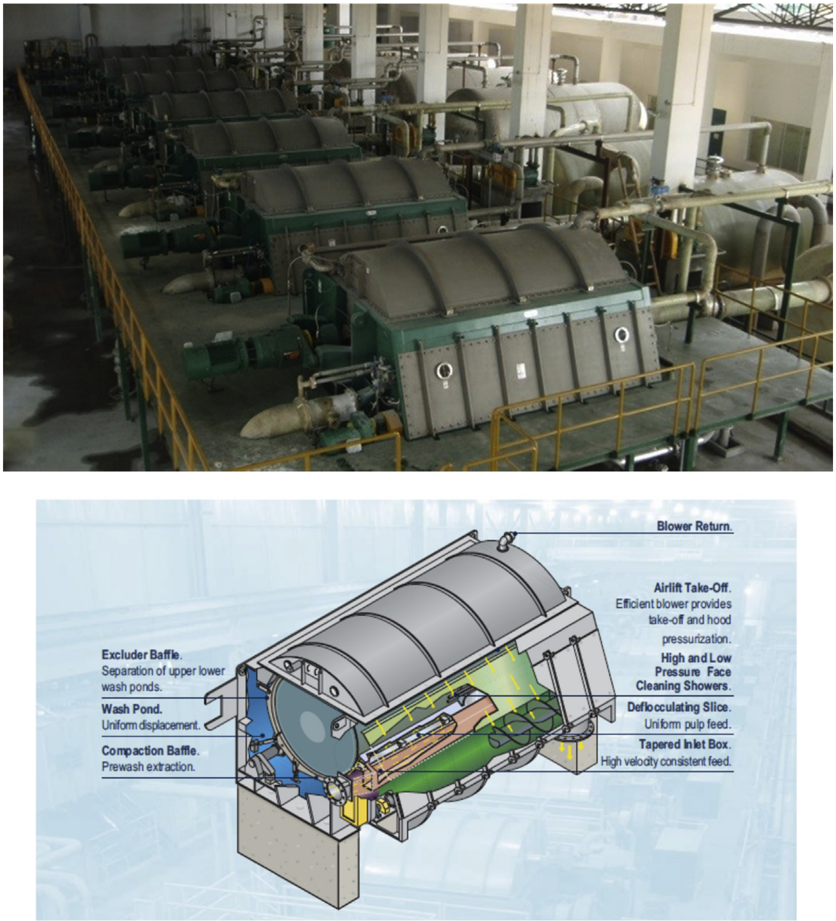


FIGURE 15.8 Compact pressurized washer. *Courtesy GLV.*

Effective silicone antifoam products have to perform well in the challenging environment of the pulp and paper industry. For this, several features are important, such as access to bubbles on the surface with low product application (product inter- and intramolecular forces need to be low). The product molecule needs to be able to rotate, allowing for the proper orientation on the bubble surface. The product molecule also needs to be incompatible with black liquor to prevent product solubilization and loss of effectiveness, stable in terms of viscosity at different temperatures, and should be able to easily distribute over the surface. Although product features such as proper formulation are important, feed points in the process are also important for successful application. Feed points are usually where foam is most problematic and can be easily identified by locations where air entrainment to the system is most severe. Silicone technology is indeed less problematic than mineral oil. Nevertheless, deposits get formed if product formulation and/or application are incorrect. To avoid or minimize potential problems when transitioning from one antifoam formulation to another, a mill should conduct

FIGURE 15.9 Kadant Black Clawson Chemi-Washer. *Courtesy Kadant.*

laboratory experiments that allow deposit potential and product effectiveness to be determined. A simple test consisting of the use of pulp mill black liquor samples heated to process temperatures with the addition of antifoam should be conducted. Shear is applied to the sample once process temperature is reached. The sample is then set aside and observed for antifoam separation and deposit formation. The same test can be conducted at different temperatures and pH to test different possible scenarios encountered in the pulp mill.

15.7 ANNOTATED BIBLIOGRAPHY

Gullichsen, J., Fogelholm C-J. (2000). Papermaking science and technology, volume 6A, chemical pulping. Helsinki, Finland.
This excellent book focuses on chemical pulping methods and also deals with pulp washing.
Miliander L (2009) Pulp Washing. Pulp and Paper Chemistry and Technology Volume 2. Pulping Chemistry and Technology, Edited by Monica Ek, Göran Gellerstedt, Gunnar Henriksson, Walter de Gruyter GmbH & Co. KG, Berlin, p. 165, ISBN 978-3-11-021,341-6.
This chapter presents washing of chemical pulp in detail, including the oxygen delignification stage.
Sixta, H. (Ed.) (2006). Handbook of Pulp. WILEY-VCH Verlag GmbH & Co. KgaA, Weinheim Germany.
This is a comprehensive handbook dealing with the traditional aspects of pulping processes. It describes all pulping processes

FIGURE 15.10A TwinRoll presses. *Courtesy Valmet.*

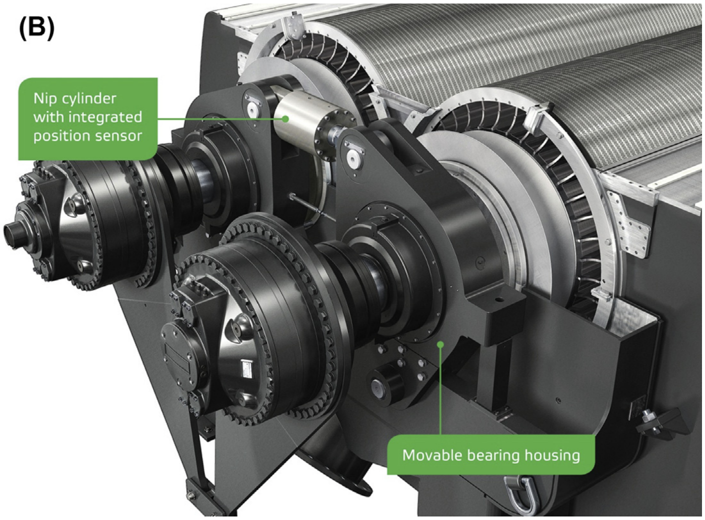


FIGURE 15.10B TwinRoll presses. *Courtesy Valmet.*

used for paper and board manufacturing, as well as waste liquor treatment, pulp bleaching, and environmental aspects, while also covering pulp properties and applications.

Smook GA (2003). Handbook for Pulp and Paper Technologists. Joint Textbook Committee of the Paper Industry of the United States and Canada, 425 p.

This book provides an introduction to the entire technology of pulp and paper manufacture, covering all aspects of pulping and papermaking.

Sillanpää, M., "Studies on washing in kraft pulp bleaching," Ph.D. thesis, University of Oulu, Department of Process and Environmental Engineering, Oulu, Finland, 2005, p. 41.

In this thesis, it is shown that brown stock washing and pulp washing between bleaching stages are distinct areas with their own specific features. They differ in terms of the composition and molecular size of the impurities in the pulp suspension. Various process conditions cause further differences between washing in bleaching and brown stock washing

Habermehl, J (2005). Silicone foam control technology for kraft brownstock washing, Solutions, Online Exclusives, 88(12): (2005). Available online at http://www.tappi.org/Bookstore/Technical- Papers/Journal-Articles/Archive/Solutions/Archives/2005/December.aspx.

This paper presents the history and use of silicones in kraft brown stock washing, beginning with a basic understanding of general antifoam requirements to clarify why silicones offer so many unique benefits.

Norden HV and Jarvekainen M (1966). Analysis of pulp washing filter, Kemian Teollisuus 23(4): 344–351.

Santos RB and Hart PW (2014). Brownstock washing – A review of the literature. Tappi Journal, January, Vol. 13 No. 1, p. 9–19.

This excellent paper reviews the work that has been performed in brown stock washing to ensure a complete understanding of the process. Because brown stock washing is one of the key aspects of a well-running integrated mill, review and understanding of brown stock washing fundamentals is important for all mill operation personnel. Good understanding of the fundamentals and current research will help a mill optimize this important unit operation.

Pulp and Paper Canada. (2006) Achieving Efficient pulp washing https://www.pulpandpapercanada.com/equipment-systems/achieving-efficient-pulp-washing-1000201800

This paper discusses ways for achieving efficient pulp washing. Proper technology can not only improve the efficiency of pulp washing but also reduce the need to vent vapors to the environment.

CHAPTER

16

Pulp Cleaning, Screening, and Fractionation

16.1 INTRODUCTION

Pulp from cooking always contains some undesirable solid material as some of the chips may not be fiberized properly and some of the pulp may not be completely in the form of individual fibers. Also, some contaminants, such as bark, sand, rocks, and tramp metal etc., may enter with chips. Deposits are formed on tanks, machinery, and pipes. These deposits may be liberated into the pulp stream in some cases. Plastic and other industrial materials can also be found in pulp suspensions. Impurities have a negative effect on the quality of the end product, and they may damage the process equipment and also cause runnability issues. All such solid contaminants have to be removed from pulp. Some contaminants can be separated from pulp on screens. Contaminants which are similar or smaller than fibers may be removed by differences in density.

The objectives of screening and cleaning are to remove these solid impurities from the pulp to protect the downstream equipment, save bleaching chemicals, and obtain a clean product. Pulp screening can be described as solid–solid separation using a screen in a liquid environment. The larger particles are retained on the screen, whereas the smaller ones selectively pass through the narrow screen apertures. The mechanism of screening is separation by size. The large pulp fiber bundles get retained on the screen, whereas small isolated fibers pass through. Screening with narrow slots is actually emerging as a challenge to centrifugal cleaning as the process of choice for contaminant removal from bleached pulp. With regard to fractionation, pressure screens and centrifugal cleaners cover different separation tasks. While screens fractionate mainly by fiber length and fiber flexibility, the cleaners fractionate mostly by wall thickness, coarseness, and fibrillation.

Pulp cleaning is characterized by solid–solid separation using centrifugal and centripetal forces in the gravity field of a hydrocyclone. Depending on the separation task, the design of the hydrocyclone is customized so that either heavyweight or lightweight particles are selectively separated from the main stream. The mechanism of cleaning is separation by specific weight. For instance, heavyweight sand can be separated from the light pulp fibers.

Screening and cleaning equipment can also be used for fractionating the pulp. During fractionation, the pulp is divided into usable portions of different properties such as fiber length or fiber wall thickness, which are separately handled downstream in the process. In chemical pulping,

Biermann's Handbook of Pulp and Paper: Raw Material and Pulp Making
https://doi.org/10.1016/B978-0-12-814240-0.00016-1

fractionation by screens has traditionally been used for high-kappa pulps. Fractionation for low-kappa pulps has gained industrial significance in the recent years. Screening operations can be located in both the unbleached and bleached sections of the fiberline. Centrifugal cleaning is mostly used for the bleached pulp, except for cleaning for sand removal, which is also used in unbleached screening systems. Demands on screening operations have increased since chlorine bleaching has been replaced by environment-friendly bleaching sequences.

Screening of the pulp is done to remove oversized and unwanted particles from good papermaking fibers so that the screened pulp is more suitable for the paper or board product in which it will be used. The biggest oversized particles in pulp are knots. Knots can be defined as uncooked wood particles. Knots consist of uncooked chips, uncooked branch knots, or poorly penetrated dense wood. The knots are removed before washing and fine screening. Knot particles are large and can be separated with screen plates with holes usually having a diameter of about 5 mm. Knots removed in screening are usually washed and returned to the digester to be recooked. Knots can also be refined and reintroduced to the screen feed flow or be removed to combustion, for instance. In low-yield pulps they are broken down in refiners and/or fiberizers. In low-yield pulps they are removed in special coarse screens called knotters.

The main purpose of fine screening is to remove shives. Shives are small fiber bundles that have not been separated by chemical pulping or mechanical action. A common definition of the shives content is material retained on a 0.15 mm or 0.25 mm slotted laboratory screen. Shives are typically stiff aggregates of 1–3 mm in length and 0.15–0.25 mm or several fibers in width.

Chop is oversize wood particle removed in screening. It is more of a problem when pulping hardwoods, as it originates mostly from irregularly shaped hardwood vessels and cells. Chop particles are shorter and more rigid than shives. Chops are cubical material originating from irregular dense sawdust and fines. Debris is the name for shives, chop, and any other material that would have any sort of bad effect on the papermaking process or on the properties of the paper produced. Shives and chops are separated with screen plates with narrow slots or small holes. The shives and chops removed in screening are usually refined and reintroduced into the screen feed flow in mills built before 1990. In mills built after 1990, the shives and chops are usually taken to oxygen delignification or removed to combustion, for instance. Dirt originates from bark, extractives, and undissolved wood compounds. Table 16.1 shows contaminants in chemical pulp. Dirt can also be sand, ash, or other inorganic contaminants. Dirt is removed and separated with cleaners.

Earlier, screening and cleaning equipment used atmospheric feed and/or discharge. However, today's pressurized systems have many advantages over their atmospheric counterparts. These are mentioned as follows:

- Higher operating consistency
- High operating temperature

TABLE 16.1 Contaminants and Debris in Chemical Pulp

Contaminants
Shives
Mini shives
Dirt
Specks

- Greater capacity
- Lack of air entrainment
- Better separation efficiency

16.2 SCREENING

Screening is a key process in pulp and paper production and is used to improve the quality of pulp destined for a wide range of pulp and paper products. The objective of screening is to remove oversize contaminants from the pulp, but now it is also finding increasing use for fiber fractionation as mentioned earlier. A product quality can be improved by fractionating fibers for targeted processing or for use in specialty paper products.

Screening equipment is an important system for pulp processing. After the black liquor is separated from the fiber in the washing section, the pulp contains coarser fibers, foreign matter, and dirt such as pieces of bark, digester brick, cement, etc. Therefore this troublesome and undesirable matter should be removed to produce first-quality pulp. Pulp screening equipment is used in this regard.

Two types of screens are being used in pulp mills. These are coarse screens and fine screens. These screens work on vibrating, shaking, gravity centrifugal and centripetal forces. The two major types of coarse screens are sliver screens and knotters. The examples of sliver screens are bull screen, rotary scraper, rotary oscillating, etc and the knotters are worm knotter, Johnson knotter screen, diaphragm screen, etc.

The major types of fine screen are Cowan, IMPCO, diaphragm or flat screen, Quiller, bird pulp screen, vertical type of centrifugal screens, inward-flow rotary type screen, bird inward-flow screen, Jones inward flow screen, Walpole outward flow screen, APMEW outward flow, APMEW inward flow, Ahlfors Swedish screens, etc. Fig. 16.1 shows IMPCO HI-Q Fine Screen from GL&V.

Most screens are pressurized and have a screen plate which is cleaned continuously by a rotating rotor. In some alternative screen designs, the screen plate rotates and is cleaned by a static element. Also, there are open unpressurized vibrating screens which are still in use. Some special screens such as knot washers are also unpressurized.

In a pressurized screen, the pulp can flow inward or outward through the screen plate. The rotor cleaning the screen plate can be located at the inlet side of the screen plate or at the accept side of the screen plate. Pulp which enters the screen or screen plate is called inlet pulp. The pulp which is able to pass through the holes or slots is called accept pulp, and the particles retained by the screen plate are called rejects. In a screen, accepted pulp fraction passes through the screen plate due to difference in pressure over the screen plate, but bigger impurities tend to remain on the screen plate. To get fibers to pass screen apertures, fiber flocs should be dispersed with rotor before single fibers can go through the screen apertures. The reject must also be removed from the surface of the screen plate so that the screen plate would not plug and prevent screening. Fig. 16.2 shows a typical screen and the principle of screening.

Pressure screens are an increasingly important unit operation in pulping, recycling, and papermaking and are found to be very effective for removing oversize contaminants which reduce the strength, smoothness, and optical properties of paper. There are several configurations for pressure screens devices (Fig. 16.3).The screen has an axial feed, a foil rotor with a conical rotor body, and a slotted screen plate. Pressure screens are also used to fractionate the pulp by fiber length, thereby allowing for

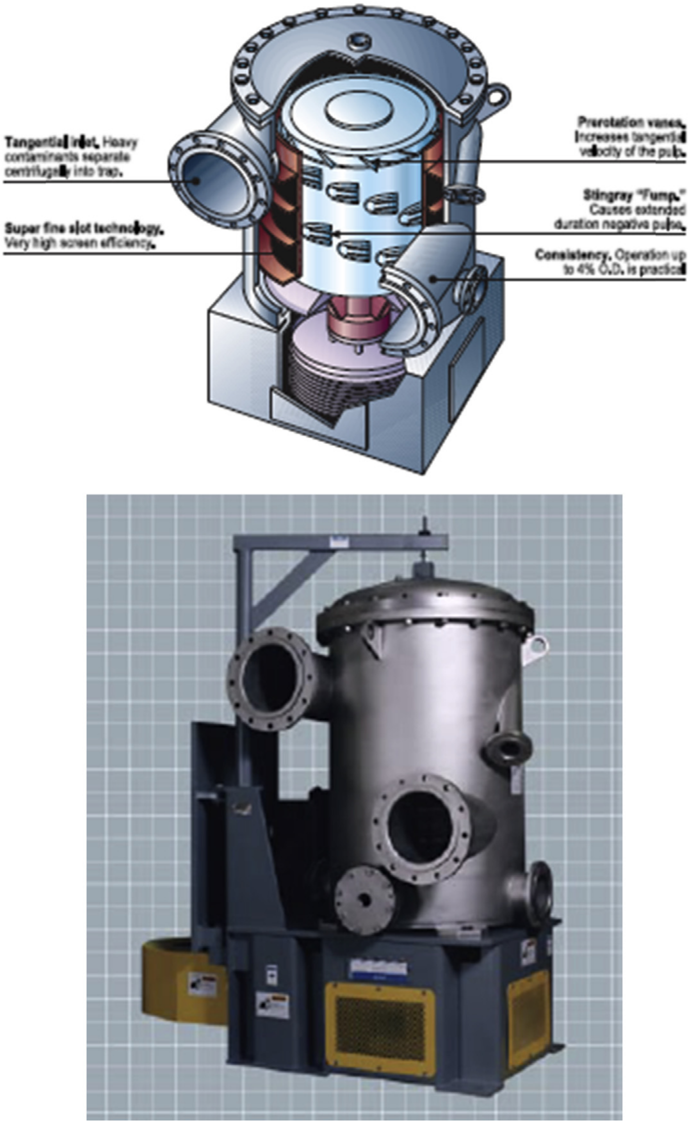


FIGURE 16.1 IMPCO HI-Q fine screen. *Courtesy GLV.*

the production of high-value products. A pressure screen contains two major components: the screen cylinder and rotor. When the unscreened pulp goes into the screen via the feed stream, the accept fibers pass through small holes or slots in the screen cylinder to the accept stream, whereas the oversized particles continue down the length of the cylinder to the reject stream. The rotor uses a foil to which it generates pressure pulses at the screen surface to

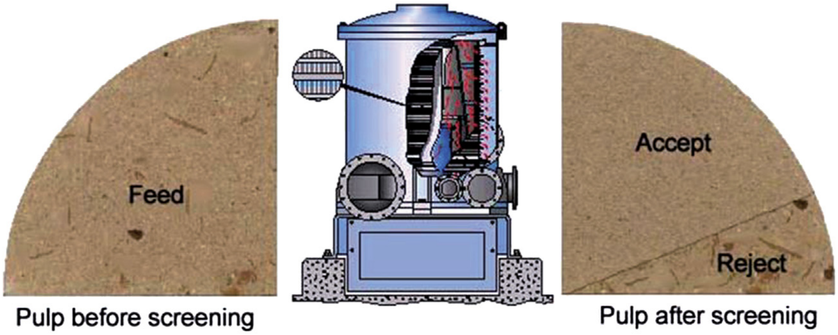


FIGURE 16.2 Principle of screening in a pressure screen. *Courtesy Metso.*

backflush the narrow slotted apertures, clearing them of accumulations which could result in plugging. The design of the rotor and speed directly affect the maximum capacity of the screen. The pressure pulsations usually contain two components. There is a negative (or suction) component which performs the backflushing action. This should be maximized. Also, there is a positive component which can cause stickies to be extruded and forced through the slot into the accept stream. This should be minimized or removed. Earlier studies into screen rotor design have revealed that increasing the magnitude of the negative pressure pulse produced by the rotor will increase the screen capacity. The magnitude of the negative pressure pulse is proportional to the square of the rotor tip speed. Pilot-scale studies show that the maximum capacity of the screen increases approximately linearly with rotor tip speed. However, the power consumed by the rotor increases with the cube of tip speed. Therefore small increases in rotor tip speed can increase power consumption and screen operating costs significantly. For improving the power-capacity relation of a screen rotor, many studies have been conducted on the effect of rotor foil design on the magnitude of the negative pressure pulse. Fig. 16.4 shows different types of rotor, and Fig. 16.5 shows rotor types with different pulsation elements.

FIGURE 16.3 Pressure screens. *Courtesy Alliance International.*

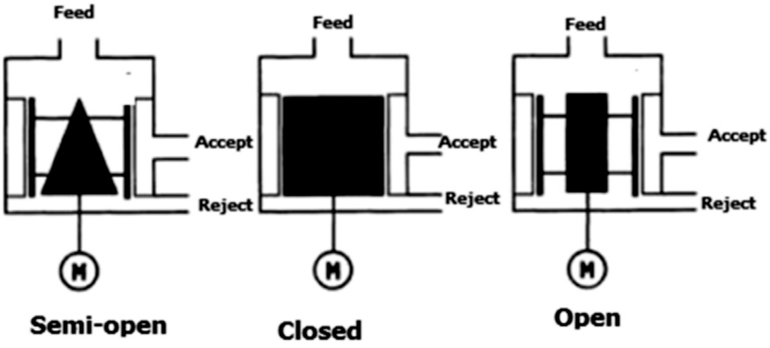


FIGURE 16.4 Different types of rotor. *Reproduced with permission from Niinimäki et al. (1996).*

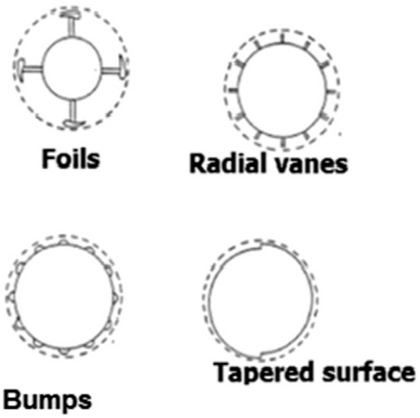


FIGURE 16.5 Rotor types with different pulsation elements. *Adapted from Bliss (1990).*

TABLE 16.2 Screening Applications

Mill Type	Screen Position	Furnish
Mechanical pulp Groundwood Thermomechanical Pressure groundwood Chemi-thermomechanical	Coarse Fine Fractionation	Softwood Hardwood
Chemical pulp Sulfite pulp Sulfate pulp	Knotter Brown stock Bleached stock Liquor filter	Softwood Hardwood
Recycled fiber Deinked pulp	Coarse Fine Fractionation	Old corrugated containers Mixed waste Old newsprint Old magazines Mixed office waste Sorted office waste Printing waste
Paper/board machine Newsprint Fine paper Cartonboard Board Tissue	Headbox Thick stock Broke Dilution Special screen	

In 2002, there were more than 250 different types of pressure screens installed in the pulp and paper mills around the world. Many of these models reflect the differing design philosophies of different manufacturers. However, this number also reflects the wide range of applications that exist within the pulp and paper industry. The operating conditions and the quality targets of the screening process actually vary with each application. In Table 16.2, the number of major product categories, the stages of screening for a particular product, and the furnishes typically used for each are presented.

16.3 SCREEN SELECTION AND FACTORS AFFECTING SCREENING PERFORMANCE

Selection of screen is a significant matter. All types of screen are not suitable for all kinds of fiber. To select a screen, several factors presented in Table 16.3 should be taken into account. Table 16.4 shows the various factors which affect the screening performance.

TABLE 16.3 Factors to Be Taken Into Consideration for Selection of Screen

Kind of fiber
Cost and repair
Power consumption
Efficiency
Capacity
Space required

TABLE 16.4 Factors Affecting the Screening Performance

Stock consistency
Type of fiber
Type and size of holes
Type of plate cleaning mechanism
Level of coarse fiber and foreign matter
Rejection rate
Flow configuration
Flow rate
Stock temperature

Water (consistency) has an important role in all the steps in the pulp screening. Water acts as a conveyer for the fiber in *screening* section. The consistency of the pulp of the storage tanks may be 3%–4%. When the pulp leaves the storage tank, the consistency should be reduced by addition of white water (previously used water). The inlet consistency of the screening equipment should be 0.35 to 0.85 for optimum result, depending on the nature of pulp. When the consistency is more than 0.85%, then the rejections will increase. The proper consistency of the stock should be 0.40%–0.50%, depending on the type of pulp screening.

Another important variable for screening performance is the diameter of the pulp screening equipment holes. It should not be more than 3/16 in. in diameter in case of coarse screen; but it is better to keep 1/8 ins in diameter. Whereas it should be 0.045 to 0.0625 in. in case of fine screen. It decides the minimum size of particle that will be rejected.

After fine screening, the rejected stock may be around 10%; it rejects such fibers that are not too coarse. Hence, the stock should be rescreened with the proper dilution to better recover. It may be coarse screen. The accepted stock of fine screening is of excellent quality for supply to the next stage.

The coarse screening removes the heavier particles, such as very coarse fibers, knots, shives, dirt, and sand, and it may be 4%–5% of the whole stock. It may differ with type of fiber and type of screening and hole diameters. The accepted stock of coarse screening is sent to the fine screening inlet side to rescreen for greater efficiency in screening section.

Besides the pulp screening equipment, the screening section may contain a centricleaner and filter for different paper grades required for producing different qualities of pulps. Centricleaners are used for separating the fine dirt from the fiber and to deliver a clean pulp suitable for bleaching.

16.4 SCREEN PLATES

Several designs of screen plate are available commercially. The screen plates can be either smooth (standard cylinder) or grooved (profile style cylinder) on the inlet surface. A grooved surface increases the capacity of the screen plate by 25%–50% or alternatively a smaller hole or narrower slot can be used. Screen plates used to separate knots have holes with a diameter of 4–6 mm. Screen plates with holes used in the fine screening of softwood pulps have holes with a diameter of 1.2–1.6 mm and in the fine screening of hardwood pulps a diameter of 1.0–1.4 mm. The holes of screen plates used in pulp screening are usually made by drilling and are conical on the back side. Screen plates with slots are made by cutting slots into the plate or by assembling a plate of wires. The slot width is in the range of 0.2–0.4 mm. Screen plates are also characterized by the percentage of open area. The percentage of open area depends on the size of openings and distance between openings. The normal range of the open area is 10%–30%. If the holes are very close, a fiber can enter two holes at once, causing fiber buildup, called stapling. Because of the risk of stapling, particularly for softwoods, a minimum distance between holes is required. This reduces the percentage of open area, particularly when small holes are used.

16.5 CENTRIFUGAL CLEANING

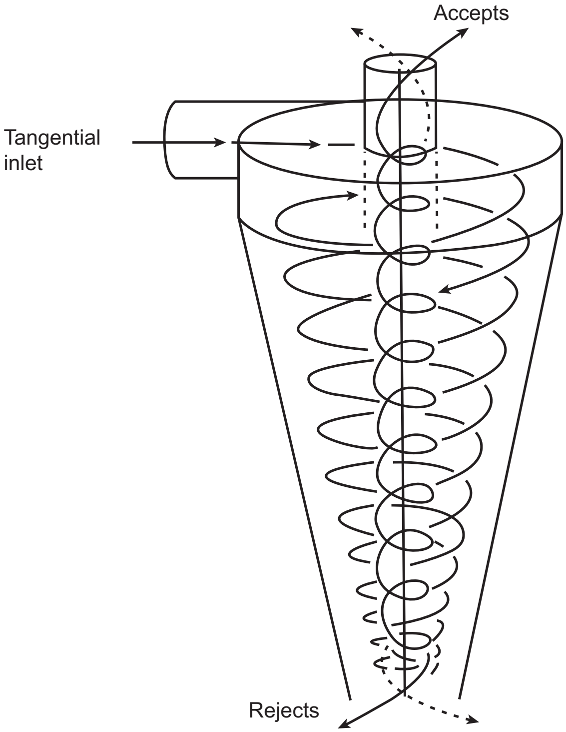


FIGURE 16.6 Schematic of a typical centrifugal cleaner.

A centrifugal cleaner (or hydrocyclone) separates components of the feed by centrifugal action. A schematic of a typical centrifugal cleaner is shown in Fig. 16.6. Cleaners are used to separate those particles which are difficult to separate with screens. Such particles in a chemical pulp fiberline are, for example, light plastic particles, bark residues, and sand. There are several names for the basic unit used in centrifugal cleaning. These are centricleaner, centrifugal cleaner, cyclone, and hydrocyclone. Generally, some kind of cleaner arrangement is required in a fiberline for producing pulp with high cleanliness and free of small particles. The cleaners are usually operated at consistencies below 1%, which make the volumes to be pumped large. The cleaners separate contaminants by centrifugal and gravitational forces; and for having large centrifugal forces, the diameter of the cleaner has to be small and the rotational speed in the cleaner has to be high. Single cleaners are thus small and have a low capacity per unit. Single cleaners are mounted in housings with many cleaners in parallel for obtaining mill installations with sufficiently high capacities. The high rotational speed inside the cleaner requires high pressure losses, and fairly high pumping costs are associated with cleaner installations.

The centrifugal action in centricleaner is not induced by rotating the equipment unlike in a centrifuge. Instead, it is induced by introducing the feed stream at relatively high velocity, tangentially into a cylindrical body. This generates a vortex, which tends to cause high-density components to move to the wall. The lower portion of the cyclone consists of a convergent cone. It is not theoretically necessary though. Material collected at the wall (the high-density fraction) is discharged from the bottom of the cone. The bulk of the flow forms an inner vortex that rises to the top of the unit and discharges through a central pipe (the vortex finder). Normally, all of the components of interest are denser than the suspending fluid (water), and all solid components will tend to be collected from the bottom (“rejects”) outlet. This includes the fiber and is responsible for the well-known “thickening effect” whereby the consistency of fiber in the rejects stream is typically about two times of that in the feed stream. So, for normal operation, all of the components are denser than water and are trying to settle. If an infinitely long residence time were available, all of the solids would report to the “rejects” outlet and no segregation would occur. In a real system, the differences in the settling rates of different solid components are relied upon.

The dense particles have to migrate through a finite distance of rotating fluid to the wall—the thickness of this rotating fluid approximates the width of the inlet flow channel. Ideally, the residence time of the hydrocyclone would be selected so that there is time for the fast settling particles (contaminants) to reach the wall and be discharged as rejects, while none of the slower settling particles (good fiber) have time to reach it. However, in practice, some of the fibers enter the hydrocyclone close to the wall and are rejected, and some of the contaminants enter the cyclone far from the wall and do not have time to migrate to it (so they are included with the accepts). Therefore separation is never perfect.

Other factors also contribute to imperfect separation. These are short-circuiting and turbulence. Some material short-circuits from the rotating outer region directly to the inner core and out through the vortex finder. Little or no separation occurs with this component. Varied factors can cause the formation of large eddies which sweep fluid from close to the wall back into the bulk region, and so negates the separation already performed on this fluid.

It is also necessary to discharge some of the inlet liquid with the rejects concentrate just to maintain movement of the rejects and avoid plugging of the bottom outlet. This fluid will have a composition similar to that of the accepts fluid, and so it represents an inevitable loss of separation efficiency.

The first two of these factors result in more contaminants appearing in the accepts than would otherwise be the case. The last factor results in the rejection of more good fiber than would otherwise occur.

16.6 PROCESSES FOR PULP SCREENING AND CLEANING

Screens and cleaners do not completely separate contaminants selectively. In the accept flow, there is always some reject, and in the reject flow, there are always accept fibers. The operation of the screen requires a low operational consistency to enable the use of screen plates with holes or slots small enough to achieve good separation efficiencies. The cleaners need to have a low operational consistency to be selective enough. Table 16.4 shows consistencies of typical pulp suspension in mill screening and cleaning installations. The pulp suspension fed into screens and cleaners is separated into two pulp streams, the accept pulp flow and the reject pulp flow. Typical reject ratios are shown in Table 16.5.

TABLE 16.5 Consistencies of Typical Pulp Suspension in Mill Screening and Cleaning Installations

3%–6% in knot separation
1%–4% in fine screening
Below 1.5% in cleaning

TABLE 16.6 Typical Reject Ratios in Different Process Stages

Typical Reject Ratios
3%–10% in knot separation
10%–20% in fine screening
15%–25% in cleaning

A high reject ratio improves the cleanliness of the accept pulp and increases the capacity of the machine. A high reject ratio, however, increases the amount of reject pulp flow to be further treated in the reject stages of the screening or cleaning plant.

Screen Rooms in a Fiberline

In a fiberline for the production of bleached kraft pulp, three screen rooms are normally needed, of which knot separation and fine screening in the brown stock area can sometimes be combined into one system. In knot separation, also called coarse screening, the pulp is screened to separate large particles of uncooked wood. The separated wood particles, mostly knots, are washed to recover accept pulp before the knots are taken to further treatment. The system also separates junk material. In the fine screening system, the pulp is screened to remove shives, chops, and other contaminants such as bark particles, plastics, and sand. Special techniques are needed to separate the light and heavy contaminants.

In the postscreening system after bleaching, the pulp is screened or cleaned to remove sand and other small particles that would be visible as dirt particles in the pulp or paper sheet. The postscreening system is usually an integrated part of the stock and short circulation system of the drying machine. Postscreening is also a barrier screening arrangement that prevents large particles from entering the pulp web; these could damage the press rolls of the pulp drying machine.

Table 16.6 shows the connection of the screening and cleaning systems of a fiberline. The postscreening stage can be bypassed if the pulp is used on-site at a paper machine that has its own adequate cleaning and screening system.

Screens and cleaners can be connected in series and in parallel. Parallel screens or cleaners are used when the capacity of a single device is not high enough to handle the total process. The reject flows are often connected in a cascade arrangement.

The process configuration of screen plants varies from mill to mill, and there are few standard solutions. Because of variations in raw materials and sources of contaminants, the screen rooms are designed to meet special local requirements.

Knot Separation

Typically, knots represent the largest fraction of impurities in the pulp coming from the digester. Knots actually are originated from the dense sections of branches and heartwood and also from oversized chips which have not been cooked down to their center. Knots are of dark color and rather large size. They can cause the failure of downstream equipment in the pulp mill if they are not efficiently removed from the pulp. Thus, knot removal (knotting) is normally carried out before washing. Knot separation from the main stream of pulp is performed in a pressure screen. The separated knots are then subjected to removal of good fibers in a secondary, atmospheric screen. Barrier screening mechanism governs both the operations.

Knot removal process uses a deknotting screen (Fig. 16.7) and knot washer. There are a number of machine alternatives available for the process. In the deknotting screen, pulp is fed tangentially, and the centrifugal forces generated by the flow speed and the rotating screen basket separate the knots to the tangential outlet. Some dilution liquor is needed to control the reject outlet flow. The foils located inside the rotating screen cylinder are stationary and generate cleaning pulses

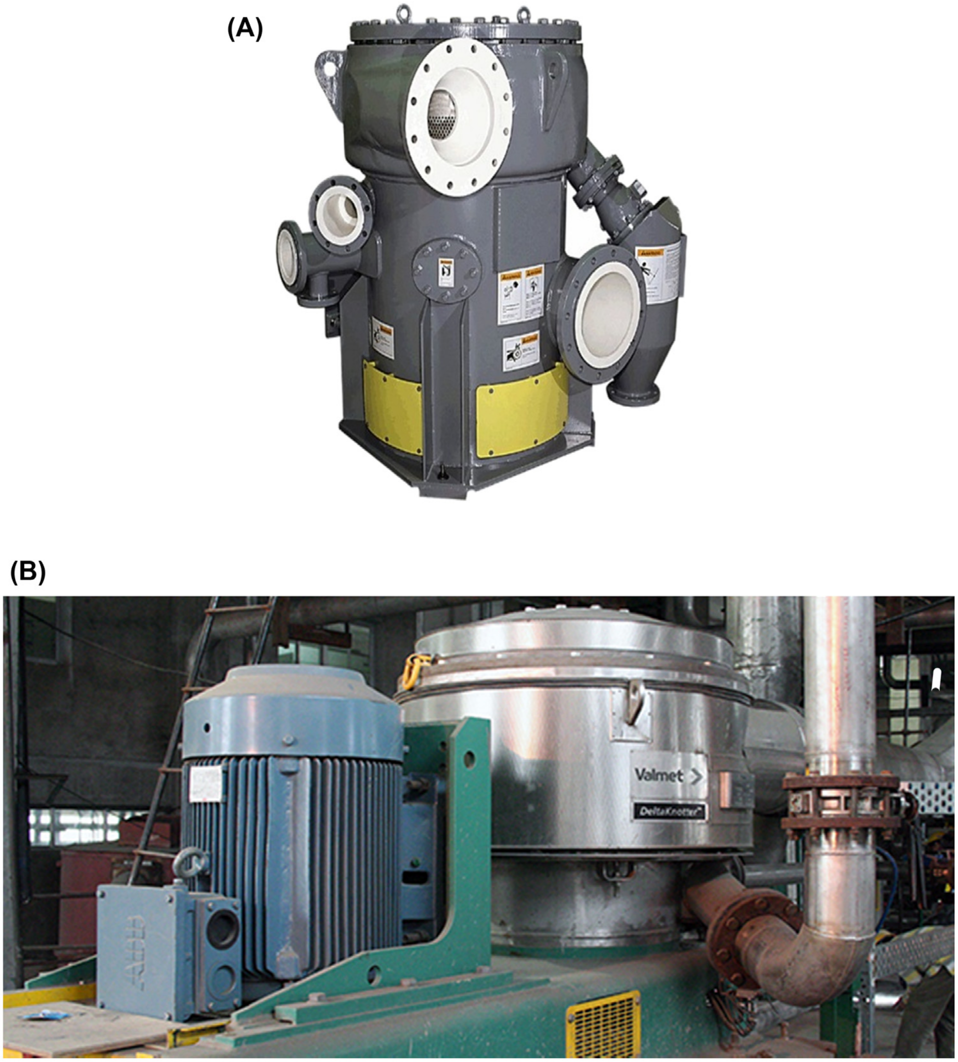


FIGURE 16.7 Knotters. (A) HI-Q Knotter. (B) DeltaKnotter. *(A) Courtesy GL&V; (B) Courtesy Valmet.*

TABLE 16.7 Screening and Cleaning Systems in a Fiberline

Coarse Stage	Junk, Knots
Fine stage	Shives, light fraction, heavy fraction
Post stage	Small impurities (bark, filler, sand); light fraction (plastics)

Knots and shives are taken back to the process and out from the process.

on the rotating cylinder. The accept fibers enter the accept chamber in the center of the machine from where there is a separate outlet.

Screening and cleaning systems in fiberline are used in coarse stage, fine stage and post stage as shown in Table 16.7.

Valmet has released a new type of combined knotter and fine screen called DeltaCombi (Fig. 16.8). This is a combined knotter and fine screen that operates in similar fashion to the DeltaScreen. In the lower section, the screen is equipped with an additional rotating screen basket with holes for knotting. The feed pulp must first pass this coarse screen basket from the outside to the inside. The pulse-generating stationary foils of the knotting section are located on the accept side of the screen basket. The coarse reject is taken out from the bottom part. The accept passing the coarse screen basket is led upwards through the rotor of the fine screen and then enters the fine screening section between the foil rotor and stationary fine screen basket.

FIGURE 16.8 DeltaCombi (combines knotter and fine screen). *Courtesy Valmet.*

The knot washers can produce knots with a solid content of above 30% and a good fiber content of less than 2%. The knot washer is a slow rotation machine that washes the fibers from the knot rejects. The pulp enters the machine from the bottom at a consistency of about 1%. The knots move up due to the action of the central screw, and the screw has wash nozzles where wash liquor is entered to wash the fibers from the knots. The fibers go out through the screen basket located around and cleaned by the central screw and are led to a separate outlet.

Brown Stock Screening

The main objective in brown stock fine screening is to separate shives. Removal of shives during screening is more difficult than that of knots. Shives cause operational problems on the paper machine. In contrast to knots, shives are mostly bleachable, but they consume higher amounts of bleaching chemicals and may still remain of darker color than the bulk of the pulp after bleaching. Shives should be removed before bleaching. Shive separation is carried out in a system consisting of a number of pressure screens. Whether shive removal follows barrier or probability screening depends on the aperture size of the screens. Shives tend to be removed increasingly by the barrier principle as the use of very narrow slotted screens is becoming common.

The shives can be refined and returned to the process, can be taken to oxygen delignification, or can be removed from the process. To enrich the shives content in the reject stream, the screening system is equipped with secondary and tertiary screening stages. More than three stages can sometimes be used.

Different kinds of contaminants such as uncooked wood particles, plastic, and sand can be separated from reject streams during fine screening. Bark originating from incomplete debarking of the wood represents one of the most challenging impurities. Bark is of dark color, has a similar density as wood, and disintegrates easily. There is actually no dedicated process for the removal of bark from pulp, but the primary removal of bark should take place in the woodyard before chipping. The remaining bark is removed from the pulp, together with other contaminants during the course of screening and cleaning.

Sand and stones mainly come along with the wood chips but may originate also from tiling or concrete tanks. Rocky material can cause equipment failure and is responsible for the wearing of equipment. The removal of stones and sand is therefore best carried out as soon as possible in the fiberline. Larger stones can be separated from the pulp by screening. Cleaning takes care of any type of rocky material, including sand. When narrow slotted screens are used in a screening application, sand is rejected on a barrier principle and carried through the subsequent screening stages. Special precautions must be taken in such a case to minimize wear in the system caused by sand accumulation.

Metals and plastic can enter the fiberline with the wood and may break away from equipment or enter the process accidentally. Like stones, metals can cause the breakdown of equipment and must be removed to protect sensitive machinery. Plastic contaminants adversely affect the quality of the final product by causing operational problems in papermaking. Because of the large density difference, metals can be easily separated from pulp by centrifugal cleaning. Plastics are generally more difficult to remove; but as certain types of plastic are less dense than pulp, they can sometimes be separated by reverse centrifugal cleaning.

Bleached Pulp Screening

The pulp needs to be cleaned to separate small colored particles before drying or papermaking. Cleaning is done in the case of bleached pulp after the bleach plant but before the pulp drying machine. When producing brown stock, the cleaning can be done in series with brown stock fine screening. The cleaning is normally done in a multistage cleaner plant at a low consistency, and the reject is removed from the process. In some installations after 1990, the first cleaner stage has been replaced by a screen equipped with narrow slots. The advantage of the system is that the consistency of the pulp can be kept at a higher level, which makes it possible to feed the pulp directly to the headbox of the pulp dryer. The cleaner consistency is usually so low that an intermediate decker is needed to raise the consistency between the cleaner plant and the headbox.

The postscreening system can be equipped with equipment for removing the junk material and plastic separation. Junk material and plastics can be separated using the cleaners designed for junk material and lightweight material separation. The screens of special design can also be used.

16.7 FRACTIONATION

Fractionation is an important objective of the screening system. In spite of the limitations placed on fractionation efficiency by screening and cleaning equipment, fractionation applications are gaining a lot of attention. The prospects of value-added, tailor-made fibers are stimulating the imagination of product developers.

In the pulp and paper industry, fiber fractionation is considered to be the process of using screens for fractionating pulp stream into two fractions. Fiber fractionation using screens is mainly based on fiber length but can also develop some differences of cross-sectional fiber dimensions, particularly if correlation exists between fiber length and the cross-sectional fiber dimensions. So far, screen fractionation has earned its biggest commercial and technical success in board mills using the recycled brown grades example, old corrugated board (OCC). After screen fractionation, thickening and refining of the long fiber fraction is performed for improving strength and print quality of the board. Multilayer applications based on these fractions have also been suggested. By the use of hydrocyclones instead of screens, a very different outcome of the fractionation process can be obtained.

Fiber fractionation is the separation of pulp fibers by quality, particularly fiber length, coarseness, or specific surface, for improving the value of the product. Value is typically realized by producing specialty products for niche markets, improving commodities, and improving uniformity. Fiber fractionation and subsequent processing of each fraction is an effective means of producing higher quality and more uniform pulp. For this reason, fiber fractionation is an important unit operation in an increasing number of pulping and papermaking applications. In thermomechanical production (TMP), fractionation of high freeness pulp and subsequent long fiber refining has shown to improve strength, whereas fractionation of low freeness pulp and long fiber refining has shown to improve optical and printing characteristics and sheet structure. In recycled fiber production, fiber fractionation and subsequent processing has shown to reduce energy consumption and improve brightness and strength. In case of softwood kraft production, fiber fractionation has been used to produce top and base stock from a single high yield cook for making multiplyboard. Also, it has been used for several other applications, including improving the reinforcing.

Pulps containing long and thick-walled fibers usually produce a higher tear index. Pulps with thin-walled fibers, and those containing fines, have higher tensile strength, internal bond strength, elongation, density, and better optical properties. The different fractions can be refined separately or treated otherwise and may then be recombined, or not. A market pulp producer having two dewatering machines may fractionate his pulp to increase the long fiber content of the furnish sent to one machine for producing a high-value reinforced pulp. A paper producer with a multilayer headbox may use the shorter fibers in the surface layers for improving sheet smoothness and optical properties, while using the longer fibers in the core for providing strength. Besides strength, fiber fractionation can also significantly improve the porosity of a pulp by removing the short fibers and fines, which reduce porosity. Overall, the fractionation of pulp creates several new opportunities for the alternative use of the fiber raw material. Nonetheless, fractionation is practicable only in mills, which can make use of all the obtained fractions.

The flow rates of the different fractions are defined by the particular application. Low reject ratio is not necessarily part of the fractionation requirements. It may be beneficial to perform fractionation using a multistage system. In contrast to contaminant removal, the efficacy of fractionation can be improved by multistage systems. The holed screens are found to fractionate better as compared with slotted ones. While feedback is very important for obtaining a higher fractionation efficiency, it has been found that both cascade and series arrangements may yield similar fractionation results at a given mass reject rate. The best obtainable fractionation occurs between about 30% and 60% mass reject ratio.

Hydrocyclones are mostly used in the pulp and paper industry to remove harmful substances from the fiber stream. In the 1960s, the ability of hydrocyclones to fractionate fibers was discovered accidentally. Earlier, the hydrocyclones were used to fractionate earlywood and latewood fibers, i.e., to separate thin-walled earlywood fibers from thick-walled latewood fibers. Later, it was found that hydrocyclones could also separate refined pulp according to the degree of fiber treatment.

Other fractionation techniques have been suggested. These are rotating atomizer, pressurized screens, the Johnson fractionator using liquid column flow or flotation. These techniques do not necessarily fractionate according to the same morphological characteristics as hydrocyclones. Fractionation using hydrocyclones makes it possible to obtain fractions with a large difference in paper properties. Significant differences in strength and surface smoothness were found when measuring the properties of handsheets made from the fine and the coarse fraction of hydrocyclone fractionated unrefined southern pine pulp. A sheet made of a high content of earlywood is dense and smooth, whereas a sheet made from latewood fibers is bulky and porous. Several patents have been granted on different hydrocyclone fractionations.

The increasing costs of raw material and energy combined with higher product quality demands have made fiber fractionation a more attractive process. Currently, the process is successfully used in removing coarse fibers in TMP production for improving product quality and saving energy. An identical approach is also used for TMP-based SC-grade production. More elaborate fractionation systems have been suggested for improving strength and reducing moisture-induced roughening of SC/LWC. The Radiclone AM80-F hydrocyclone developed by Kadant Noss AB is being used commercially (Fig. 16.9).

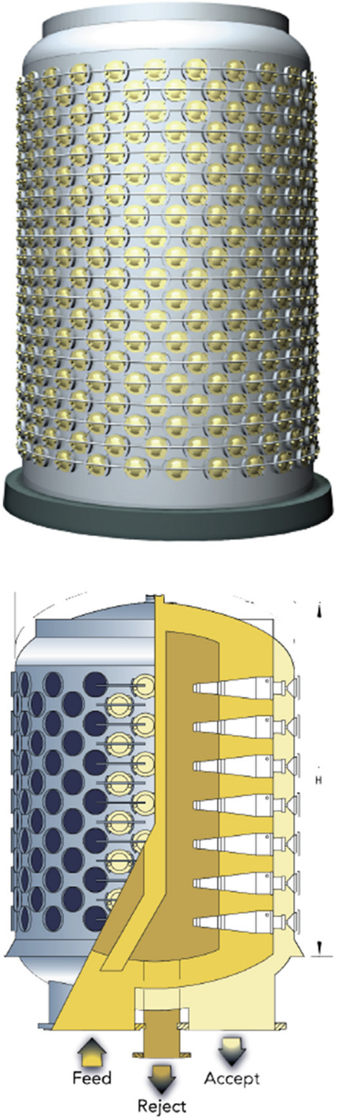


FIGURE 16.9 RADICLONE AM80. *Courtesy Kadant.*

There exist a large number of proposed future application scenarios for fractionation. Superior newsprint paper can be produced by combining multilayer forming technology with fractionation of TMP. A similar approach was suggested for production of improved multiplyboard. Furthermore, a patent US5582685 describes how fractionation can be used for the production of tissue paper at a reduced cost. Fractionation of the stock in the approach flow system in multilayer board production machines has been proposed.

Technical possibilities of eucalyptus pulp differentiation by hydrocyclone fractionation have been studied. The possibility to bleach or to enzymatically treat the fractions separately has also been examined. The economical circumstances today sometimes motivate hydrocyclone fractionation, but its widespread application is still restricted by its disadvantageous operating characteristics and its poor fractionation efficiency. For reaching an acceptable efficiency, fractionation hydrocyclones have to be operated at a low feed concentration and also as multistage processes. This in turn requires the use of an auxiliary equipment to handle and redistribute large quantities of water.

16.8 PRESSURE SCREENING VERSUS FRACTIONATION

The objective of fractionation is to classify the pulp selectively according to certain fiber properties and then to separate the flows accordingly. The separated fractions can then be used in custom-made paper products after further processing or directly. The objective of screening is to remove impurities from the pulp and to further treat the impurities. The impurities are removed from the system in case of recycled fiber. These two process stages are now very commonly linked in recycled fiber lines, particularly in the case of manufacture of linerboard. There is no established correct consistency for fractionation and screening. Excellent results for brown recycled fiber fractionation have been obtained within the range of 1.5%–2%. Fine screening with a slot basket is conducted either at a low consistency of around 1% or at a medium/high consistency of 3%–4%. Pressure screening involves either of the following two main approaches to the process:

- barrier screening
- probability screening

In simple terms, barrier screening (shown on the left side of Fig. 16.10) uses narrow slots, a low reject rate, and strong rotor foils. It ensures that particle dimensions are all greater than the size of the slots, meaning that particles too large to pass through are screened out. Probability

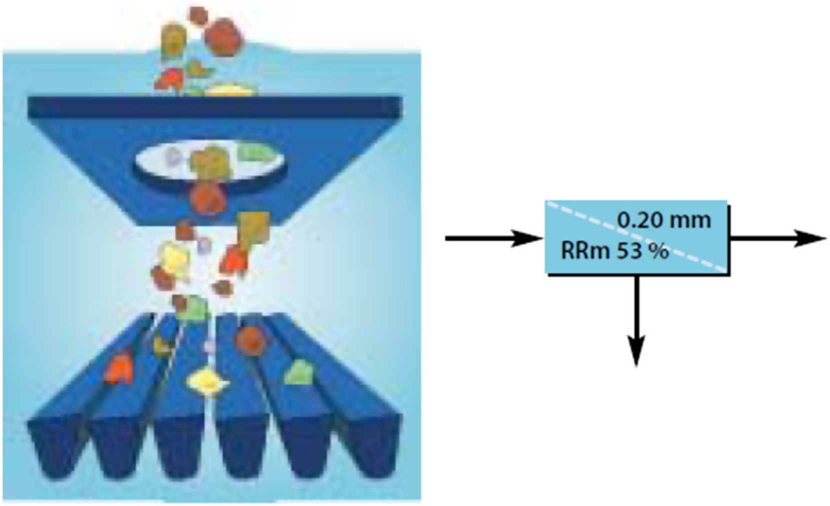


FIGURE 16.10 Barrier type (left) and fractionating probability screening (above). *Reproduced with permission from Lipponen (2003).*

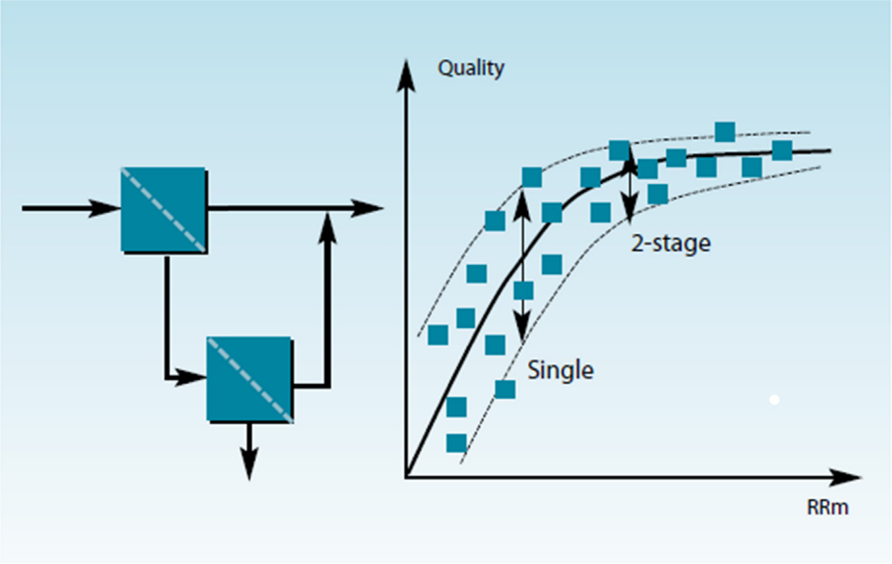


FIGURE 16.11 Two-stage fractionation produces more homogenous fractions. *Reproduced with permission from Lipponen (2003).*

screening (shown on the right side of Fig. 16.10) gives a good description of fractionation. The process operates with a high reject rate and is gentle. Probability screening ensures that at least one dimension of the removable particle is larger than the slot. A two-stage system allows operation with high reject rates on the horizontal section of a quality curve, as shown in Fig. 16.11. The system can then be optimized for the desired quality and required amount and is therefore more flexible.

16.9 ANNOTATED BIBLIOGRAPHY

Andersson R (2010). Evaluation of two hydrocyclone designs for pulp fractionation, Licentiate Thesis 2010, Royal Institute of Technology School of Chemical Science and Engineering, Department of Fibre and Polymer Technology, Stockholm, Sweden
In this thesis, evaluation of two hydrocyclone designs for pulp fractionation has been studied. The fractionation performance of the novel design was benchmarked against that of a conventional, best available technology (BAT) design. In terms of fractionation efficiency, the BAT design performed better. However, the fractions produced with the novel hydrocyclone had a much smaller difference in concentration, implying a much less pronounced enrichment of fines in the fine fraction.

Bergström J (2007). Flow field and fibre fractionation studies in Hydrocylone. Doctoral Thesis at Royal Institute of Technology, School of Chemical Science and Engineering, Department of Fibre and Polymer Technology, Stockholm Sweden.
Hydrocyclones can be used to fractionate fibers according to their papermaking potential. In this thesis, flow field and fiber fractionation studies are presented.

Bliss T (1990). Screening in the stock preparation system. Proc. Stock Preparation Short Course, Atlanta, GA, USA, 59–75.

This article presents the details of screening in the stock preparation system.

Lipponen J (2003). Narrow-Slot Basket. Technologies Open Door. To Better Fractionation, Screening. MARCH 2003 PaperAge, page no. 19–22

This article discusses some of the latest screening innovations and focuses on technological development in the screening of brown recycled fibers

Metso Application Report (2011) Screening 2611/04/03 EN • 9/2011 http://valveproducts.metso.com/documents/neles/ApplicationReports/2611_Pulp/2611_04_03en.pdf.

This report discusses principle of screening in a pressure screen and centrifugal cleaner and its operational principle.

Niinimäki J, Dahl O, Hautala J, Tirri T & Kuopanportti H (1996). Effect of feed construction on the efficiency of pressure screening. TAPPI Journal 79(11): 119–123.

This study evaluated the effects of feed direction and existence of feed chamber using long fiber yield and shive removal efficiency. Feed direction influenced partial distribution in the radial direction of the screen basket. Feed construction affects screening efficiency. Constructions without a feed chamber offer the greatest advantage.

Olson JA (2001). Fibre Length Fractionation Caused by Pulp Screening, Slotted Screen Plates. Journal of Pulp and Paper Science VOL. 27 NO. 8, 255–261.

Fiber length fractionation caused by pulp screening and slotted screen plates are presented in this paper. Fiber fractionation and selective processing of each fraction produces higher quality and more uniform pulp. Engineering efficient pressure screening systems require appropriate performance equations.

Sixta, H. (Ed.) (2006). Handbook of Pulp. WILEY-VCH Verlag GmbH & Co. KgaA, Weinheim Germany, pp. 69–107, (Chapter 3).

This is a comprehensive handbook dealing with the traditional aspects of pulping processes. It describes all pulping processes used for paper and board manufacturing, as well as waste liquor treatment, pulp bleaching, and environmental aspects, while also covering pulp properties and applications.

Smook GA (2003). Handbook for Pulp and Paper Technologists. Joint Textbook Committee of the Paper Industry of the United States and Canada, 425 p.

This book provides an introduction to the entire technology of pulp and paper manufacture, covering all aspects of pulping and papermaking.

Vinson KD (1996). Method for producing a cellulose pulp of selected fiber length and coarseness by a two-stage fractionation, Patent US5582685.

Cellulosic pulps of selected fiber morphology are disclosed as having a coarseness less than a threshold coarseness level. The threshold coarseness level is a function of average fiber length. These cellulosic pulps are particularly useful for producing paper structures such as tissue paper. A method for producing the cellulosic pulps is also disclosed.

CHAPTER

17

Kraft Spent Liquor Recovery

17.1 CHEMICAL RECOVERY

Chemical recovery is the process in which the inorganic chemicals used in pulping are recovered and regenerated for reuse. This process results in (1) recovery of the inorganic cooking chemicals, (2) generation of large amounts of heat energy by burning the organic materials derived from the wood, (3) reduction in air and water pollution by converting the waste products into useful (or at least harmless) materials, (4) regeneration of the inorganic chemicals into pulping chemicals. In summary, the recovery process for kraft pulping is (1) concentration of black liquor by evaporation; (2) combustion of strong black liquor to give the recovered inorganic chemicals in the form of smelt; the smelt, Na_2S and Na_2CO_3, dissolved in water gives green liquor; (3) preparation of the white cooking liquor from green liquor; this is done by converting the Na_2CO_3 to NaOH using $Ca(OH)_2$, which is recovered as $CaCO_3$; (4) recovery of by-products such as tall oil, energy, and turpentine; (5) regeneration of calcium carbonate, $CaCO_3$, to calcium hydroxide, $Ca(OH)_2$. Storage at all of the above steps allows the overall operation to continue even though one component requires servicing or is not operating smoothly and also accommodates surges in the system. Storage capacity of 3–24 h is common; longer down times of essential components may result in the shutdown of the entire mill. It is not uncommon, however, for a mill to ship black liquor to a nearby mill for recovery and exchange it for fresh liquor during recovery boiler rebuilding. Fig. 17.1 shows the kraft liquor recovery cycle from the point the pulp and liquor leave the blow tank to the point the liquor is ready for the green liquor clarifiers.

17.2 PULP WASHING

Pulp Washers (Brown Stock Washers)

Pulp washers are almost always drumflow or counterflow washers for separating spent pulping chemicals. Pulp washers use countercurrent flow between stages such that the pulp moves opposite in direction to the flow of wash water as described in Chapter 12, Volume 1. This design allows for the most removal of pulping chemicals (for recovery) and lignin (to reduce bleaching chemical demand or improve papermaking with brown papers) with the least amount of water. The dilution factor is a measure of the amount of water used in washing compared with the amount theoretically required to displace the liquor from the thickened pulp; it is reported as mass of water per mass of dry pulp. A low dilution factor decreases the energy requirements of the multiple-effect evaporators (MEEs). Using more washers increases removal of pulping chemicals with less water dilution but increases capital and

https://doi.org/10.1016/B978-0-12-814240-0.00017-3

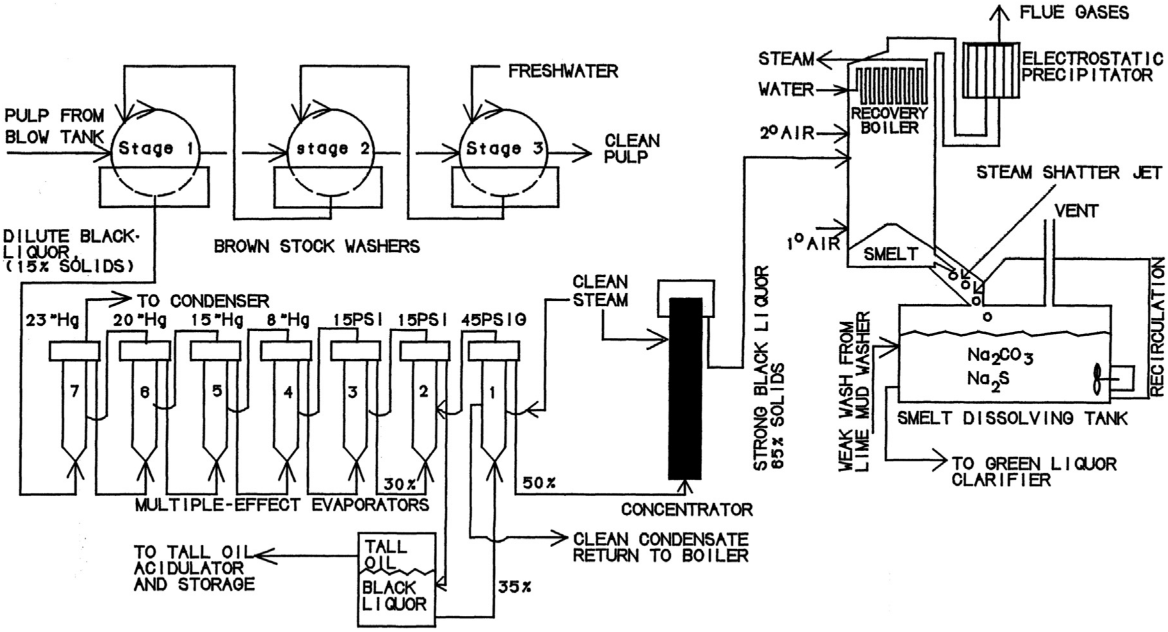


FIGURE 17.1 The liquor recovery cycle in a kraft mill before causticizing. (Not to scale and liquor storage points are not shown.)

operating costs. Usually three or four washers in series are used with about 2–3 tons of water being added to the black liquor per ton of pulp to recover over 96% of the pulping chemicals. Washing of some entrained material occurs at the repulpers (shown in Fig. 17.2) used between the washers. The two fundamental controls are drum speed and stock inlet flow rate. Soda loss in the pulp is traditionally measured as lb/ton pulp on a Na_2SO_4 basis. This alone is not a good indicator of washing efficiency because 12–15 kg/t (25–30 lb/ton) soda (as Na_2SO_4) is chemically bound to the pulp, presumably to the carboxylate groups much like an ionic exchange resin. Resinous species such as the pines tend to foam and require larger washers and filtrate tanks or the use of large amounts of defoamers. Linerboard mills often use excess paper machine white water in the brown stock washers because it is not overly contaminated with filler and additives. A *drop leg* is used to siphon the water from the washer so that a vacuum pump is not usually required. The bottom end of the drop leg goes to a filtrate storage tank that is designed to prevent air from entering the bottom end of the drop leg. The drop leg supplies a vacuum on the order of 24 kPa below atmospheric pressure (7 in. Hg below atmospheric pressure) for the first stage, 30 kPa (9 in. Hg) for the second stage, and 40 kPa (12 in. Hg) for the third stage. The overall drop leg length is about 12–14 m (40–45 ft) with 3 m (10 ft) within the filtrate tank yielding an effective length of 10 m (30–35 ft). The actual vacuum is lowered proportionally to the air bubble content of the pulp slurry. The drop leg is ideally a vertical drop. If a horizontal section is needed, it should be exactly horizontal and placed at least 7 m (22 ft) below the washer. Drop legs that are not entirely horizontal or vertical allow air to separate from the stock and rush upward, thereby accumulating and decreasing the vacuum.

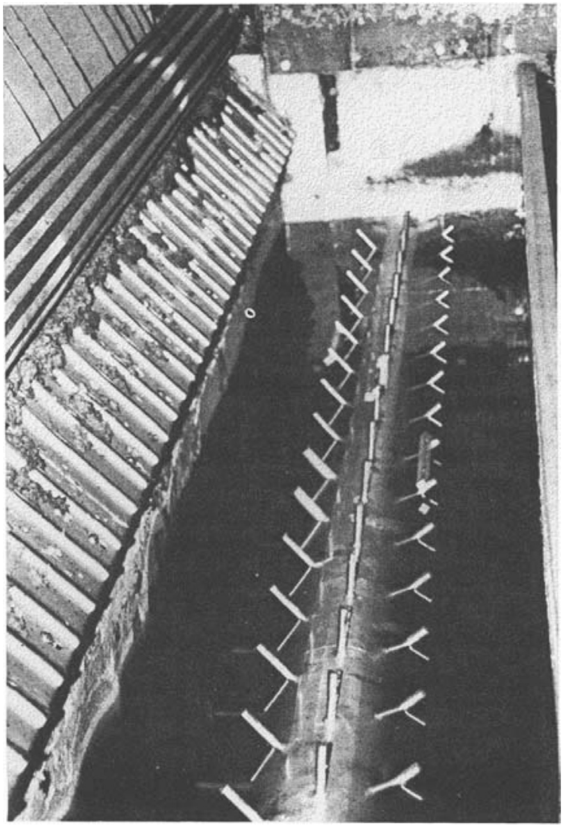


FIGURE 17.2 A repulper after a pulp washer.

17.3 LIQUOR EVAPORATION

Black Liquor Behavior During Evaporation

It is desirable to concentrate the solids of the black liquor as much as possible to make heat recovery from liquor combustion as efficient as possible, but when the black liquor reaches high solids contents, the viscosity increases drastically (Chapter 13, Volume 1). Combustion of highly concentrated black liquor leads to higher temperatures in the lower part of the furnace, which increases the rate of smelt reduction and decreases sulfur emissions. Black liquor is most often burned at 65%–73% solids content in conventional commercial systems. Some systems allow black liquor combustion at 75%–80% solids content, but only a few mills use these systems. Sometimes the viscosity of certain black liquors (e.g., from straw pulping) can be decreased by holding the concentrated black liquor at 115°C (240°F) for several hours. Like any aqueous solution, the boiling point of black liquor increases with increasing solids content. The boiling point rise (relative to water) is about 3°C (6°F) at 33% solids, 8°C (14°F) at 50% solids, 13°C (23°F) at 67% solids, 17°C (30°F) at 75% solids, and 21°C (37°F) at 80% solids. This is the overall solids content; not all of this is actually in solution because, when black liquor is concentrated above 55%, burkeite ($2Na_2SO_4 \cdot Na_2CO_3$), etc. precipitates as scale.

Multiple-Effect Evaporators

MEEs contain several units (effects) that are connected in series by vapor piping. The water vapor boiled off from the liquor in one effect acts as heating steam in the steam chest of the following effect. Most black liquor is concentrated in MEEs.

MEEs are used for black liquor processing. The term multiple effect comes from the multiple effective use of energy to perform the evaporation task. In such a configuration, live steam is condensed only in the first effect evaporator, producing vapors that are then sent to condense in a second effect where additional evaporation takes place. The process can then be repeated until reaching the last effect evaporator where the vapors produced are condensed in a condenser using cooling water. Steam generation in the kraft mill is a significant operating expense, and every effort should be made to conserve its use. The evaporation plant is by far the major consumer of that steam for the removal of water from the weak black liquor. Economic operation of the evaporator is therefore predicated on the multiple effective use of the heat available from the steam and therefore on the number of effects in the MEE.

The MEEs are a series of four to eight evaporators with indirect heating for removing water from the dilute black liquor coming from the pulp washers. Traditionally, long-tube vertical (LTV) bodies were used, but recently, falling film evaporators have also been installed. Later effects are operated under vacuum to achieve evaporation within the desired temperature range. The black liquor leaves at 50% solids. In North America, the water evaporated from the concentrated black liquor of one effect is used as steam in the previous effect. (In Europe, the operation is often partially cocurrent to avoid scaling that occurs when the hottest steam contacts the most concentrated liquor). Stated conversely, each effect acts as a surface condenser for the previous effect. Fig. 17.3 shows the arrangement of a set of evaporators. For example, 100 lb of black liquor containing 15 lb of solids and 85 lb of water is evaporated to 30 lb; with a steam economy of 5.0 it would take 14 lb of steam to remove the 70 lb of water. The steam economy is about 0.8 per effect. An overall steam economy of 4–5, depending on the number of effects, is normally good for mill operation. If this stage is a bottleneck, lower steam economy is sacrificed for higher throughput. The initial steam introduced at the first effect comes from the boiler, and its condensate is returned to the boiler. The subsequent condensates are contaminated with volatile black liquor components and are usually sent to the sewer.

$$\text{steam economy} = \frac{\text{water mass evaporated}}{\text{mass of steam used}}$$

Long-Tube Vertical Bodies

The climbing film, LTV evaporator has become the standard system for concentrating black liquor. These evaporators came into use during the 1920s and 1930s. The LTV evaporator is still the most widely used type of evaporator.

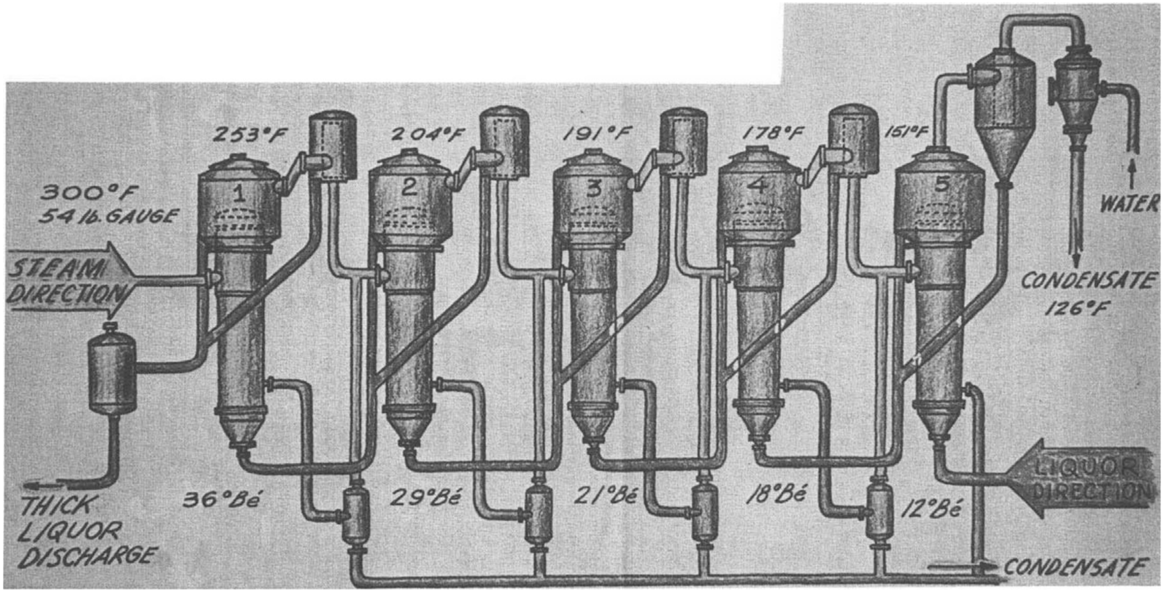


FIGURE 17.3 Five-effect black liquor concentration. *From J. Ainsworth,* Papermaking, *©1957 Thilmany Paper Co., with permission.*

Traditionally, each effect consists of a LTV evaporator (Fig. 17.4). Several LTV bodies are shown in Fig. 17.5. Black liquor rises up the heat exchanger area until it reaches the vapor dome at the top. In the vapor dome, steam flashes from the black liquor and is pulled by vacuum to the next effect as the steam source. The shell of the evaporator is usually 12.5-mm (0.5 in.) steel plate. The heat exchanger consists of 2 in. diameter tubes from 14 to 32 ft long. Stainless steel is often used in the first two effects where the liquor is warmest and most concentrated. The first effect is operated at 50 psig and 150°C (300°F), whereas the last effect is about 27 in. Hg vacuum and 46°C (115°F).

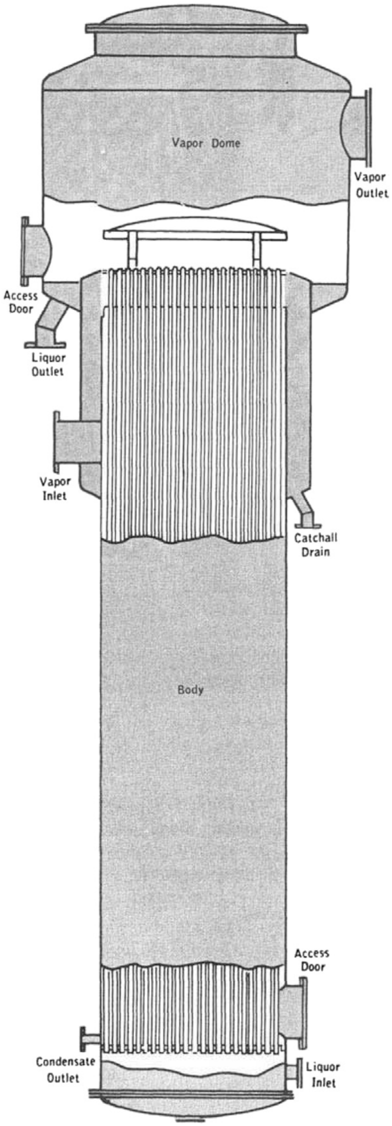


FIGURE 17.4 Long-tube vertical evaporator. *Reprinted from* Making Pulp and Paper, *©1967 Crown Zellerbach Corp., with permission.*

Falling Film Evaporators

Falling film evaporators are used much like conventional evaporators, except the mechanism of evaporation in each stage is different. These evaporators are being used in many countries to produce black liquor slurry with up to 80% solids content for firing in the recovery boiler (Vakkilainen and Holm, 2000). This evaporator design relies either on tubes or on plates as heat transfer surfaces. In tubular units, liquor is processed on the inside of the surface, whereas in plate designs, the liquor is processed on the outside of the heat transfer surface.

In each stage, steam (or sometimes hot water in the first stage) is used as the heat source and flows between stainless steel plates about 30 mm (1.25 in.) apart. Large banks of these plates are aligned radially outward in each effect. Dimples in the metal plates keep the plates a fixed distance apart and increase the strength of the metal plates. Fig. 17.6 shows a section of the plates.

The black liquor is introduced at the top of the evaporator and flows down the opposite side of the metal plates where the dimples help spread the black liquor into a thin film. The falling film plate design allows for selective condensation of the vapors boiled from the black liquor of previous effects. About 65% of the methanol and BOD is concentrated in 6% of the overall condensate stream in the upper portion of the plates to give *foul condensate segregation.* The remaining condensate is collected from the lower

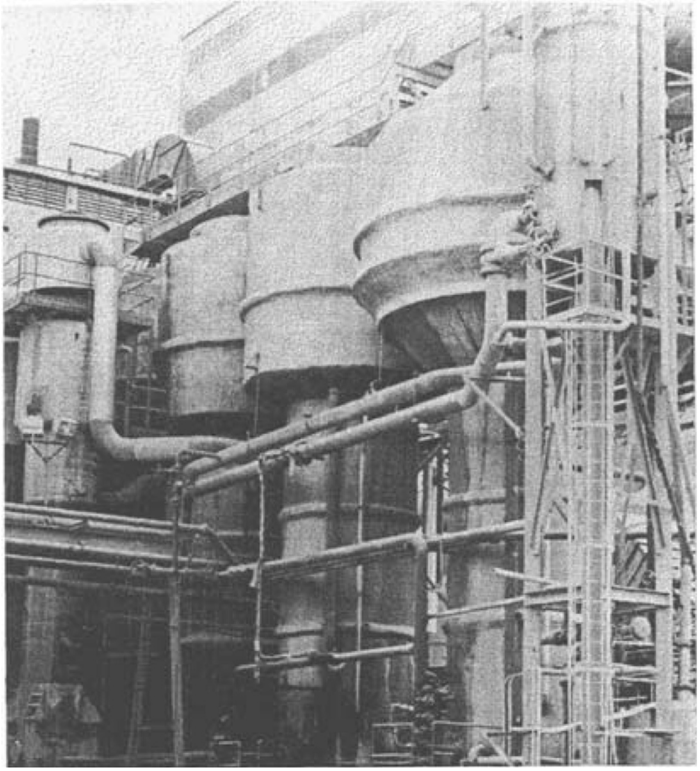


FIGURE 17.5 A series of long-tube vertical bodies (the multiple-effect evaporators).

portion of the plates and is suitable for brown stock washing.

Falling film plate evaporators are less subject to fouling than LTV and require boilouts much less often. They also operate at a lower overall vacuum than conventional evaporators with the last stage operating at 26 in. Hg. Black liquor must be recirculated within each stage. For example, the fourth stage of one operation uses 10,000 gal/min recirculation with a liquor feed of 900 gal/min at 14% solids and an outlet of 450 gal/min at 26% solids. Some of the fourth effect concentrated liquor can be used to concentrate the infeed of the third effect because liquor at low to intermediate concentrations tends to foam, a big problem with large recirculation rates. Falling film evaporators can be used in conjunction with blow heat recovery at mills using batch digesters because lower temperature gradients are required. The steam discharged during blowing is used to heat large quantities of water. The hot water is then used in liquor evaporation until the next digester blow reheats it. This provides a leveling effect for the intermittent heat generation of blowing with batch digesters.

Direct Contact (Cascade) Evaporator

The direct contact evaporator is a chamber where black liquor of 50% solids content directly contacts the hot flue gases from the recovery furnace. The final black liquor concentration is 65%–70% solids. This method is now obsolete because high sulfur emissions result as the hot CO_2-containing flue gases strip sulfide from the

FIGURE 17.6 A small section of a falling film evaporator plate (wood-grain table background).

black liquor. Also, indirect concentrators allow higher energy recoveries. A few mills that have recovery boilers installed before the early 1960s still use this method. This process, before being replaced by concentrators, required partial *black liquor oxidation.* In this process, the black liquor enters a chamber where it is mixed with air (or oxygen) to convert reduced sulfides, such as $(CH_3)_2S$ and S^{2-}, to oxidized forms of sulfur and thereby minimize sulfur emissions (Chapter 15, Volume 2). The reason this is required is that the CO_2 in the flue gases exists as the acid H_2CO_3, which lowers the pH of black liquor, stripping H_2S from it. This process is not necessary with indirect concentrators because the pH of the black liquor remains high before combustion. Three types of direct contact evaporators have been used:

- Cascade evaporators (CE)
- Cyclone evaporators (B&W)
- Venturi scrubbers (B&W)

Concentrators, Indirect Concentrators

Indirect concentrators (used in so-called *low odor recovery boilers)* are forced circulation or falling film steam heated evaporators used to concentrate black liquor in the range where burkeite precipitates as scale. Because concentrators are more energy efficient and environmentally sound than direct contact evaporators, they have largely replaced direct contact evaporators since their introduction in the mid-1960s. The final solids content of the black liquor is about 65%−70% with a fuel value of 14−16 MJ/kg (6000−7000 Btu/lb) compared with coal that is 32 MJ/kg (14,000 Btu/lb). Although a very high solids content in black liquor is desired to increase combustion efficiency, the viscosity increases quickly with solids contents above 65% −70%, and the black liquor becomes too thick to pump even at elevated temperatures.

Tall Oil

Tall oil is a by-product mixture of saponified fatty acids (30%−60%), resin acids (40%−60%, including mostly abietic and pimaric acids), and unsaponifiables (5%−10%) derived from the wood extractives of softwoods. Crude tall oil is isolated from acidified skimming of partially concentrated black liquor. It is collected and refined at special plants. The refined products are sold commercially for soaps, rosin size, etc. Typically, 30−50 kg/t (60−100 lbs/ton) on pulp may be recovered from highly resinous species representing about 30%−70% recovery. It is recovered from mills pulping resinous species such as the southern pines. The pulp and paper industry recovers about 450,000 tons of crude tall oil annually.

Turpentine

Turpentine is a mixture of volatile extractives (monoterpenes) collected during digester heating. In batch digesters, most of it is collected before the digester temperature reaches 132°C (270°F). It is collected from the digester relief gases and sold for solvents and limited disinfectants used in household pine oil cleaners. Because terpenes are volatile, the recovery can decrease by 50% with outside chip storage of a few weeks. It is often standard practice at mills recovering turpentine to use a portion of green (fresh) wood chips in the digester feed to reduce turpentine loss, while the balance is used from chips rotated in inventory. Fresh wood of loblolly and short leaf pines yield about 6—12 L/t (1.5—3 gal/ton) air dry pulp, whereas slash and longleaf pine yield 10—18 L/t (2.5—4.5 gal/ton). The US pulp industry recovers about 30 million gallons of turpentine annually.

Kraft Lignin

Some black liquor is recovered by acidification and used as dispersants, phenol-formaldehyde adhesive extenders, and binders in printing inks. For example, Indulin is Westvaco's trade name for kraft lignins of various grades. Dimethylsulfoxide (DMSO, a solvent and controversial healing remedy) can also be recovered from kraft lignin. However, kraft lignin is not isolated and marketed to the same degree that lignosulfonates from sulfite pulping methods have been. Calcium lignosulfonates were a waste problem, which were marketed as a "solution in search of a problem."

17.4 RECOVERY BOILER

Recovery Boiler or Recovery Furnace

The development of the recovery boiler by Tomlinson in conjunction with Babcock & Wilcox in the early 1930s led to the predominance of the kraft process. Fig. 17.7 shows a typical recovery boiler design, while Fig. 17.8 compares two types of boilers with widespread use. Fig. 17.9 shows a recovery boiler building at a brown paper mill. The purpose of the recovery boiler is to recover the inorganic chemicals as smelt (sodium carbonate and sodium sulfide), burn the organic chemicals so they are not discharged from the mill as pollutants, and recover the heat of combustion in the form of steam. The latter is accomplished by large numbers of carbon steel tubes filled with circulating water or steam to recover heat from the walls of the recovery boiler and the flue gases. Fig. 17.10 shows some banks of tubes to be installed into a recovery boiler.

In Finland and Sweden, the outer surfaces of these tubes are clad with stainless steel to greatly increase their life. Some recovery boilers in the United States are equipped with stainless steel clad tubes as well, but it is not a widespread practice. Combustion Engineering has used a "chromizing" process where chromium is incorporated "in" the surface to produce a stainless steel—like surface. The recovery boiler or furnace burns the concentrated black liquor by spraying it into the furnace through side openings (Plate 17.1). The water evaporates, and the organic materials removed from the wood form a char and then burn. There are three zones: The upper section is the *oxidizing zone*, the middle section (where the black liquor is injected) is the *drying zone*, and the bottom section is the *reducing zone* where, in a bottom bed of char, the sulfur compounds are converted to Na_2S. The remaining NaOH and sodium salts of organic acids are converted to Na_2CO_3. These sulfur- and sodium-based inorganic materials leave as molten slag that is directed to the green liquor dissolving tank (Plate 17.2). Because of the possible adverse reaction of molten smelt with water, all recovery boilers have an *emergency shutdown procedure* in the event of trouble! The recovery

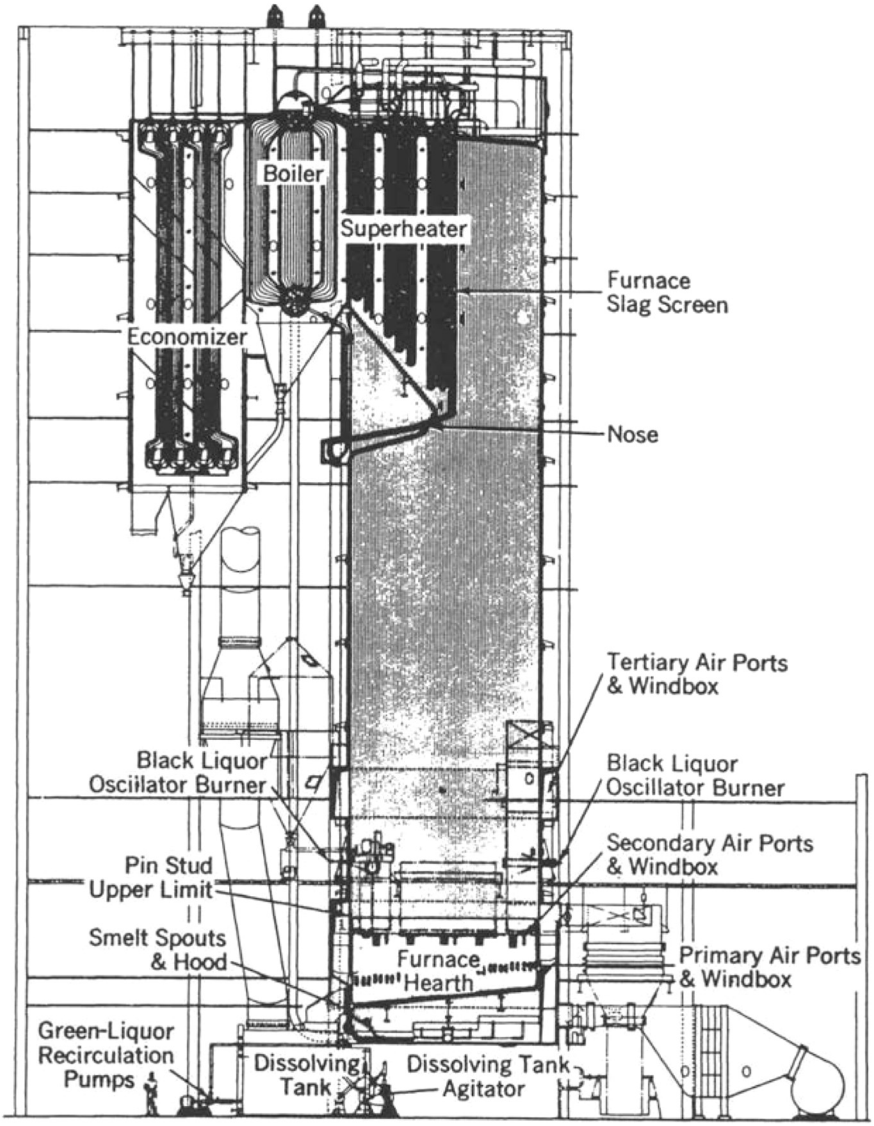


FIGURE 17.7 Kraft recovery boiler from Babcock & Wilcox. *From Stultz, Steven and Kitto, John B (1992).*

boiler is the largest, single, most expensive piece of equipment in a kraft mill costing over \$100 million; hence, in many mills the recovery boiler limits the maximum production. The newest recovery boilers may support 2500–3000 tons of pulp production per day. The overall chemical reactions in the recovery boiler in addition to combustion are: conversion of sodium salts:

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$

reduction of makeup chemical:

$$Na_2SO_4 + 4C \rightleftarrows Na_2S + 4CO$$

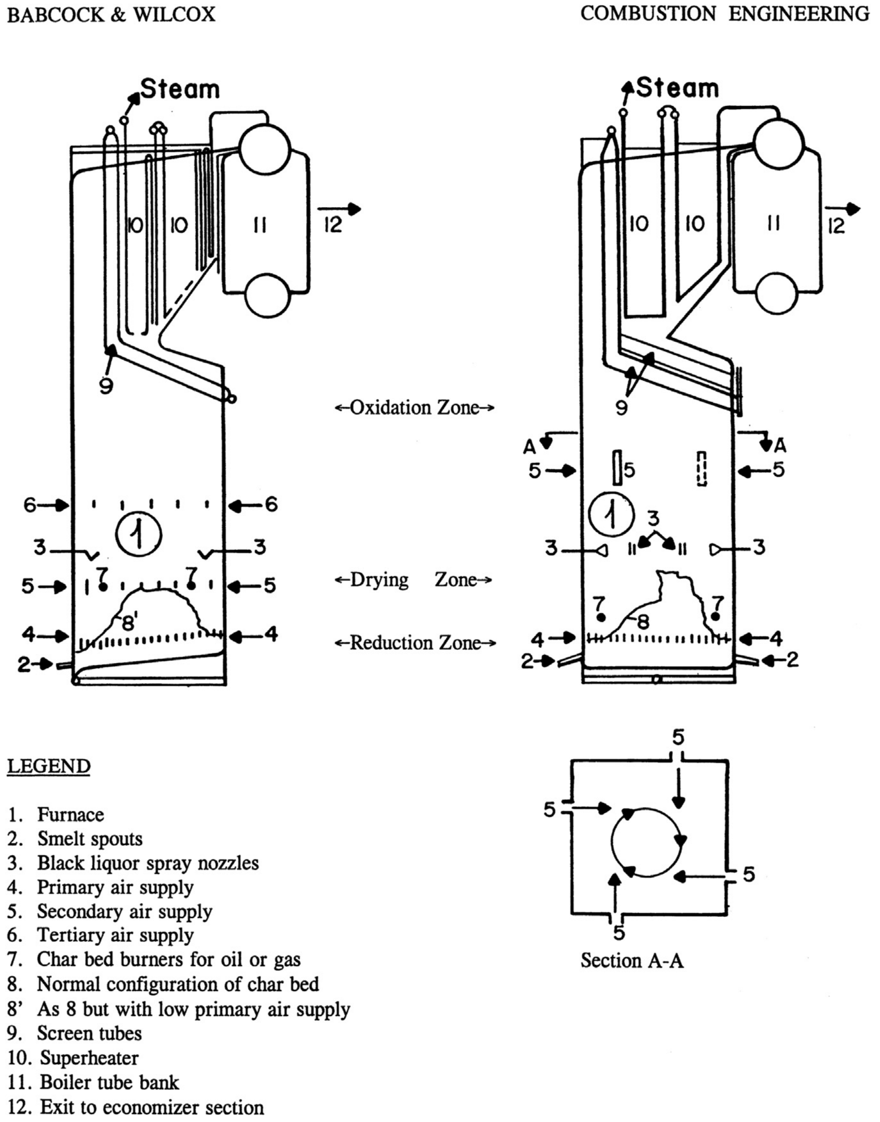


FIGURE 17.8 Principal design and air distribution of two recovery boiler designs. *From Stultz, Steven and Kitto, John B (1992).*

The lower zone is deficient in oxygen, so reduction reactions occur. This allows the sulfur in the smelt to occur as Na_2S and not $Na_2S_2O_3$ or Na_2SO_4, which would be unsuitable for fresh liquor. About 40%—50% of the air required for combustion is added by forced draft fans at the primary vents at the bottom of the recovery boiler. The primary air supply is preheated to 150°C (300°F) and burns the organic compounds, leaving smelt, but maintains reduction conditions. The upper zone begins above the region of secondary air supply and has about 10% −20% excess air above that required for complete combustion of the organic materials. The

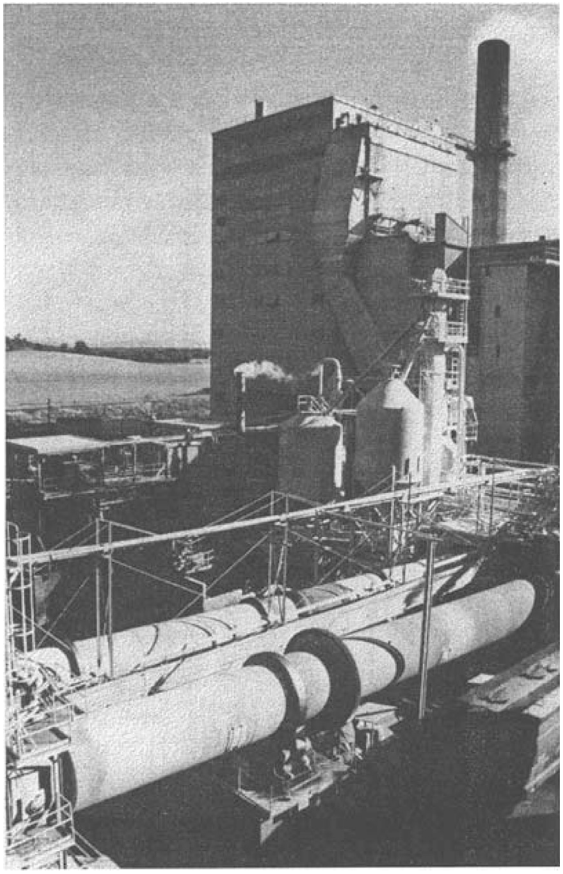


FIGURE 17.9 Kraft recovery boiler in the background and two limekilns in the foreground.

top zone must be under oxidative conditions to prevent carbon monoxide emissions. The flue gases are drawn away from the recovery boiler at the exit of the electrostatic precipitator; this maintains an air pressure below ambient so that gases will be sucked into the boiler in the vicinity of the black liquor nozzles to improve the safety of the operation. Some example reactions in each zone are:

Oxidation zone:

$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2$$

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O$$

$$Na_2S + 2O_2 \rightarrow Na_2SO_4$$

$$H_2S + 1\tfrac{1}{2}O_2 \rightarrow SO_2 + H_2O$$

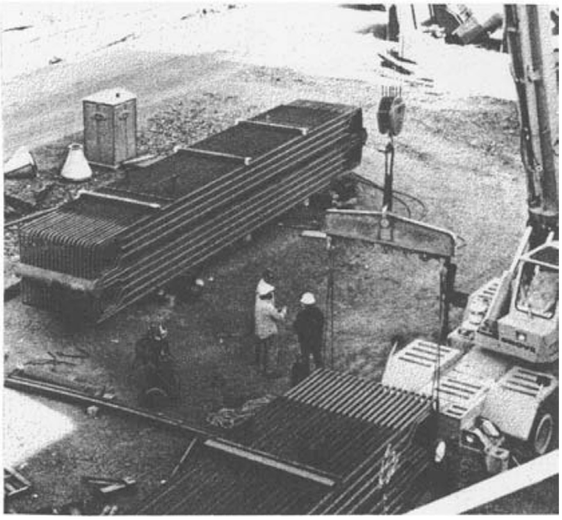


FIGURE 17.10 A small portion of the heat recovery tubes to install in a recovery boiler rebuild.

Drying zone:

$$\text{Organics} \rightarrow C + CO + H_2$$

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$

Reduction zone:

$$\text{Orgaincs} \rightarrow C + CO + H_2$$

$$2C + O_2 \rightarrow 2CO$$

$$Na_2SO_4 + 4C \rightarrow Na_2S + 4CO$$

$$C + H_2O \rightarrow CO + H_2$$

The low secondary air supply of the B&W boilers is placed about 2 m (6 ft) above the primary air supply. This air acts as secondary air along the walls of the boiler, but as primary air in the char bed and, therefore, controls the height of the bed. Additional secondary air is needed; it is called tertiary air. (By definition all nonprimary air is secondary air.) In the CE boilers a tangential air supply is used to produce a rotary movement of the furnace gases (EPA, 1976).

The maximum combustion temperature occurs between the plane of black liquor entry and plane of secondary air entrance. Firing black liquor at 65% solids leads to a maximum

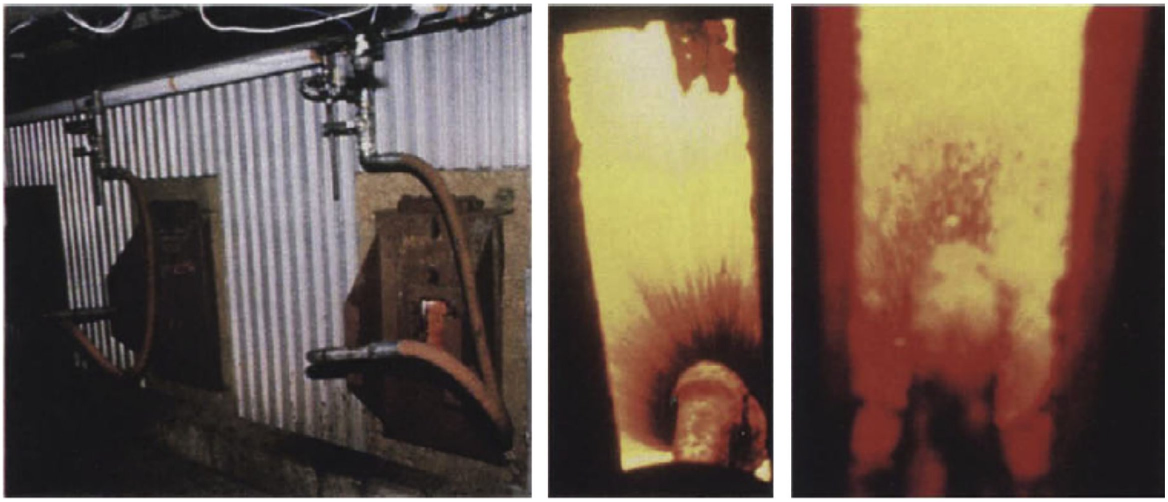


PLATE 17.1 Some black liquor guns of a kraft recovery boiler. The inserts show the liquor being fired into the furnace.

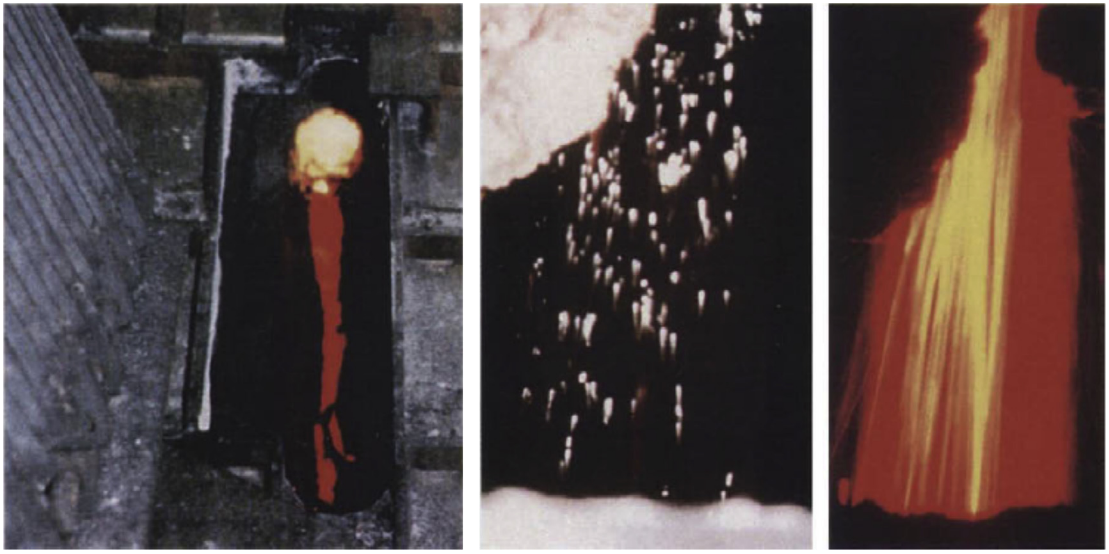


PLATE 17.2 Several views of smelt flowing from the bottom of a kraft recovery boiler.

combustion temperature of 2000–2400°F, whereas combustion at 70% solids leads to combustion temperatures greater than 2500°F. Cameras are used to monitor the appearance, size, and position of the char bed at the bottom of the recovery boiler to properly control liquor combustion.

Heat Recovery

The maximum temperature in the recovery boiler is about 1100–1300°C (2000–2400°F) for black liquor burned at 65% solids. The heat of combustion of the organic materials is transferred to tubes filled with water in several areas:

in the walls of the recovery boiler, in the *boiler* section, and in the *economizer* section. The economizer section is a final set of tubes (from the point of view of the exhaust gases, but the first tubes the water travels through) used in more recent recovery boilers to warm water for various processes. The *thermal efficiency*, defined below, is the proportion of heat recovered as steam and is about 60%. Most of the heat loss occurs as steam in the flue gases from water in the black liquor.

$$\text{thermal efficiency} = \frac{\text{heat to steam}}{\text{total heat input}}$$

The minimum temperature of the exhaust gases is 130°C (265°F) to prevent condensation of corrosive materials and to insure the exhaust will go upward beyond the smokestack. The combustion gases cool by radiation to about 870°C (1600°F) before entering the convection heating tubes. Temperatures above this, which might result by overloading the recovery boiler, do not allow complete combustion of the organics, which causes fouling of the screens and superheater tubes by tacky soot particles. The flue gases are cooled to about 450°C (850°F) after the boiler and to 160°C (320°F) after the economizer. (With direct contact evaporation, the flue gases leave the economizer section at 400°C.) About 6000–7000 kg/t (12,000–14,000 lb/ton) steam on pulp are produced by the recovery boiler.

Cogeneration

Cogeneration is the process of producing electricity from steam (or other hot gases) and using the waste heat as steam in chemical processes. In contrast, a stand-alone power-producing plant typically converts less than 40% of the heat energy of fuel (coal, natural gas, nuclear, etc.) into electricity. The remaining heat is simply lost to the heat sink; the heat sink lowers T_{cold} to increase the efficiency and is usually a large body of water where the effects of thermal pollution must be considered. The *Carnot cycle*, which predicts the maximum possible efficiency for the conversion of heat to work, of a heat engine is:

$$e_{\text{rev}} = 1 - T_{\text{cold}}/T_{\text{hot}} = (T_{\text{hot}} - T_{\text{cold}})/T_{\text{hot}}$$

where T is expressed in an absolute temperature scale such as Kelvin, T_{hot} is the temperature of the steam entering the turbine, and T_{cold} is the temperature of the steam exiting the turbine. Because pulp mills (both chemical and most mechanical) can use the steam coming out of the turbine and would produce steam in any case, these mills can essentially convert heat energy into electricity with over 80% efficiency. Surprisingly, many pulp mills do not cogenerate. This is particularly true in the northwestern United States where electric companies and relatively cheap hydroelectricity have discouraged this.

Electrostatic Precipitators (Cottrell)

Electrostatic precipitators (ESP, Fig. 17.11) consist of chambers filled with metal plates, charged with high DC voltage (30,000–80,000 V) through which exhaust gases from the recovery furnace pass. The chambers remove solid materials (particulates) in the gas stream that acquire a charge from the high voltage and collect on the plates, thereby

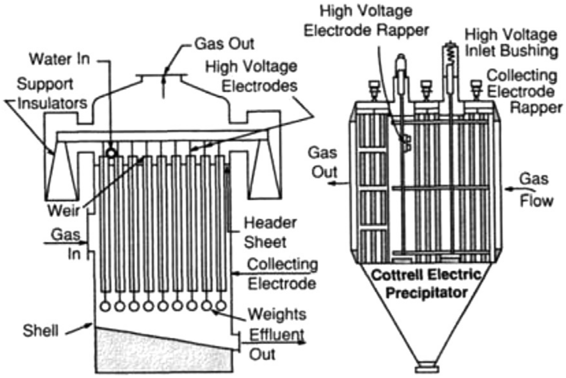


FIGURE 17.11 Cottrell electrostatic precipitator. *Redrawn from J. Ainsworth,* Papermaking, *1957 Thilmany Paper Co., with permission.*

purifying the stream before it is discharged into the atmosphere. Removal of over 99% of the particulates over 0.1/μm can be achieved. The current required is on the order of 500 mA/1000 m^2 (50 mA/1000 ft^2) of plate area. Rapping the plates with a shock wave dislodges the particulates into a collecting tray placed below them. Much of the material collected is sodium sulfate and sodium carbonate, typically 5–20 kg (10–40 lb) per ton pulp, which is returned to the recovery boiler. Electrostatic precipitators are now used on many new limekilns as well.

17.5 COOKING LIQUOR REGENERATION—THE CAUSTICIZING PROCESS

Chemical Recovery

The chemical recovery cycle is summarized in Fig. 17.12. Inorganic pulping chemicals are recovered from the furnace as a molten smelt (Na_2CO_3 and Na_2S) that falls to the bottom of the furnace. These are dissolved in water to give green liquor. The combination of molten smelt and large quantities of water in the heat exchanger tubes make recovery boilers potentially explosive, a critical concern at all times. The green liquor is treated with $Ca(OH)_2$ to regenerate the NaOH. The $CaCO_3$ that is formed must go through the limekiln to generate CaO that is later dissolved in water to regenerate $Ca(OH)_2$.

Green Liquor (Dissolving) Tank

Water (from the dregs washer) fills the green liquor dissolving tank, which is located below the kraft recovery furnace, where the molten slag is added through the smelt spout to form green liquor (mainly Na_2CO_3 and Na_2S). A *steam shatter jet* and recirculated green liquor impinges on the smelt stream to break it into small pieces. If the steam shatter jet fails, major explosions

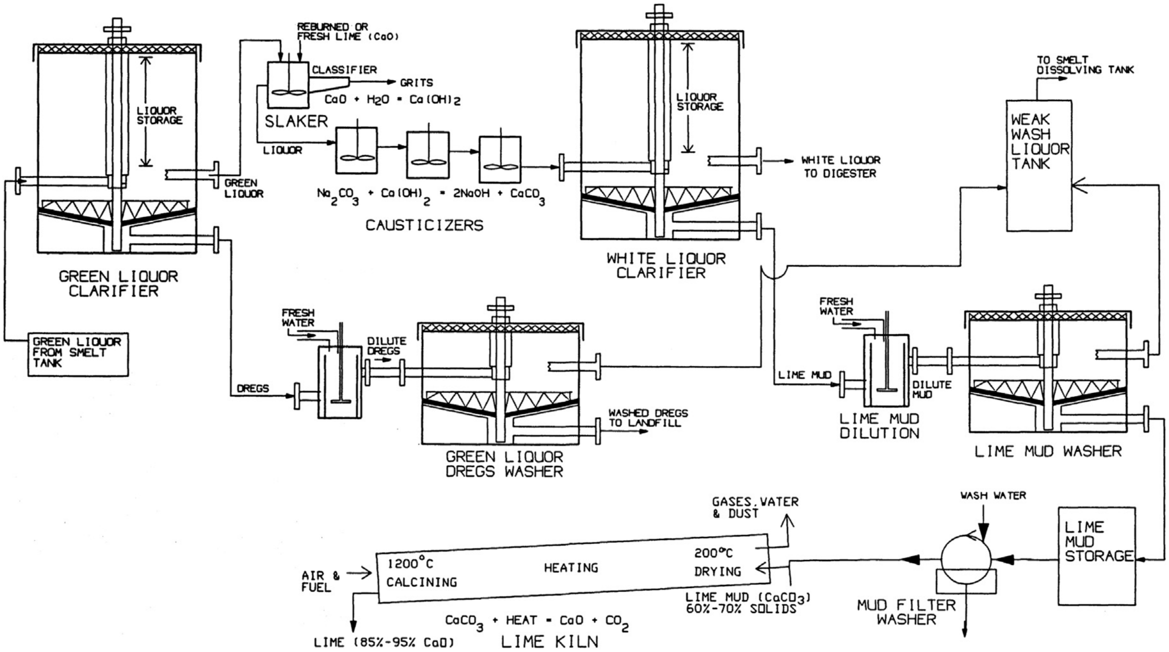


FIGURE 17.12 A summary of the causticizing process of a kraft mill.

become probable. The green liquor then goes to the green liquor clarifier tank. The density of the green liquor at this point is used as a process control variable of green liquor concentration.

Green Liquor Clarifier

The green liquor clarifier is a settling tank used to remove *dregs* by sedimentation before the green liquor is recausticized as shown in Fig. 17.13. It can also serve as a storage tank for green liquor and should provide at least 12 h supply of green liquor. Since the mid-1960s, single-compartment clarifiers have been used in place of the older multicompartment clarifiers. Overflow rates on the order of 0.6 m/h (2 ft/h) and retention times over 2 h are used. The dregs settle to the bottom where rakes move them to the outlet. If green liquor clarification is not used or is inadequate, these inert materials build up in the lime, decreasing the *lime availability.* The green liquor clarifier/storage unit should be insulated to limit heat loss of the green liquor coming from the smelt dissolving tank at 85–95°C (185–205°F). Most mills now use polymeric additives to help green liquor clarification.

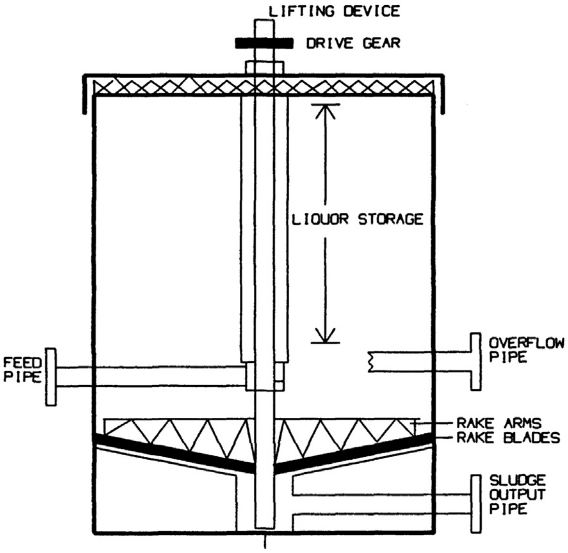


FIGURE 17.13 A single-compartment gravity sedimentation (settling) clarifier and storage unit suitable for green or white liquor.

Green Liquor Dregs and Dregs Washer

The green liquor dregs are undissolved materials in the green liquor. The dregs are about 0.1% of the liquor and consist of carbon (50% or more) and foreign materials (mainly insoluble metal carbonates, sulfates, sulfides, hydroxides, and, especially from nonwood fibers, silicates) to give a black bulky material. Incomplete combustion of organic materials in the recovery boiler can lead to inert carbon particles that leave with the smelt and greatly increase the amount of dregs. The metal salts arise from nonprocess elements (impurities) of the wood and corrosion products of the processing equipment, particularly from the recovery boiler. Improvements in the design of the recovery boiler have decreased the dregs yield to less than 4 kg/t (8 lb/ton) pulp. The dregs are washed in a dregs washer, often a drum filter or sedimentation washer (Fig. 17.14) where about 90%–95% of the sodium chemicals are removed, of which there is about 1–4 kg (2–9 lb) (Na_2O basis) per ton of pulp in the dregs before the washers.

Slaker

The slaker is a chemical reactor in which lime is mixed with green liquor (Fig. 17.15). The reaction temperature is 99–105°C (210–220°F). Using a high temperature and lime directly from the kiln gives a lime mud that settles well. The lime, CaO, forms slaked lime, $Ca(OH)_2$, and much of the causticizing reaction occurs here where the retention time is 10–15 min. These two chemical equations are shown below:

Slaking reaction:

$$CaO + H_2O \rightarrow Ca(OH)_2$$

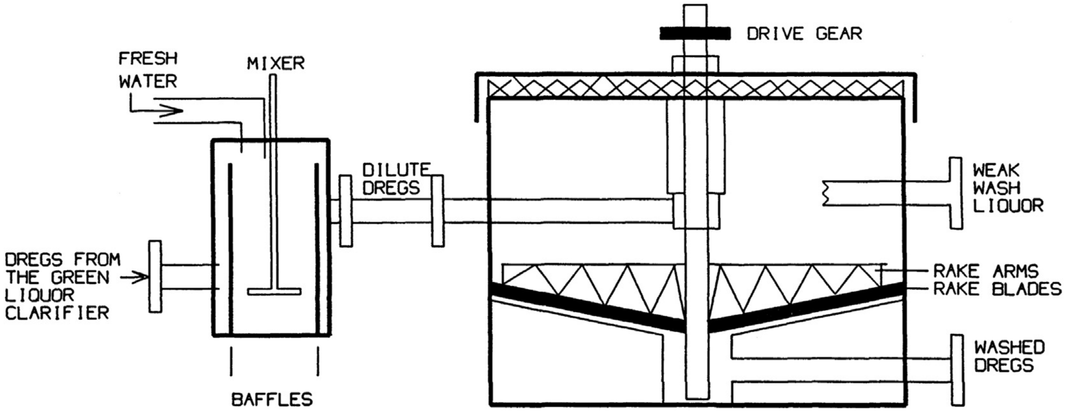


FIGURE 17.14 Sedimentation type green liquor dregs washer.

Causticizing reaction:

$$Ca(OH)_2 + Na_2CO_3 \rightleftarrows 2NaOH + CaCO_3(s)$$

Grits (large, unreactive lime particles and insoluble impurities corresponding to about 0.5%—2% of the lime feed) are removed here by the *classifier*, which uses a raking action. The grits are often sent to landfills although a few mills will send them through a ball mill and use them to neutralize the acid effluent of the bleach plant. The extent of the causticizing reaction (and therefore the causticizing efficiency in the white liquor) depends on the concentration of the initial Na_2CO_3 and the amount of lime used. With concentrations below 16% of actual chemical, the theoretical conversion is over 90%. At concentrations above this, the theoretical conversion drops off quickly. It is desired to have about 1% excess lime. Much more than this increases the turbidity of the white liquor and decreases the filtration rates of the lime mud. Commercially, about 75%—85% of the ultimate level of conversion is achieved in the agitator section of the slaker. The causticity efficiency should be 3%—4% below the equilibrium value to avoid excess liming.

Causticizers

The causticizers are two to four continuous flow, stirred reactors that are used to complete the causticizing reaction (Fig. 17.16). The contents are stirred with a pitched blade turbine at 70—80 rpm. The liquor/lime slurry flows through them in series with a total retention time of 1.5—2.5 h. The internal surfaces must be stainless steel or another corrosion resistant material.

White Liquor Clarifier

The white liquor clarifiers are settling tanks (gravity sedimentation) used to remove the lime mud ($CaCO_3$) from the white liquor. The clarified liquor should have turbidity below 100 ppm. The lime mud leaves with a solids content above 35% to minimize entrained soda that is removed in the lime mud washer. Like the green liquor clarifiers, white liquor clarifiers with single compartments with at least 12 h storage (see Fig. 17.13) are now much more common than the multicompartment clarifiers. Poor lime settling may be a result of excess lime to the slaker (more than 1% excess), a low lime availability (below 80%—85% that is indicative of a high level of contaminants because of inadequate removal of dregs and/or grits or incomplete slaking due to overloading the limekiln), a high percentage of low reactivity unburned fresh lime (i.e., purchased lime that has not been through a limekiln or is aged),

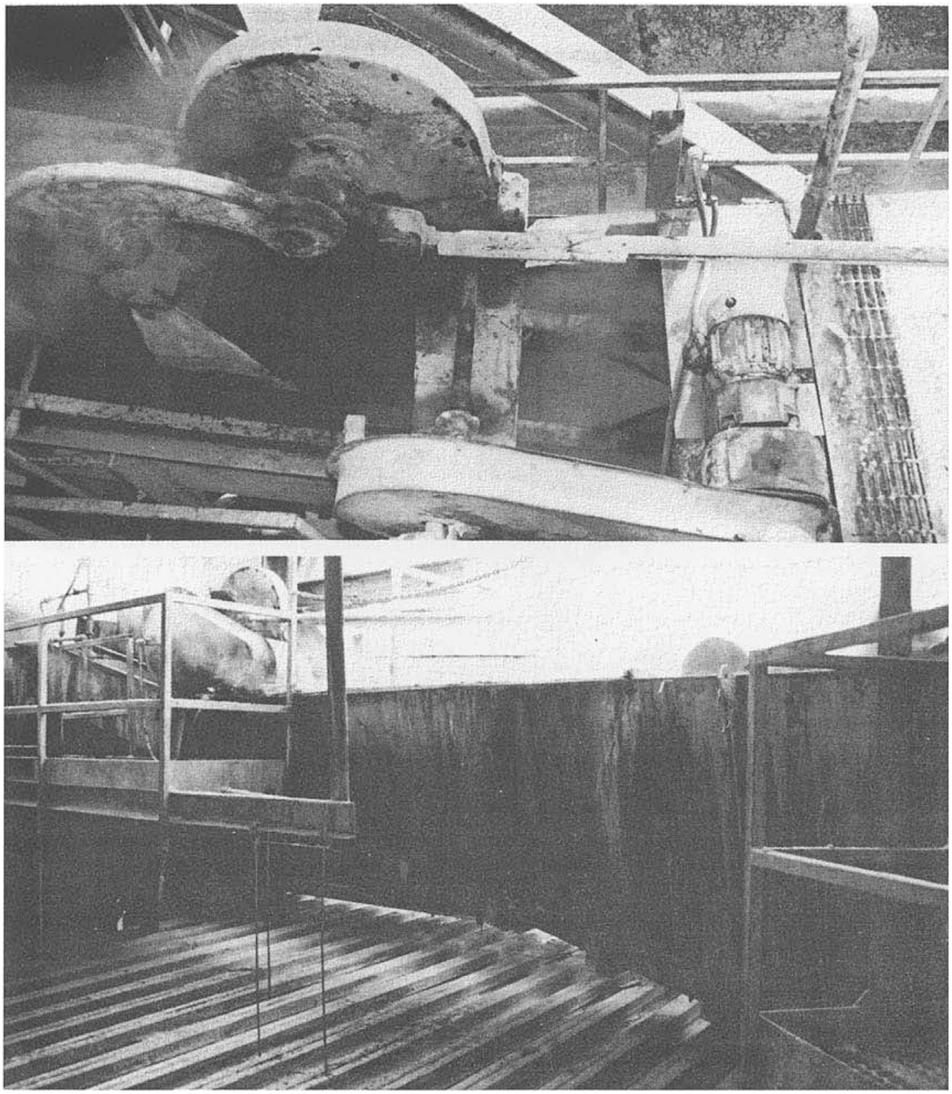


FIGURE 17.15 The top (top) and side (bottom) views of a slaker.

or inadequate white liquor clarification or clarifier operation. Lime burned at too low a temperature gives much mud of high viscosity; lime burned at too high a temperature gives a slow causticizing reaction and a slow settling lime mud with entrained alkali. Polymeric additives are often used to help white liquor clarification.

White Liquor Pressure Filters

Recently, some mills have been installing white liquor pressure filters after the white liquor clarifiers to supply additional clarification. Typically the filters have polypropylene filter tubes through which the white liquor flows under a pressure of 140—210 kPa (20—30 psig)

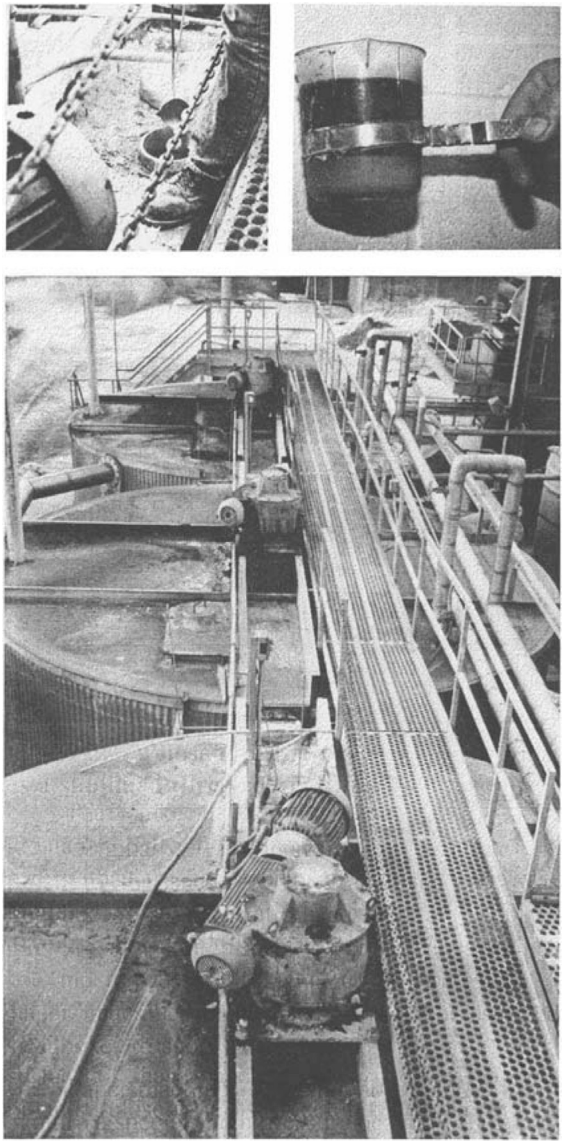


FIGURE 17.16 The causticizers (bottom). Top: The left insert shows a sample drawn for quality analysis, and the right insert shows proper sample settling.

to trap further lime mud. A reverse, flushing cycle removes the embedded lime mud that is added to the bulk of the lime mud (from the white liquor clarifiers) before the lime mud washers.

Lime Mud Washer

The lime mud washer removes most of the 15%–20% entrained alkali (Na_2O basis) from the lime mud, usually by sedimentation washing. It is typically a settling tank (or two in series) where fresh (makeup) water is used to wash the lime mud. If it were not removed, the Na_2S would cause slagging in the kiln, and reduced sulfur compounds would be released as H_2S. About 1% alkali on lime mud remains after washing. The liquor (weak wash or weak white liquor) is then used to dissolve smelt from the recovery boiler. It is important to maintain a proper water balance during lime mud washing to avoid formation of excess weak wash. This must be sent to the sewer with loss of valuable chemical that creates a disposal problem.

Lime Mud Filter

Thick lime mud from storage is diluted to 25%–30% solids (as measured by an X-ray detector) before going to the lime mud filter. The lime mud filter is a rotary drum vacuum filter washer used for final lime washing and thickening to 60%–70% solids before the lime enters the kiln. Centrifuges have been installed instead of drum vacuum filter to thicken lime, but they have lower water removal, leading to increased energy costs and lower limekiln throughput.

Limekiln

The primary function of the limekiln is to convert calcium carbonate to calcium oxide for reuse in the causticizing process. The process involves heat and mass transfer between the kiln, fuel, primary and secondary air, drying of lime mud, and calcining of calcium carbonate. It is important to have a comprehensive understanding of the following processes for diagnosing operational problems; improving energy consumption; increasing production reducing emissions; increasing refractory life; reducing process instabilities; improving the product quality; and optimizing the kiln operations.

Rotary limekilns in the pulp and paper industry are large steel tubes that are lined on the inside with refractory bricks. These kilns range in size from 7 ft (2.1 m) in diameter by 175 ft (53 m) long to 13.5 ft (4 m) in diameter by 400 ft (122 m) long. The refractory lining is from 6 in. (15.2 cm) to 10 in. (25.4 cm) thick. Production capacities for these units range from 50 t/day (45 mt/day) to 450 t/day (400 mt/day) of CaO. Fig. 17.17 shows schematic of the exterior and interior of limekiln. Rotary limekilns are slightly inclined from the horizontal and are slowly rotated on a set of riding rings. Lime mud is introduced at the uphill, feed end and slowly makes its way to the discharge end because of the inclination and rotation. A burner is installed at the discharge end of the kiln where fuel is burned to form an approximately cylindrical flame. Heat transfer from this flame and the hot combustion gases that flow up the kiln dries, heats, and calcines the counterflowing lime solids.

The weight of the kiln is supported on riding rings that encircle the kiln. These riding rings contact carrying rolls supported by concrete piers. A large electric motor operating through a reducing gearbox and pinion drives the main gear attached to the kiln. Typically, the kiln is driven at speeds of 0.5—2 rpm, often with variable speed arrangements (Adams, 1996). Typical transit times for the lime through the kiln are from 1.5 to 4 h under normal operating conditions. This is set by the speed and by the slope of the kiln, which is between 1.5 and 3 degrees (5/16—5/8 in./ft). The rotation of the kiln requires the use of hoods and seals at each end for connection to stationary ancillary equipment. At the hot end, the firing hood provides support for the burner and the flame management equipment and also the openings and passages for the discharge of the reburned lime product. At the cold end, the hood provides openings for a lime mud feed screw or belt, a connection to

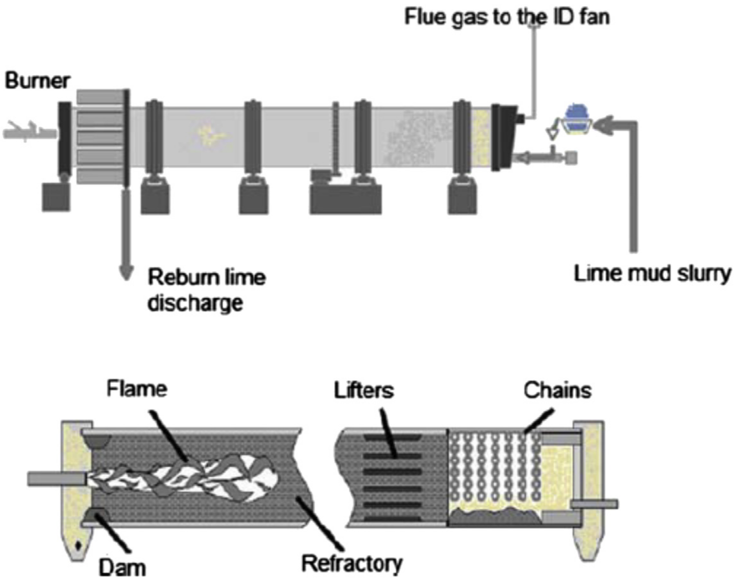


FIGURE 17.17 Schematic of the exterior and interior of a modern rotary lime reburning kiln. *ID*, induced draft. *Based on Adams, T.N., 1996. Lime kiln principles and operations. 1996 Kraft Recovery Short Course, Orlando, FL, 8—11 January.*

the induced draft fan and an important seal to limit the flow of tramp air. In older installations this hood is often an enlarged chamber in which dust and mud can be sluiced out of this area. Newer installations incorporate smaller hoods to improve the seal and reduce the length of the mud screw or belt. The burner and flame play an important role in product quality and refractory service life.

As with all combustion fired heat exchange equipment, higher flame temperatures mean higher production capacity and efficiency. However, excessive temperatures cause refractory damage and overburned, slow-reacting lime product. This trade-off in performance results in a compromise in flame length. Shorter flames are too hot and cause refractory damage and overburned lime, whereas longer flames cause some loss in production capacity and efficiency and loss of control of the product quality. A compact, medium-length flame approximately three times the kiln diameter in length is a good trade-off between efficiency and refractory service life. However, irrespective of the shape, the flame must not touch the refractory, or serious refractory washing will occur. At the cold end of the kiln, the relatively low gas temperature restricts heat transfer. To improve this, a section of chain is hung from the shell in this part of the kiln. This chain is made up of links that are typically 3/4 in. × 3 in. Hangers attach lengths of this chain directly to the kiln shell either from one end or both ends. When the chain is hung from one end it is referred to as curtain chain, and when hung from both ends it is most often called a garland system.

Wet lime mud is fed into the high end of the kiln, and the solid phase moves countercurrent to the flow of hot gases as the kiln rotates. The transfer of heat into the mud at the cold end is optimized by providing extended surface area, usually by means of steel chains attached to the kiln shell and hanging in the hot gases. In the hotter zones of the kiln, the metal shell is lined with refractory brick. As its temperature is increased, the lime mud material becomes plasticized and forms into pellets, aided by the rolling and lifting action of the kiln (Adams, 1996). Normally, the size of the aggregates ranges up to about 3 cm in diameter. Occasionally, the pellets keep on growing to form large balls or adhere to the brick to form rings. The soda content of the lime mud has a significant effect on its aggregating properties during the reburning operation and is typically controlled to less than 1% sodium oxide. The hot end of the kiln is typically maintained at 1150−1250°C by firing oil or gas. Without reclaiming heat from the kiln product, the reburned lime would be discharged at a temperature of about 950°C. Most modern kilns are equipped with integral tube coolers to recover the major portion of this heat in direct contact with part of the entering air. These coolers are attached to the discharge end of the kiln in such a way that the calcined lime falls into one of the coolers; it then reverses direction and flows countercurrent to the air to the opposite end of the cooler where it is discharged at a temperature of about 350°C. Air is supplied to the kiln by a forced draft fan, but the major work is done by the induced draft fan that pulls the combustion gases through the kiln. The gases leaving the kiln are laden with lime mud dust and should be cleaned up before discharge. In most cases, the dust is removed in a suitably designed scrubber, most commonly a venturi-type. The electrostatic precipitators have become the equipment of choice for this service, especially for the largest size kilns. Fig. 17.18 shows Abdritz's lime reburning kiln system.

Some mills with short limekilns or where the limekiln is bottleneck and higher throughput is required use *flash driers* to dry the lime mud to less than 1% moisture content before it enters the kiln. In flash drying, the exit gases of the kiln (much hotter than 200°C because dry mud is being fed into it) are used to dry the lime mud. The lime mud is combined with the gases in a mixer. The flue gases and water vapor are then separated from the lime mud in a cyclone.

FIGURE 17.18 Andritz's lime reburning kiln system ensures reliable and energy efficient production of high-quality lime for the recausticizing operation. *Courtesy: Andritz*

Heat is recovered from the flue gases and hot burned lime of the limekiln. A development of the early 1980s is the discharging of the hot, burned lime product through about 8—10 *integral tube coolers* forming a ring around the limekiln on the outer side of the discharge end. Secondary air flows through these tubes in the opposite direction as the lime so that it is preheated, thereby increasing the combustion temperature or lime throughput. However, the lime must remain above 320°C (600°F) so it will slake well. Sulfur oxides are not emitted to a large extent because the CaO is a good scavenger for the highly acidic forms of these compounds and $CaSO_3$ and $CaSO_4$ are formed. Emissions of nitrogen oxides are high because of the excess air and high combustion temperatures. See Chapter 15, Volume 2 for more information. Pure oxygen gas has been used as a partial substitute for air to decrease H_2S generation from the lime mud and increase lime mud throughput rates. Ring formation within the limekiln is part of the territory. If it becomes a severe problem, expensive shutdowns may result. Ring formation can result (Tran and Barham, 1991) when noncondensable gases are introduced to the limekiln, and the ring occurs from the formation of $CaSO_4$. The use of a Total Reduced Sulfur (TRS) scrubber column for the Non-Condensible Gases (NCG) before their introduction to the limekiln can drastically decrease ring formation. The exhaust gases must be treated to remove particulate matter. Usually a venture scrubber (Fig. 17.19) is used. The flue gases flow through a constriction on the order of 1 ft^2 with the introduction of a water spray to trap the particulates. In the mid-1970s, a few mills started using electrostatic precipitators (ESP, Fig. 17.11) to treat the limekiln exhaust gases. ESP have many advantages over the venturi scrubbers, including cleaner exhaust gases, easier control of the system, and low exhaust fan power requirements because the exhaust is not forced through a narrow

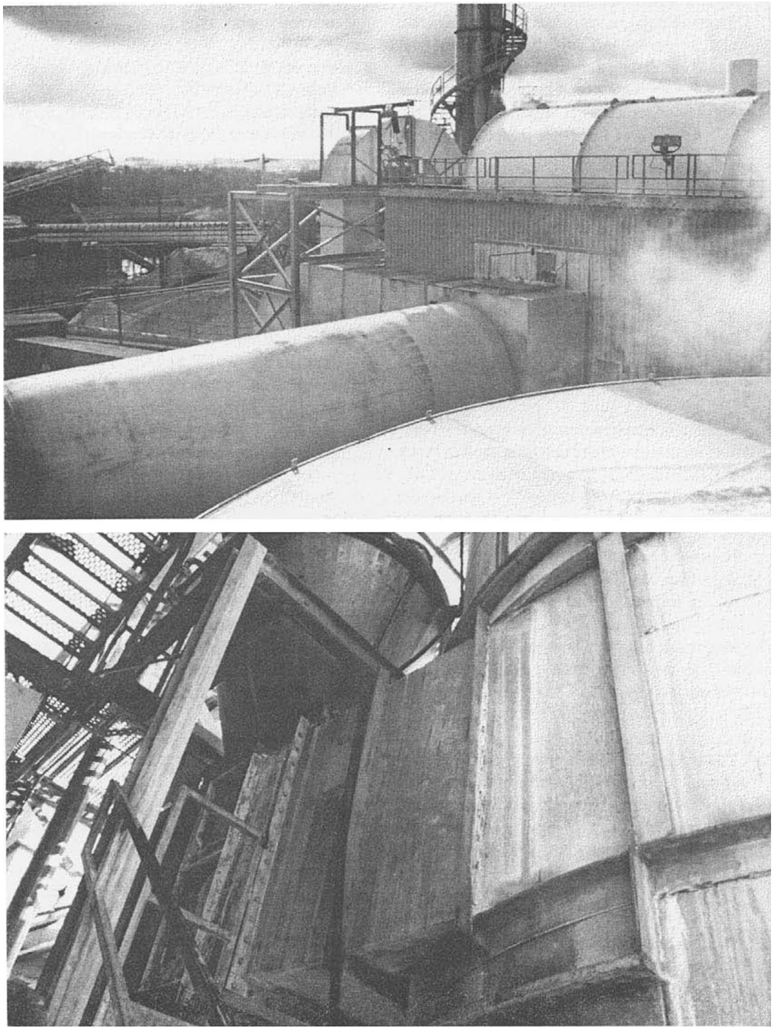


FIGURE 17.19 The top view shows the limekiln duct carrying the flue gases to the venturi scrubber (bottom) and from the scrubber to the chimney.

constriction. Now most new systems use electrostatic precipitators to capture the particulates.

Salt Cake (Na_2SO_4)

Salt cake is the makeup chemical for the kraft process that is used to replace chemicals lost (mostly through the pulp) in pulping. About 50–100 lb/ton pulp is normally dissolved in the concentrated black liquor just before spraying into the recovery furnace. The name "sulfate" process was derived from the use of this salt as a makeup chemical; however, sodium sulfate is *not* involved in the actual pulping process. The makeup chemical can be other chemicals as well.

Cross Recovery

Cross recovery is the collection of waste NSSC liquor and burning it in a nearby kraft mill. Kraft mills recover the sodium and sulfur as Na_2S and Na_2CO_3 after the recovery furnace. The kraft mill pays the Neutral sulfite semichemical (NSSC) mill for Na_2SO_4, which allows the NSSC mill to purchase fresh cooking chemicals (sulfur and either NaOH or Na_2CO_3).

17.6 ANNOTATED BIBLIOGRAPHY

U.S. Environmental Protection Agency, Environmental pollution control. Pulp and Paper Industry, Part I, air, EPA-625/7-76-001 (1976).

Krotscheck, A.W., Sixta, H., 2006. Recovery (Chapter 9). In: Sixta, H. (Ed.), Handbook of Pulp. WILEY-VCH Verlag GmbH & Co. KgaA, pp. 995–1024.

Adams, T.N., 1996. Lime kiln principles and operations. 1996 Kraft Recovery Short Course, Orlando, FL, 8–11 January.

Bajpai, P., 2008. Chemical Recovery in Pulp and Paper making. PIRA International, UK, 166 pp.

Vakkilainen, E.K., 2000. Chemical recovery. In: Gullichsen, J., Paulapuro, H. (Eds.), Papermaking Science and Technology Book 6B. Fapet Oy, p. 7 (Chapter 1).

Vakkilainen, E.K., 2007. Modern recovery practices and state-of-the-art technology. International Chemical Recovery Conference: Efficiency and Energy Management, Quebec City, QC, Canada, 29 May–1 June, pp. 15–201.

Ragnar, M., Henriksson, G., Lindstrom, M., Süttinger, R., 2000. Pulp In book: Ullmann's Encyclopedia of Industrial Chemistry. Wiley-VCH. Available from: https://doi.org/10.1002/14356007.a18_545.pub3.

Bajpai P (2017). Pulp and Paper Industry *Chemical Recovery*. 1st Edition ELSEVIER Inc. USA.

Brown Stock Washing

Crotogino, R.H., N.A. Poirier, and D.T. Trinh, The principles of pulp washing, *Tappi J.* 70(6): 95–103(1987).

This is an excellent overview of pulp washing from the theoretical and equipment perspectives.

Perkins, J.K., Ed., *1982 Brown Stock Washing, Short Course Notes*, TAPPI Press, Atlanta, GA, 1982, 49 p.

This is a very useful introduction to brown stock washing. Descriptions of Chapters 1–9 follow. Perkins, J.K and K.M. Jackson, The washing of brown stock, pp 1–6 (Chap. 1), gives a historical overview of the basic washing methods; Perkins, J.K., Rotary filter washing equipment, pp 7–9 (Chap. 2), has 10 figures with descriptions of the title equipment; Hough, G.W., Auxiliary components and design for vaccum filter washing systems, pp 11–16 (Chap. 3), addresses stock flow, drop legs, seal chambers, and seal tanks; McSweeney, J.M., Control and instrumentation, pp 17–20

(Chap. 4); Smyth, Jr., J.A., The mathematics and variables of countercurrent brown stock washing, pp 21–26; Guillory, A.L., Sorbed soda and its determination, pp 27–31 (Chap. 6); Guillory, A.L., Brown stock washer efficiency and physical testing, pp 33–37 (Chap. 7); Perkins, J.K., Analyzing and troubleshooting a washing system, pp 39–45 (Chap. 8); and Perkins, J.K., Newly introduced methods of brown stock washing, pp 47–48 (Chap. 9).

Phillips, J.R., and J. Nelson, Diffusion washing system performance (plus a simplified method for estimating saltcake loss from any equipment combination. *Pulp Paper Can.* 78(6):T123-T127(73–76) (1977).

This article includes a brief review of the equipment.

Norden, H.V., V.J. Pohjola, and R. Seppanen, Statistical analysis of pulp washing on an industrial rotary drum. *Pulp Paper Mag. Can.* 74(10):T229–T337(83–91) (1973).

Regression analysis showed the dependence of the underflow leaving the drum on various factors.

Harvin, R.L. and W.F. Brown, *Tappi J.*, 36(6): 270–274(1953).

The specific heat of black liquor is fairly linear from 1 cal/g at 0% solids to 0.70 at 60% solids.

Black Liquor Evaporation

Gudmundson, C, H. Alsholm, and B. Hedstrom, Heat transfer in industrial black liquor evaporator plants, *Svensk Papperstidning.* Part I, 75(19):773–783(1972); Part II, 75(22):901–908(1972).

The overall heat transfer coefficient in climbing film evaporators is dependent on the heat flux; boiling point of the liquid; and the liquid feed rate, temperature, viscosity, and surface tension. Foaming flow produces remarkable heat transfer, especially at low heat flux, compared with nonfoaming flow. The error between calculated and measured data was less than 15% for 95% of the data.

Jaakola, H., Hatano, T., 2007. Black liquor evaporation to high dry solids with crystallization technology. Jpn. Tappi J. 61 (5), 9–12.

Falling Film Evaporators

Shalansky, G., D. Burton, and B. Lefebvre, Northwood pulp & timber's experience using the falling film plate type evaporator for high solids concentration of kraft black liquor, *Pulp Paper Can.* 93(1):51–56(1992).

This is a very useful article on the subject with some nice figures to demonstrate the concepts.

Wei, X., Huang, K., 1993. A new plate-type falling film evaporating plant of Gingzhou paper mill. China Pulp Pap. 12 (5), 3–9.

Fosberg, T.M., Claussen, H.L., 1982. Falling-film evaporators recover chemicals efficiently. TAPPI. 65 (8), 63.

Meng, M.X., Hsieh, J.S., 1995. Falling-film black liquor evaporation. 1995 Pulping Conference, Chicago, IL, USA, 1–5 October, Book 1.

Black Liquor Properties

Lowendahl, L., G. Petersson, and O. Samuelson, Formation of carboxylic acids by degradation of carbohydrates during kraft cooking of pine, *Tappi J.* 59(9): 118–120(1976).

The amounts of 26 organic acids in black liquor are given.

Venkatesh, V and X.N. Nguyen, 3. Evaporation and concentration of black liquor, in Hough, G, Ed., *Chemical Recovery in the Alkaline Pulping Process,* TAPPI Press, Atlanta, 1985, pp 15–85.

A general presentation of black liquor properties is given, including specific gravity as a function of solids content, boiling point rise, specific heat, viscosity, chemical composition, and thermal conductivity.

Harvin, R.L. and W.F. Brown, *Tappi J*, 36(6): 270–274(1953).

The specific heat of black liquor is fairly linear from 1 cal/g at 0% solids to 0.70 at 60% solids.

Recovery Boiler

Taylor, S.S., Good firing practices unprove boiler safety, *Am. Papermaker*, 52(4, mislabeled as 3 in the front):39–42(1989).

Koncel, J.A., Preventive maintenance can end smelt-water explosions, *American Papermaker*, 54:(8):26–27(1991).

The cause of 125 BLRB explosions is itemized along with a six-step emergency shutdown procedure. Useful guidelines for preventing smelt-water explosions are found here. "Industry statistics show that smelt-water explosions take place in 1 of every 72 operating BLRBs each year."

Bauer, D.G., and W.B.A. Sharp, The inspection of recovery boilers to detect factors that cause critical leaks, *Tappi J.* 74(9): 92–100(1991).

This is a technical article along these lines that should be in the library of anyone responsible for recovery boiler safety.

Causticizing

Mehra, N.K, C.F. Cornell, and G.W. Hough, Chap. 5. Cooking liquor preparation, in Hough, G, Ed., *Chemical Recovery in the Alkaline Pulping Process*, TAPPI Press, Atlanta, 1985, pp 191–256.

A good discussion of the theoretical causticizing efficiency as well as material and energy balances for liquor and lime cycles is presented here.

Daily, CM. and J.M. Genco, Thermodynamic model of the kraft causticizing reaction, *J. Pulp Paper Sci*, 18(1):J1–J10(1992).

The thermodynamics of the causticizing reaction has been modeled based on K.S. Pitzer's method to predict the ratio of the activity coefficients of hydroxyl and carbonate anions in strong electrolyte solutions. Overflow decreased from 1.35% to 0.26%, whereas the slurry solids concentration of the underflow increased from 32% to 44% using a 100% recycle rate [*Tappi J.* 75(3):20(1992)].

Lewko, L.A. and B. Blackwell, Lime mud recycling improves the performance of kraft recausticizing, *Tappi J.* 74(10): 123–127(1991).

This claims to improve the causticizing process by recycling some of the lime mud to the slaker. This might be important at a mill that is limited by the limekiln or lime mud washing. It also will decrease the dead load slightly in the recovery boiler and lead to a small increase in boiler capacity. In Table 11 the "common overflow" units should be mg/L, not g/L. Reports after this paper tell of a mill whose free lime mud content in the white liquor clarifier. Although not discussed in this paper, it would seem that high-sulfur-content coals might actually be burned in a recovery boiler with sulfur recovery in the smelt.

Cogeneration

Price, K.R. and W.A. Anderson, New cogeneration plant provides steam for Oxnard papermaking facility, *Tappi J.* 74(7): 52–55(1991).

Here cogeneration using the GE LM2500, which is a modification of the GE CF6-6 aircraft engine used in DC-10 jet aircraft, is described.

Limekilns

Amer. Papermaker, 55 (1): 3A–35(l992).

This article describes the use of ESP in a new limekiln.

Tran, H.N. and D. Barham, An overview of ring formation in lime kilns, *Tappi/*. 74(1): 131–136(1991).

Miscellaneous

Sell, N. and J. C. Norman, Reductive burning of high-yield pulp by the addition of pulverized coal, *Tappi J.* 75(10): 152–156. Stultz, Steven C and Kitto, John B (1992). Steam its generation and use, 40th edition 929 p. ISBN 0-9634570-0-4. Pulverized coal was added to pulp liquor (from a mill that makes 78% yield sodium bisulfate hardwood pulp) to help recover the sulfur as sulfide (77%) and sulfite (20%) instead of sulfate, which is the typical recovery product for sulfur at these mills. Vakkilainen, E.K., Holm, R., 2000. Firing very high solids black liquor in recovery boilers. Engineering Conference, Atlanta, GA, 1721 September, 8 pp.

EXERCISES

General

1. What are the three main objectives in the chemical recovery cycle?
2. Write the chemical equations as indicated.
    a. Reaction of NaOH in the recovery boiler:
    b. The formation of white liquor from green liquor:
    c. The regeneration of calcium so it can be used in reaction (b):
    d. Concentration of black liquor from 15% to 50% solids:
3. Where is turpentine recovered during kraft pulping? Where is tall oil collected?
4. What is cross recovery?

Pulp Washing

5. Indicate the effect of a high dilution factor in pulp washing on the following:

	Increase	Decrease
a. Sodium loss	__	__
b. Evaporation cost	__	__
c. Bleaching cost	__	__

6. The steam economy of the MEEs is 4.24; suppose the dilution factor in the brown stock washers goes from 3 tons water per ton pulp to 4 tons water per ton pulp. How much more steam is required to process a ton of pulp?

Liquor Concentration

7. What are the two types of bodies used in MEEs?
8. Black liquor is first concentrated to about 45%–50% solids using the MEEs. Final concentration is achieved by direct contact evaporators or by concentrators. Since the late 1960s, direct contact evaporators have not been installed in pulp and paper mills. Why is this the case?
9. Why is the concentration of black liquor usually limited to about 65%–75% solids before combustion in the recovery boiler? Why would a higher solids content be desirable?

Recovery Boiler

10. Describe the location of the oxidation and reduction zones in the recovery boiler. Give some examples of chemical reactions that occur in each of these zones.
11. What is the purpose of the electrostatic precipitator after the recovery boiler?
12. What would happen to the sodium sulfide if it was oxidized in the bottom of the recovery boiler? Is this beneficial?

Lime Cycle

13. What are the three zones in the limekiln in terms of what is happening to the lime?

14. What are the consequences of not removing the dregs from the green liquor?

Causticizing

15. Of what is the causticizing efficiency of white liquor a measure?

Miscellaneous

16. It has been a long practice at many mills to add some black liquor to the white liquor and chips before pulping. What are some possible advantages of adding black liquor to the digester as part of the digester charge?

CHAPTER

18

Alternative Chemical Recovery Processes

18.1 INTRODUCTION

The kraft process is the dominating pulping process, which accounts for almost 60% of all mechanical and chemical pulp produced worldwide. In this process, pulp is produced by digesting wood chips at high temperature and pressure in a sodium hydroxide solution called white liquor to dissolve the wood lignin and other organic wood substances and to liberate the wood fibers that form the pulp and finally paper. The spent pulping liquor, called kraft black liquor, contains about half the mass of the dissolved wood substances and most of the pulping chemicals. The dissolved wood material has a significant heating value, and the pulping chemicals are used to produce new white liquor, which is of great economical and environmental importance. This process of recovering the black liquor is an important part of the kraft process, and it has served the industry very well. However, conventional kraft recovery process has several major drawbacks as shown in Table 18.1.

Extensive research toward alternative processes has been conducted over the past three decades. The new recovery methods, which are in use or currently under development, can be divided into two groups:

1. Methods that introduce gasification technologies, i.e., replace the conventional recovery boiler and thereby possibly eliminate the smelt explosion hazard.
2. Methods that introduce alternative causticization processes, i.e., an alternative method of chemical conversion of sodium carbonate to sodium hydroxide.

These methods replace the conventional lime-causticizing process and thus eliminate the complicated and energy-intensive lime cycle. New recovery methods can include combinations of these two groups.

18.2 ALTERNATIVE TECHNOLOGIES

Several different alternative black liquor recovery processes have been developed over the years. They can roughly be divided into processes for the chemical recovery (i.e., alternative causticization processes) and the energy recovery (i.e., gasification processes) of black liquor. The alternative causticization and gasification processes can also be combined. The drawbacks of the conventional recovery process listed earlier have been the drivers for development of these new concepts.

Biermann's Handbook of Pulp and Paper: Raw Material and Pulp Making
https://doi.org/10.1016/B978-0-12-814240-0.00018-5

TABLE 18.1 Drawbacks of Conventional Kraft Recovery Process

Smelt-water explosion hazard (safety)
Emission of reduced sulfur gases (environmental impacts)
Too high capital costs (economy)

Gasification Processes

Black liquor gasification (BLG) is a promising technique for pulp mills for the generation of a surplus of electrical energy or the production of biofuel. The principle of BLG is the process of converting concentrated black liquor into inorganic compounds (mainly sodium and sulfur) appropriate for the recovery of cooking chemicals and combustible fuel gas, comprising mainly hydrogen and carbon monoxide.

The developments in gasification technology have been conducted over years for efficient recovery of bio-based residues in the chemical pulp mills. BLG has been a popular topic in several conferences on biorefining, engineering, pulping, and environmental matters. Several studies have been conducted to analyze the technical, economic, and climate change mitigation performance of gasification process, and a number of pilot plants have been successfully operated. There has been more focus on possible integration of gasification process for increased energy self-sufficiency. This serves as a base for a modern biorefinery concept at the pulp mills, coproducing pulp, and valuable energy products. To add more value to the integrated pulp mills, the research and development in the area of BLG has been focused on increased power production from integrated BLG system switching a pulp mill from a net electricity importer to exporter; utilization of surplus BL energy for biofuel production and potentially converting a modern Kraft mill to become biofuel supplier in the future energy system; improved performance of the combined heat and power systems using integration of the BLG with a gas turbine; evaluation of advanced power cycles for potential increase in electricity surplus, including combined cycle (CC), steam-injected gas turbine (STIG) cycle, evaporative gas turbine or humid air turbine (EvGT or HAT) cycles; assessment of BLG technology in terms of technical, economic, and climate change mitigation; integration of pulp mills with carbon dioxide mitigation technologies; cost-competitiveness of electricity or biofuel production via BLG; and resolving the material challenges of BL gasifier refractory lining.

The two main technologies are pressurized and atmospheric gasification, being commercialized by Chemrec AB and ThermoChem Recovery International (TRI) respectively.

BLG technologies are distinguished into two major classes:

- Low-temperature gasification: Low-temperature gasifiers operate at 600−850°C, below the melting point of inorganics, thus avoiding smelt-water explosions.
- High-temperature gasification: High-temperature gasifiers generally operate in the range of 900−1000°C and produce a molten smelt.

The MTCI Technology

Manufacturing and Technology Conversion International (MTCI) has developed a pulse-enhanced, indirectly heated, fluidized bed gasifier that is used at Norampac and Georgia-Pacific pulp mills. In the late 1996, Weyerhaeuser at New Bern had run small-scale MTCI system at the mill and processed 2 tonnes/h of black liquor solids (BLS). The MTCI technology uses low-temperature gasification with a bubbling fluidized bed steam reformer operating at 580−620°C (Fig. 18.1).

The bed is indirectly heated by several bundles of pulsed combustion tubes, which burn some of the gas produced. Black liquor is sprayed into the fluidized bed, where it coats the solids and is quickly dried and pyrolyzed. The remaining char reacts with steam to produce a hydrogen-rich fuel gas. Part of the bed material is

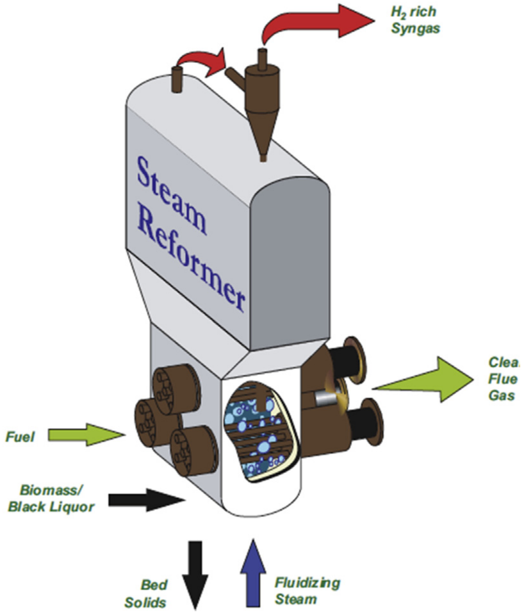


FIGURE 18.1 The steam reformer of TRI. *Reproduced with permission from IEA Bioenergy (2007). Black Liquor Gasification Summary and Conclusions from the IEA Bioenergy ExCo54 Workshop.*

continuously removed, dissolved in water, and cleaned off unburned carbon to obtain green liquor. The resultant gas is passed through a cyclone to separate the solids and then goes to a heat recovery steam generator. Part of the steam generated is used in the gasifier as both reactant and fluidizing medium. The gas continues through a venturi scrubber and a gas cooler, before removal of the hydrogen sulfide in a scrubber using some of the green liquor. The cleaned gas contains about 73% hydrogen, 14% carbon dioxide, 5% methane, and 5% carbon monoxide. The heating value of the gas is high at ~13 mJ/Nm^3. It can be burned in an auxiliary boiler, used in a fuel cell to generate electricity, or, if pressurized, it can be fired in a gas turbine.

The Chemrec Technology

Chemrec is working on both an atmospheric and a pressurized version of a high-temperature downflow entrained flow reactor. The atmospheric version is mainly intended as a booster to give additional black liquor processing capacity, whereas the pressurized version is more advanced and could replace a recovery boiler or function as a booster. In the atmospheric system, black liquor is fed as droplets through a burner at the top of the reactor. The droplets are partially combusted with air or oxygen at 950–1000°C and atmospheric pressure. The heat generated sustains the gasification reactions. The salt smelt is separated from the gas, falls into a sump, and dissolves to form green liquor. The gas produced passes through a cooling and scrubbing system to condense water vapor and remove hydrogen sulfide. The gas has a low heating value (~2.8 mJ/Nm^3) and is suitable for firing in an auxiliary boiler. It consists of 15%–17% carbon dioxide, 10%–15% hydrogen, 8%–12% carbon monoxide, 0.2%–1% methane, and 55%–65% nitrogen. The thermal efficiency is quite low. An atmospheric Chemrec Recovery Booster system with a firing rate of 270 t of dry solids per day has been in use at Weyerhaeuser's New Bern mill since 1997, although it was shut down between 2001 and 2003 because of extensive cracking in the reactor shell. During this period, the gasifier was rebuilt with a new reactor vessel and modified refractory lining design and has operated well since then. The pressurized system is similar but operates at a pressure of 30 atm. The salt smelt is separated from the gas in a quench device. The gas cleanup system is more advanced, cleaning the gas of fine particles and condensed hydrocarbons. The sulfur-rich gas stream, separated in an absorber/stripper system, can be used to prepare advanced pulping solutions. The gas produced has a higher heating value (~7.5 mJ/Nm^3) and can be, for example, fired in a gas turbine to produce electricity or used to produce biofuels such as methanol or dimethyl ether (DME). The exhaust from the turbine is passed through a heat recovery steam generator. The thermal efficiency is above 80%. A pressurized system has been built under the

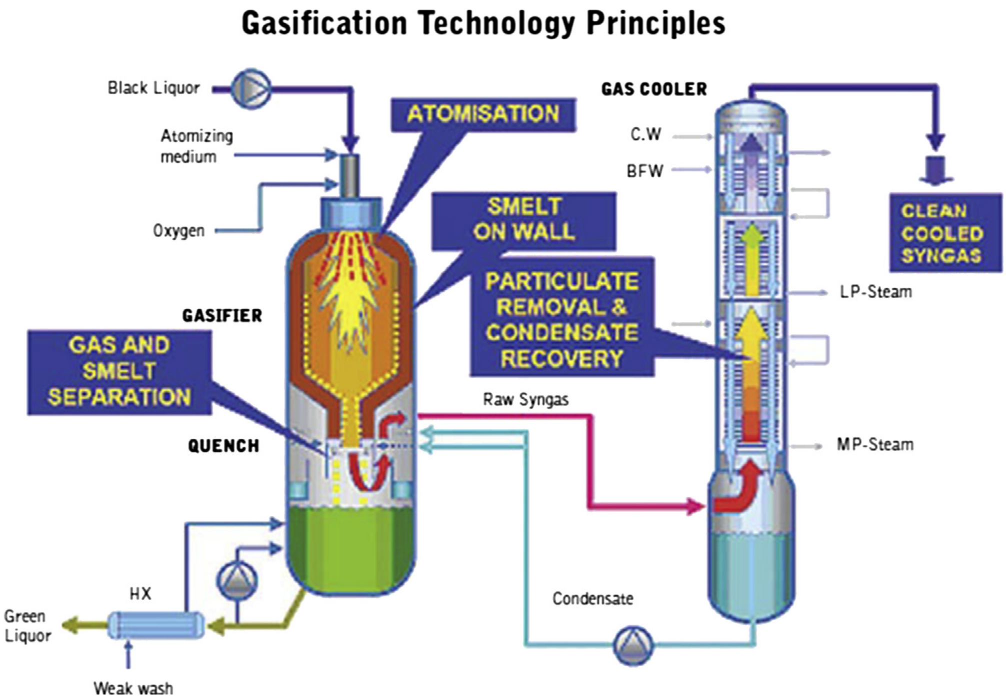


FIGURE 18.2 The pressurized black liquor quench gasifier (showing cooling of the green liquor) and the countercurrent gas cooler in a Chemrec-type of pressurized black liquor gasification plant. *MP*, medium pressure steam; *LP*, low pressure steam. *Reproduced with permission from IEA Bioenergy (2007). Black Liquor Gasification Summary and Conclusions from the IEA Bioenergy ExCo54 Workshop.*

Swedish national BLG program (2004–06) in Piteå, Sweden. It is a development plant built for 20 t dry solids per day. The system includes the processes of gasification and quenching, gas cooling, and gas cleaning. The gas produced contains about 41% hydrogen, 31% carbon dioxide, 25% carbon monoxide, 2% methane, and 1.4% hydrogen sulfide. The aim of the program is a verified process that will be ready for scale-up (by 15 times) and an optimized integration of the process with the pulping cycle. Fig. 18.2 shows the Chemrec DP-1 plant. The Chemrec system for BLG with an integrated combined cycle (BLGCC system) (Fig. 18.3) has several advantages over recovery boilers, the most significant being a dramatically improved electricity yield.

The Chemrec BLG methanol/DME fuel (BLGMF) system combines BLG with a chemical synthesis plant for production of green automotive fuels. The new combined pulp and chemicals production facility requires additional energy to compensate the pulp mill for the withdrawal of the new green automotive fuels. The efficiency of the Chemrec BLGMF system is very high, and the cost of these fuels from a full-scale unit is competitive with petroleum-based alternatives. The Chemrec BLGH2 system utilizes the syngas from the black liquor gasifier as feedstock for novel green hydrogen production. The cost of a full-scale pressurized BLG unit is estimated to be slightly higher than that of a new conventional recovery boiler although a BLGCC system does have the potential to double the amount of net

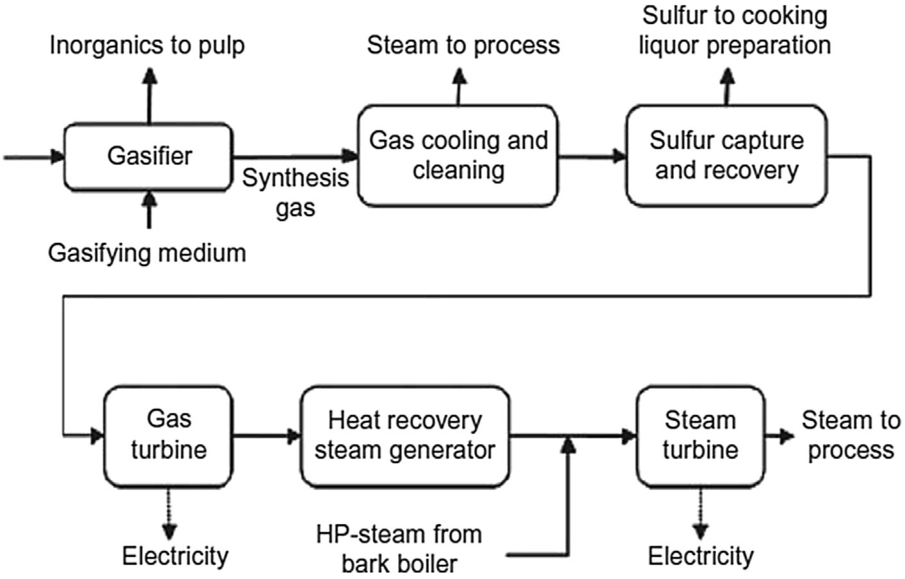


FIGURE 18.3 Integrated gasification and combined cycle. *Reproduced with permission from Naqvi et al. (2010).*

electrical energy for a kraft pulp mill compared with a modern recovery boiler with a steam turbine. For a more closed system with less need of steam, increase in electrical energy will be even higher. Another advantage of the pressurized BLG process is the increased control of the fate of sulfur and sodium, which can be used to improve the pulp yield and quality for the mill. This control is very important for the quality of green liquor and is quite limited with a conventional recovery boiler. One disadvantage of gasification is that it increases the causticization load although BLG has a lower requirement for salt cake makeup than do recovery boilers. Even though the pressurized BLG process does have a lot of advantages over the recovery boiler, there are still a number of uncertainties for this technology. BLG is still a developing technology, and only small commercial atmospheric units, processing around 100—350 t of dry solids per day, have been built. Similar-sized pressurized demonstration units do not yet exist, and it will be some time before reliable large units are available. BLG can produce more electricity, but current commercial atmospheric processes are not as energy efficient as the kraft recovery boiler process. The black liquor gasifier needs to operate under pressure to have an electricity advantage. Many issues with the technology remain unresolved. These are: finding materials which survive in a gasifier; mitigating the increased causticization load; how to start up and shut down; tar destruction; alkali removal and achieving high reliability.

The full impact of BLG on recovery cycle chemistry needs to be carefully studied with commercial units. The first large demonstration units will cost two to three times as much as a conventional recovery boiler, and although this will improve with time, the price will hinder the progress of BLG. A small black liquor gasifier with a commercial gas turbine of 70 MWe requires a mill size of more than 500,000 t of air-dried pulp per annum. Commercial gasifiers probably need to be more than 250 MWe in size. It is therefore expected that full-sized black liquor gasifiers will be built in new greenfield mills rather than as replacement units for old recovery boilers.

Environmental Impact

BLG can help sustain forests and generate ultraclean biofuels. Not only does the process have high-energy feedstock flexibility, it can also produce a variety of green fuels, including DME, methanol, ethanol, synthetic diesel, synthetic gasoline, and biogas. Biofuels from a BLG process excel in terms of well-to-wheel carbon dioxide emission reduction and energy efficiency. This was confirmed by an extensive European study conducted by the research institutes of the auto and refinery industries and the Joint Research Centre of the European Commission. This study included many different feedstocks, conversion processes, and fuel products. Both synthetic diesel and DME from forest harvest residues over the BLG route showed among the highest well-to-wheel greenhouse gas reduction and energy efficiency.

The total available black liquor volume in the United States is with the conversion efficiency of this process, equivalent to approximately 5 billion gallons per year as ethanol. The renewable fuel standard calls for 16 billion gallons of cellulosic biofuels by 2022 so that this route can give a significant contribution to meeting this target. The US pulp and paper companies today are meeting fierce competition from low-cost producers overseas and from alternative solutions in both packaging and printed media. Mill operators and their investors now have a viable option for breathing new life into the industry by transforming mills into biorefineries that use this fuels-from-the-forest process. This transformation completely changes a pulp mill's competitive position by adding 30% to 50% of profitable revenue with the typical 25% to 40% internal rate of return. It also makes needed reinvestment possible by replacing aged recovery boilers with high-maintenance costs and low performance. In many cases, the fuel plant investment can also be used to provide additional recovery capacity allowing for higher pulp production. Mills producing as little as 500 tons of BLS per day are viable as fuels-from-the-forest biorefineries using this method. Most mills are significantly larger. At the minimum capacity size, such a biorefinery mill would produce upward of 8 million gallons a year of green motor fuel calculated as gasoline equivalents. In a mill investing in second-generation biofuels technology, jobs are not only preserved, but additional jobs are created, mainly for the extraction of biomass from the forest and also to operate and maintain the biofuels plant. Other economic and public opinion benefits are significant as well, such as possible tax benefits and air emission reductions.

The most significant environmental impact caused by BLG will occur in air emissions. Compared with the current recovery technology, the IGCC system could produce low emissions of several pollutants—such as sulfur dioxide, nitrogen oxide, carbon monoxide, volatile organic compounds, particulates, and total reduced sulfur gases—and overall reductions in carbon dioxide emissions. Even with improved add-on pollution control features, the recovery boiler system still causes higher overall emissions than does the IGCC system. Table 18.2 shows environmental impact of different emissions along with relative emission rates for both recovery boilers and gasifiers.

Whether BLG is conducted at high or low temperatures, it is still superior to the current recovery boiler combustion technology. The thermal efficiency of gasifiers is estimated to be 74% compared with 64% in modern recovery boilers, and the IGCC power plant could potentially produce two times the electricity output of recovery boiler power plants, given the same amount of fuel.

Nonconventional Causticization Technologies

Two basic types of alternative causticization processes are being considered: direct causticization and autocausticization processes. An oxide

TABLE 18.2 Environmental Impact of Different Emissions

		Relative Emissions	
Pollutant	**Relative Environmental Impact**	**Recovery Boilers**	**Gasification Technology**
Wastewater	Medium–high	Low	Very low–low
Solids	Very low	Low	Low
NO_x	High	Medium	Very low
SO_2	High	Low	Very low
CO	Low	Medium	Very low
VOCs	High	Low	Very low
Particulates	High	Low –medium	Very low
CH_4	Low–medium	Low	Very low
TRS	Low	Low	Very low
HAPs	Medium–high	Low	Very low

Based on Larsen et al. (2003).

is used as the causticizing agent in both the cases. If the oxide is soluble in water it is called autocausticization, and direct causticization if insoluble.

Direct Causticization

In direct causticization the oxide is insoluble in alkaline solutions and precipitates during the dissolution phase. The causticizing agent is a metal oxide agent, such as titanium oxide, manganese oxide, and iron oxide. Titanate is considered to be the most promising agent for direct causticization in kraft pulping. The hydrated metal oxide complex can easily be recovered from the white liquor and be recycled. Overall advantages to direct causticization include the elimination of the lime cycle, reduction in dead load of sodium carbonate, and the high concentration of sodium hydroxide in the recovered white liquor. However, the price of metal oxide causticizing agents can be quite high, and the possible dead load of metal oxide is not known. Also a method of separating the dregs from the recycled metal oxide has to be developed in order for direct causticization to be a viable option. This could be attractive when the need for causticization exceeds the capacity of the lime furnace, which may happen, for example, when a recovery boiler is replaced by a gasifier. Proposed oxides for autocausticization in the literature are phosphorous oxide, silicon dioxide, aluminum oxide, and boric oxide. Borates are the most promising ones for kraft pulping.

Partial Borate Autocausticization

Partial borate autocausticization improves the limekiln and recausticization operations by reducing causticizing loads and the amount of lime processed through the system. This technique makes possible to produce caustic directly in the recovery boiler. This process occurs when sodium borates are added to the kraft liquor at substoichiometric levels. A portion of the sodium carbonate is causticized in the recovery boiler. The causticization of the remaining sodium carbonate is completed in a conventional recausticizing plant of the pulp mill with a reduced quantity of lime. This technology appears as an attractive option, particularly for kraft pulp mills, where incremental causticizing and limekiln capacity are required. Mill-scale trials have shown that there are no major side effects on the mill operations. Borate present in cooking liquor increases pulp yield, decreases rejects, improves the selectivity of lignin removal, can increase pulp viscosity at the same kappa number, and does not require capital investment because the autocausticizing reaction occurs in the existing recovery boiler. The principal autocausticizing reaction that takes place in the recovery boiler furnace occurs between sodium metaborate and sodium carbonate in the molten smelt to form trisodium borate.

The critical parameters of the process are the temperature and Na/B ratio in the black liquor. Trisodium borate reacts with water in the smelt dissolving tank to form sodium hydroxide and regenerate $NaBO_2$. The success of the technology depends greatly on whether the boron-containing black liquor can be effectively processed in a recovery boiler and on the degree of completion of the reactions that produce trisodium borate in the boiler. Promising environmental benefits are connected with a reduction of the emissions from the limekiln and a reduced consumption of energy or fuel by a limekiln. Several mill trials with partial borate autocausticization have been conducted, and the problems encountered have been resolved. The technology is now being used at several mills in Sweden, Brazil, Indonesia, and the United States. The results show that the technology works. It allows the lime consumption to be reduced by an amount proportional to the level of autocausticization (depending on the Na/B M ratio in the liquor cycle). No negative effect has been found on pulp properties, equipment corrosion, digester operations, pulp washing, black liquor evaporation, recausticizing, and limekiln operations. For a greenfield kraft pulp mill, with proper equipment design and operation, the technology has the potential to eliminate completely the causticization plant and limekiln, making the kraft process much simpler short-term trials to evaluate the effect of the technology on specific parts of the mill and long-term trials to demonstrate the overall effects of the technology on the mill operations. At autocausticization levels up to 25%, no undesired effects could be observed on digesters, pulp quality, brown stock washing, black liquor evaporation, lime recausticization, or limekiln operations. The most apparent effect of autocausticization on the liquor cycle is the increase in total inorganic salts in the system. This leads to an increase in the throughput of solids for evaporators, concentrators, and recovery boilers. Because of the endothermic nature of the autocausticization reaction, the black liquor heating value decreases. The evaporation load is not affected, however, and so the temperature may decrease in the recovery boiler. Even though the conversion of autocausticization to be sensitive to operation conditions, especially temperature, they claim that the overall impacts on the recovery boiler are manageable. Partial borate autocausticizing may offer cost savings and environmental benefits to kraft pulp mills that are recausticizing-limited by relieving production bottlenecks in the liquor cycle without costs for the capacity growth of the conventional causticization plant and limekiln. The benefits are obtained through decreasing the limekiln load and fuel usage or reducing fresh lime purchases and lime mud disposal. Some benefits also result from the increase in pulp yield at the digester and/or potential decrease in alkali charge. However, addition of borate increases the solids content in fired black liquor, especially at high levels of autocausticizing, and may result in a decrease in black liquor heating value and in steam production.

Borate Autocausticization With Black Liquor Gasification

A study was undertaken into the potential synergy between BLG and borate autocausticizing. Using experimental and theoretical results for the combined gasification—autocausticizing process, a model was established with focus on a Chemrec-type booster gasifier with partial autocausticizing. A detailed study was undertaken on the chemical recovery aspects and energy consequences. According to this it appears that autocausticizing takes place in an atmospheric gasifier. The results were obtained with a thermodynamic equilibrium calculation where reaction restraints, i.e., reaction kinetics, were not taken into account. In a gasifier, there is no char bed where the solid carbon reacts with the present dioxide, keeping the pressure of carbon dioxide low. Therefore the gas phase characteristics are important for the equilibrium of the autocausticization reactions. The reaction $Na_2B_4O_7 + Na_2CO_324 \rightarrow NaBO_2 + CO_2$ is highly reversible. As a result, especially in a pressurized gasifier, the high partial pressure of carbon dioxide may hamper the borate autocausticization. However, this is still to be examined. Three in situ causticizing processes (titanate, manganate, and borate) were examined for both high- and low-temperature gasification of black liquor. The borate and titanate options were found to be effective autocausticizing and direct causticizing agents. These two cases were examined for integration into a gasification-based recovery island using the Larson black liquor cost-benefit study as a reference case for economic forecasting. Whereas using the titanate direct causticizing process yielded a net present value (NPV) of USD 25 million, using the existing lime cycle plus borate autocausticizing for extra capacity yielded an NPV of USD 16 million.

18.3 ANNOTATED BIBLIOGRAPHY

Bajpai P (2016). Pulp and Paper Industry: Chemical Recovery, Elsevier inc. USA.
This book examines the scientific and technical advances that have been made in chemical recovery, including the very latest developments. It looks at general aspects of the chemical recovery process and its significance, black liquor evaporation, black liquor combustion, white liquor preparation, and lime reburning.
Bajpai P (2013). Black Liquor Gasification. Elsevier Science B.V, UK.
This book provides a detailed account of black liquor gasification processes for the production of energy and chemicals from black liquor.
Björk M, Sjögren T, Lundin T, Rickards H, Kochesfahani S (2004). Partial Borate Autocausticizing Proven a Success in Europe, vol. 1. International Chemical Recovery Conference, Charleston, SC.
This paper describes the first European full-scale partial borate autocausticizing trial commenced in November 2002 at the Stora Enso Norrsundet mill and has been running continuously and successfully since that time. The objective was to off-load the limekilns and reduce the amount of fresh purchased lime and subsequent disposal costs. The total lime requirement was reduced by about 7%, whereas the autocausticizing level was typically 9%–11%. Overall, the presence of sodium borate in the liquors had little effect on the mill operations, and the pulp properties and quality were unaffected. There was some indication of higher pulp yield.
Brown C, Landälv I, (2001). The Chemrec Black Liquor Recovery Technology—A Status Report. International Chemical Recovery Conference, Whistler, Canada.
This report focuses on the status of "The Chemrec Black Liquor Recovery Technology."
Brown CA, Gorog JP, Leary R, Abdullah Z (2004). The Chemrec Black Liquor Gasifier at New Bern—A Status Report. International Chemical Recovery Conference, Charleston, SC.
Chemrec (2013). http://www.Chemrec.se/.
Chemrec's atmospheric Booster at Weyerhaeuser's New Bern mill, NC, USA, was started in December 1996. After initial periods of difficulties especially with the ceramic containment material of the reactor vessel, the plant has been in commercial operation for many years and tracked the mills' chemical recovery needs.
EIPPCB (2015). Best Available Techniques (BAT) Reference Document for the Production of Pulp, Paper and Board. http://eippcb.jrc.ec.europa.eu/reference/BREF/PP_revised_BREF_2015.pdf. Ekbom
The BAT reference document entitled "Production of Pulp, Paper and Board" forms part of a series presenting the results of an exchange of information between EU Member States, the industries concerned, and nongovernmental organizations promoting environmental protection.

Grigoray O (2009). Gasification of Black Liquor as a Way to Increase Power Production at Kraft Pulp Mills, Master's thesis. Lappeenranta University of Technology, Faculty of Technology. 2009, 86.

This study is focused on the opportunity to improve the power performance from black liquor at Kraft pulp mills. It includes an overview of a traditional recovery system, its development, and indication of the integral drawbacks that provoke the search for more efficient methods of black liquor treatment. It also investigates black liquor gasification as a technology able to increase electric energy generation at pulp mills.

Hoddenbagh JA, Wilfing K, Miller K, Hardman D, Tran H, Bair C (2001). Borate Autocausticizing—A Cost Effective Technology, International Chemical Recovery Conference, Whistler, BC, Canada, 11–14, June 2001, pp. 345–353.

It has been demonstrated that borates can be effectively used in the kraft recovery cycle to increase the amount of caustic available in the smelt through a process known as borate partial autocausticizing. Borate autocausticizing process has the potential to replace a significant portion of the caustic required for the bleaching of bleached chemithermomechanical pulp.

IEA Bioenergy (2007). Black Liquor Gasification Summary and Conclusions from the IEA Bioenergy ExCo54 Workshop.

This publication provides a summary and the conclusions from a workshop organized by IEA Bioenergy. The purpose of the workshop was to present the developments of black liquor gasification for the production of energy and/or biofuels for transport and discuss the remaining barriers, either technical or strategic, that need to be overcome to accelerate the successful demonstration of black liquor gasification technologies and subsequently their penetration in the market.

Kochesfahani, S.H, Bair, C.M, Kirk, M, (2006). Partial borate autocausticizing, a new technology in chemical recovery. Appita. vol. 59 (no. 2), 130–135.

Partial borate autocausticizing provides incremental recausticizing capacity. Based on the mill trial experience and material balance calculations, the borate autocausticizing is expected to have no negative effect on pulp properties, equipment corrosion, digester operations, pulp washing, black liquor evaporation, lime recausticizing, and limekiln operations.

Larson, ED, McDonald, GW, Yang, W, Frederick, WJ, Iisa, K, Kreutz, TG (2000) A cost-benefit assessment of BLGCC technology. TAPPI J. 83 (6), 1–15.

Black liquor gasification/combined cycle technology represents a significant discontinuous innovation in the way in which pulp mills recover chemicals and generate power. The value of the additional power, the impact liquor cycle changes on operating costs, and the difference in capital costs when compared with conventional Tomlinson boiler technology are quantified in this paper.

Larsen E, Consonni S, Katofsky R (2003). A cost benefit assessment of biomass gasification power generation in the pulp and paper industry, Final Report, Princeton Environmental Institute, 8 October 2003.

This study examines in greater depth the prospective costs and benefits of commercializing black liquor gasification combined cycle (BLGCC) cogeneration system.

Lindberg D, Perander L, Backman R, Hupa M, Kochesfahani S, Rickards H (2005). Borate autocausticizing equilibria in recovery boiler smelt. Nordic Pulp Pap. Res. J. Vol. 20 (2), 232–236.

The borate autocausticizing reactions in the recovery boiler smelt have been studied by thermal analysis and thermogravimetry. The study shows that high temperatures increase the conversion of the borates, whereas high potassium concentration in the smelt and high carbon dioxide in the gas decrease the conversion.

Lindblom M (2006). Chemrec pressurized black liquor gasification—status and future plans. Seventh International Colloquium on Black Liquor Combustion and Gasification, Jyväskylä, Finland, 31 July−2 August 2006.

Status and future plans of Chemrec pressurized black liquor gasification are presented.

Naqvi M, Yan J, Dahlquist E, (2010). Black liquor gasification integrated in pulp and paper mills: a critical review. Bioresour. Technol. 101 (21), 8001−8015.

This paper presents an extensive literature review of the research and development of various BLG technologies over recent years. In addition, the potential areas of research and development in BLG required to solve the critical issues and to fill research knowledge gaps are addressed and highlighted.

Nilsson, LJ, Larson, ED, Gilbreath, KR, Gupta, A, (1995). Energy Efficiency and the Pulp and Paper Industry. ACEEE, Washington, DC/Berkeley CA.

This study examines the processes and technologies used in the pulp and paper industry, their industry use, and energy savings and cogeneration potential. It also reviews advanced technologies, decision-making, and policy options for encouraging greater energy savings and improved cogeneration systems.

Nohlgren I (2002). Recovery of Kraft Black Liquor With Direct Causticization Using Titanates, Ph.D. Disseration, Lulea University of Technology.

The feasibility of direct causticization of kraft black liquor using titanates has been evaluated in this thesis. This has been done by studying the kinetics of the reaction between sodium trititanate and sodium carbonate and describing the kinetics by appropriate reaction models. Three different chemical recovery processes have been compared from an energy point of view: the conventional kraft recovery cycle using lime, the borate causticization process (as an add-on to conventional kraft recovery process), and the titanate causticization process combined with black liquor gasification.

Nohlgren, I, (2004). Non-conventional causticization technology: a review. Nordic Pulp Pap. Res. J. Vol. 19 (4), 467−477.

In this paper, a review of the available literature on the topic nonconventional causticization technologies has been carried out. The different technologies are described, discussed, and summarized. In addition, a short description of the conventional causticization technology is given as background and for comparison.

Nohlgren, I, Sinquefield, S, (2004). Black liquor gasification with direct causticization using titanates: equilibrium calculations. Indus. Eng. Chem. Res. 43, 5996−6000.

Different alternatives to the conventional recovery of spent pulping liquors in the kraft pulping process have been studied by equilibrium calculations. These calculations were performed using FactSage.

Nohlgren, I, Sinquefield S, (2007). High temperature, high pressure black liquor gasification with borate autocausticizing. International Chemical Recovery Conference: Efficiency and Energy Management, Quebec City, QC, Canada, 29 May−1 June 2007, pp. 233−241.

High-temperature, high-pressure black liquor gasification with borate autocausticizing has been examined in this study.

Patrick K, Siedel B, (2003). Gasification edges closer to commercial reality with three new N.A mills startups. Paper Age, October 2003.

The start-up of few commercial-scale gasification units is described.

Tran H, Mao X, Cameron J, Bair CM (1999). Autocausticizing of smelt with sodium borates. Pulp Pap. Can. Vol. 100 (9), T283–T287.

The autocausticizing technology, involving the use of borate to "causticize" sodium carbonate (Na_2CO_3) in the soda or kraft smelt directly in the recovery boilers, was reviewed by reexamining the basic reactions between Na_2CO_3 and sodium borates ($NaBO_2$ and $Na_2B_4O_7$) at high temperatures. The results show that in air, both $NaBO_2$ and NaB_4O_7 react readily with molten Na_2CO_3 at any Na:B molar ratio, and the reaction product is likely to be trisodium borate, not disodium borate. The reaction kinetics depends strongly on the sample size, temperature, and the CO_2 concentration in the gas.

Tran, HN, Mao X, Lesmana, N, Kochesfahani, S.H, Bair, C.M. and McBroom, R, (2001). Effect of partial borate autocausticizing on Kraft recovery operations. International Chemical Recovery Conference, Whistler, BC, Canada, 11–14 June 2001, pp. 337–343.

Trials on partial borate autocausticizing conducted at several kraft pulp mills showed that lime consumption was lowered, and there were no effects of borate on pulp quality, effluent quality, chemical recovery process equipment, and digester and limekiln operations. Several problems were experienced during operation of evaporators, recaust plants, and recovery boilers, but most have been overcome.

Whitty K, Baxter L (2001). State of the art in black liquor gasification technology. Joint International Combustion Symposium, Kauai, Hawaii, 9–12 September 2001.

State of the art in black liquor gasification technology is presented. Two companies appear to be on the brink of commercializing black liquor gasification. MTCI's fluidized bed steam gasification process has been developed to the point where MTCI now has five commercial projects under way. Chemrec has sold an atmospheric version of their high-temperature entrained flow gasifier, and development of the pressurized version is entering the final predemonstration phase. If progress in these technologies continues, gasifiers should be a proven alternative to the recovery boiler within the next decade.

Whitty K, Verrill CL, (2004). A historical look at the development of alternative black liquor recovery technologies and the evolution of black liquor gasifier designs. International Chemical Recovery Conference, Charleston, SC, 6–10 June 2004.

This paper reviews nearly two dozen of these alternative technologies, describing the processes and identifying why development was ultimately abandoned. Common threads are recognized: low-temperature processes have problems achieving good conversion while avoiding ash agglomeration; high-temperature processes suffer material problems caused by extremely corrosive conditions. The two gasification processes now under development are approaching commercial viability.

CHAPTER

19

Pulp Bleaching

19.1 INTRODUCTION

Bleaching

Bleaching is the treatment of wood (and other lignocellulosic) pulps with chemical agents to increase their brightness. Bleaching of chemical pulps involves a much different strategy than bleaching mechanical pulps. Bleaching of chemical pulps is achieved by lignin removal. Lignin removal in chemical pulps leads to greater fiber—fiber bonding strength in paper, but the strong chemical used in bleaching chemical pulps decreases the length of cellulose molecules, resulting in weaker fibers. Bleaching mechanical pulps is achieved by chemically altering the portions of the lignin molecule that absorb light (i.e., have color). Obviously, lignin removal in mechanical pulps is counterproductive; bleaching mechanical pulps is referred to as *lignin-preserving.* Sometimes bleaching mechanical pulps is called "brightening" to distinguish it from bleaching of chemical pulps.

Brightness

Brightness is a term used to describe the whiteness of pulp or paper, on a scale from 0% (absolute black) to 100% (relative to an MgO standard, which has an absolute brightness of about 96%) by the reflectance of blue light (457 nm) from the paper. See Chapter 2, Volume 2 for more details on these tests. The approximate brightness levels of some pulps are as follows:

Unbleached kraft	20%
Unbleached sulfite	35%
Newsprint	60%
Groundwood	65%
White tablet paper	75%
High grade bond	85%
Dissolving pulp	90%

Color Reversion

Color reversion is the yellowing of pulps on exposure to air, light, heat, certain metallic ions, and fungi because of modification of residual lignin forming chromophores. Mechanical pulps are particularly susceptible to color reversion, although chemical pulps may experience this when exposed to high temperatures.

Consistency

Bleaching stages are carried out at consistencies from 3% to 20%. Higher consistencies of 10%—20% are used with chemicals such as

https://doi.org/10.1016/B978-0-12-814240-0.00019-7

oxygen, peroxide, and hypochlorite, which react with the lignin slowly. By using high consistencies, higher concentrations of the bleaching agent are realized for a given chemical loading, which increases the reaction rate.

19.2 BLEACHING MECHANICAL PULPS

The separation of wood fibers during mechanical pulping processes is achieved mainly by mechanical means, such as grinding and refining. As a result, these pulps are collectively called mechanical pulps and they include the following:

- Stone groundwood pulp
- Thermomechanical pulp
- Chemi-thermomechanical pulp
- Alkaline peroxide mechanical pulp

The world total design capacity for mechanical pulps is about 38.2 million ton/year. Like chemical pulps, lignin again is the main contributor to the color of mechanical pulps. The brightness increase for mechanical pulps and other high-yield pulp is achieved by modifying the lignin structures (chromophores) in the pulp furnish. The process sometimes is referred to as brightening to distinguish it from lignin-removing bleaching methods for chemical pulps. Commercial brightening agents are hydrogen peroxide and sodium hydrosulfite (sodium dithionite).

Mechanical pulps are bleached with chemicals designed to alter many of the chromophores. Chromophores are most often conjugated double bond systems arising in the lignin of pulps. Other chromophores such as sap stain induced by microorganisms, dirt, metal ions such as ferric that complex with lignin, and water impurities may impart color to paper. Bleaching of mechanical pulps involves masking the lignin that is present instead of removing the lignin as is the case for bleaching chemical pulps. To emphasize this distinction, bleaching mechanical pulps is often referred to as *brightening*.

Brightening mechanical pulps is accomplished with reducing agents, such as dithionite, or oxidants, such as hydrogen peroxide, often in a single-stage process. Fairly limited brightness improvements are realized (6%–12% typically), with a maximum brightness of 60%–70% in a single stage or up to 75% in a two-stage process. The pulp brightness also depends on the wood species from which the pulp was derived. Brightened mechanical pulps are subject to *color reversion*. As the lignin is largely decolored, but not removed, there is only a small loss of yield. If two stages are used, the oxidative stage is used before the reductive stage or else the oxidant will undo what the reductive compound accomplished.

Dithionite, Hydrosulfite Bleaching

Hydrosulfite, sometimes also referred to as dithionite, is a strong reducing agent. In the mill, usually sodium hydrosulfite is used (although zinc hydrosulfite was also used earlier). Hydrosulfite bleaching (Y) is preferred over peroxide bleaching if only modest brightness gains (e.g., 4–8 International Standard Organization [ISO] units) are required. Hydrosulfite selectively converts the chromophores into colorless or less colored structures, with almost no dissolution of pulp components, thus is a lignin-preserving bleaching chemical. The reactive species in a Y stage is believed to be a sulfur dioxide radical ion, which is formed through homolytic splitting of the weak sulfur to sulfur bond in hydrosulfite. The sulfur dioxide radical ions will then attack the chromophoric systems and convert them to the structures that are essentially colorless. The commercial hydrosulfite, whether in powder or solution form, often contains bisulfite, which also contributes to the discoloration of chromophores. An important consideration in a Y stage is to exclude air/oxygen from the system as much as possible to avoid loss of bleaching power. The hydrosulfite bleaching can be performed in a refiner, a stock chest, or a specially designed tower. The temperature is usually in the range of 50–70°C, the pH ~6, and the bleaching time ~60 min, although the brightness development is extremely rapid.

Hydrosulfite bleaching is carried out with 0.5%–1.0% dithionite on wood. Previously, zinc dithionite was used because it is very stable. However, zinc is toxic to fish; therefore the sodium form has replaced the zinc form. Zinc dithionite was prepared in the pulp mill from zinc and sulfur dioxide as follows:

$Zn + 2SO_2 \rightarrow ZnS_2O_4$. Bleaching is carried out at pH 5–6 with chelating agents such as ethylenediaminetetraacetic acid (EDTA) or sodium tripolyphosphate (0.1%–0.2% on pulp) to prevent metal ions such as iron(III) from coloring the pulp. Bleaching is often carried out in the refiners. The reaction time is on the order of 10–30 min. The brightness gain is only 5%–8%. Dithionite reacts with oxygen, so bleaching with it is carried out at 4% consistency; consistency below this is unnecessarily dilute, so reaction with dissolved oxygen consumes dithionite. Consistency above 4% leads to entrained air that consumes dithionite. (The solubility of oxygen in the atmosphere is only a few milliliters of gas per liter of water at 25°C [77°F] and decreases with increasing temperature; thus, entrained oxygen is more significant than dissolved oxygen at high consistencies for dithionite degradation.) Using temperatures as high as 70°C (158°F) reduces the oxygen solubility in water. Fig. 15.1 (Chapter 15, Volume 2) shows the solubility of oxygen (from air) in water as a function of temperature.

Sometimes dithionite is added between the refiner plates where temperatures above 100°C (212°F) cause steam to displace air. Dithionite ion reduces lignin and is itself oxidized to sulfite ion. If hydrogen peroxide and dithionite are used in a two-stage process, the dithionite must be the second stage or hydrogen peroxide will reoxidize those moieties reduced by the dithionite. The reaction of dithionite is shown as follows:

$$S_2O_4^{2-} + 2H_2O \rightarrow 2HSO_3^- + 2H^+ + 2e^-$$

Peroxide Bleaching

The peroxide bleaching chemistry for chemical and mechanical pulps is very different. For the chemical pulp, the goal is to maximize the removal of lignin, whereas for mechanical pulp the objective is to brighten the pulp with almost no dissolution of wood constituents, thus preserving pulp yield. The brightening of (chemi)mechanical pulps is achieved by selectively eliminating chromophores. During bleaching, perhydroxyl anion, which is a strong nucleophile, converts the electron-rich chromophores, typified by α, β-unsaturated aldehydes and ketone, and phenolic ring-conjugated ethylenic or carbonyl groups to their nonchromophoric counterparts. The peroxide bleaching is usually carried out by mixing the pulp fibers with the bleach liquor containing hydrogen peroxide, caustic soda, sodium silicate (41°Be), water, and sometimes epsom salts. The resulting mixture is then sent to a bleaching tower for 1–5 h, at 50–80°C. At the completion of the required time, some acids, typically SO_2 water, are used to lower the pH to 4.0–6.5. In a modern mill, a press, such as a twin-roll press, is used to increase the pulp to a consistency of 25%–35%, which allows the removal of much of the undesired material, such as anionic trashes, from the pulp. Several factors influence the performance of a peroxide stage, including consistency, retention time, and temperature. If the pulp consistency is >18%, the process is usually referred to as high consistency (HC) technology, whereas the medium consistency (MC) process is usually operated at 10%–12% pulp consistency.

Some metal ions, such as Fe^{3+}, Mn^{2+}, and Cu^{2+}, catalytically decompose hydrogen peroxide, so peroxide bleaching is carried out with agents that deactivate these metal ions.

$$H_2O_2 \xrightarrow{Fe^{3+}} H_2O + 1/2O_2$$

Chelating agents, such as EDTA, have the added gain of preventing pulp discoloration by binding with ferric ion that would otherwise form a colored complex with the phenolic lignin structure. Sodium silicate (5% on wood) is also used (usually after the addition of magnesium ion). The mechanism for inactivating the ions by sodium silicate is not clear; it may precipitate the ions, but, strictly speaking, it is not a chelating agent. Buffering action is required to keep the pH high even as organic acids are produced as a result of some carbohydrate degradation. Sodium silicate acts as a buffering agent. Bleaching conditions are 0.5%–3% peroxide and 0.05% magnesium ion (to mitigate carbohydrate degradation by oxygen under alkaline conditions) on pulp, temperature of 40–60°C (104–140°F) (about 20°C lower than with chemical pulps as lignin removal is not the goal), pH of 10.5–11, consistency of 10%–20%, 1–3 h retention time, with a brightness gain of 6%–20%. Hydrogen peroxide with sodium hydroxide and/or sodium peroxide is used to produce the high pH that is necessary to produce the active perhydroxyl ion, HOO^-. The formation of the perhydroxyl ion is as follows:

$$H_2O_2 \rightleftarrows HOO^- + H^+ \quad pK_a = 11.65 \text{ @ } 25°C$$

Some carbohydrate degradation occurs and is responsible for about half of the peroxide consumed. Pine and fir are difficult to brighten. Color reduction occurs by altering chromophoric groups such as orthoquinones. The pulp is sometimes subsequently treated with SO_2 to neutralize OH^- and reduce any residual peroxide.

Chelation (The Q Stage)

Transition metal ions, such as manganese, iron, and copper, can induce peroxide decomposition under the typical peroxide brightening conditions, thus decreasing the process efficiency and increasing the cost. Therefore it is important that transition metal ions be removed from pulp fibers before a peroxide stage. Organic compounds containing both amines and carboxylic acids in the structures, such as diethylenetriaminepentaacetic acid (DTPA) and EDTA, are the main chemicals used to remove transition metal ions from mechanical pulp in a pretreatment stage called the chelation stage (Q). Either DTPA or EDTA can form highly stable complexes with transition metal ions. Typically, the penta sodium salt of DTPA is used. The chemical is usually mixed thoroughly with the stock before a hydrogen peroxide stage (P). A convenient procedure for this is to add the chelant to the low consistency stock in the cleaning system or when the stock is delivered to the decker/press. The chelated metals are then removed in the dewatering stage via a press or decker. The total transition metal ion concentration in the treated pulp would be significantly reduced.

19.3 MEASUREMENT OF LIGNIN CONTENT

General Considerations

The measurement of lignin in chemical pulps is a vital tool to monitor the degree of cook (extent of delignification during pulping) or to measure residual lignin before bleaching and between various stages of bleaching to monitor the process, although pulp brightness between bleaching stages is often used to control the bleaching operation. As most of the lignin remains in mechanical pulps and bleached mechanical pulps, it is not measured in these pulps.

Lignin is easily measured indirectly by measuring the amount of an oxidant (such as chlorine or potassium permanganate) consumed by lignin in a sample of pulp of known mass. Fig. 19.1 is a comparison of several cooking degree numbers. Methods based on consumption of potassium permanganate (Kappa and K numbers) are the most common ones used. The idea (Fig. 19.2) is to treat the pulp with an excess of permanganate ion (or chlorine for Roe or C number) for a specified period of time to oxidize the lignin. After the specified reaction time, the residual permanganate (or chlorine) is determined by indirect titration; i.e., the excess permanganate converts iodide to iodine, and the iodine is titrated with thiosulfate (Chapter 21, Volume 2).

Other methods of lignin measurement are included here, as they appear in some of the older literature or have laboratory uses.

Kappa Number

The kappa test is an indirect method for determining lignin by the consumption of permanganate ion by lignin. The Kappa number is the number of milliliters of 0.1 $KMnO_4$ consumed by 1 g of pulp in 0.5 *N* sulfuric acid after a 10 min reaction time at 25°C (77°F) under conditions such that one-half of the permanganate remains unreacted. The 50% residual permanganate is titrated to determine the exact consumption. Experimentally, 30%–70% excess is common with factors to convert this to 50%. TAPPI Standard T 236 is based on this procedure. The Kappa number test can be used on bleached pulps, unbleached pulps, and high-yield chemical pulps by use of a single scale,

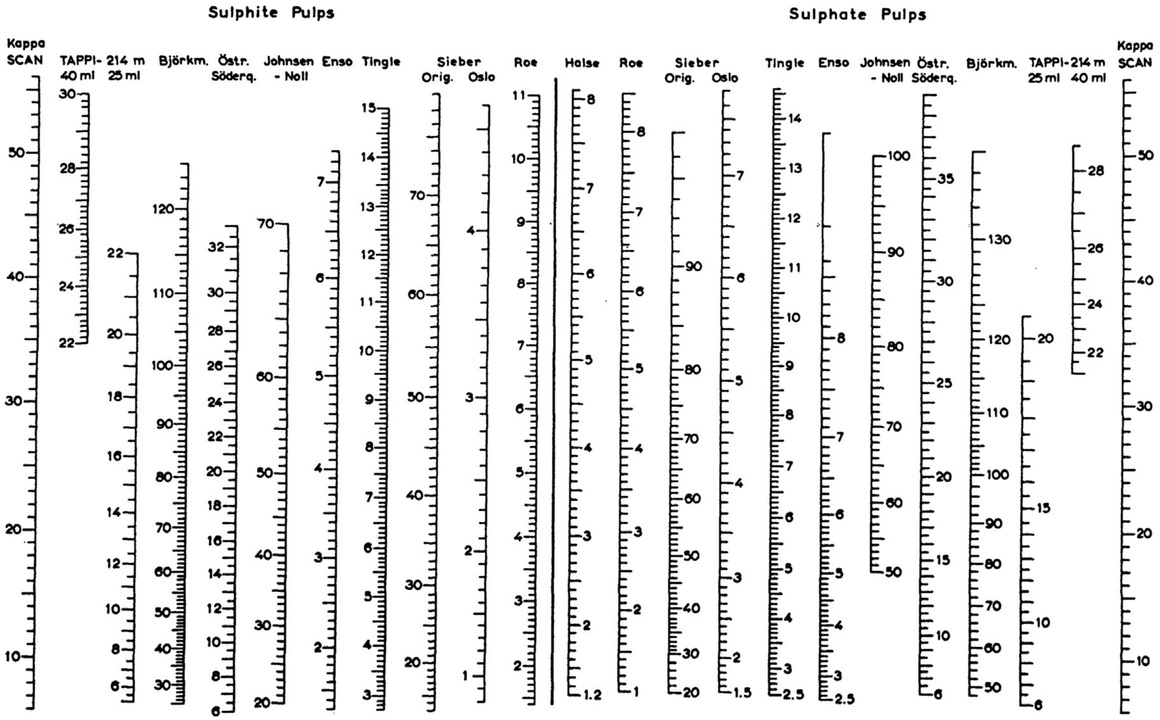


FIGURE 19.1 Comparison of cooking degree numbers. *Reprinted with permission from Alander, P., I. Palenius and B. Kyrklund, The relationship between different cooking degree numbers, Paperi ja Puu (8):403–406(1963).*

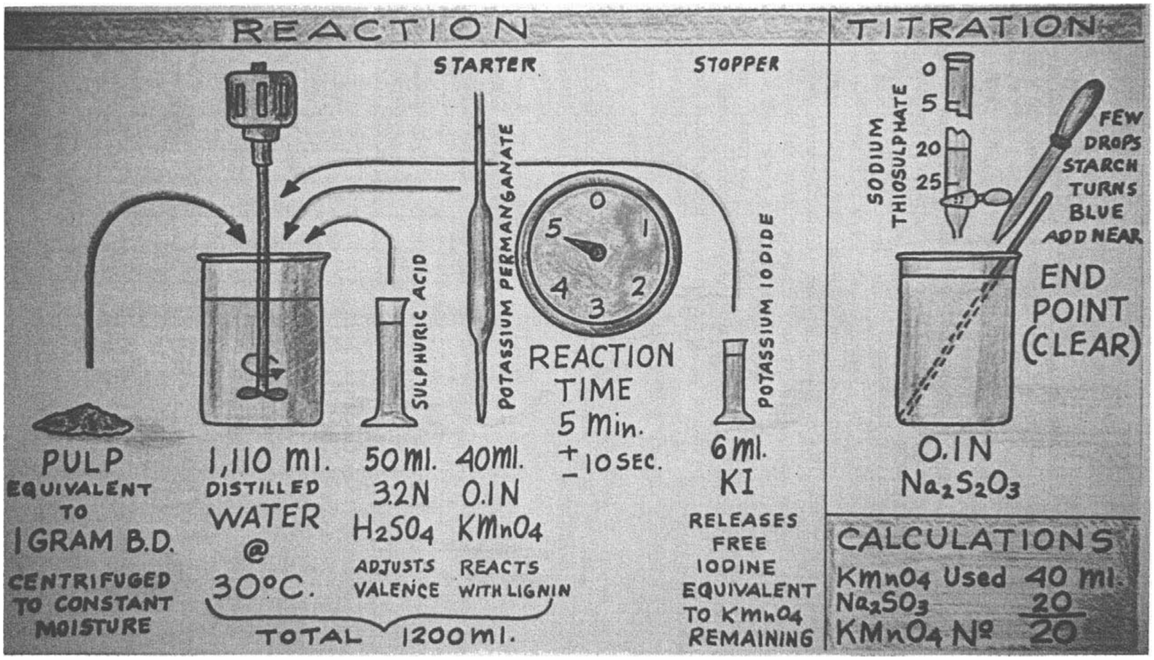


FIGURE 19.2 Lignin content with permanganate (40 mL K number). *From J. Ainsworth,* Papermaking, *©1957 Thilmany Paper Co., with permission.*

with bleached pulps always giving low numbers and unbleached pulps giving high numbers, unlike the K number. A variety of lignin contents are accommodated by varying the amount of pulp used in the test but keeping the amount of $KMnO_4$ constant. It is useful to know how these tests correspond to actual lignin content. This is achieved by measuring the lignin content of pulps gravimetrically and relating this to the Kappa number. The Klason lignin procedure is described below.

Klason lignin is considered to be essentially the same as the actual lignin content. Alander, Palenius, and Kyrklund (1963) give the following relationship for sulfite and kraft chemical hardwood pulps: Klason lignin, % = 0.15 × Kappa number. This relationship is approximately correct for softwoods as well. Chiang et al. (1987) found the coefficient of 0.159 for Douglas fir and 0.168 for western hemlock. The authors related Kappa number to the sum of Klason lignin and acid-soluble lignin (which are defined later).

Permanganate Number, K Number

The permanganate (or K) number is really four different tests. A constant amount of pulp is used with either 25 mL (for bleached pulp), 40 mL (Fig. 19.2), 75 mL, or 100 mL (for high yield pulps) of permanganate. Results of the 100 mL K number test are not easily compared to the results of the 75 mL (or any other) K number test, so there is no continuum or results for all types of pulps as with the kappa test. Guillory (1982) gives the relationship in the equation: log(Kappa number) = 0.837 + 0.0323 (40 mL K number) Therefore a 40 mL K number of 10 corresponds to a Kappa number of 14.5, 20 (40 mL K number) corresponds to 30.4 Kappa number, and 30 (40 mL K number) corresponds to 64.1 Kappa number.

Roe Number

The Roe number is a measure of lignin content by the number of grams of gaseous Cl_2 consumed by 100 g dry pulp at 25°C (77°F) in 15 min. TAPPI Standard 202 (now withdrawn) was one method. Alander, Palenius, and Kyrklund (1963) give the following relationship for hardwood pulps:

$$\text{Roe number} = 0.158 \times \text{kappa} - 0.2\ (\text{kraft})$$

$$\text{Roe number} = 0.199 \times \text{kappa} + 0.1\ (\text{sulfite})$$

Chlorine Number, C, Hypo Number

The chlorine number is a test method similar to that of Roe, except the ClO_2 is generated in situ by acidification of sodium hypochlorite. TAPPI Standard T 253 uses this method to determine a hypo number. The following empirical equation relates the chlorine number to the Roe number. Chlorine number $= 0.90 \times$ Roe number.

Klason Lignin, Acid-Insoluble Lignin

Klason lignin is the residue obtained after total acid hydrolysis of the carbohydrate portion of wood. It is a gravimetric method for determining lignin directly in woody materials, for example, by TAPPI Standard T 222. This method is not used for routine quality control in the mill but has uses in the laboratory. Wood meal or pulp is treated with 72% sulfuric acid at 20°C (68°F) for 2.0 h followed by dilution to 3% sulfuric acid and refluxing for 4 h. The lignin is filtered in a tared crucible, washed, dried, and weighed. The isolated lignin in this manner is degraded considerably; nevertheless, it corresponds (by weight) closely to the original amount of lignin in the sample. Some of the lignin, especially in sulfite or hardwood pulps, remains soluble (called acid-soluble lignin) and can be estimated spectrophotometrically in the UV region. In the wood chemistry literature many modifications of the hydrolysis conditions exist, but the difference in the amount of lignin isolated is probably not appreciable. For example, the primary hydrolysis may be carried out for 1.5 h at 25°C (77°F) or 1 h at 30°C (86°F); the secondary hydrolysis is often carried out at 4% or 6% H_2SO_4 for 3–4 h, but TAPPI Standards seldom offer such flexibility.

19.4 BLEACHING CHEMICAL PULPS

Cellulose Viscosity

The cellulose degree of polymerization in low yield pulps and bleached pulps is very important as these processes lower the degree of polymerization of cellulose to the point where the paper strength properties are adversely affected. Cellulose viscosity of mechanical pulps and high yield pulps are not measured, as it is usually quite high and not a factor in the strength properties of papers derived from these pulps. Cellulose viscosity is measured by dissolving the pulp in cupriethylenediamine solution and measuring the viscosity of the solution (TAPPI Standards T 254 and T 230). See Chapter 1, Volume 2 for more detail.

Full Chemical Pulp Bleaching

Chemical pulp bleaching is accomplished with various compounds containing chlorine or oxygen and alkali extractions in several stages. Fig. 19.3 indicates why several stages with different compounds are used. The use of three to seven stages increases the efficiency of bleaching by reducing the amount of chemical required. This is due to the complex nature of lignin; each bleaching chemical is going to react differently with lignin. As lignin is a complex molecule with different types of linkages, the use of different chemicals will break various types of bonds. For example, a large increase in brightness is achieved by using relatively small amounts of ClO_2 in a later stage that could only be achieved using massive amounts of additional Cl_2 in stage 1; use of large amounts of chlorine in stage 1 would also cause much carbohydrate degradation. Plate 19.1 shows handsheets made from pulp at various stages of the bleaching process. Plate 19.2 shows several washers of a four-stage bleach plant. As chemical pulps are dark to begin with, bleaching increases brightness up to 70% with a maximum brightness of about 92%. Unlike bleached mechanical pulps, the high brightness is stable as the lignin is removed. Bleached chemical pulps are insensitive to color reversion, but high temperatures may induce some color reversion. Lignin removal is accompanied by significant losses of pulp yield and strength of the individual fibers. However, the strength of fiber–fiber bonding increases after bleaching. Bleaching of chemical pulps involves the use of chemicals which are more specific to lignin removal than to carbohydrate degradation compared with the chemicals used in pulping. If this were not true, one could simply continue the pulping process to remove more lignin. On the other hand, bleaching is

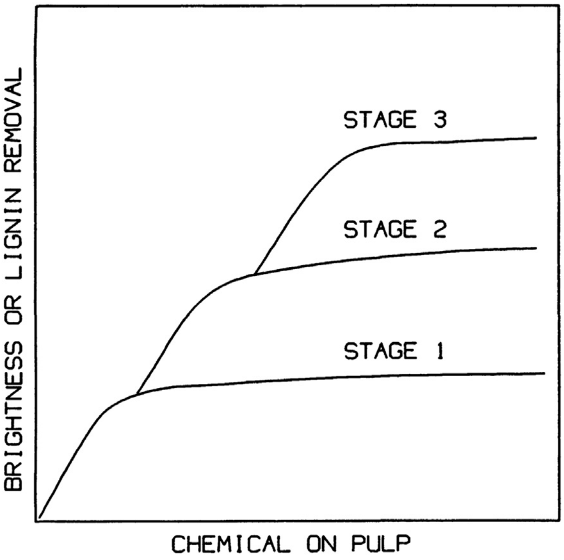


FIGURE 19.3 Hypothetical increased brightness versus chemical usage for three stages of bleaching.

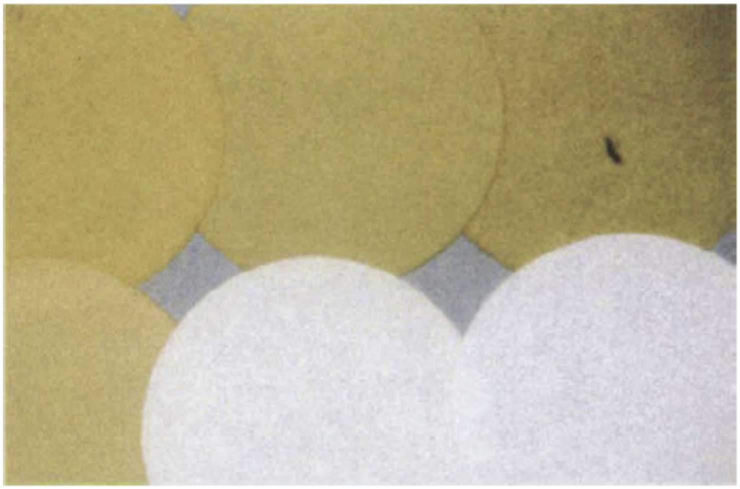


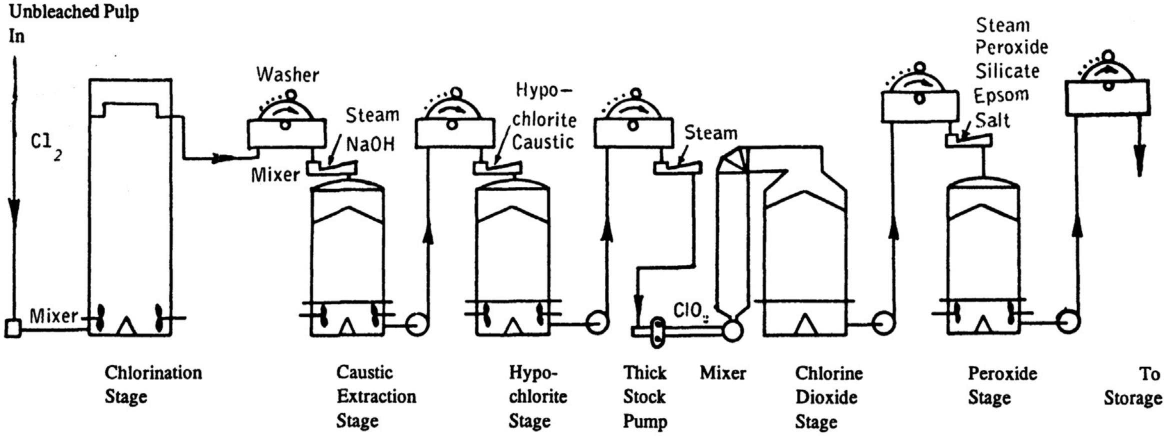
PLATE 19.1 Handsheets at various stages of bleaching. From upper right, counterclockwise the pulp samples are (1) unscreened, (2) screened, (3) after chlorination, (4) after alkali extraction, (5) after hypochlorite treatment, and (6) after hydrogen peroxide bleaching.

PLATE 19.2 Several stages of washing in a four-stage bleach plant.

much more expensive than pulping for a given amount of lignin removal. Within the range of useable bleaching chemicals, some are very specific to lignin removal while others are much less specific and cause appreciable carbohydrate degradation and diminished yield. For example, oxygen and chlorine are relatively inexpensive but not particularly selective for lignin removal. These chemicals are used in the early stages of bleaching to remove most of the lignin. Residual lignin is removed in later stages with expensive but highly selective bleaching agents such as chlorine dioxide, hypochlorite, and hydrogen peroxide. Table 19.1 is a summary of conditions used in various bleaching stages. Bleaching letters are explained below. Typical sequences are CEH (C: Chlorination; E: Extraction; H: Hypo) to a brightness of 84%–86% or CEHD (C: Chlorination; E: Extraction; H: Hypo; D: Chlorine dioxide) or CEHHD (C: Chlorination; E: Extraction; H: Hypo; H: Hypo; D: Chlorine dioxide) to a brightness of 92%. Fig. 19.4 shows the layout of a CEHDP sequence. Each stage consists of a pump to mix the chemical with the pulp, a retention tower to provide time for the bleaching chemical to react with the pulp

TABLE 19.1 Summary of Conditions Used in Various Bleaching Stages of Chemical Pulps

General Conditions ↓	C Stage	E_1 Stage	H Stage	D Stage	P Stage	O Stage
Chemical addition (on pulp)	3%–8%	2%–3%	2% (as Cl_2)	0.4%–0.8%	1%–2% Na_2O_2; Mg^{2+}; silicate	2%–3% 0.4–0.8 MPa 60–120 psi Mg^{2+}
Pulp consistency (%)	3–4	10–18	4–18	10–12	10	20–30 10–12
pH	0.5–1.5	11–12	8–10	3.5–6	8–10	10–12
Temperature (°C)	20–30	50–95	35–45	60–80	60–70	90–110
Time (h)	0.3–1.5	0.75–1.5	1–5	3–5	2–4	0.3–1.0



	Chlorination Stage	Caustic Extraction Stage	Hypochlorite Stage	Chlorine Dioxide Stage	Peroxide Stage
Time, hr:	1 hr	1-2 hr	2-4 hr	5 hr	4 hr
Temp., °F:	ambient	160	90	160	160
Cons.:	3.0%	12%	12%	12%	12%
pH:	1.5	10.5	9.0	3.0	10.5
Bright., %:	20%-25%	30%-35%	65-75	85%-90%	90%-92%

FIGURE 19.4 CEHDP sequence used to bleach pulp to 90%–92% brightness. *Reprinted from* Making Pulp and Paper, *©1967 Crown Zellerbach Corp., with permission.*

PLATE 19.3 A bleach tower of a hypochlorite stage.

(Plate 19.3), and a washer (Fig. 19.5) to remove the bleaching chemicals and solubilized pulp components. Diffusion washers may also be used (but are much less common) and are similar to those discussed in Chapter 12, Volume 1 in regard to pulp washing.

C Stage, Chlorine (Greek Chloros, Greenish Yellow)

Normally, chlorine is the first bleaching stage, where unbleached pulp is treated with elemental chlorine, Cl_2, that is either gaseous or in solution,

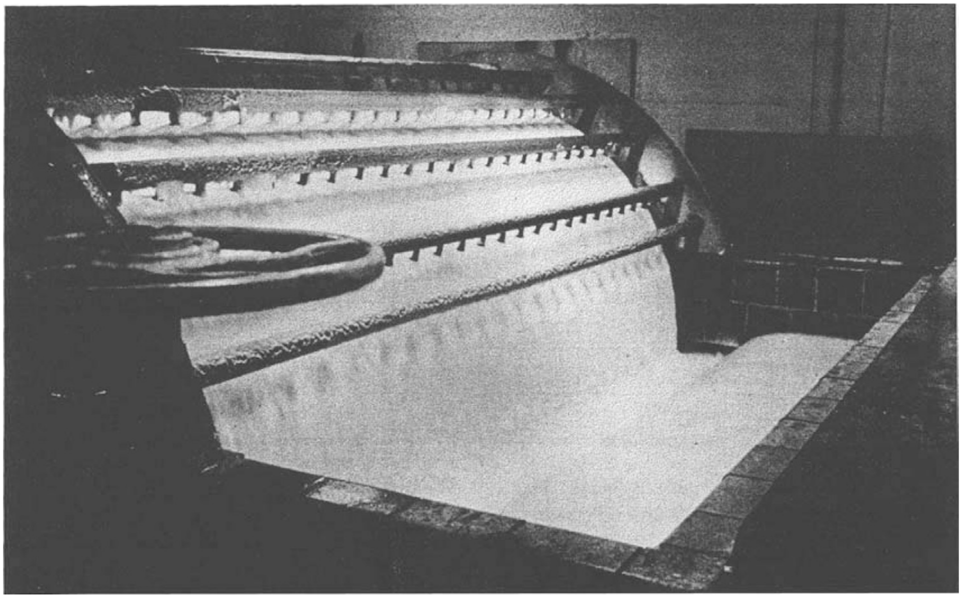


FIGURE 19.5 An open, bleach washer of the vacuum drum type. Modern washers are enclosed.

at a pH of 0.5–1.5. Bleaching is carried out with a pulp consistency of 3%–4%, ambient temperature as the reaction is quick, and a retention time of 0.3–1.0 h. Pressurized, upflow reactors are used as the solubility of chlorine in water is low (4 g/L at Sewage Treatment Plant, STP). Chlorine application is 6%–8% on softwood kraft pulps or 3%–4% on sulfite or hardwood kraft pulps. Elemental chlorine was the first agent used to chemically bleach cellulose fibers (cotton, not wood) and has been used since shortly after its discovery in 1774 by Scheele. Its large-scale use commercially for pulp bleaching had to wait until stainless steel was available in the 1930s. Chlorine is manufactured concomitantly with sodium hydroxide by electrolysis of sodium chloride; as these two chemicals are produced together, one often speaks of the chlor-alkali industry. One method of producing these chemicals is shown in Fig. 19.6. The production of chlorine is summarized as follows:

$$2NaCl + 2H_2O + \text{elect.} \rightarrow Cl_2 + 2NaOH + H_2$$

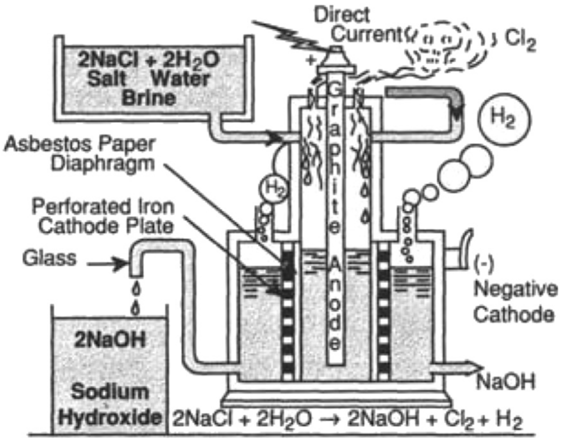


FIGURE 19.6 A method of NaOH and Cl_2 manufacture. *Redrawn from J. Ainsworth,* Papermaking, 1957 *Thilmany Paper Co., with permission.*

Chlorine is not overly specific to lignin, and much carbohydrate degradation occurs through its use. The chlorine reacts with lignin by *substitution* of hydrogen atoms for chlorine atoms (particularly on the aromatic ring), *oxidation* of lignin moieties to carboxylic acid groups, and, to a small extent, *addition* of chlorine across carbon–carbon double bonds (Fig. 19.7). The substitution reactions (Fig. 19.8) are probably the most important in the ultimate lignin removal. It has been known for a long time that chlorine is first rapidly depleted by the pulp and then is depleted much more slowly. This indicates several types of reactions are occurring. Fig. 19.9 shows how chlorine reacts with pulp as a function of time. The substitution and addition reactions are much faster than the oxidation reactions and do not leave Cl^- in solution, whereas oxidation reactions do. This is the basis for determining the type of reaction occurring. Oxidation includes reactions with both lignin and carbohydrates. Oxidation of the carbohydrates leads to a decreased cellulose viscosity and decreased pulp strength.

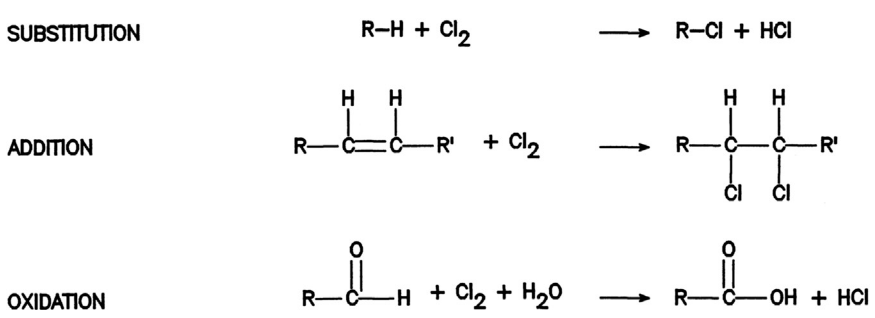


FIGURE 19.7 Examples of Cl_2 reactions with lignin. Oxidation reactions occur with both lignin and carbohydrates. In the case of the latter, significant decreases in pulp strength result.

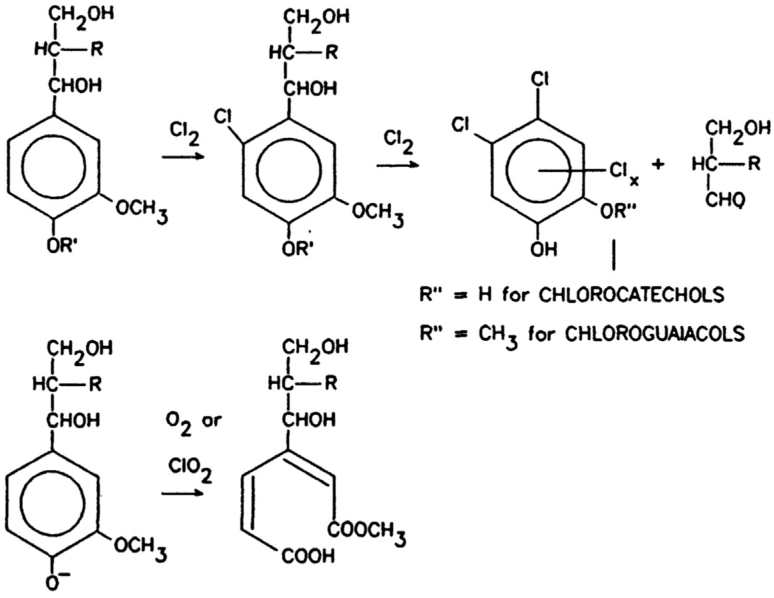


FIGURE 19.8 Example reactions of bleaching agents with lignin.

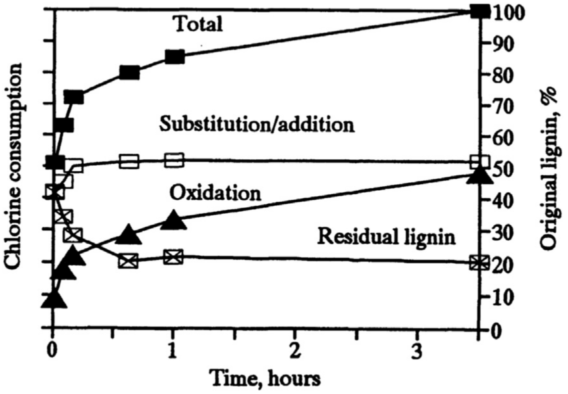


FIGURE 19.9 Reaction of excess Cl_2 and sulfite pulp with time. The top three curves use the left scale. The bottom curve (right scale) is residual lignin after NaOH extraction. *After Giertz (1951).*

The species hypochlorous acid (HClO) (Fig. 21.1, Volume 1 shows its formation vs. pH) especially contributes to oxidative degradation of the carbohydrates; therefore chlorination is carried out above pH 0.5 (to avoid acid hydrolysis of cellulose) and below pH 1.5 (to avoid carbohydrate degradation by oxidation). Also, sodium hypochlorite bleaching is carried out with excess NaOH to avoid carbohydrate oxidation by HClO. According to Giertz (1951), the actual species causing oxidation may be a complex of HClO and hypochlorite ion as the pH of maximum degradation is 6.5–7.5 and not 4–5, where hypochlorous is at a maximum (Fig. 21.1, Volume 1). In the past, the amount of chlorine added to pulp was controlled by measuring the residual chlorine after the chlorination stage. In fact it is better to avoid adding excess chlorine, particularly at elevated chlorination temperatures, so that the substitution reactions occur to completion (rapidly), but oxidation reactions are controlled by not allowing residual chlorine to be present. As Fig. 19.9 shows, the oxidation reactions do not increase the amount of lignin removed in the alkali extraction of sulfite pulp; however, this is less true for kraft pulps because of their highly condensed nature (O'Neil et al., 1962). For the same reason, kraft pulps require longer chlorination periods than sulfite pulps, 60–90 min versus 15–45 min, respectively. The practice of substituting about 10% of Cl_2 with ClO_2 (CD) has been practiced for a long time, as it results in a stronger pulp by avoiding overchlorination.

Lignin is not removed to a large degree in this stage, and the pulp actually gets darker (with a characteristic orange color). The pulp is diluted to 1% consistency and washed to remove acid which would otherwise consume alkali in the next stage. The lignin removal and brightness increase actually occur in the alkali extraction stage that invariably follows the chlorination stage. Chlorination produces chlorinated organic materials including a very small amount of dioxin, which has led to the use of other chemicals to replace a part or all of the chlorine use in bleaching (e.g., O and CD bleaching stages). Dioxin and bleaching is discussed in Chapter 15, Volume 2. Many mills are using high chlorine dioxide substitution. Chlorine-free bleaching sequences are used commercially for sulfite pulps at a few mills. Papers made from these pulps are promoted as "environmentally friendly" or words to that effect.

It is difficult to make bright grades of kraft pulps without the use of chlorine, but it is possible if a system is designed specifically for this purpose. The future will bring many changes in this area.

CD Stage

The CD stage is a modification of C stage bleaching, where some of the chlorine is replaced with ClO_2. ClO_2 acts as a scavenger of chlorine radicals in this stage. Substitution of 10% of the chlorine with chlorine dioxide is used to prevent over-chlorination. Substitution of 50% or more of chlorine with chlorine dioxide at many mills is becoming common to reduce production of dioxins and other chlorinated organic chemicals. One problem is that as Cl_2 and NaOH are both derived from electrolysis of NaCl, a slackening in the Cl_2 market will mean much higher NaOH prices. Other industries have taken advantage of excess Cl_2 supplies, such as the polymer industry in the manufacture of polyvinyl chloride and other chlorinated polymers, which has mitigated this effect.

E Stage

The E stage is *extraction* of degraded lignin compounds, which would otherwise increase the chemical usage in subsequent bleaching stages, with caustic (NaOH) solution. It follows the C stage and sometimes other stages of bleaching. When it follows the C stage (E_1), it is used at 2%–3% on pulp, often with a downflow tower because of the HC of pulp (10%–18%), with a temperature of 50–95°C (120–200°F) and a reaction time of 0.75–1.5 h. High temperatures and alkali loading up to 5% are used to remove hemicelluloses for dissolving pulps or absorbent pulps. In later E stages, alkali is used at less than 1% on pulp. The alkali displaces chlorine and makes the lignin soluble by reactions such as:

$$\text{Lignin} - \text{Cl} + \text{NaOH} \rightarrow \text{Lignin} - \text{OH} + \text{NaCl}$$

The lignin in the E_1 effluent gives a dark color that is ultimately responsible for much of the color of the final mill effluent. Recently oxygen gas has been incorporated into this stage (0.5% on pulp) at many mills and the term EQ applied.

H Stage

The H stage consists of bleaching with hypochlorite solution, usually as the sodium salt NaClO; this is the same chemical found in household liquid bleach. This stage is carried out at 4%–18% consistency, 35–45°C (95–113°F), 1–5 h, and pH 10. The process is often controlled by measuring the oxidation-reduction potential. It is important to maintain the pH above 8 because below this pH hypochlorite is in equilibrium with significant amounts of HClO (Fig. 21.1, Volume 1), which is a powerful oxidant of carbohydrates, with an E° of 1.63 V. As the pH is high, lignin is continuously extracted as it is depolymerized. Hypochlorite reacts principally by oxidation. About 1% on wood (based on chlorine) is used. This chemical is more selective than elemental chlorine but less selective than chlorine dioxide; consequently, the use of hypochlorite has decreased since the advent of chlorine dioxide. Cellulose is oxidized along its chain, forming aldehyde groups and making random cleavage more likely. Calcium hypochlorite was discovered in 1798 by dissolving Cl_2 in an aqueous slurry of calcium hydroxide and was the principal bleaching agent of the industry for a century. Sodium hypochlorite, which is now used as it leads to less scaling, is made from chlorine as follows:

$$Cl_2 + 2NaOH \rightarrow NaOCl + NaCl + H_2O$$

D Stage

The D stage involves bleaching with chlorine dioxide. Chlorine dioxide (first studied for pulp bleaching in 1921 by Schmidt and used for commercial pulp bleaching in the mid-1940s) is relatively expensive but highly selective for lignin. This makes it very useful for the latter bleaching stages where lignin is present in very low concentrations. It is explosive at concentrations above 10 kPa (1.5 psi, or 0.1 atm); hence, it cannot be transported and must be manufactured on site. Its solubility is 6 g/L at 25°C with a partial pressure of 70 mm Hg. It is used at consistencies of 10%–12%, 60–80°C (140–176°F), for 3–5 h at a pH of 3.5–6. It is used at 0.4%–0.8% on pulp. Downflow towers are used to decrease the risk of gas accumulation. The D stage is useful for reducing shive contents.

$ClO_2 \rightarrow 1/2Cl_2 + O_2$ (Undesirable breakdown above 100 torr pressure)

$2ClO_2 + H_2O \rightarrow HClO_3 + HClO_2$ (slow, undesired decompostion in soln.)

Chlorine dioxide may react in two steps. In the first step ClO_2^- is formed; this then reacts under acidic conditions to form Cl^-. Thus,

$$ClO_2 \rightarrow ClO_2^- \rightarrow Cl^-.$$

It reacts by oxidation; one reaction is shown in Fig. 19.8.

P Stage

Bleaching with hydrogen peroxide, H_2O_2, is not common for chemical pulps. (But this is changing somewhat as mills look for chlorine-free systems.) It is usually used for brightening mechanical pulps, but when it is used to bleach chemical pulps it appears as the last stage of a sequence such as C-E-H-P or C-E-H-D-P. It is used at 10% consistency, 60–70°C (140–160°F), pH of 8–10, for 2–4 h. It is an expensive bleaching agent but may be used more frequently as the use of elemental chlorine decreases. Peroxide oxidizes carbonyl groups of carbohydrates (produced by oxidants such as hypochlorite) to carboxylic acid groups. Its use with chemical pulps is fairly similar to that with mechanical pulps, except for a higher temperature.

O Stage, Oxygen Pulping and Bleaching

Oxygen bleaching or pulping is the delignification of pulp using oxygen under pressure (550–700 kPa or 80–100 psi) and NaOH (3%–4% on pulp). Oxygen bleaching has been used commercially since the late 1960s. This is an odorless, relatively pollution-free process used before chlorination at high consistencies (20%–30%) or MCs (10%–15%). Delignification is carried out at 90–130°C (195–266°F) for 20–60 min. The key to the use of O_2 delignification was the discovery that small amounts of magnesium ion (0.05%–0.1% on pulp) must be present to protect the carbohydrates from extensive degradation. This is the most inexpensive bleaching chemical to use but also the least specific for lignin removal. A considerable decrease in cellulose viscosity accompanies this process. Bleaching may be thought of as extended delignification, that is, an extension of the pulping process. Many mills have considered using an oxygen delignification step after pulping but before the traditional chlorination first step of bleaching. Some call it oxygen delignification; others call it oxygen bleaching. Many mills have added oxygen to the first alkali extract step, designated as the E step, because it is not a major change to the process and saves bleaching chemicals in subsequent stages. Oxygen is even less specific at lignin removal than chlorination, so it is used to decrease the softwood pulp Kappa number from 30 to 35 after pulping (20–24 for hardwoods) to 14–18 after the oxygen bleaching stage. Bleaching to Kappa numbers below this leads to unacceptable losses of the cellulose viscosity. The effluent of oxygen delignification can be used in the brown stock washers or otherwise ultimately sent to the recovery boiler because there is no chloride ion present that would lead to high dead loads and corrosion in the recovery boiler. Reducing the amount of lignin removed by the chlorination step by half reduces by half the color and biological oxygen demand from the bleach mill water discharge after secondary treatment. Environmental considerations are the main reason for using oxygen bleaching. The bleach plant produces mush of the color of the final mill discharge. There are two main methods of oxygen bleaching: MC and HC. The HC process is at 30% consistency and 90–110°C (195–230°F) in a pressurized reactor. In the MC process pulp at 10%–15% consistency (the normal consistency as it comes off the drum washers) is used. While HC oxygen bleaching is more common, there are some difficulties with it. The gas in the reactor contains high concentrations of oxygen and volatile organic chemicals such as methanol, ethanol, and acetone that are potentially explosive; it is difficult to evenly distribute NaOH and O_2; and the pulp is saturated with oxygen which tends to cause foaming on the pulp washers. Studies indicate that the temperature of oxygen bleaching is important to the selectivity of the process with better selectivity at 100°C (212°F) than 130°(266°F). Partial pressure of oxygen above 200 kPa (30 psig) leads to little increase in the rate of delignification.

Ozone Bleaching

The development and utilization of ozone treatment technology in the bleaching process in the pulp and paper industry has allowed recycling of waste streams from the bleach plant, producing dramatic reductions in the volume of liquid effluent and with pollutants, such as biological oxygen demand, chemical oxygen demand, color, and organochlorine compounds. Ozone is being used by several mills to produce fully bleached hardwood and softwood pulps that have mechanical properties compatible with most paper-making applications. Significant progress has been made in the optimization of both elemental chlorine-free (ECF) and totally chlorine-free (TCF) sequences (Hostachy and Serfass, 2006). When compared with the industrial development of oxygen delignification, which was initiated more than 40 years ago, the implementation of ozone for pulp bleaching has grown quite rapidly. Ozone can be used in both chemical and mechanical pulping and has enabled many pulp mills to improve product quality, environmental, and process performance. Significant progress has been made in the use of ozone for emerging green bleaching practice, favoring on-site chemicals production, including complete reuse of byproducts, minimizing the ecological footprint and reducing operating costs. Extended ozone delignification offers the possibility to reduce the effluent to be treated, as the filtrate from the ozone stage and further alkaline stages can be circulated back to the recovery boiler. In addition to hardwood and softwood pulps, ozone is also a promising option to bleach nonwood pulps. Ozone generation requires limited space. It is found to efficiently delignify all types of chemical pulps and is used either at medium or high pulp consistency in ECF and TCF bleaching. Charges of ozone typically used are lower than 6—7 kg/t of pulp. As ozone is a very efficient delignifying agent, it can partially or totally replace chlorine dioxide in an economical way. It is a highly competitive bleaching chemical that, when compared at equal bleaching power, is typically 1.2—1.5 times less costly than chlorine dioxide (Bajpai, 2012). ECF sequences combining ozone and chlorine dioxide are economically competitive with sequences using chlorine dioxide only, even when capital expenses for modifying process equipment are taken into consideration. They have the advantage of improved performance and added flexibility in regard to effluent characteristics and position the mill on the pathway to (nearly) effluent-free bleaching. In combination with (pressurized) hydrogen peroxide, ozone makes it possible to produce fully bleached TCF pulp while maintaining expenditures in bleaching chemicals at levels that are comparable, if not lower, than those pertaining to ECF bleaching.

Ozone can be used in both chemical and mechanical pulping and has enabled many pulp mills to improve product quality, environmental, and process performance (Hostachy, 2010c). Significant progress has been made in the use of ozone for emerging green bleaching practice, favoring on-site chemicals production, including complete reuse of by-products, minimizing the ecological footprint and reducing operating costs. Today, the overall concept is based on 100% oxygen recycling as each oxygen molecule is used twice; first to produce ozone and then for other applications such as oxygen delignification, white liquor oxidation, and effluent treatment. Extended ozone delignification offers the possibility to reduce the effluent to be treated, as the filtrate from the ozone stage and further alkaline stages can be circulated back to the recovery boiler. In addition to hardwood and softwood pulps, ozone is also a promising option to bleach nonwood pulps. Ozone generation requires limited space and can enable the pulp mill to improve its independence from the chemical market. It has been demonstrated that by taking into account carbon emission for bleaching chemicals production, supply chain, and local energy requirement, implementing green beaching with ozone can reduce carbon emissions up to 60% compared with conventional chemistry mainly based on chlorine dioxide. Moreover, implementing green bleaching practices does not have to mean sacrificing pulp quality but actually opens up opportunities to develop new paper grades.

Ozone is found to efficiently delignify all types of chemical pulps. It is used either at medium or high pulp consistency in ECF and TCF bleaching sequences. Charges of ozone typically used are lower than 6–7 kg/t of pulp. Indeed, as ozone is a very efficient delignifying agent, it can partially or totally replace chlorine dioxide in an economical way (1 kg of ozone replaces about 2 kg of pure chlorine dioxide). The effluent from ozone prebleaching can be used in brown stock countercurrent washing and taken to the chemical recovery system, providing its acidic nature is taken into account. The implementation of ozone for pulp bleaching has grown quite rapidly when compared with the industrial development of oxygen delignification.

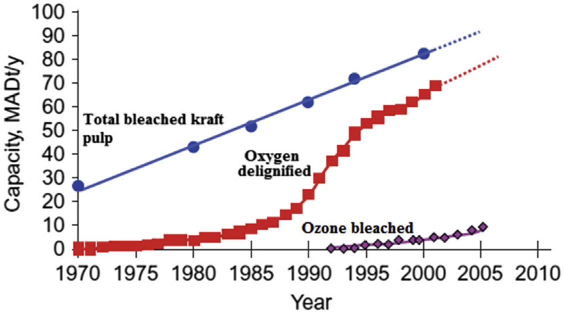


FIGURE 19.10 Evolution of the ozone bleached pulp. *Based on Hostachy and Serfass (2006).*

When compared with the industrial development of oxygen delignification, which was initiated more than 40 years ago, the implementation of ozone for pulp bleaching has grown quite rapidly (Fig. 19.10). The main reason underlying this evolution is the necessity to respond to growing environmental awareness, reflected both in regulatory constraints and market demands. The fact that ozone is finding growing acceptance as a bleaching chemical compatible with these requirements results from a combination of advances with regard to the bleaching process and associated equipment on the one hand and ozone production and handling on the other. Recent advances in ozone generation, and in particular the development of Ozonia's AT95 technology, as well as the lowering of oxygen cost by means of on-site production, have established ozone as a highly competitive bleaching chemical.

While it may come as no surprise that TCF sequences combining ozone and hydrogen peroxide are significantly less costly than those employing hydrogen peroxide only, it should be stressed that ECF sequences that combine ozone with chlorine dioxide are more cost-effective than ECF sequences using only chlorine dioxide. Ozone is today about 1.5 times less expensive than chlorine dioxide, when compared on the basis of the same costing structure, i.e., allowing for operating expenses and investment costs in both cases and at equal bleaching power.

Peroxy Acid Bleaching

A peroxy acid, or peracid, is an acid that contains a perhydroxyl group (−OOH). The common ones are peracetic acid and the Caro's acid (peroxymonosulfuric acid). They are powerful oxidizing agents. Caro's acid, H_2SO_5, is a dibasic acid in which the protons are attached to the oxygen of the hydroxyl group and the perhydroxyl group. The Caro's acid anion, HSO_5^-, is a considerably weaker acid than HSO_4^-, the anion of sulfuric acid. In pulp bleaching, peracetic acid can function as a delignifying or a brightening agent. Typically, the delignification conditions for peracetic acid are given below:

- initial pH 6−7
- temperature 70−80°C
- reaction time 60−180 min at MC

The peroxy acetic acid consumption is 3-kg/delignified kappa unit. As a brightening agent, peracetic acid improves brightness, brightness reversion, and other optical properties of the bleached pulp. As a postbrightening agent, peracetic acid can be applied in the high density storage tank for the production of wood-free paper at integrated pulp and paper mills or at paper mills using market pulp. At near-neutral pH levels, the brightening effect of peracetic acid is very rapid. Most of the improvement in optical properties occurs during the first few minutes, even at low temperatures and consistencies. In this application, 1−2kg peracetic acid per ton of pulp is sufficient to increase ISO brightness by 1.5−2.5 units. Also, it is found that the residual peracetic acid efficiently prevents microbial growth in paper machines. Furthermore, peracetic acid can limit brightness reversion of the bleached pulp and inhibits brightness reversion during beating. It is also shown to be effective in bleaching pigments and fillers. It should be noted that peracetic acid and Caro's acid have similar effects as delignifying and bleaching agents. Neither has common usage in the industry.

Elemental Chlorine-Free Processes

The focus on reduction in adsorbable organic halides (AOX) in bleach effluents has promoted ECF and TCF bleaching processes. ECF bleaching is a chlorine-free process in that no elemental (molecular) chlorine is used in the bleaching sequences. Although the term ECF does not specify it, typically chlorine dioxide is the principal bleaching agent for these processes.

ECF pulp, bleached with chlorine dioxide, continues to grow and is now dominating the world bleached chemical pulp market. Demand for ECF increased dramatically over the last 2 decades. ECF market share continues to grow in all pulp-producing regions. This trend will continue as all new production planned in all producing regions will incorporate ECF bleaching.

In North America, ECF production represents 96% of bleached chemical pulp production. Other regions are well on their way to replacing pulps bleached with molecular chlorine with ECF. This trend is expected to continue as new mills planned in Germany, Chile, Brazil, and Asia incorporate ECF bleaching.

The worldwide growth in ECF is increasing, while TCF production has not increased substantially since 1995. The amount of pulp produced in ECF sequences is more than 10 times the amount produced in TCF sequences. Both ECF and TCF processes are expected to yield less pulp per ton of wood fibers than conventionally bleached pulp because the use of increased number of bleach/wash stages result in greater fiber loss. TCF, which has the most protracted bleached cycle, has the lowest yield. Industry opinion is divided as to the relative merits of ECF and TCF processes.

Field studies, research and chemical analysis over the last 2 decades, have shown that treated wastewater from well-managed pulp and paper mills using ECF bleaching is virtually free of dioxin and persistent bioaccumulative toxic substances. The remaining chlorine containing organic substances resulting from ECF bleaching have a composition similar to those found in nature, degrade naturally, and do not persist in the environment. They present a negligible environmental risk to aquatic ecosystems. This research has been confirmed in ecosystem simulations comparing wastewaters from ECF bleaching with other nonchlorine bleaching concepts, including TCF. These investigations have reached a common conclusion. Studies comparing ECF and TCF effluents confirmed the absence of significant differences in biological effects in the aquatic environment.

ECF bleaching is being performed on both conventional and reduced kappa pulps. Table 19.2 shows the examples of ECF bleaching sequences.

Market pulp quality from ECF bleaching is excellent. Mill studies in Canada and the United States have shown high brightness, 89%–90% ISO, and high strength (burst, tear, tensile, viscosity) pulps are produced with ECF. ECF production does not require low lignin content of unbleached pulps and therefore has higher yield than today's TCF pulping and bleaching processes. For existing mills, conversion to ECF has been relatively easy for the following reasons:

- Many mills had existing chlorine dioxide generators that could be upgraded to the required production for relatively low capital cost
- Existing bleach plants were totally compatible
- Bleaching cost increased modestly, 5%–10%

TABLE 19.2 Few Examples of ECF Bleaching Sequences

OD(EOP)D
D(EO)DD
D(EOP)D
C/D(EO)D
AD(EO)DOD
(EO)DD
O(AD) (EOP)D
(EOP)D(PO)D

ECF, elemental chlorine-free.

ECF is integral to achieving the vision of minimum impact. A minimum impact pulp and paper mill maximizes wood yield; makes high quality paper that is easily recycled; maximizes energy production from biomass; minimizes water consumption, solid waste, and air emissions; treats and disposes of waste optimally; and creates sustainable value to society. Pulping and bleaching strategies incorporating ECF produce strong softwood fibers, minimizing the reinforcing fiber requirements for many paper grades such as lightweight coated. It has also been recognized that in combination with enhanced pulping, ECF manufacturing has a higher yield, using the least amount of wood compared with other pulping and bleaching techniques. Finally, ECF is compatible with, and at the leading edge of, so-called "closed loop" strategies for reducing wastewater from bleaching. Along with efficient wastewater treatment, closed loop strategies are providing optimal solutions for protecting and sustaining the receiving water ecosystem.

Modified Elemental Chlorine-Free Sequences

The current trend today is the use of modified ECF sequences, i.e., sequences which still use chlorine dioxide but not in the conventional manner of DEDED or ODED sequences. The key here is to make them as efficient as chlorine-containing sequences. The use of chlorine dioxide and ozone in combination—in (DZ) or (ZD) stages—has started to appear over the last few years. Indeed, basic chemistry tells us that the reactions of these two chemicals on lignin complement each other, as with the case of chlorine and chlorine dioxide combinations (DC), for example. It makes the process more efficient than DO or Z alone. The other interest in combining the use of ozone and chlorine dioxide lies in the fact that the required operating conditions (temperature and pH) are similar for the two chemicals, making it possible to run (DZ) or (ZD) stages with no intermediate washing. The criterion in the process is the replacement ratio, i.e., the amount of chlorine dioxide replaced by 1.0 kg of ozone. Ozone and chlorine dioxide (as pure chlorine dioxide) being of the same order of cost today, a replacement ratio higher than one means a reduction in chemical cost.

Totally Chlorine-Free Processes

The TCF bleaching processes do not use chlorine dioxide or any other chlorine containing chemicals. In the TCF process, only oxygen-based chemicals are used. These are oxygen molecules, hydrogen peroxide, ozone, and peroxy acids. The TCF technology is often used in combination with extended delignification in the pulping process.

In TCF bleaching, unpressurized (P) and pressurized (PO) peroxide stages, the slightly peracetic acid stage (Paa), and ozone stages (Z) are used. Transition metals contained in the pulp are first removed in a chelating stage (Q). Alternatively, acid hydrolysis can remove metals without the conventional chelating agent in a broad pH range. Oxygen delignification (often multistage) always precedes TCF bleaching. Applicable sequences are shown in Table 19.3. A high final brightness is also possible with sequences containing only alkaline bleaching stages, but these stages are most suitable as oxygen chemical sequences in fiberlines that also bleach pulp with the use of chlorine chemicals. Typical chemical consumption (kg/adt) in oxygen chemical bleaching of softwood kraft pulp of Kappa number 10%—88% ISO brightness is given in Table 19.4.

Peroxide and oxygen are not sufficient to delignify the pulp further when the Kappa number of the pulps is low. Ozone or peracids are more efficient delignifying chemicals and can be used to reduce the Kappa number to a low level before the final brightness increase in the PO stage. The chemical charges and process conditions will obviously vary depending on wood species, degree of system closure, etc. The brightness development in TCF sequence depends on the proportions of various chemicals used.

Today's TCF sequences are less selective than ECF and therefore have not been able to retain high strength values at full brightness. Several studies have shown that TCF tear strength at high brightness is 10% lower than ECF, and the pulps have lower fiber strength. The lower strength has implications for paper machine productivity and virgin fiber requirements in

TABLE 19.3 Few Examples of TCF Bleaching Sequences

OQ(PO) (PO)
O(ZQ) (PO) (ZQ) (PO)
O(Q) (PO) (ZQ) (PO)
OQ(PO) (PaaQ) (PO)
OQ(EOP) (PaaQ) (PO)

TCF, totally chlorine-free.

TABLE 19.4 Typical Chemical Consumption (kg/adt) in TCF Bleaching of Softwood Kraft Pulp (Kappa Number 10)

Chemicals	Chemical Consumption (Kg/adt)
H_2O_2	20
NaOH	32
O_2	6
O_3	5
H_2SO_4	20
EDTA	2

EDTA, ethylenediaminetetraacetic acid; *TCF*, totally chlorine-free.

recycled grades and recyclability. TCF production requires low lignin content of unbleached pulps and therefore has lower yield than today's ECF pulping and bleaching processes. Studies show TCF bleaching of 8 Kappa number pulp increases overall wood consumption up to 10% as compared with an ECF bleaching of 30 Kappa number pulp (30–32). In a tour of Scandinavian mills, mill experience confirmed the yield loss. All of the mills that produced any TCF pulp noted its lower strength properties.

For most existing mills, conversion to TCF is relatively difficult for the following reasons: the capital cost to convert ranges from $40 million to $190 million US; operating costs increase $20—$75 U.S. per ton (34–35); and existing bleach plants have insufficient retention time for efficient hydrogen peroxide bleaching. These estimates in operating cost increases have been by mills that produce both ECF and TCF. An Austrian mill which modernized its bleach plant to produce ECF determined that the incremental bleaching cost for TCF would be $60 US per ton.

The superiority of TCF over ECF bleaching in terms of environmental impact is questionable. There are some significant disadvantages in TCF bleaching, which explains the lack of interest still being expressed by most of the pulp producers. The most important of these is that bleaching a kraft pulp to high levels of brightness (90% ISO) is not possible without sacrificing some strength properties. The problem of cellulose degradation during TCF bleaching has been extensively studied.

Taking an OPZ(EO)P sequence, it was shown that each stage might contribute to some cellulose depolymerization. One critical factor is the amount of ozone introduced in the sequence. For charges higher than 5–6 kg/ton, the cellulose may be slightly depolymerized and oxidized. This last effect makes the pulp sensitive to any alkaline environment such as (EO)P, which leads to further chain cleavage by a mechanism that has already been well documented.

Consequently, despite the fact that such a sequence was close to optimum efficiency in terms of delignification (ozone is ranked in the same category as chlorine) and bleaching power, it is penalized by the occurrence of several degradation mechanisms taking place on cellulose in a synergistic way. One possible solution to the problem of cellulose degradation during TCF bleaching to 90% ISO is to limit the charge of ozone and to introduce some nondegrading bleaching agents in the sequence. The only reagents that demonstrate this property so far are the peroxyacids (peroxyacetic and peroxymonosulfuric acids). But more research is required to reduce the chemical cost to acceptable levels when peroxyacids are used.

Enzyme Bleaching

Two different strategies have been developed in using enzymes for chemical pulp bleaching:

1. hemicellulases (particularly xylanases) as a pretreatment for enhancing the chemical removal of lignin in multistage bleaching sequences
2. ligninases or laccases for direct delignification

The first one has led to a successful commercial mill-scale process, whereas the latter is still in the exploratory stage and awaits possible commercialization. The benefit in using enzyme for pulp bleaching depends on the bleach sequence used, the residual lignin content of the pulp, the final target brightness, and environmental concerns of the mill. The main goals have been directed toward reducing the charge of chlorine-containing chemicals in the bleach plant and lowering the AOX content of the bleach effluent. Enzyme has been used in conventional chlorine-containing sequences, such as (C/D) EDED, in ECF and TCF sequences. For more details see Chapter 24, Volume 1.

19.5 NEW DEVELOPMENTS

Dimethyldioxirane Delignification

Dimethyldioxirane (DMD) has been demonstrated to be a very selective delignification agent. It is a source of active oxygen, can be generated from acetone and peroxymonosulfate, and employed in-situ. Upon oxidation of a substrate with DMD, oxygen is transferred to the substrate and acetone is regenerated. In this reaction, DMD can transfer a single activated oxygen atom onto aromatic and unsaturated substrates, and acetone acts as a catalyst in the reaction. DMD as a pulp bleaching agent was tested for the first time by Lee et al. (1994) at Paprican and at the University of Missouri, St. Louis. The way in which the agent selectively delignified the chemical pulp was found to be similar to that of chlorine and chlorine dioxide. Elucidation of the pulp reaction mechanisms remains a subject of research activity. The commercialization of this technology remains to be seen.

DMD can be applied in two ways, as a delignifying agent or as an activating agent, before oxygen or alkaline hydrogen peroxide bleaching stages. In delignification studies, Lee et al. (1994) achieved a Kappa number reduction of greater than 80%, and the viscosity was the same as that achieved by bleaching with chlorine-containing compounds. Qin et al. (1999a) studied eucalyptus kraft pulp treated with 5% DMD, followed by caustic extraction, and the resulting pulp had the same Kappa number as a corresponding batch of the same pulp treated with oxygen, while the viscosity and delignification selectivity were superior to that of oxygen delignification. As an activating agent, DMD pretreatment before alkaline hydrogen peroxide bleaching was shown to be effective (Qin et al., 1999b, Abou-Youset and Hussein, 2001). Although there has been considerable study of DMD bleaching, only a few studies have considered the use of DMD treatment for dissolving pulp bleaching. So research on this effective and selective reagent applied in dissolving pulp bleaching will benefit the development of both textiles and cigarette filter tips industries.

Hydrogen Peroxide Activators

Nitrilamine (cyanamide) can be added to a hydrogen peroxide stage to increase the brightness threshold by 2–3 points. This effect will allow the mill either to lower peroxide charges or to attain higher brightness pulps. The charged nitrilamine would be consumed in the bleaching reaction and converted to urea. The use of tungstate and molybdate catalysts to activate acidic hydrogen peroxide for delignification reactions has also been investigated (Kubelka et al., 1992). Similarly, transition metal–substituted polyoxometalate cluster ions have been proposed primarily for use as delignifying agents (Weinstock et al., 1993). Polyoxometalate cluster ions are inorganic analogs of the organic platforms known to control the activity of transition metals in enzymes that selectively catalyze the oxidation of lignin. The polyoxometalate cluster can be reoxidized after reaction with lignin for recycle and reuse. Air and hydrogen peroxide have been used to reoxidize the catalyst. It has been shown that application of a silicon-tungsten-manganese-based cluster ion to an oxygen-delignified softwood kraft pulp at 125°C for 2 h decreases the Kappa number from 35 to 5 and only reduces the viscosity slightly (from 34 to 27 cP). Most of the work in this area is still at the development stage.

19.6 ANNOTATED BIBLIOGRAPHY

General Aspects

O’Neil, F.W., K. Sarkanen, and J. Schuber, Bleaching, in *Pulp and Paper Science and Technology*, Vol. 1, Libby, C.E., Ed. McGraw-Hill, New York, 1962, pp 346–374.
A good overview of bleaching chemistry.

Singh, R.P., Ed., *The Bleaching of Pulp*, Tappi Press, Atlanta, 1979, 694 pp.
While many recent developments in oxygen delignification, decreased use of elemental chlorine, dioxin formation, etc. are not covered, this text is an excellent reference for the topic. It is well illustrated and also covers equipment.

Bajpai, P (2012). *Environmentally Benign Approaches for Pulp Bleaching second ed*. Elsevier B.V, 406 pp.
This book focuses on environmentally friendly technologies that can help solve some of the problems associated with conventional bleaching technologies.

Reeve DW, In: Dence, C.W., Reeve, D.W. (Eds.), *Pulp Bleaching—Principles and Practice*. Tappi Press, Atlanta, p. 261 (1996a).

European Commission, July 2000. Reference Document on Best Available Techniques in the Pulp and Paper Industry.

Kappa Number, Permanganate Number, K Number

Alander, P., I. Palenius and B. Kyrklund, The relationship between different cooking degree numbers, *Paperi ja Puu* (8):403–406(1963).

Chiang, V.L., H.J. Cho, R.J. Puumala, R.E. Eckert, and W.S. Fuller, *Tappi J.* 70(2): 101–104(1987).

Guillory, A.L., *1982 Brown Stock Washing,* Tappi Press, Atlanta, Georgia, p 29.

Chlorination, Organochlorine Compounds

Giertz, H. W., Delignification with bleaching agents, in E. Hagglund, Ed., *Chemistry of Wood,* Academic Press, New York, 1951, pp 506–530.

Pryke, D.C., Mill trials of substantial substitution of chlorine dioxide for chlorine: Part II, *Pulp Paper Can,* 90(6):T203-T207(1989).

Reeve, D.W., Organochlorine in paper products, *Tappi J.* 75(2):63–69(1992).
The chlorinated organic compounds in bleached papers do not seem to be a health hazard because of the low concentration of mobile species and low fraction that might be transferred to the user.

Bajpai, P., Bajpai, P.K., 1996. Organochlorine Compounds in Bleach Plant Effluents—Genesis and Control. In: Pira International U.K., p. 127.

Bajpai, P., Bajpai, P.K., 1997. Reduction of Organochlorine Compounds in Bleach Plant Effluents. In: Eriksson, K.-E. (Ed.), Biotechnology in Pulp and Paper Industry (special edition) for Advances in Biochemical Engineering and Biotechnology. Springer Verlag, Berlin, p. 213.

Hise, R.G., R.C. Streisel, and A. M. Bills, The effect of brown stock washing, split addition of chlorine, and pH control in the C stage on formation of AOX and chlorophenols during bleaching, *Tappi J,* 75(2):57–62(1992). (Also in *1991 TAPPI Pulping Conference Proceedings.*)
Split addition of chlorine and other modifications of pulping and bleaching can decrease the production of dioxins and other chlorinated organic compounds. This is a useful work with 20 references.

Oxygen Supply, Oxygen Bleaching, and Delignification

Baeuerlin, C.R., M.H. Kirby, and G. Berndt, Vacuum pressure swing adsorption oxygen for oxygen delignification, *Tappi J.*, 74(5): 85–92(1991).
Oxygen for use at rates above 130 tons/day is usually produced by cryogenic distillation of air on-site. Oxygen for use at rates below 15 tons/day is best supplied by having oxygen delivered by truck or rail. For intermediate levels of oxygen supply, an on-site vacuum pressure swing adsorption

unit may be economical. The system works by adsorbing N_2, CO_2 and H_2O from air with synthetic zeolite sieves.

Coetzee, B., Continuous sapoxal bleaching operating, technical experience, *Pulp Paper Mag. Can,* 75(6):T223-T228 (1974).

The first commercial mill to use oxygen delignification was the Enstra mill of Sappi in South Africa where, notably, water is in short supply. The successful operation of this process at Sappi led to the widespread use of oxygen delignification and is reported in detail here. There are well over 100 articles on the subject in the primary literature of the last 20 years. Some recent general articles on oxygen bleaching follow.

Shackford, L.D. and J.M. Oswald, Flexible brown stock washing eases implementing oxygen delignification. *Pulp & Paper* 61(5): 136—141(1987); no references.

Kleppe, P.J. and S. Storebraten, Delignifying high-yield pulps with oxygen and alkali, *Tappi J,* 68(7):68—73(1985).

This publication reports the results of 4 years of production experience at a mill using medium consistency oxygen bleaching.

Enz, S.M. and F.A. Emmerling, North America's first fully integrated, medium-consistency oxygen delignification stage, *Tappi J.* 70(6): 105—112(1987).

This is a very good summary of operating conditions and results for hardwood pulp.

Althouse, E.B., J. H. Bostwick, and D.K. Jain, Using hydrogen peroxide and oxygen to replace sodium hypochlorite in chemical pulp bleaching, *Tappi J.* 70(6): 113—117(1987).

This is a review article with 10 references that concludes, in general, that using less hypochlorite at equal brightness gives higher pulp viscosity for kraft and sulfite pulps.

Tench, L. and S. Harper, Oxygen-bleaching practices and benefits: an overview, *Tappi J.* 70(11):55—61(1987).

This is a worldwide survey of mills using the title method.

Idner, K., Oxygen bleaching of kraft pulp: high consistency versus medium consistency, *Tappi* 7. 71(2):47—50(1988).

This article concludes that a slightly higher pulp viscosity is achieved with medium consistency than with high consistency oxygen bleaching.

Homsey, D., A.S. Perkins, J. Ayton, and M. Muguet, A mill survey of oxygen utilization in extraction and delignification processes, *Tiqfpi J.* 74(6):65—72(1991).

This is a practical discussion on oxygen delignification from mill experiences, especially for medium consistency mills, the growth of which has been spurred by the development of mixers for dispersing oxygen into pulp.

Hsu, C.L. and J.S. Hsieh, Advantages of oxygen versus air in delignifying pulp, *Tappi J.* 69(4): 125—128(1986).

van Lierop, B., N. Liebergott, and G. J. Kubes, Pressure in an oxidative extraction stage of a bleaching sequence, *Tappi J.* 69(12): 75—78(1986).

Gellerstedt, G. and E.-L. Lindfors, Hydrophilic groups in lignin after oxygen bleaching, *Tappi J,* 70(6): 119—122(1987).

Hsu, C.L and J.S. Hsieh, Oxygen bleaching kinetics at ultra-low consistencies, *Tappi J.* 70: (12): 107—112(1987). This is a laboratory study conducted at 0.4% consistency.

Ozone Bleaching

Byrd, Jr., M.V., J.S. Grazel, and R.P. Singh, Delignification and bleaching of chemical pulps with ozone: a literature review, *Tappi J.* 75(3):207—213(1992).

Byrd, Jr., M.V. and K.J. Knoernschild, Design considerations for ozone bleaching, A guide to ozone use, generation, and handling, *Tappi J.* 75(5): 101—106(1992).

Gottlieb, P.M., P.E. Nutt, S.R. Miller, and T.S. Macas, Mill experience in high—consistency ozone bleaching of southern pine pulp, *Tappi J*, 77(6): 117–124(1994).

Liebergott, N., B. van Lierop, and A. Skothos, The use of ozone in bleaching pulps, *TAPPI Proceedings 1991 Pulping Conference*, pp. 1–23 (81 references). The article was reprinted in two parts in *Tappi J.* 75(1): 145–152(1992) and 75(2): 117–124.

O'Brien, J., PaperAge tours Union Camp's Franklin, Va., ozone bleaching facility, *PaperAge* 109(7):9–12(July, 1993).

Young, J., Lenzing mill bringing second ozone bleaching line on stream. *Pulp & Paper* 66(9):93–95(1992).

Carre G, Wennerström M. (2005): Ozone bleaching – An established technology, IPBC, Stockholm, Sweden, 144–149.

Garcia J C; Lopez F; Perez A; Pelach M A; Mitje P; Colodette J L (2010). Initiating ECF bleaching sequences of eucalyptus kraft pulps with Z/D and Z/E stages.

Hostachy J C and Serfass R 2006 Ozone bleaching - State of the art and new developments. http://otsil.net/articles/ozone%20bleaching%20State%20of%20Art%20TECHNOLOGY%20.pdf

Hostachy, J.C., Apr. 18–21, 2010c. Use of Ozone in Chemical and High Yield Pulping Processes: Latest Innovations Maximizing Efficiency and Environmental Performance. In: 64th Appita Annual Conference and Exhibition. Melbourne, Australia, 349–354.

Gullichsen, J. "Fiber Line Operations". In: Chemical pulping – Papermaking Science and Technology, Gullichsen, J. and Fogelholm, C.-J. (Ed.), Fapet Oy, Helsinki, Finland: Book 6A, p. A19 (2000).

Chirat C, Nyangiro D., Struga B., Lachenal D. (2005): The use of ozone on high kappa softwood and hardwood kraft pulps to improve pulp yield, IPBC, Stockholm, Sweden, 74–80.

Lindstrom L-A; Norden S; Wennerstrom M (2007). High consistency ozone bleaching: present status and future, IPPTA vol. 19, no. 1, Jan.–Mar. 2007, pp 83-86.

Hypochlorous Acid Bleaching, MONOX—L

Klykken, P.O. and Hurt MM, Molecular chlorine free bleaching with MONOX-L, *1991 TAPPI Pulping Conference Proceedings*, pp. 523–532.

Hurst, M.M., R Korhonen, K. Vakeva, and R. Yant, High brightness pulp bleaching with Monoox-L, *PulpPaperCan*, 93(11): 41–44(1992).

Hypochlorous acid is purported to be an effective bleaching agent when used with a proprietary additive (said to be a C-2 monoalkyl amine) that protects cellulose from acid hydrolysis. (One wonders if this additive might be useful during chlorine bleaching.) A mill trial using this process is described here. This method helps keep chlorine and caustic use balanced. The production of dioxins is said to be low. Use of a weak hypo by-product from the ClO_2 generators is also helpful.

Chlorine Dioxide Bleaching

Schmidt, E., *Ber.* 54:1860 (1921); 56:25(1923).

Wilson, R., J. Swaney, D.C. Pryke, C.E. Luthe, and B.I. O'Connor, Mill experience with chlorine dioxide delignification, *Pulp &. Paper Can.* 93(10):T275-T283(1992).

This article is a good starting point with 42 references.

Chlorine Monoxide Bleaching

Bolker, H.I. and N. Liebergott, Chlorine monoxide gas a novel reagent for bleaching pulp. *Pulp Paper Mag. Can*, 73(11) 82–88(1972).

Chlorine monoxide, Cl_2O, was found to be an effective bleaching agent at 15%—30% consistency and could replace chlorine dioxide in later bleaching stages. For example, chlorinated, extracted sulfite pulp could be brought to 94 brightness with a single stage using 0.6% Cl_2O on pulp. Chlorinated, extracted kraft pulp was brought to 82 brightness when treated with 1% Cl_2O for 1 min; a second stage brought the brightness to 94%. Strength properties of the pulps were as good as those pulps bleached with chlorine dioxide. With unbleached kraft pulp, 2% Cl_2O was more effective than bleaching with 5.9% Cl_2, with 94% less color in the effluent.

Peracids

Ricketts, D.J., 1997. Role of Peracids Revisited for Delignification, Bleaching. In: Patrick, K.L. (Ed.), Advances in Bleaching Technology. Miller Freeman Books, San Francisco, Calif., p. 56.

Anderson, J.R., Webster, J.R., Amini, B., Wang, S., Chang, H.-m., Jameel, H., 1993. Peracids: A Further Step in the Evolution to TCF Chemical Pulp Bleaching. In: 47th Appita Annual General Conf. Proceedings, vol. 2. APPITA, Parkville, Victoria, Australia, p. 461.

Barros, D.P., Silva, V., Hamalainen, H., Colodette, J.L., May 2010. Effect of Last Stage Bleaching with Peraceticacid on Brightness Development and Properties of Eucalyptus Pulp. BioResources 5 (2), 881—889.

ECF and TCF Bleaching

Pryke DC (2003). ECF is on a roll: it dominates world bleached pulp production, Pulp Pap. Int. 45(8): 27—29.

Takagi H. The impact of elemental chlorine free bleaching on effluent characteristics, Jpn Tappi J. vol. 61, no. 7, July 2007, pp 46—50.

Loureiro P E G; Ferreira P J; Evtuguin D V; Carvalho M G V S. Effect of the final ECF bleaching stage on the Eucalyptus kraft pulp properties: a comparison between hydrogen peroxide and chlorine dioxide, International pulp bleaching conference, Quebec City, QC, Canada, 2—5 June 2008, pp 259—264.

Loureiro P E G; Santos A S M; Evtuguin D V; Carvalho M G V S. The influence of ECF bleaching history on the performance of a final hydrogen peroxide stage, Appita vol. 64, no. 1, Jan.—Mar. 2011, pp 83—88.

Alliance for Environmental Technology (2007). Trends in World Bleached Chemical Pulp Production: 1990—2007.

AMEC and Beca AMEC (2006). Review of ECF and TCF Bleaching Processes and Specific Issues Raised in the WWF Report on Arauco Valdivia. Prepared for Resource Planning and Development Commission. Tasmania, Australia. May 2006.

Andrew J; Chirat C; Mortha G; Grzeskowiak V. Modified ECF bleaching sequences for South African hardwood kraft pulps, International pulp bleaching conference, Quebec City, QC, Canada, 2—5 June 2008, pp 55—60.

Pryke, D.C., Farley, B. and Wolf, A., "Implementation of ECF Bleaching at Mead Paper Co., Chillicothe, Ohio." Proceedings, Tappi Pulping Conference. October 1995.

Xylanase Treatment

Daneault C, Leduc C, and J.L. Valade JL, The use of xylanases in kraft pulp bleaching: a review, *Tappi J.* 77(6):125—131(1994).

Enzymatic bleaching pretreatments (hypothetically) rely on breaking lignin–carbohydrate bonds in pulp.

Bajpai, P., 2012. Biotechnology in Pulp and Paper Processing. Springer Inc., New York, US, pp. 412.

Senior, D.J. and J. Hamilton. Biobleaching with xylanases brings biotechnology to reality, *Pulp & Paper 66(9):* 111–114(1992).

Dimethyl Dioxirane Delignification

Lee CL, Preprints, International Pulp Bleaching Conference, 1994, p. 273.

Lee CL, Hunt K, Murray RW. Annual Meeting - Technical Section, Canadian Pulp and Paper Association (pt B), B1–B8A (1993).

Qin WJ, Cui G, Liang WZ, Yu HS (1999a). *Journal of Cellulose Science and Technology* 7(2), 16–21 (1999a).

Qin WJ, Cui G, Liang WZ, Yu HS (1999b) *Chemistry and Industry of Forest Products* 19(3), 11–15.

Abou-Youset, Hussein. Journal of Korea Technical Association of the Pulp and Paper Industry 33(5), 25–29 (2001).

Hydrogen Peroxide Activators

Kubelka V, Francis RC, and Dence CW (1992), Delignification with acidic hydrogen peroxide activated by molybdate *J. Pulp Paper Sci.* **18**(3), 108.

Weinstock IA, Minor, JL, Reiner, RS, Agarwal, UP, Atalla, RH (1993). Raman and UV Visible Spectroscopic Studies of a Highly Selective Polyoxometalate Bleaching System. In Proceedings of the 1993 Pulping Conference, Atlanta, GA, USA, November 1993; pp. 519–532.

EXERCISES

1. What is the fundamental difference in approach to bleaching chemical pulps versus mechanical pulps?
2. In what types of pulps is color reversion a problem and why?
3. How is the lignin content of pulp measured as a quality control measure for the pulping process?
4. To approximately what percentage of lignin in pulp does a Kappa number of 30 correspond for a softwood pulp?
5. What is cellulose viscosity, and what is its ibid. significance?
6. Why is chlorine bleaching always followed by alkali extraction?
7. Would chlorine be used as a bleaching agent in stage 5 of a bleaching sequence? Why or why not?
8. Why are pH control and chlorine addition of critical concern during chlorine bleaching?
9. At what consistencies, temperatures, chemical usage etc. is oxygen delignification carried out for the MC and HC methods? What are the advantages of oxygen delignification? What are the disadvantages?
10. What are the advantages and disadvantages of bleaching in several stages?
11. Why is buffering action important during bleaching with sodium hypochlorite?
12. Why is the effluent from E_1 after chlorination not normally used in the brown stock washers?
13. Discuss how water can be conserved in the bleach plant.
14. Discuss how oxygen bleaching can conserve water, decrease color from the mill effluent, and save on chemical costs.

CHAPTER

20

Hexenuronic Acid and Their Removal

20.1 INTRODUCTION

Eucalyptus kraft pulps have become important raw materials for a wide range of printing and writing papers, specialty papers, and tissue papers. Because of the rapid growth in consumption of these papers, increasing demands have been placed on the development of technologies for pulping and bleaching of hardwood (HW) eucalypts. The focus of this development has been improved quality, particularly in terms of higher brightness levels, and also papermaking properties, reduced effluent emissions, and cost-efficient pulp production. In terms of the bleaching process, fundamental research largely focused on lignin chemistry, but now intensive investigations have been directed toward carbohydrate chemistry. It has been found that hemicelluloses affect a variety of important properties throughout the pulping, bleaching, and papermaking process.

Hemicellulose is a complex component of lignocelluloses. It is a heteropolysaccharide, consisting of pentoses, hexoses, and glucuronic acids. The most abundant hemicellulose in hardwoods is O-acetyl-4-O-methyl glucuronoxylan, whereas arabino-4-O-methyl glucuronoxylan forms a major part of the softwood (SW) hemicelluloses. During kraft pulping, extensive modification of the hemicelluloses takes place as a result of the dissolution of low molecular weight chains, end-initiated depolymerization reactions (primary peeling), and alkaline hydrolysis of glycosidic bonds, leading to secondary peeling and a reduction in the degree of polymerization. In addition, part of the 4-O-methyl glucuronic acid side groups, which also undergo alkaline dissolution along with the degradation/dissolution of the xylan chain, is converted to hexenuronic acids (HexA) (Fig. 20.1).

The presence of HexA in kraft pulps has become an active area of research and has been shown to have important implications for the manufacture of bleached chemical pulps. The amount of HexA produced in the pulp has been shown to be affected by pulping conditions such as temperature, pulping time, ionic charge, hydroxyl ion concentration, sulfidity, and liquor-to-wood ratio. HexA has been found to be unreactive in alkaline oxygen and peroxide bleaching stages, but because of its unsaturated nature it reacts readily with chlorine dioxide, chlorine, ozone, and peracids.

20.2 SIGNIFICANCE OF HEXENURONIC ACID

The presence of HexA groups in pulp results in increased consumption of potassium permanganate in the Kappa number test because of the well-known fact that permanganate

https://doi.org/10.1016/B978-0-12-814240-0.00020-3

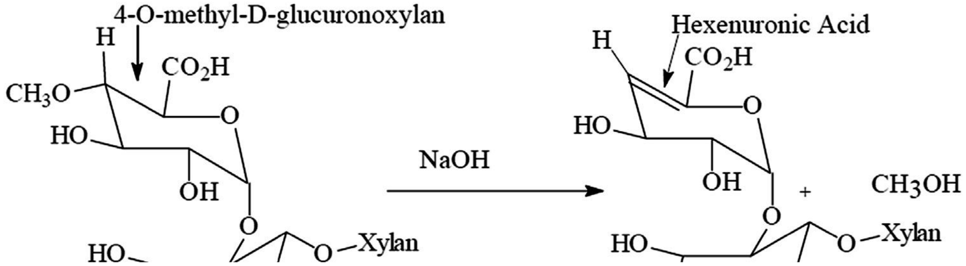


FIGURE 20.1 Conversion of 4-O-methyl glucuronic acid to hexenuronic acid during kraft pulping. Based on Clayton (1963).

reacts with carbon–carbon double bonds. Because Kappa number measurements are widely used to evaluate the efficiency of delignification in pulping and bleaching processes, the presence of these unsaturated constituents will affect the results of this analysis and give erroneously higher measurements for the amount of residual lignin in the pulp. It has been found that 10 mmol of HexA contributed to 1.05 Kappa units. In some studies, a value of 0.86 Kappa units has been quoted. HexA belongs to a class of compounds that contain enol ether or unsaturated carboxylic acid groups. These functional groups strongly affect the reactivity and stability of HexA and are the targets of both electrophilic and nucleophilic attack. As a result, chlorine dioxide and other electrophilic bleaching chemicals, such as chlorine, ozone, and the peracids, react with the “ene” functionality of HexA groups. This means that during delignification, bleaching chemicals are not consumed. This leads to higher bleaching chemical consumptions, increased effluent emissions, and increased production costs. Consumption of other bleaching chemicals such as hydrogen peroxide are affected indirectly because HexA results in a strong affinity of kraft pulps for certain transition metals that are mainly bound to the uronic acid groups. These metal ions, with manganese (II) being the most harmful, are known to catalyze the degradation of hydrogen peroxide during peroxide bleaching. The HexA groups have, however, been reported to be unreactive in alkaline oxygen and peroxide bleaching stages. The brightness reversion of kraft pulps is mainly because of the presence of residual lignin, chlorinated extractives, or oxidized carbohydrate units. Carboxylic acids and their counterions have, in the past, also been reported to affect brightness reversion. The yellowing tendency of kraft pulps has been especially shown to be proportional to the uronic acid content, and the removal of HexA, in particular, has been shown to improve the brightness stability of these pulps. Table 20.1 shows effects of HexA in bleaching.

TABLE 20.1 Effects of HexA in Bleaching

Increased consumption of bleaching agents to reach target brightness
Increased contribution to AOX and calcium oxalate in effluent
Increased binding of transition metal ions
Increased brightness reversion
May contribute to the formation and deposition of oxalates on bleaching equipment

20.3 METHODS FOR DETERMINATION OF HEXENURONIC ACID

Several methods have been developed to quantify the HexA content in kraft pulps. Most of these methods are based on the hydrolysis of HexA in the pulp followed by the analysis of the degradation products using ultraviolet spectroscopy and/or chromatography.

Spectroscopic method is based on the selective hydrolysis of HexA with formate buffer solution. The amount of HexA removed is calculated from the absorption maximum at 245 nm, which originated from the major hydrolysis product, 2-furancarboxylic acid.

Another spectroscopic method is based on the selective hydrolysis of HexA using a mercuric chloride—sodium acetate mixture as the hydrolysis solution. HexA was measured directly at 260 nm. A dual wavelength (260 and 290 nm) spectroscopic technique to eliminate spectral interference resulting from leached lignin in the hydrolysis solution has been also described.

Colorimetric method is based on the selective hydrolysis of the glucosidic link between HexA and the xylan chain. This technique involved several treatment steps with mercuric acetate, sodium arsenite, periodate, and reaction with thiobarbituric acid to yield a pink product. Quantification was carried out by chromatographic separation and/or ultraviolet—visible (UV-Vis) spectroscopy, with an absorption maximum at 550 nm.

Various cellulolytic and hemicellulolytic enzymes are used for the hydrolysis of the pulp polysaccharides. HexA-substituted oligosaccharides in the hydrolysate are then quantified by high-performance anion-exchange chromatography (AEC) coupled with pulsed amperometric detection (HPAEC-PAD).

Sulfuric acid is used for the selective hydrolysis of HexA groups to its degradation products, 2-furoic and 5-formyl-2-furoic acid. The degradation products were separated by AEC and quantified using suppressed conductivity detection.

A method simultaneously determines both residual lignin and HexA in kraft pulps by UV spectroscopy. In this method, the pulps are dissolved in cadoxen solution, and the pulp-cadoxen solutions were scanned in the 205—500 nm range.

UV resonance Raman (UVRR) spectroscopy is used for the determination of lignin and HexA. UVRR spectra are collected at wavelengths of 244 and 257 nm, and the data are calibrated using the partial least squares regression method for obtaining good predictability.

A Fourier transform infrared (FTIR) spectroscopic method is used for determining HexA content and Kappa number of high yield kraft pulps. In this method, pulp handsheets are scanned in the transmission mode in the wave number range 4000—800 cm. Based on the transmission spectra and using a multivariate analysis, the Kappa number and HexA content of the pulps are predicted.

Another method involves determining lignin and HexA content of bleached hardwood kraft pulps (BEKPs). The method is based on UVRR spectroscopy. The lignin content of the pulps are determined from the aromatic band heights of the UVRR spectra, and HexA content is simultaneously determined from the UVRR band heights of unsaturated C=O and C=C structures.

20.4 REMOVAL OF HEXA

Because of the problems encountered in bleaching operations, removal of HexA is very much important. Low HexA pulps are likely to provide a cleaner production opportunity and to be cost-effective due to lesser consumption of bleach chemicals and pollution. Removal of HexA can be carried out by either bleaching at acidic conditions or by acidic treatment at high temperature without bleaching chemicals. The reactive double bond in the HexA reacts with several bleaching chemicals such as chlorine, chlorine dioxide, ozone, and peracid but not with alkaline oxygen and hydrogen peroxide. Therefore, peroxide-bleached kraft pulps, especially HW kraft pulps with high HexA content, show low brightness stability. In bleached pulp, remaining HexA and carbonyl groups could be responsible for brightness reversion. The carbonyl groups are formed, for example, in ozone stages but can be removed in alkaline environment, i.e., hydrogen peroxide and alkaline extraction stages. Chlorine dioxide is able to eliminate structures such as double bounds and carbonyl groups. Furthermore, according to the literature it can be advantageous with adsorbed calcium in the pulp for decreasing brightness reversion.

Other ways of reducing HexA is either by modifying the pulping conditions or through mild acid hydrolysis. There are a number of hot acid or hot D in operation or coming into operation in BEKP mills.

Hot Acid Pretreatment or Combined Hot Acid and Chlorine Dioxide Stage

The removal of HexA by acid hydrolysis before bleaching offers several advantages. One of the major general advantages of acid hydrolysis, and the subsequent removal of HexA, is the reduction of bleaching chemical costs. The amount of furan derivatives produced during acid hydrolysis correlated linearly with the decrease in Kappa number of both unbleached and oxygen-bleached softwood and hardwood pulps. Depending on the type of pulp, the selective hydrolysis treatment removed 20–60 meq HexA per kilogram of pulp and reduced the Kappa number by 2–7 units. This resulted in a 30%–40% decrease in chemical consumption during ECF bleaching of birch kraft pulps. Use of an acid stage (at 90°C and pH 3–3.5) resulted in savings in chlorine dioxide up to 13%–17%, viscosity reductions of 105–115 dm^3/kg, and yield losses between 2.2% and 1.9%. Another study used an acid stage at 90°C and pH 3.5 and found that the acid stage reduced the Kappa number by 5 units with a selectivity of 50 dm^3/kg per Kappa number reduction (i.e., 250 dm^3/kg viscosity loss).

The presence of HexA is found to be a dominant component of the pulp Kappa number for HW kraft pulps, whereas for SW kraft pulps, it is found to be a minor component. Acid hydrolysis studies on HW kraft pulps showed that it may be possible to reduce the apparent pulp Kappa number by 35%–50% with a mild acid treatment before bleaching. The level of HexA in an HW kraft pulp can be influenced by the extent of delignification.

The conditions for mild hydrolysis are pH 3–3.5, temperature 85–95°C. The removal of HexA by acid hydrolysis before bleaching offers several advantages. One of the main advantages of acid hydrolysis, and the subsequent removal of HexA, is the reduction of bleaching chemical costs. Depending on the type of pulp, the selective hydrolysis treatment removes 20–60 meq HexA per kg of pulp and reduced the Kappa number by 2–7 units. This resulted in a 30%–40% decrease in chemical consumption during ECF bleaching of birch kraft pulps. The use of acid stage increases bleach pulp production, improves digester Kappa number, and improves acid washing of calcium salts. A hot acid stage is also operating at the Klabin Bacell, Camacari, Brazil, BEKP mill (TCF sequence OOAZP), and has been trialled at the VCP, Luiz Antonio, Brazil, BEKP mill (ECF sequences (O/O)A(ZD) (EOP)D and (O/O)AD(EOP) (ZD)) and CENIBRA, Bel Oriente, Brazil, BEKP mill (ECF sequence OADEDED). A kraft eucalyptus fiberline at Aracruz, Barra do Riacho, Brazil, used a hot acid stage, (AD)hot(EOP)(DD). Around 15%–20% savings in chlorine dioxide consumption somewhat reduced AOX formation, higher chemical oxygen demand (COD) COD formation, and less brightness reversion when compared with an initial D0 stage. Hot acid stages do not brighten the pulp although efficient in removing HexA and thus reducing the chlorine dioxide and decreasing the brightness reversion. In addition, such stages may decrease pulp yield, strength, and refinability and also require significant capital for installation. The savings in chlorine dioxide vary considerably and depend on eucalyptus species, number of bleaching stages, bleachability of the pulp, and process conditions in pulping. Thus, despite a few application in the Brazilian BEKP mills, adoption of acid hydrolysis as a standalone stage, Ahot or (AD)hot, has not been widespread and is debatable as an environmental measure.

A study was undertaken into a modified approach to the hot chlorine dioxide bleaching process, involving dividing the treatment into two separate phases. In the first phase, at about 60°C, chlorine dioxide was allowed to react, whereas in the second phase, at approximately 90°C, the acid hydrolysis of HexA was carried out. Heating after the first phase is performed at the top of an upflow–downflow type reactor. Results show that the chlorine dioxide requirement to reach a specific target brightness in the modified approach was the same as or slightly lower than that usually required and that the final viscosity was higher.

High-Temperature Chlorine Dioxide Stage

This technique is similar to (AD)hot technology (acid hydrolysis followed by chlorine dioxide without interstage washing), except that the addition of chlorine dioxide occurs at the beginning of the stage. The DHT (Hot chlorine dioxide) stage is based on the principle that the reaction rate of chlorine dioxide with lignin is faster than that with HexA. Hence, the majority of the chlorine dioxide is consumed by lignin at the beginning of the reaction, while the HexA are eliminated later through acid hydrolysis at high temperature and long exposure. The main motivations for applying the DHT stage in ECF bleaching of eucalyptus kraft pulps are potential reductions in capital costs (shorter sequences), operating costs, and increased pulp brightness stability. The DHT stage is more efficient than a conventional first D stage (D0). It decreases bleaching chemical costs and the formation of AOX in ECF bleaching. This is particularly true for three-stage sequence bleaching, which requires an extracted Kappa number of ∼3.5. However, the DHT stage usually negatively affects the pulp yield, viscosity/strength, and refinability, which can offset the economic gains. Moreover, the filtrate, rich in metal ions and organic matter (increased COD formation), may be difficult to manage. For long sequences, four to five stages, the gains due to a DHT stage can be negligible and, probably, do not justify its implementation. However, it must be considered that this technology can be a unique alternative in bleaching eucalyptus pulp to 90% ISO brightness, with acceptable chemical consumption in a three-stage bleaching sequence. Shorter sequences are being used to reduce the capital costs. There are some kraft eucalyptus mills operating or coming into operation with bleach plants, including a DHT stage, e.g., CENIBRA, Bel Oriente, Brazil, DHT(EO)DED (2002); Ripasa, Limeira, Brazil, DHT(OP)D (2003); CMPC, Santa Fé, Chile, DHT(EOP)D (2003/2004); Suzano, Mucuri (Bahia Sul), DHT(EOP)D(PO) (2004); and Mondi, Richards Bay, South Africa, DHT(OP)DD (2005). Despite the positive effects of Ahot, (AD)hot and DHT, possible drawbacks are increased yield loss (increased wood consumption), decreased pulp viscosity/strength and refinability, and increased COD in bleach plant effluents. The positive and negative effects of the three modes of “hot acid” or hot D stages vary considerably depending on the eucalyptus species, the number of bleaching stages, the bleachability of the pulp, and the process conditions in pulping and bleaching. Usually both the advantages and drawbacks are more accentuated for Ahot and (AD)hot than for DHT. There are a number of "hot acid" or hot D in operation or coming into operation in BEKP mills. The rationale for, and effects from, the implementation of any of the stages must be evaluated from case to case.

Ozone Stage

Ozone bleaching is found to be very effective in removing the HexA. Three types of prebleaching for removing HexA has been suggested: high consistency ozone bleaching, ZeTrac; chlorine dioxide bleaching at a conventional temperature, D(EOP); and chlorine dioxide bleaching at a high temperature (85–90°C, 60–120 min), (D/A)(EOP). The HexA content of the pulp was reduced in the prebleaching for all three alternatives. Comparing hot(D/A) with conventional D after prebleaching, the HexA reduction was more effective in (D/A), as expected, but with ozone bleaching the reduction was even more effective. Prebleaching with ozone reduced the HexA content with 89%–95% compared with 65%–73% with (D/A). Performing the (D/A) stage at an even higher temperature and longer retention time could increase the efficiency for removing HexA. However, results in the literature show that a more powerful (D/A) stage (95°C and 180 min) will decrease bleaching yield and beatability. Comparing ozone bleaching and hot chlorine dioxide bleaching, (D/A), in prebleaching, the ozone stage is more efficient than the (D/A) stage for reducing the HexA content. The use of ozone stage for lower brightness reversion by removal of HexA is most efficient when ozone is used in prebleaching. As ozone bleaching gives carbonyl groups in the pulp, it is important to have a stage or stages that decompose these groups in final bleaching. Efficient alternatives are, for example, chlorine dioxide by (Dn)D or by using peroxide as a last bleaching stage, DP.

The effects of the ozone stage consistency on delignification efficiency subsequent to the removal of HexA in the course of elemental chlorine-free (ECF) bleaching of eucalyptus kraft pulp has been assessed. The inclusion of an acid hydrolysis stage before the ozone phase was examined to better evaluate the removal of HexA. The results obtained show that the ozone stage was less efficient when HexA are removed, but the ozone stage carried out at high consistency was much less affected. The reduction of Kappa number was 29% greater with high consistency ozone bleaching than that with medium consistency. The inclusion of an acid hydrolysis stage allowed a reduction of up to 48% in the active chlorine charge in the bleaching process. The OAZhcDPp sequence with ozone at high consistency proved to be the most efficient in the consumption of chlorine dioxide and hydrogen peroxide.

Peracids

Peracids can also react with uronic and HexA groups mainly linked to xylans (Fig. 20.2). Peracetic acid (Paa) participation in an electrophilic reaction with the double bond in HexA, promoting its hydroxylation, as the nucleophilic attack secondary to the carbonylic groups, formed after hydrolysis of the hydroxylated compounds (Fig. 20.3). These reactions compete with each other and with electrophilic reactions between

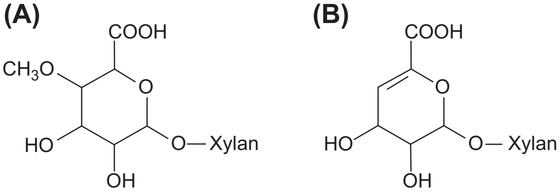


FIGURE 20.2 (A) 4-O-methyl-α-D-glucuronic acid and (B) 4-deoxyhex-4-enuronic acid.

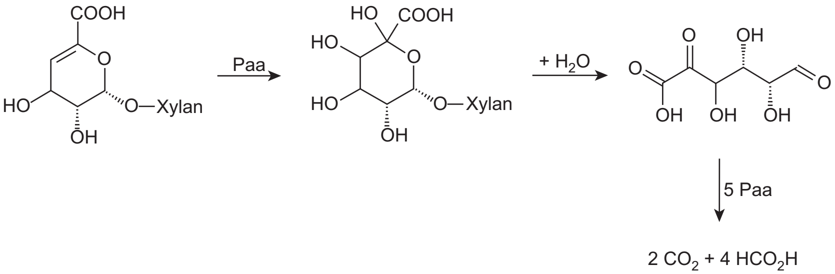


FIGURE 20.3 Hexenuronic acid oxidation by peracetic acid (Paa). *Based on Heikkilä et al. (1998).*

Paa and lignin. Thus, previous removal of uronic acids can favor lignin removal and bleaching efficiency with Paa.

Peroxymonosulfuric acid (Ps) effectively removes HexA even at low concentrations, and such effect is enhanced at higher temperature (Table 20.2). Ps acts both on lignin and on HexA, leading to reductions in unbleached pulp lignin content and a reduction on the chlorine dioxide bleaching demand. However, at high Ps load, cellulose could be degraded, resulting in poor mechanical properties after bleaching. Reductions in chlorine dioxide demand consumption reduced AOX generation during pulp bleaching (Table 20.3). Moreover, total phenols concentrations in bleaching effluents also dropped as a result of Ps pretreatment. Chlorine dioxide demand consumption was reduced by 42%—77% as a result of such pretreatment, with a proportional reduction in AOX generation and phenolic compounds release. Finally, effluent total organic carbon (TOC) concentrations seem to be a function of the Ps load during pretreatment.

Use of peroxymonosulfuric acid bleaching in laboratory experiments and pulp mill trial to evaluate the capability to degrade HexA has been examined. Oxygen BEKP was treated using peroxymonosulfuric acid under several pH and the reaction mechanism examined. Peroxymonosulfuric acid stage (Px stage) bleaching was examined in a mill where the bleaching sequence of hardwood was A-Z/D-Eop-D. Lignin degradation proceeded at almost the same rate from pH 1.5 to 5. It was found that pH 3 was the most effective to degrade HexA and that HexA was degraded by electrophilic attack of

TABLE 20.2 Peroxymonosulfuric Acid Treatment of Unbleached Kraft Pulp

Ps Load % (w/w dpb)	T (°C)	Kappa	HexA (mmol/kg)	Lignin (mmol/kg)
Reference pulp		9.7	43	53
0.20	93	5.3	21	19.3
0.20	100	3.8	9	24.5
0.20	107	3.5	7	13.8
0.36	65	7.2	26	—
0.36	85	6.7	25	—
0.36	100	3.9	9	—
0.53	20	7.0	34	—
0.53	60	6.3	30	—
0.53	100	3.3	8	—
0.60	93	4.8	19	13.9
0.60	100	3.3	8	16.0
0.60	107	2.2	2	—
1.00	93	4.1	14	2.7
1.00	100	2.8	6	—
1.00	107	2.0	0	8.2

Based on Petit-Breuilh et al. (2003).

TABLE 20.3 Effect of Peroxymonosulfuric Acid Pretreatment on Effluent Bleaching Composition

%Ps (dpb)	T (°C)	Color (ppm)	Phenol (ppm)	AOX (ppm)	COD (ppm)	TOC (ppm)	ClO_2 Savings in Bleaching
References pulp		167	6.3	2.1	413	153	
0.2	93	142	4.3	1.4	300	162	42%
0.2	100	127	3.8	–	335	–	57%
0.2	107	135	3.5	1.3	324	123	60%
0.6	93	129	3.9	–	268	182	44%
0.6	100	185	5.3	–	304	189	57%
0.6	107	165	4.3	–	304	–	76%
1.0	93	185	–	1.5	444	506	54%
1.0	100	135	4.0	–	357	468	68%
1.0	107	173	4.7	0.93	321	461	77%

Based on Petit-Breuilh et al. (2003).

peroxymonosulfuric acid. The peroxymonosulfuric acid treatment in low pH resulted in a decrease of fiber quality, whereas the peroxymonosulfuric acid treatment in high pH resulted in an increase of pulp brightness. One important factor was reaction temperature, which controls the reaction rate of peroxymonosulfuric acid. Higher temperature resulted in higher reaction rate. Reaction time was another important factor. Results showed that more than 60 min was required in the sufficient degradation of lignin and HexA. Based on these results, it has been concluded that optimum conditions for reaction were pH between 2 and 4, temperature between 60 and 90°C, and treatment time over 60 min. A simple, compact, mill scale peroxymonosulfuric acid generator was also developed. Following a successful trial, peroxymonosulfuric acid bleaching stage was installed in one of Oji Paper Co. Ltd's mills where the bleaching sequence of hardwood is A-Z/D-Eop-D. Chlorine dioxide has been reduced with no serious problems in the bleaching sequence.

TABLE 20.4 Combination of A- and Paa-Stages in Bleaching of Birch Kraft Pulp

Stage	–	Paa	A	A+Paa
Paa (%)	–	2.0	–	1.35
(mmol/kg)		263		178
Kappa number	11.8	6.1	8.2	3.7
HexA (meq/kg)	49.2	7.9	22.2	3.1
Brightness (% ISO)	42.9	58.0	45.8	62.7
Formic acid (mmol/kg)	–	47	22	33

Based on Bajpai (2012).

Reduction in HexA in eucalyptus kraft pulps occurs with the use of electrophilic bleaching chemicals. Paa, persulfuric acid, and other mild electrophiles are seen to decrease HexA content relative to residual lignin during bleaching of the pulps. Diffusion control reduces the selectivity of extremely powerful electrophiles toward HexA.

Significant reduction in HexA is obtained by using a combination of acid and peracetic stage in bleaching of birch kraft pulp (Table 20.4).

Comparison of combined Paa and chlorine dioxide bleaching stages of unbleached and oxygen delignified HW and SW kraft pulps with conventional chlorine dioxide and Paa stages as to Kappa number and viscosity reduction, selectivity, and reduction of HexA content was made. The combined stages were more efficient in Kappa number reduction than those with only chlorine dioxide. Part of the increased Kappa number reduction was due to an improved degradation of HexA. The stages where chlorine dioxide was added before the Paa showed a higher selectivity than those in which the chemicals were added simultaneously; in turn, the latter were more effective than the "pure" chlorine dioxide (D, D0) and Paa stages. However, Paa and chlorine dioxide appear to react with each other, leading to the degradation of both bleaching chemicals. The market price for Paa is currently much higher than that for chlorine dioxide, and it is doubtful whether the benefits of Paa addition can justify the extra cost. However, if the market price for Paa reduces due to an increased consumption or improved production methods, the technique might be interesting, particularly for special applications, and also when high brightness stability or a combination of high strength and high brightness are desired.

Enzymes

Enzymes, xylanase- and laccase-mediator system, are also found to be effective in removing HexA from kraft pulp. Xylanase treatment reduced the HexA content although the results were dependent on the type of xylanase used. However, enzymatic removal of xylans can also impact on refining properties of pulps and paper properties. Use of bacterial xylanases from families 11 and 5 improved delignification and bleaching, whereas a synergistic effect of the enzymes was observed on several pulp and paper properties. The xylanases enhanced the release of xylooligosaccharides branched with HexA, producing fibers with a reduced HexA and xylose content. On the other hand, these effects were found to be dependent on the xylanase used, with the family 11 enzyme being more efficient than the family 5 xylanase. Effluent properties were affected by the enzymatic sequences because of the dissolution of lignin and xylooligosaccharides, while some changes in the fiber morphology were also produced without affecting the final paper strength properties.

In another study, the two commercial xylanases were effective in increasing delignification (9%) and brightness (3% ISO). Its effectiveness was related to its greater action on releasing the xylan polymer, thus producing also a strong decrease in the HexA contents during the enzymatic stage (15%). All xylanases produced morphological changes in the fiber surfaces, but only with X_C cracks and holes that improved the diffusion of reactives were observed. The best bleaching results were obtained with the XD sequence.

Xylanase pretreatment enhanced the effect of the laccase-mediator system in reducing the content of a residual lignin and releasing more HexA. A similar brightness and smaller Kappa number could be obtained by using 30% less laccase, 80% less HBT, and a 45% shorter reaction time.

An enzymatic method for removal of HexA from kraft pulp has been developed. The removal of HexA by the laccase/violuric acid treatment resulted in a bleaching effect comparable with that of approximately one alkaline hydrogen peroxide stage and was not detrimental to the pulp. In addition to the bleaching effect and decrease of HexA, the laccase/violuric acid treatment also had a positive effect on the tensile index.

Use of laccase from *Trametes villosa* and the mediator hydroxbenzotriazole (HBT) in TCF pulp removed HexA by 23% and reduced brightness reversion by 8.4%. Assessment of the effect of HexA on pulp refining revealed that these oxidizable structures introduced hydrophilicity in the pulp. It was found that removing HexA from TCF pulp altered its refining outcome in regard to drainability and water retention capacity. In addition, it resulted in paper with comparable strength-related properties that required no additional refining energy.

Removal of HexA may aid in improving the bleaching performance and brightening effect of xylanases. HexA, because of the presence of unsaturated carboxylic acid group and enol ether, is reactive with nucleophilic and electrophilic chemicals, substantially affecting pulp bleaching. It has the ability to alter the optical properties of bleached pulps, as it decreases brightness and increases brightness reversion. Xylanase pretreatment is used to enhance brightness development during chemical bleaching. HexA was observed to have vital influence in brightness development of chemical pulps during xylanase-aided biobleaching.

New enzyme-based delignification/bleaching methods have been developed for the slow generation of oxidizing compounds. These methods have been developed with the assistance of the hydrolase-mediated oxidation system (HOS), other dioxirane-producing and peroxynitrous acid (PNA)-producing systems, new laccase-based oxidation procedures with special activating compounds, laccase/lipase-based procedures for the generation of fatty hydroxamic acids as laccase activators. A comparison has shown that similar delignification results can be obtained with all the methods tested. Results obtained with two enzymatic systems (HOS, PNA) with and without strong acid posttreatment, in comparison with strong acid treatment alone, removed most of the HexA in this pulp. Extended HOS and HOS alone in combination with a slight acid posttreatment resulted in significant saving of the strength properties of the pulp at almost the same HexA removal rates.

Other Methods

Japanese researchers studied the potential of UV irradiation to degrade HexA of ECF-BEKP. UV treatment significantly reduced HexA content under the acidic conditions, while the most suitable wavelength appeared to be 254 nm. Acidic papers produced from UV-irradiated pulps exhibited inhibition of yellowing induced by HexA in the aging test. It has been concluded that UV irradiation has the potential to be developed as a method for inhibiting the yellowing of HexA-containing acidic paper.

20.5 ANNOTATED BIBLIOGRAPHY

Aracri E, Vidal T (2010). Xylanase- and Laccase-Aided Hexenuronic Acids and Lignin Removal from Specialty Sisal Fibres. International Journal of Engineering Science, Nov, 2010, vol. 48, no. 11, pp. 1233–1241.
The effectiveness of the combined use of xylanase and laccase for the removal of hexenuronic acid (HexA) and lignin from sisal pulp fibers.

Bajpai PK, Bajpai P, Anand A, Sharma N and Mishra OP (2005), Hexenuronic acids in different pulps and its removal. Proc. Paperex 2005 India (seventh International Conference on Pulp Paper and Conversion Industry), New Delhi, Dec 3–5, 2005, p. 393–405.
This paper reports hexenuronic acids in different pulps and their method of removal.

Bajpai (2012). Environmentally Benign Approaches for Pulp Bleaching, second Edition. Elsevier Inc. USA.
This book focuses on environmentally friendly technologies that can help solve some of the problems associated with conventional bleaching technologies.

Buchert J, Teleman A, Harjunpaa V, Tenkanen M, Viikari L and Vuorinen T (1995). Effect of Cooking and Bleaching on the Structure of Xylan in Conventional Pine Kraft Pulp, Tappi Journal, 78(11): 125–130.
The effect of cooking and bleaching on the structure of xylan in conventional pine kraft pulp is presented in this paper.

Cadena EM, Vidal T, Torres AL (2010). Influence of the hexenuronic acid content on refining and ageing in eucalyptus TCF pulp, Bioresour. Technol. vol. 101, no. 10, May 2010, pp 3554–3560.
This paper reports that by using an enzyme-mediator treatment (laccase from *Trametes villosa* and the mediator hydroxybenzotriazole), brightness reversion

caused by the presence of hexenuronic acids can be alleviated.

Call HP (2002) Delignification/bleaching and removal of hexenuronic acids with the aid of hydrolase and oxidoreductase-activated oxidation reactions, Cost workshop Biotechnology in the pulp and paper industry. Cost E23 Action, Poster Session, Grenoble, France, 28–29 Nov. 2002, no. 4, 6 pp.

Delignification/bleaching and removal of hexenuronic acids using hydrolase and oxidoreductase-activated oxidation reactions is discussed in this paper.

Chai XS, Luo Q, Yoon SH and Zhu JY (2001a). The Fate of Hexanuronic Acid Groups During Kraft Pulping of Hardwoods, Journal of Pulp and Paper Science, 27 (12): 403–406.

The fate of hexanuronic acid groups during kraft pulping of hardwoods is examined in this study. HexA content in hardwood pulps continued to increase with delignification and did not decrease until much later in the pulping process. The variations in wood species contributed not only to the HexA content but also to the time-dependent HexA content profile.

Chai XS, Zhu, JY and Li J (2001b). A Simple and Rapid Method to Determine Hexenuronic Acids Groups in Chemical Pulps, Journal of Pulp and Paper Science 27 (5): 165–175.

This paper describes a new procedure to determine hexenuronic acid (HexA) groups in kraft pulp. The method is based on the highly selective hydrolysis of HexA from a pulp sample in a mercuric chloride–sodium acetate solution.

Chakar FS, Allison L, Ragauskas, AJ, McDonough, TJ and Sezgi U (2000). Influence of Hexenuronic Acids on US Bleaching Operations, Tappi Journal, 83(11): 62.

Effect of HexA on the US pulp bleaching operations in DFRC project F015 is discussed. The impact on pulp bleachability, methods of HexA generation and removal, and their impact on pulp properties are discussed.

da Silva MR, da Silva FJ (2003). The role of ozone in removal of hexeneuronic acids and delignification during ECF bleaching of eucalyptus kraft pulp, Papel vol. 64, no. 3, Mar. 2003, pp 89–95.

The role of ozone in removal of hexenuronic acids and delignification during ECF bleaching of eucalyptus kraft pulp is discussed in this paper.

Eiras KMM and Colodette, JL (2003). Eucalyptus Kraft Pulp Bleaching with Chlorine dioxide at High Temperature, Journal of Pulp and Paper Science, 29(2): 64–69.

Bleaching of eucalyptus kraft pulp with chlorine dioxide at high temperature for the removal of hexenuronic acids is examined.

Evtuguin DV, Daniel, AID. and Pascoal Neto C (2002). Determination of hexenuronic acid and residual lignin in pulps by UV spectroscopy in cadoxen solution. J. Pulp and Paper Sci. 28(6): 189–192.

A new method for the simultaneous determination of hexenuronic acid and residual lignin in kraft pulps by UV spectroscopy in cadoxen solutions is proposed. Unbleached or partially bleached hardwood or softwood pulps soluble in cadoxen can be analyzed. The HexA content determined by this new method is about 5% higher that that obtained by the conventional acid hydrolysis technique.

Fagerstrom R, Tenkanen M, Kruus K, Buchert J (2001). Removal of hexenuronic acid side groups from kraft pulp by laccase-mediator treatment. Eighth International conference on biotechnology in the pulp and paper industry, Helsinki, Finland, 4–8 June 2001 edited by Vahala P, Lantto R, pp 225–227.

Removal of hexenuronic acid side groups from kraft pulp by laccase-mediator treatment is discussed in this paper.

Fatehi P, Malinen R O, Ni Y (2009). Removal of hexenuronic acid from eucalyptus kraft pulps during chlorine dioxide—based and ozone-based ECF bleaching sequences Appita vol. 62, no. 3, May 2009, pp 212—218.

This paper focuses on the determination of hexenuronic acid content in the chlorine dioxide—based and ozone-based bleaching sequences for eucalyptus kraft pulps and the effect of acid hydrolysis (for HexA removal) on the selectivity and bleaching of these two bleaching sequences.

Furtado FP, Evtugin, DV. and Gomes, TM (2001). Effect of the Acid Stage in ECF Bleaching of Eucalyptus globulus Kraft Pulp Bleachability and Strength, Pulp and Paper Canada, 102(12): 93—96.

The effect of hot acid stage before ECF bleaching of eucalyptus globules pulp on yield, mechanical properties, and bleach chemical consumption was examined in this study. The hot acid stage in combination with DEDED sequence resulted in decrease in the Kappa number and active chlorine consumption.

Gellerstedt, G. and Li, J (1996). An HPLC Method for the Quantitative Determination of Hexeneuronic Acid groups in Chemical Pulps, Carbohydrate Research, 294: 41—51.

An analytical method for the quantitative determination of hexenuronic acid groups has been developed. The procedure involves a selective hydrolysis with mercuric acetate of the glucosidic linkage between the hexenuronic acid group and the xylan chain followed by oxidation with periodates to form beta-formyl pyruvic acid. The latter is reacted with thiobarbituric acid, and the red-colored adduct formed is separated by reverse phase HPLC and quantified by measuring the absorbance at 549 nm.

Granstrom A, Roost C, Eriksson T, Larsson P, Gellerstedt G (2000). Influence of hexenuronic acid groups on the thermal yellowing of TCF-bleached birch kraft pulps, Sixth European workshop on lignocellulosics and pulp (EWLP 2000). Advances in lignocellulosics chemistry towards high quality processes and products, Bordeaux, France, 3—6 Sept. 2000, pp 343—346.

Investigation was carried out on the variables influencing the thermal yellowing of TCF-bleached birch kraft pulps. Temperature and hexenuronic acid content have been found to be the most influential parameters, followed by aging time and pH.

Heikkilä, M, Räsänen, E, Stenberg, H, and Vuorinen, T (1998). Competing electrophilic and nucleophilic reactions of peracids, In: Proc. Intl. Pulp Bleaching Conf, Helsinki, 139—144.

Peracetic acid (Paa) participation in an electrophilic reaction with the double bond in hexenuronic acid, promoting its hydroxylation, as the nucleophilic attack secondary to the carbonylic groups, formed after hydrolysis of the hydroxylated compounds has been discussed. These reactions compete with each other and with electrophilic reactions between Paa and lignin.

Henricson K, Pikka O, Kauppinen M (1999). Selective hydrolysis of hexenuronic acid groups in mill scale bleaching of hardwood pulp, sixth International conference on new available technologies, Stockholm, Sweden, 1—4 June 1999, pp 158—163.

Method for selectively removing HexA through a mild acid hydrolysis of kraft pulps is reported. The potential of the method as a part of ECF and TCF bleaching sequences was studied with several Finnish companies. During the selective hydrolysis, HexA was converted to furan derivatives that could be quantified from the hydrolyzate by UV spectroscopy. The amount of the furan derivatives correlated linearly with the decrease in Kappa number of both

unbleached and oxygen-bleached softwood and hardwood pulps.

Hoang, V, Bhardwaj, N.K. and Nguyen, KL (2005). An FTIR method for determining the content of hexenuronic acid (HexA) and Kappa number of a high yield Kraft pulp. Carbohydr. Polymers 61: 5–9.

This paper defines FTIR method for determining HexA content and Kappa number of high yield kraft pulps. Pulp handsheets were scanned in the transmission mode in the wave number range of 4000–800 cm^{-1}. Based on the transmission spectra and using a multivariate analysis, the Kappa number and HexA content of the pulps were predicted.

Ikeda T, Ohi H (2003). Brightness stability and hexenuronic acid content of totally chlorine-free hardwood bleached pulp, 12th International symposium on wood and pulping chemistry (ISWPC), Madison, WI, USA, 9–12 June 2003, vol. I, pp 219–222.

In this study, TCF bleaching sequences in light of the chemical behavior of hexenuronic acid in kraft pulps were examined. The results were used to develop an acid treatment in which 70% of the hexenuronic acid in kraft pulp was removed and full bleaching followed treatment by ozone and the hydrogen peroxide. The brightness stability of the pretreated pulps was found to be superior.

Jaaskelainen, A-S, Saariaho, A-M. and Vuorinen, T. (2005). Quantification of lignin and hexenuronic acid in bleached hardwood Kraft pulps: A new calibration method for UVRR spectroscopy and evaluation of the conventional methods. J. Wood Chem. and Technol. 25: 51–65.

A method was developed to determine lignin and HexA content of bleached hardwood kraft pulps. The method was based on UVRR spectroscopy. The lignin content of the pulps were determined from the aromatic band heights of the UVRR spectra, and HexA content was simultaneously determined from the UVRR band heights of unsaturated C=O and C=C structures.

Jiang, Z. –H, Van Lierop, B. and Berry, R (2000). Hexenuronic Acid Groups in Pulping and Bleaching Chemistry, Tappi Journal, 83(1): 167–175.

This study reported that by using the selective hydrolysis, chlorine dioxide consumption can be reduced by 6.8 kg ClO_2/ton of pulp in case of hardwood pulps.

Jiang, Z-H, Audet, A, Sullivan, J, Van Lierop, B. and Berry, R. (2001). A new method for quantifying hexenuronic acid groups in chemical pulps. J. Pulp and Paper Sci. 27(3): 92–97.

In this method, sulfuric acid was used for the selective hydrolysis of HexA groups to its degradation products, 2-furoic and 5-formyl-2-furoic acid. The degradation products were separated by anion-exchange chromatography (AEC) and quantified using suppressed conductivity detection.

Juutilainen S, Vuorinen T, Vilpponen A, Henricson K, Pikka O. Combining chlorine dioxide bleaching of birch kraft pulp with an a-stage at high temperatures TAPPI pulping conference, Orlando, FL, USA, 31 Oct.–4 Nov. 1999, vol. 2, pp 645–651.

This study showed that the selective hydrolysis of hexenuronic acid of hardwood kraft pulp may be coupled with chlorine dioxide prebleaching at high temperatures. A D/A/D sequence combines (1) oxidation of phenolic lignin structures at high pH, (2) hydrolysis of HexA, and (3) oxidation of nonphenolic lignin structures.

Katsukwawa S, Miyawaki S, Koyanagi T (2010). Development of techniques to remove hexenuronic acid by UV irradiation, 77th pulp and paper research conference, Tokyo, Japan, 17–18 June 2010, pp 20–25.

Potential of UV irradiation to degrade hexenuronic acid (HexA) of elemental chlorine-free bleached hardwood kraft pulp

was seen. UV treatment significantly reduced HexA content under the acidic conditions, while the most suitable wavelength appeared to be 254 nm.

Kumar S, Mishra SP, Mishra OP Bajpai P, Tripathi S, Bajpai P.K and Varadhan R (2007). Hot chlorine dioxide versus conventional D_O stage in ECF bleaching of kraft pulps. IPPTA J. 19(1), 87—91.

A comparison between conventional ECF bleaching and the hot chlorine dioxide bleaching was made. With the use of D_{HT} stage, total chlorine dioxide consumption reduced.

Li, J. and Gellerstedt, G (1997b). The Contribution to Kappa Number from Hexenuronic Acid Groups in Pulp Xylan, Carbohydrate Research, 302(3—4): 213—218.

This study showed that high temperature ClO_2 bleaching has higher bleaching efficiency than the low temperature conventional sequence. For the oxygen delignified kraft pulps (Kappa number 10.2), the former sequence saves more than 20% chlorine dioxide charge compared with the later one when reaching the same high brightness (88% ISO). Low pH value in D0 stage of high-temperature bleaching promotes the delignification and hydrolysis processes.

Pereira M, Melo R, Daza C (2003). Influence of removal of hexenuronic acid in the bleaching of Eucalyptus kraft pulp, Celul. Pap. (Chile) vol. 19, no. 2, May—June 2003, pp 14—18.

The removal of hexenuronic acids in the production of elemental chlorine-free pulp from eucalyptus through an acid preliminary stage and the use of high temperature in the first step of chlorination with chlorine dioxide have been examined. The consumption of chlorine dioxide was significantly lower than in a conventional bleaching sequence, and the content of heavy metals was reduced.

Petit-Breuilh X, Melo R, Zaror C (2003). Environmental implications of hexenuronic acid removal from Eucalyptus globulus kraft pulp using peroxymonosulfuric acid, 36th pulp and paper annual congress: ABTCP 2003, Sao Paulo, Brazil, 13—16 Oct. 2003, 8 pp.

The use of peroxymonosulfuric acid for removal of HexA was examined in this study. Ps acts both on lignin and on HexA, leading to reductions in unbleached pulp lignin content and a reduction on the ClO_2 bleaching demand.

Ragnar M, Backa S (2004). Hot chlorine dioxide bleaching: a modified approach. 2004 TAPPI Fall technical conference, Atlanta, GA, USA, 31 Oct.—3 Nov. 2004, 5 pp.

A modified approach to the hot chlorine dioxide bleaching process, involving dividing the treatment into two separate phases, was undertaken in this study. Chlorine dioxide requirement to reach a specific target brightness in the modified approach was the same as or slightly lower than that usually required and that the final viscosity was higher.

Saariaho, A-M, Hortling, B, Jaaskelainen, A-S, Tamminen, T. and Vuorinen, T. (2003). Simultaneous quantification of residual lignin and hexenuronic acid from chemical pulps with UV resonance Raman spectroscopy and multivariate calibration. J. Pulp and Paper Sci. 29(11): 363—370.

UVRR spectroscopy was used for the determination of lignin and HexA. UVRR spectra were collected at wavelengths of 244 and 257 nm, and the data were calibrated using the partial least squares regression method to obtain good predictability.

Siltala M, Winberg K, Henricson K, Lönnberg B (1998). Mill Scale Application for Selective Hydrolysis of Henxenuronic Acid Groups in TCF Bleaching of Kraft Pulp. Int. Pulp Bleaching Conference, June 1—5, Helsinki, p 279—287.

At Wisaforest pulp mill, selective hydrolysis of hexenuronic acid groups in the production of TCF-bleached birch pulp was studied. Kappa reduction of 3.5 corresponding to a 70% HexA reduction was achieved in 7 h at 86°C at pH 3.5. The A star stage replaced a chelation stage in the bleaching sequence. Postyellowing was decreased when the HexA groups were removed from the pulp.

Tavast D, Brannvall E, Lindstrom ME, Henriksson G (2011). Selectiveness and efficiency of combined peracetic acid and chlorine dioxide bleaching stage for kraft pulp in removing hexeuronic acid, Cellul. Chem. Technol. vol. 45, no. 1–2, Jan.–Feb. 2011, pp 89–95.

Comparison of combined peracetic acid and chlorine dioxide bleaching stages of unbleached and oxygen delignified hardwood and softwood kraft pulps with conventional chlorine dioxide and Paa stages were made. The combined stages were more efficient in Kappa number reduction than those with only chlorine dioxide.

Tenkanen, M, Gellerstedt, G, Vuorinen, T, Teleman, A, Perttula, M, Li, J. and Buchert, J (1999). Determination of Hexenuronic Acid in Softwood Kraft Pulps by Three Different Methods, Journal of Pulp and Paper Science, 25(9): 306–311.

Three methods for the detection of hexenuronic acid in unbleached and bleached softwood kraft pulps were compared. The methods were based on total enzymatic hydrolysis of pulp combined with high-performance anion-exchange chromatography of the liberated HexA-substituted xylooligosaccharides, selective acid hydrolysis of pulp combined with UV spectroscopy of the hydrolysis products, and selective mercuric acetate hydrolysis of pulp combined with colorimetric determination of the hydrolysis products. The results obtained by the three methods correlated well with each other.

Tomoda I, Uchida Y (2008). Peroxymonosulfuric acid bleaching: the brief of bleaching reaction and the result of mill trials, International pulp bleaching conference, Quebec City, QC, Canada, 2–5 June 2008, pp 177–180.

Peroxymonosulfuric acid bleaching was used to degrade hexenuronic acid. The treatment in low pH resulted in a decrease of fiber quality, whereas the treatment at high pH resulted in an increase of pulp brightness. More than 60 min was required for the sufficient degradation of lignin and HexA. Following a successful trial, peroxymonosulfuric acid bleaching stage was installed in one of Oji Paper Co. Ltd's mills.

Valls C, Vidal T, Roncero MB (2008). Elimination of hexenuronic acids by different enzymatic treatments, International pulp bleaching conference, Quebec City, QC, Canada, 2–5 June 2008, pp 233–236.

Different enzymatic treatments were used for bleaching eucalyptus pulp in elemental chlorine-free and total chlorine-free sequences. All the xylanases were found to be effective.

Valls **C** and Roncero MB (2009). Using both xylanase and laccase enzymes for pulp bleaching, Bioresource Technology. 100: 2032–2039.

Both xylanase and laccase enzymes for pulp bleaching were studied. Xylanase pretreatment enhanced the effect of the laccase-mediator system in reducing the content of a residual lignin and releasing more HexA. A similar brightness and smaller Kappa number could be obtained by using 30% less laccase, 80% less HBT, and a 45% shorter reaction time.

Vuorinen T, Fagerström P, Buchert J, Tenkanen M, Teleman A (1999). Selective Hydrolysis of Hexenuronic Acid Groups and its Application in ECF and TCF Bleaching of Kraft Pulps, J. Pulp Paper Sci, 25:5, pp. 155–162.

A method for selectively removing HexA through a mild acid hydrolysis of kraft pulps is reported. The amount of HexA removed correlated linearly with a decrease in Kappa number. Depending on the type of the pulp, the kappa number was reduced by 2—7 units. The removal of HexA significantly reduced chemical consumption in ECF and TCF bleaching sequences.

Wane G, Germgard U (2009). Pulp and fibre surface properties of bleached hardwood kraft pulps: the influence of an a-stage. Pap. Puu vol. 91, no. 7—8, pp 58—64.

Hexenuronic acid content can be reduced by introducing a selective, hot, hydrolysis step into the bleaching sequence.

CHAPTER

21

Bleaching and Pulp Properties Calculations

21.1 DILUTION WATER CALCULATIONS

The water per ton of pulp ratio (V) is solved from the consistency (c) as $V = (100\text{-}c)/c$.

EXAMPLE 1

After the brown stock washers, the consistency of unbleached pulp is 11.2%. Calculate the volume of water (in m^3/t ovendry pulp) required to dilute the slurry to 3% consistency for chlorination.

Solution

At 11% consistency, there are 89 t water/(11 t pulp) = 8.09 t water/t pulp. At 3% consistency, there are 97 t water/(3 t pulp) = 32.33 t water/t pulp. Therefore 32.33–8.09 = 24.24 t water/t pulp to be added. Because 1 t = 1000 kg = 1 m^3 of water, this is 24.24 m^3 of water per metric ton of pulp.

21.2 CHLORINE BLEACHING

The pH is of utmost importance in chlorine bleaching for several reasons. First, the form of chlorine in solution is dependent on the pH according to the following equilibrium reactions.

$$\begin{aligned} &Cl_2 + H_2O \rightleftarrows H^+ + Cl^- + HOCl \\ &K_a = 3.9 \times 10^{-4} \text{at } 25^\circ C \end{aligned} \qquad (21.1)$$

$$\begin{aligned} &HOCl \rightleftarrows H^+ + OCl^- \\ &K_a = 3.5 \times 10^{-8} \text{at } 18^\circ C \end{aligned} \qquad (21.2)$$

From these equilibria, Fig. 21.1 can be constructed in the manner of Giertz (1951). This is very similar to other diprotic acids plotted in Chapter 13, Vol. 1 except the three species that are plotted together. Determining the concentration of the actual species at low pH is tricky because chlorine is a moderately strong acid (and so its ionization alters the pH significantly) and three species are formed by the ionization instead of two. First, the concentration of chlorine in water at 25°C is 0.091 M at saturation (i.e., 1 atm pressure of Cl_2). (Like the solubility of CO_2, the solubility of Cl_2 is highly pH dependent.) The pH of saturated chlorine water is calculated as follows:

$$K_a = [HOCl][H^+][Cl^-]/[Cl_2] = \frac{[H^+]^3}{(0.091 - [H^+])}$$

Solving for $[H^+]$ gives $[H^+] = 0.029\ M$. Therefore, a saturated chlorine solution in water,

https://doi.org/10.1016/B978-0-12-814240-0.00021-5

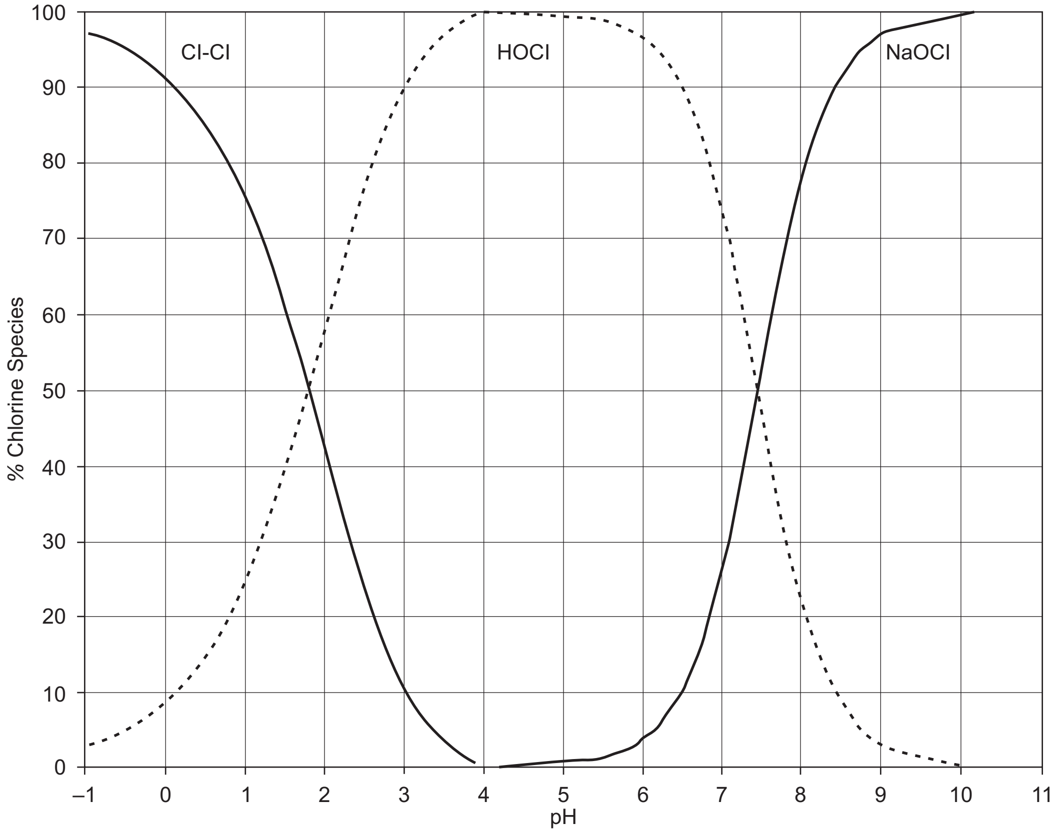


FIGURE 21.1 Chlorine species as a function of pH in saturated chlorine water (0.05 *M* Cl_2) at 25°C. Obviously the total solubility is pH dependent, with NaOCl being very soluble at the higher pHs.

without addition of acid or base, has a pH of -log 0.029 or 1.54, an actual chlorine concentration $[Cl_2]$ of 0.062 *M*, a hydrochloric acid concentration of 0.029 *M*, and a hypochlorous acid concentration of 0.029 *M*. The concentration of chlorine species will be considered using 0.05 *M* Cl_2 initially because this will not exceed the saturated pressure of chlorine at any pH, as a function of pH. Acid or base can be hypothetically added without dilution to achieve pHs, as shown in Fig. 21.1. Initially $[Cl_2] = 0.028$, $[H^+] = 0.022$, and the pH is 1.66. The ratio of Cl_2 to HOCl as a function of pH (where the source of the acid is immaterial) is solved in the following manner, where $x = [HOCl] = [Cl^-]$:

$$K_1 = \left[H^+\right]x^2/(0.05 - x)$$

$$\left[H^+\right]x^2 + K_1x - 0.05K_1 = 0$$

This equation is easily solved at various pHs by use of the quadratic equation. (At pH = 0, $x = 0.00423$ *M*. At pH 1.66, $x = 0.0222$ in agreement with the calculation above.)

When 0.05 *M* NaOH is added, all of the Cl_2 is converted to HOCl and the pH is of the weak acid system HOCl. HOCl is easily handled as any other weak acid. The pH is then calculated from Eq. (20.5) as -log $(K_a \times C)^{1/2} = 4.38$. When 0.10 M NaOH is present, the chemical is essentially all OCl^- and the pH is given as:

$$\left(14 - (K_b \times [OCl^-])^{1/2}\right) = 10.08$$

The pH at intermediate amounts of base is given in the form of the Henderson–Hasselbalch equation (see Eq. 21.2 for this equation); consequently, the ratio of HOCl to OCl^- is not concentration dependent (except for the effect of activity coefficients) from pH 5–9.

$$\begin{aligned} pH &= pK_a + \log(C_{A^-}/C_A) \\ &= 7.46 + \log([OCl^-]/[HOCl] \end{aligned}$$

Because the actual concentration of chlorine species is pH dependent, pulp bleaching with chlorine is also pH dependent. The desired reaction of substitution occurs most rapidly at the lowest pH values; however, acid hydrolysis of cellulose and hemicellulose also increases with decreasing pH. (Acid hydrolysis leads to a decrease in the cellulose viscosity.) The hydrolysis of chlorine is also temperature dependent. Rydholm in *Pulping Processes* (p. 920) gives the hydrolysis constants of Cl_2 as a function of temperature; they are 1.45×10^{-4} at 0°C and 9.75×10^{-4} at 60°C.

21.3 CHLORINE DIOXIDE

The action of ClO_2 has been studied in detail by Schmidt (1923). He found ClO_2 to be highly reactive with aromatics and phenolics but not reactive with carbohydrates. Today, ClO_2 is used in the later bleaching stages because it is very selective for lignin removal. It is also being used in early stages for environmental reasons. Chlorine dioxide can be produced from chlorite by oxidation with hypochlorite or reduction with suitable reducing agents (Giertz, 1951). Chlorine dioxide formation by reduction of sodium chlorate in acidic aqueous solutions occurs with different reducing agents that give rise to many processes, as shown in Table 21.1. Chlorine is reduced from a valence of +5 in chlorate to a valence of +4 in chlorine dioxide. Chlorate is produced by the disproportionation reaction as follows:

$$\begin{array}{cccc} 3ClO^- & \rightarrow & 2Cl^- & ClO_3^- \\ +1 & & -1 & +5 \end{array}$$

The overall reaction is as follows:

$$NaCl + 3H_2O + \text{electricity} \rightarrow NaClO_3 + 3H_2$$

Chlorine dioxide is also produced by the *Lurgi* process from Cl_2, H_2O, and electricity. The chlorine dioxide is produced by the same

TABLE 21.1 Formation of ClO_2 by Reduction of $NaClO_3$

	Reducing Agent		
Name of Process	**Species**	**Change of Valence**	**Chemical Equation**
Mathieson	SO_2	$S: +4 \rightarrow +6$	$2NaClO_3 + SO_2 + H_2SO_4 \rightarrow 2ClO_2 + 2NaHSO_4$
Solvay	CH_3OH	$C: -2 \rightarrow +4$	$6NaClO_3 + CH_3OH + 6H_2SO_4 \rightarrow 6ClO_2 + CO_2 + 6NaHSO_4 + 5H_2O$
Rapson	HCl	$Cl: -1 \rightarrow 0$	$2NaClO_3 + 4HCl \rightarrow 2ClO_2 + 2NaCl + Cl_2 + H_2O$
R-2, R-3, SVP	NaCl	$Cl: -1 \rightarrow 0$	$NaClO_3 + NaCl + H_2SO_4 \rightarrow ClO_2 + 1/2Cl_2 + Na_2SO_4 + H_2O$

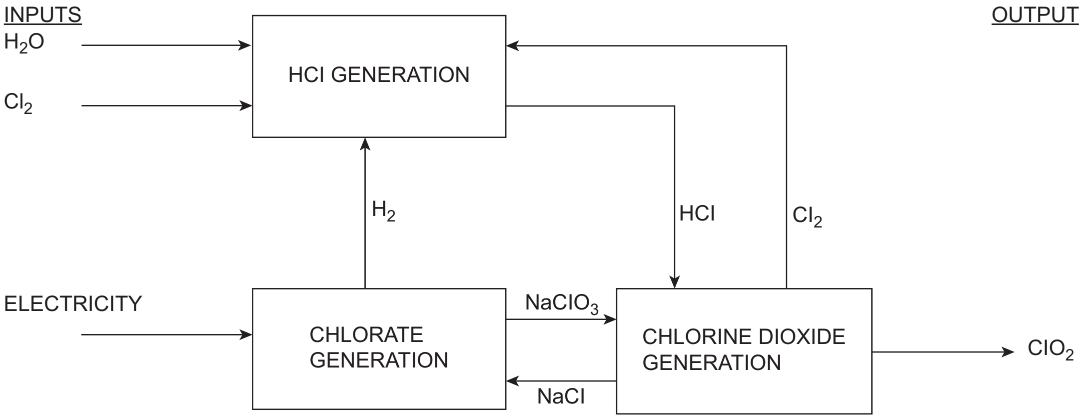


FIGURE 21.2 Chlorine dioxide generation from Cl_2, H_2O, and electricity by the Lurgi process.

reaction as the Rapson process. The NaCl and Cl_2 products of this reaction are used to generate additional chlorine dioxide. Also $NaClO_3$ is generated by electrolysis. Fig. 21.2 shows the process that is electrical intensive and uses 8–9000 kWh/t of ClO_2.

21.4 CHEMICAL ANALYSIS OF BLEACHING LIQUORS AND CHLORINE EQUIVALENCY

The determination of active bleaching agents is performed by iodometric titrations. The bleaching solution is added to an aqueous solution containing excess potassium iodide (KI). The KI is oxidized to iodine while the bleaching agent is reduced. The amount of iodine liberated is measured by titration with thiosulfate using a starch indicator to observe the final disappearance of iodine. In the case of chlorine, the reactions are as follows:

$$Cl_2 + 2I^- \rightarrow 2Cl^- + I_2 \qquad (21.3)$$

$$I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6 \qquad (21.4)$$

Bleaching chemicals are normally expressed as amount of "available chlorine." This allows bleaching chemicals to be considered in terms of their equivalent weights. Table 21.2 shows the conversions for several bleaching agents. Keep in mind that in Eq. (21.3), 1 mol of KI reacts with 1 mol of electrons; therefore, the equivalent weight of KI is equal to its formula weight. On the other hand, 1 mol of I_2 reacts with 2 mol of electrons in Eq. (15.4), and the equivalent weight of I_2 is one-half of its formula weight. It should be clear that the equivalent weight of Cl_2 is one-half of its formula weight.

EXAMPLE 2

Write the balanced reaction of chlorine dioxide with iodide.

Solution

$$2ClO_2 + 10I^- + 8H^+ \rightarrow 2Cl^- + 5I_2 + 4H_2O$$

EXAMPLE 3

Suppose a chemical loading of 2% NaClO on pulp (as chlorine) is desired. What is the actual amount of NaClO that should be used?

Solution

2% as Cl_2 × (37.25 g NaClO)/(35.5 g Cl_2) = 2.1% NaClO as NaClO.

Problem

Suppose 2% ClO_2 as chlorine is desired. What should the actual concentration be? Answer: 0.76% ClO_2.

TABLE 21.2 Equivalent Weights of Bleaching Chemicals

		Equivalent Weight		Gravimetric Factors		
Bleaching Agent	**Chemical Equation**	**As Formula Weight**	**g/Equivalent**	**To Cl_2**	**From Cl_2**	***E*°, *V***
Chlorine	$Cl_2 + 2e \rightarrow 2Cl^-$	FW/2	35.5	1.000	1.000	1.36
Hypochlorite	$NaOCl + H_2O + 2e \rightarrow NaCl + 2OH^-$	FW/2	37.25	0.953	1.049	0.89
Hypochlorous acid	$HOCl + H^+ + e \rightarrow 1/2Cl_2 + H_2O$; then Cl_2 reaction as above	FW/2	26.25	1.352	0.739	1.63; 1.36
Chlorine dioxide	$ClO_2 + 4H^+ + 5e \rightarrow Cl^- + 2H_2O$	FW/5	13.5	2.630	0.380	1.27
Chlorine monoxide	$Cl_2O + 4e \rightarrow Cl^-$	FW/4	21.75	1.632	0.613	
Sodium chlorate	$NaClO_3 + 6e \rightarrow Cl^-$	FW/6	17.75	2.029	0.493	
Oxygen	$O_2 + 2H_2O + 4e \rightarrow 4OH$	FW/4	8.00	4.438	0.225	0.41[a]
Iodide (sodium)	$I_2 + 2Na^+ + 2e \rightarrow 2NaI$	FW	149.89	0.237	4.222	0.620

[a] *In 1* N *NaOH.*

EXAMPLE 4

Given the data in the following table, fill in the blank spaces.

Stage	**C**	**E**	**H**	**D**
Chemical input on pulp, % as Cl_2	6	3	3	2
Chemical input on pulp, % true	?	?	?	?
Yield per stage, %	99	96	97	98
Cumulative yield, %	?	?	?	?
Pulp input, kg	1000	?	?	?
Pulp output, kg	?	?	?	?
Chemical input, kg	?	?	?	?

Solution

Chlorine and caustic are expressed "as is," so the chlorine input would be 6% of the pulp charged and the caustic input would be 3% of the charge. Hypochlorite and chlorine dioxide charges are given in terms of equivalent chlorine and must be converted as explained.

Hypochlorite: 3% (as $Cl_2 \times 1.049 = 3.15\%$) (as NaClO) based on pulp.

Chlorine dioxide: 2% (as $Cl_2 \times 0.380 = 0.76\%$) (as ClO_2) based on pulp.

The yield per stage is the ratio of output per stage to the input per stage, and the cumulative yield (for the entire bleaching sequence) is the ratio of the final output to the input of the first stage of bleaching. It is also the sequential product of the yields per stage:

Cumulative yield stage 1: $100\% \times 0.99 = 99\%$

Cumulative yield stage 2: $100\% \times 0.99 \times 0.96 = 95.0\%$ … and so forth for each stage.

The pulp input and pulp output per stage can be calculated by using the above percentage figures. What comes out of one stage must be the input for the following stage. The chemical input per stage is figured from the pulp input times the chemical charge (percentage) per stage:

C stage: 1000 kg × 6% = 60 kg Cl_2 as Cl_2.

E stage: 990 kg × 3% = 29.7 kg NaOH as NaOH.

H stage: $950 \times 3.15\% = 29.9$ kg NaClO as NaClO.

D stage: $922 \times 0.76\% = 7.0$ kg ClO_2.

Final pulp yield: $1000 \times 0.99 \times 0.96 \times 0.97 \times 0.98 = 903$ kg bleached pulp.

The completed chart appears as follows:

Stage	**C**	**E**	**H**	**D**
Chemical input on pulp, % as Cl_2	6	3	3	2
Chemical input on pulp, % true	6.0	3.0	3.15	0.76
Yield per stage, %	99	96	97	98
Cumulative yield, %	99	95	92.2	90.3
Pulp input, kg	1000	990	950	922
Pulp output, kg	990	950	922	903
Chemical input, kg	60	29.7	29.9	7.0

Problem

Complete the following table:

Stage	**C**	**E**	**H**	**D**
Chemical input on pulp, % as Cl_2	5	2.5	3.7	1.5
Chemical input on pulp, % true	?	?	?	?
Yield per stage, %	98.5	97	98	99
Cumulative yield, %	?	?	?	?
Pulp input, kg	1000	?	?	?
Pulp output, kg	?	?	?	?
Chemical input, kg	?	?	?	?

21.5 CANADIAN STANDARD FREENESS CORRECTION EQUATIONS

The Canadian Standard Freeness (CSF) is a commonly used indicator of the level of refining. The test calls for determining freeness at 20°C and 0.30% consistency; however, tabular corrections are given for temperatures from 10 to 30°C and 0.20%–0.40% consistency. These tables are time-consuming to use and are unnecessary with the use of computerized electronic spreadsheets.

Two equations (Biermann and Hull, 1992) have been formulated to correct freeness values above 50 CSF; one for consistency, Eq. (21.5), and one for temperature, Eq. (21.6). Although these equations are awkward, once entered into the spreadsheet they can be used to automatically correct freeness. Tables 21.3 and 21.4 are abbreviated versions of the correction tables generated from Eqs. (21.5) and (21.6), respectively.

$$\text{CSF corr} = (\text{cons} - 0.30) \times 590 \times \left(1 + \frac{0.4 - \text{cons}}{0.2} \times \frac{\text{CSF}}{1000}\right) \times \left(1 - \frac{(\text{CSF} - 390^2)}{\text{CSF}^{0.2} \times 87000}\right) \tag{21.5}$$

TABLE 21.3 Canadian Standard Freeness (CSF) Consistency Correction Table

	Consistency (%)				
CSF	**0.2**	**0.25**	**0.30**	**0.35**	**0.40**
50	−23	−12	0	12	23
80	−34	−17	0	13	26
100	−36	−19	0	19	36
150	−49	−24	0	23	45
200	−58	−28	0	26	51
250	−66	−31	0	29	55
300	−72	−34	0	30	57
350	−76	−36	0	32	59
400	−80	−37	0	32	59
450	−82	−38	0	32	58
500	−82	−38	0	32	57
550	−81	−37	0	30	54
600	−79	−36	0	29	51
650	−74	−34	0	27	46
700	−68	−31	0	24	41

From Eq. (21.5).

TABLE 21.4 Canadian Standard Freeness (CSF) Temperature Correction Table

	Temperature (°F)				
CSF	**10**	**15**	**20**	**25**	**30**
50	11	6	0	−6	−11
80	20	10	0	−10	−20
100	25	12	0	−12	−25
150	33	16	0	−16	−33
200	38	19	0	−19	−38
250	42	21	0	−21	−42
300	44	22	0	−22	−44
350	46	23	0	−23	−46
400	46	23	0	−23	−46
450	46	23	0	−23	−46
500	44	22	0	−22	−44
550	42	21	0	−21	−42
600	40	20	0	−20	−40
650	37	18	0	−18	−37
700	33	16	0	−16	−33

From Eq. (21.6).

$$\text{CSF corr} = (20 - t) \times 4.6 \times \left(1 - \frac{(400 - \text{CSF})^2}{\text{CSF}^{0.25} \times 61000}\right) \tag{21.6}$$

Recent work (Sundrani et al., 1993) shows that the freeness tables supplied with the TAPPI and CPPA methods give corrections with an absolute value below what they should be for kraft pulps. The correction tables were developed with stone groundwood and, for the higher freeness values, sulfite chemical pulps in the 1930s. There is no original data in the literature, and there is no indication of the algorithm used to generate the tables. Because the viscosity of water decreases exponentially with temperature, there is no reason to believe that the temperature correction table should be symmetrical, as it is given in these standards.

21.6 COMPUTER SIMULATION OF FIBER CLEANING SYSTEMS

When evaluating the overall cleaning efficiency of a system of vortex cleaners containing primary, secondary, tertiary, and, perhaps, higher order banks before the paper machine, one soon discovers that the calculations are tedious and that evaluating numerous configurations or flow rates is laborious. It is very easy to simulate the overall performance using simple computer programs. BASIC will be used here because many personal computers are equipped with this tool.

The philosophy of evaluating these systems is as follows: Do not try to solve the problem; simply define the system and put a specified number of fibers or dirt particles through the system, solve the approximate accept and reject rates, run the system enough times so that the solution converges to the desired answer within a tolerance limit, and count where the particles come out. It is convenient to have 100 particles exit the system so that the various exit points can be calculated as percentages. Two programs must be made: one for the dirt particles and one for the fibers because they behave differently.

An example will be used to show the principle. We will simulate the operation of a system containing primary, secondary, and tertiary cleaners. In each of these sections, 75% of the dirt particles are rejected. The fiber reject rate is 10% for the primary cleaners, 15% for the secondary cleaners, and 20% for the tertiary cleaners. The primary accepts leave the cleaning system and go to the paper machine. The primary rejects go to the secondary inlet, the secondary rejects go to the tertiary inlet, and the tertiary rejects are sewered. The secondary accepts go to the primary inlet. Initially we will study a system where the tertiary accepts go to the secondary inlet. (We will then reinvestigate the system with the tertiary accepts going to the primary inlet.)

Table 21.5 is the program with the results of the run to simulate the fibers. Table 21.6 shows the results of the same system from the point of view of the dirt particles. The outputs of each cleaner bank are shown when fibers are used because this reflects the size of each bank that will be required.

When the tertiary rejects go to the secondary inlet, the overall fiber reject rate is 0.377% and the overall dirt reject rate is 67.50%. To simulate the system where the tertiary accepts go to the primary inlet, changes must be made in three lines of both programs. The changes are

TABLE 21.5 The Simulation of a Cleaning System With Fibers

```
10   REM THIS PROGRAM HAS PRIMARY, SECONDARY, AND TERTIARY CLEANERS
     FOR FIBER. THE TERTIARY REJECTS GO TO THE SECONDARY CLEANERS.
20   FIBER = 100: REM 100 FIBERS MEANS OUTPUTS WILL BE PERCENTAGES
30   PRI.RATE = 0.9: REM THE FIBER ACCEPT RATE OF THE PRIMARY CLEANERS
40   SEC.RATE = 0.85: REM THE FIBER ACCEPT RATE OF THE SECONDARY CLEANERS
50   TER.RATE = 0.8: REM THE FIBER ACCEPT RATE OF THE TERTIARY CLEANERS
60   PRI.IN = FIBER
70   TOLER = 0.005: REM THE ERROR BETWEEN ITERATIONS SHOULD BE LESS THAN 0.005%
     BEFORE STOPPING THE PROGRAM
80   ITERATE = ITERATE +1: REM THE PROGRAM WILL RETURN HERE BETWEEN ITERATIONS
90   PRINT "ITERATION = "; :PRINT USING "##"; ITERATE; :PRINT "; FIBERS IN = "; :PRINT USING
     "####.##"; PRI.IN;
100  PRI.ACC = PRI.IN * PRI.RATE
110  PRI.REJ = PRI.IN – PRI.ACC
120  ACCEPTS = PRI.ACC
130  SEC.IN = PRI.REJ + TER.ACC
140  SEC.ACC = SEC.IN * SEC.RATE
150  SEC.REJ = SEC.IN – SEC.ACC
160  TER.IN = SEC.REJ
170  TER.ACC = TER.IN * TER.RATE
180  TER.REJ = TER.IN – TER.ACC
190  REJECTS = TER.REJ
200  PRINT "; ACCEPTS = "; :PRINT USING "###.##"; ACCEPTS; :PRINT "%; REJECTS = "; :PRINT
     USING "###.##"; REJECTS; :PRINT"%"
210  IF ABS((FIBER + SEC.ACC)-PRI.IN)<TOLER GOTO 240
220  PRI.IN = FIBER + SEC.ACC
230  GOTO 80
```

TABLE 21.5 The Simulation of a Cleaning System With Fibers—cont'd

```
240     PRINT ″PRIMARY ACCEPTS = "; PRI.ACC; "%; "; "PRIMARY REJECTS = "; PRI.REJ; "%;
        "."SECONDARY ACCEPTS = "; SEC.ACC; "%; "; "SECONDARY REJECTS = "; SEC.REJ; "%;
        ","TERTIARY ACCEPTS = "; TER.ACC; "%; "; "TERTIARY REJECTS = "; TER.REJ; "%; "

RUN

ITERATION = 1;     FIBERS IN = 100.00;     ACCEPTS = 90.00%;     REJECTS = 0.30%

ITERATION = 2;     FIBERS IN = 108.50;     ACCEPTS = 97.65%;     REJECTS = 0.36%

ITERATION = 3;     FIBERS IN = 110.24;     ACCEPTS = 99.22%;     REJECTS = 0.37%

ITERATION = 4;     FIBERS IN = 110.60;     ACCEPTS = 99.54%;     REJECTS = 0.38%

ITERATION = 5;     FIBERS IN = 110.67;     ACCEPTS = 99.61%;     REJECTS = 0.38%

ITERATION = 6;     FIBERS IN = 110.69;     ACCEPTS = 99.62%;     REJECTS = 0.38%

PRIMARY ACCEPTS = 99.61916%;            PRIMARY REJECTS = 11.0688%
SECONDARY ACCEPTS = 10.69104%;          SECONDARY REJECTS = 1.886653%
TERTIARY ACCEPTS = 1.509322%;           TERTIARY REJECTS = 0.3773306%

Ok
```

TABLE 21.6 The Simulation of a Cleaning System With Dirt Particles

```
10      REM THIS PROGRAM HAS PRIMARY, SECONDARY, AND TERTIARY CLEANERS FOR
        DIRT. THE TERTIARY REJECTS GO TO THE SECONDARY CLEANERS.

20      DIRT = 100: REM 100 DIRT PARTICLES MEANS OUTPUTS WILL BE PERCENTAGES

30      PRI.RATE = 0.25: REM THE DIRT ACCEPT RATE OF THE PRIMARY CLEANERS

40      SEC.RATE = 0.25: REM THE DIRT ACCEPT RATE OF THE SECONDARY CLEANERS

50      TER.RATE = 0.25: REM THE DIRT ACCEPT RATE OF THE TERTIARY CLEANERS

60      PRI.IN = DIRT

70      TOLER = 0.005: REM THE ERROR BETWEEN ITERATIONS SHOULD BE LESS THAN 0.005%
        BEFORE THE PROGRAM ENDS

80      ITERATE = ITERATE +1: REM THE PROGRAM RETURNS HERE EACH ITERATION

90      PRINT ″ITERATION = "; :PRINT USING "##"; ITERATE; :PRINT "; DIRT IN = "; :PRINT USING
        "####.##"; PRI.IN;

100     PRI.ACC = PRI.IN * PRI.RATE

110     PRI.REJ = PRI.IN − PRI.ACC

120     ACCEPTS = PRI.ACC

130     SEC.IN = PRI.REJ + TER.ACC

140     SEC.ACC = SEC.IN * SEC.RATE

150     SEC.REJ = SEC.IN − SEC.ACC
```

Continued

TABLE 21.6 The Simulation of a Cleaning System With Dirt Particles—cont'd

```
160                 TER.IN = SEC.REJ
170                 TER.ACC = TER.IN * TER.RATE
180                 TER.REJ = TER.IN – TER.ACC
190                 REJECTS = TER.REJ
200                 PRINT "; ACCEPTS = "; :PRINT USING "###.##"; ACCEPTS; :PRINT "%; REJECTS = "; :PRINT
                    USING "###.##"; REJECTS; :PRINT"%"
210                 IF ABS((DIRT + SEC.ACC)-PRI.IN)< TOLER GOTO 240
220                 PRI.IN = DIRT + SEC.ACC
230                 GOTO 80
240                 END
RUN
ITERATION = 1;      DIRT IN = 100.00;      ACCEPTS = 25.00%;      REJECTS = 42.19%
ITERATION = 2;      DIRT IN = 118.75;      ACCEPTS = 29.69%;      REJECTS = 58.01%
ITERATION = 3;      DIRT IN = 125.78;      ACCEPTS = 31.45%;      REJECTS = 63.94%
ITERATION = 4;      DIRT IN = 128.42;      ACCEPTS = 32.10%;      REJECTS = 66.17%
ITERATION = 5;      DIRT IN = 129.41;      ACCEPTS = 32.35%;      REJECTS = 67.00%
ITERATION = 6;      DIRT IN = 129.78;      ACCEPTS = 32.44%;      REJECTS = 67.31%
ITERATION = 7;      DIRT IN = 129.92;      ACCEPTS = 32.48%;      REJECTS = 67.43%
ITERATION = 8;      DIRT IN = 129.97;      ACCEPTS = 32.49%;      REJECTS = 67.47%
ITERATION = 9;      DIRT IN = 129.99;      ACCEPTS = 32.50%;      REJECTS = 67.49%
ITERATION = 10;     DIRT IN = 130.00;      ACCEPTS = 32.50%;      REJECTS = 67.50%
Ok
```

identical in both programs. The corrected lines read:

```
130     SEC.IN = PRI.REJ
210     IF ABS((DIRT + SEC.ACC +
         TER.ACC)-PRI.IN) < TOLER GOTO 240
220     PRI.IN = DIRT + SEC.ACC + TER.ACC
```

When the modified programs are run, the fiber reject rate is 0.332% and the dirt reject is 62.79%. In the first system the selectivity (the dirt reject rate divided by the fiber reject rate) is 179, and in the second system the selectivity is 189. When primary accepts are not treated further in a cleaning system with tertiary cleaners, the tertiary rejects should go to the secondary cleaners not the primary cleaners because 67.5% of the dirt will be removed compared with 62.8%, whereas the fiber reject rate changes very little. When the secondary accepts are returned to the primary cleaners, the tertiary accepts should always go to the secondary inlet; the reason is that the dirt particles must then go through two sets of cleaners before being accepted rather than just going to the primary cleaners where they have a relatively good chance of being accepted.

Once one has learned how this technique is used, it is easily modified to accomplish numerous chores. For example, one might try altering the flow rates or reject rates in different banks of cleaners. The model can be made more complex by actually defining a distribution of dirt or fiber particle sizes with different reject rates for each particle size range. The technique can also be adapted to screening, cleaning, deinking, and other systems. The limits are defined only by the ingenuity of the programmer. If systems get too complicated, one should consider using commercial simulation programs.

21.7 PAPER MACHINE CALCULATIONS

The relationships between basis weight, consistency, paper machine width and speed, and production rates are easily derived. It is assumed that the speed of the stock exiting the headbox is approximately equal to the speed of the machine wire. The volumetric flow rate may be expressed as a function of the three primary paper machine dimensions or in terms of the dry fiber rate and pulp consistency at the headbox.

$$\text{Volumetric flow rate} = \text{PM speed} \times \text{PM width} \times \text{slice height} \tag{21.7}$$

$$\text{Mass flow rate} = (\text{dry fiber rate})/(\text{consistency}) \tag{21.8}$$

In Eq. (21.8), one must report the consistency in units of mass per volume (such as kg/m^3) to obtain the volumetric flow rate in units of volume. Often the consistency is reported as a mass % such as 0.4% (implying 0.4 kg dry pulp per 100 kg pulp slurry). If one is not careful, errors in calculations will occur because 10 kg/m^3 is 1% consistency! The dry fiber rate is easily given in terms of basis weight and machine production in area (Eq. 21.9). Eq. (21.10) shows the relationship between slice height and consistency.

$$\text{Dry fiber rate} = \text{basis weight} \times \text{PM speed} \times \text{PM width} \tag{21.9}$$

$$\text{Basis weight} = \text{slice height} \times \text{consistency} \tag{21.10}$$

As with any equation, when solving these equations, one must be careful to insure that consistent units are used throughout the solution. In Eq. (21.10) the slice height is conveniently expressed in meters and the consistency in kg/m^3. The basis weight is solved in terms of kg/m^2, which is easily converted to g/m^2.

The speed of the stock exiting the headbox is usually within 5% of the machine wire speed. As shown in Chapter 5, Volume 2, the pressure in the headbox is dependent on the wire speed. Some speed is lost because of friction. The amount of this loss is dependent on the slice geometry.

EXAMPLE 5

What is the speed of a paper machine producing 500 MT per day of paper that is 50 g/m^2 and makes paper 10 m wide?

Solution

The dry fiber rate is:

$$500{,}000\ \text{kg}\cdot\text{day}^{-1}(86{,}400\ \text{s}\cdot\text{day}^{-1}) = 5.79\ \text{kg/s}.$$

$$5.79\ \text{kg s}^{-1}/(0.050\ \text{kg m}^{-2}) = 115.8\ \text{m}^2/\text{s}.$$

Because the width = 10 m, the speed = 11.6 m/s.

Problem

What is the slice opening for this machine if the consistency is 0.5%? Answer: 0.01 m, which is the basis weight divided by the consistency.

EXAMPLE 6

Derive the relationship between slice velocity and machine speed assuming no frictional losses.

Solution

The potential energy of a given mass of pulp slurry is *mgh*, where *m* is the mass, *g* is the acceleration due to gravity, and *h* is the height of the headbox (or a pressure that can be converted to an equivalent height). The potential energy is converted to kinetic energy that is given as $\frac{1}{2}mv^2$, where v is the velocity of the slice that is approximately equal to the velocity of the machine. The slice velocity is realistically given with a term for energy loss (C_q). C_q is approximately 0.85–0.90 for a tapered slice and 0.65–0.75 for a slice with an abrupt opening (as viewed from the inside). Therefore

$$\frac{1}{2}mv^2 = mgh$$

$$v = \sqrt{2gh} \tag{21.11}$$

$$\text{actually, } v \approx C_q\sqrt{2gh}$$

EXAMPLE 7

The pressure of a headbox corresponds to a height of 10 m. If 50% of the potential energy is converted to kinetic energy, what is the velocity of the slice?

Solution

$$\frac{1}{2}mv^2 = 0.5 \times mgh$$

$$v = \sqrt{0.5} \times \sqrt{2gh}$$

$$v = 9.9\text{m/s}$$

21.8 PROPERTIES OF DILUTE PULP SLURRIES, FLOCCULATION

The behavior of dilute slurries of pulp (0.1%–3% or higher) is critical to paper formation on the paper machine. (It is also important in pulp pumping, mixing, and screening but receives less attention in these applications.) This area is complex, and there are few resources that give a good overview to it. The results of some studies are given in this section, but this is only a starting point of a complex area.

One important aspect of dilute pulp slurries is the tendency for pulp fibers to flocculate, which leads to poor paper formation on the paper machine. Flocculation is a nonuniform fiber distribution, or clustering, in the slurry. Kerekes (1983) gives a review with 32 references on fiber flocculation with particular attention to the presence of decaying turbulence, which is applicable to many areas of pulp processing such as flow beyond the holey roll in the headbox, at impeller tips of mixers and pumps, and perforated screens.

Mason (1954) showed that the critical concentration (c_o) for flocculation is inversely dependent on the square of the axis ratio (the length divided by the width) of the fiber. For example, the calculated c_o on a volume basis for a L/w of 100 is 0.0015% and for a L/w of 60 is 0.0042%.

Jokinen and Ebeling (1985) list some ways of decreasing flocculation. These include reducing the pulp consistency (which is why headbox consistencies are about 0.5%), lowering the temperature of the pulp suspension, reducing fiber length (such as with increased refining or using hardwood instead of softwood), increasing the pH, using anionic polymers, and using high stock velocities and turbulent flow (such as holey rolls in headboxes). The authors experimentally evaluated the relative importance of these factors and concluded that fibers flocculate for mechanical reasons. Flocculation is most effectively decreased by decreasing the consistency, using shorter fibers (but this decreases paper strength), and adding anionic polymers of high molecular weight such as polyacrylamide.

Kerekes and Schell (1992) indicate that *uniformity* of fiber distribution and *mobility* of fibers in suspension both contribute to good formation. *Superposition*, the piling of fibers on the wire during sheet formation, also affects formation. The authors develop a mathematical model called the crowding factor (the number of fibers within the spherical volume formed by the diameter of a fiber) to describe fiber flocculation. They tested their model with a variety of fiber types and include some stunning pictures of fibers in slurries.

Gorres et al. (1989) used a simulation model to predict paper formation based on fibrous floe characteristics. Smith (1986) compared handsheets as a way to rank formation potentials.

21.9 STRENGTH OF WET FIBER MATS

Introduction

In their classic study, Lyne and Gallay (1954) measured the wet strength of pulp webs and various types of glass fibers to determine the relative effect of surface tension and hydrogen bonding on the wet web strength. Their results are shown in Fig. 21.3 for groundwood and sulfite pulps and Fig. 21.4 for glass fiber webs.

Based on their results, the authors conclude that up to 20%—25% solids, the fibers are held together by surface tension forces. Surface tension forces decrease with increasing solids beyond this point (as observed by the unmodified glass fibers), but hydrogen bonding begins and the strength increases as the water is removed.

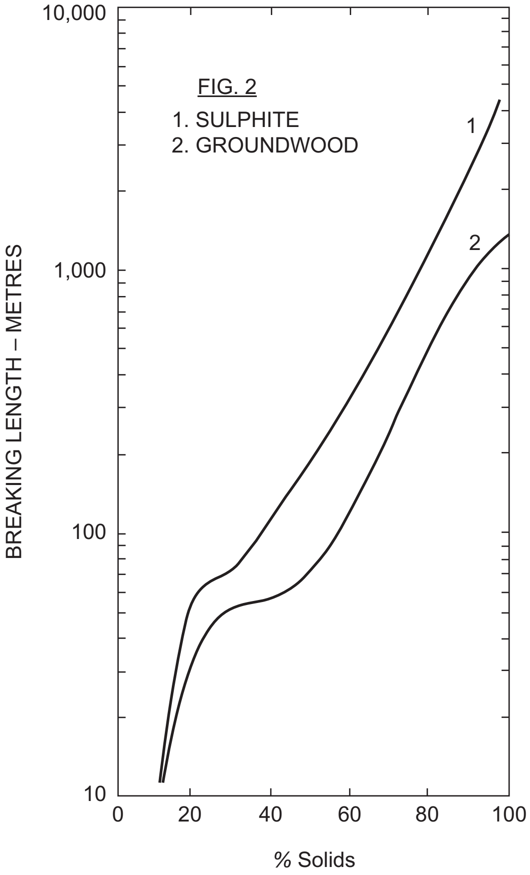
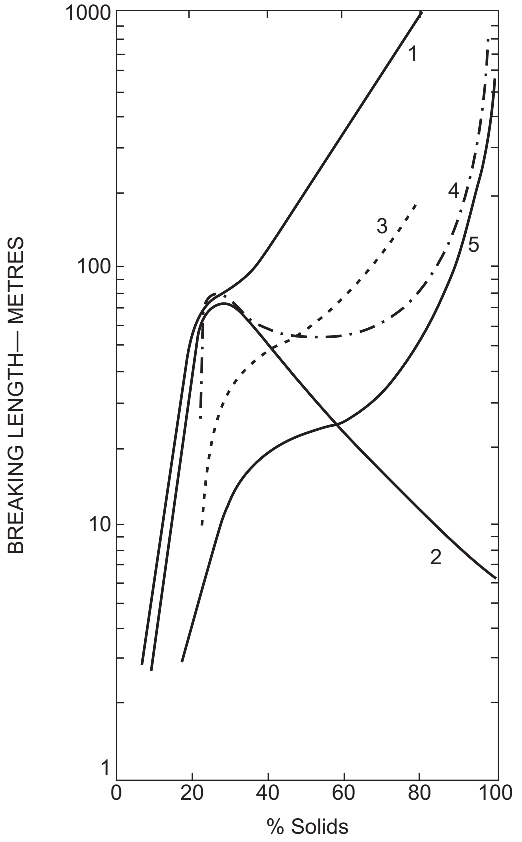


FIGURE 21.3 Strength of pulp webs with increasing dryness. *©1954 TAPPI. Reprinted from Lyne and Gallay (1954) with permission.*

The authors also demonstrate that papers formed from liquids of lower surface tension than water do not achieve nearly the strengths of paper formed from water. It would be ideal if paper could be dry-formed like most fiberboards, but this is not possible when hydrogen bonding provides the interfiber bonding in the final product. However, pulps are sometimes dried from acetone in the laboratory so that they remain bulky for subsequent work. Even just lowering the surface tension of water to



1) sulfite pulp, 2) 2.5 μm untreated glass fibers, 3) HF treated glass fibers, 4) glass fibers with sodium silicate adhesive, and 5) as 3 with gelatine adhesive.

FIGURE 21.4 Strength of fiber webs with increasing dryness. *©1954. TAPPI. Reprinted from Lyne and Gallay (1954) with permission.*

33 dyn/cm (from 73 dyn/cm at 18°C) by the addition of 0.1% surfactant decreases the ultimate breaking length of a groundwood paper from 300 to 95 m. Making the surface of pulps hydrophobic with mineral oil also drastically decreased the strength of paper made from them. (Freeze-drying of pulp slurries also gives a very weak fiber mat.)

By the same token, normal paper formed from water does not lose much strength when exposed to liquids of low surface tension and polarity, such as toluene (28 dyn/cm) or hexane (18.5 dyn/cm). Paper loses moderate amounts of its strength in solvents capable of hydrogen bonding, such as methanol (23 dyn/cm), even if the surface tension is not particularly high. Paper loses most of its strength in water (unless treated with special wet strength agents).

Surface Tension Effects

Obviously the surface tension of the liquid from which the fiber mat is formed is of central importance to the papermaking process. The pulp fibers must approach each other within a few tenths of a nanometer to form hydrogen bonds. The fiber surfaces approach each other when dried from liquids of high surface tension. Tremendous forces from capillary action and hydrogen bonding bring the fiber surfaces very close together.

Swanson (1961) discusses some of the surface tension forces in wet webs. Fig. 21.5 shows how

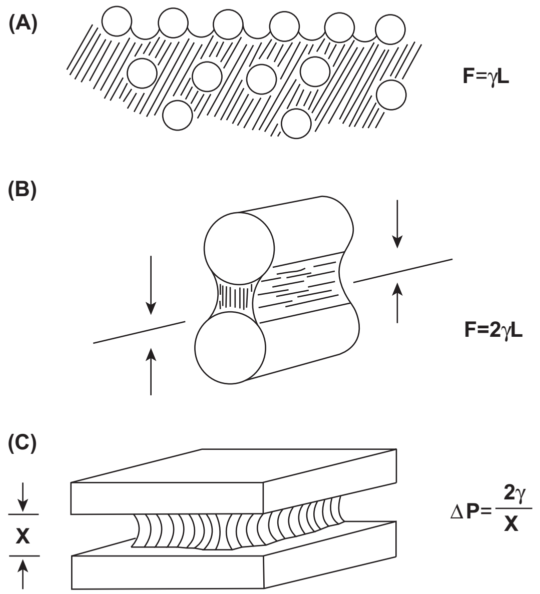


FIGURE 21.5 Surface tension forces during paper drying. *©1961 TAPPI. Reprinted from Swanson (1961) with permission.*

some of these forces act. The three diagrams are in order of decreasing water content and increasing forces: In part (A) the web is about 8% solids, or the consistency on the fourdrinier wire in the hivacs. The force in (B) with a surface tension of 75 dyn/cm for water and a fiber diameter of 0.03 mm would be about 5 kPa; with fibrillation the diameter may be effectively 0.003 mm, giving a force of 50 kPa (7 psi). In the region of 20%–25% solids, the water becomes discontinuous and the surface tension forces decrease and (C) applies. As the film thickness decreases, the pressure may reach 1 or 200 atmospheres.

21.10 FIBER PHYSICS

Introduction

Some basic aspects of wood and fiber physics important to understanding paper were presented in Section 2.7.

The Strength of Individual Fibers

Often the strength differences in the machine direction and cross-machine direction of paper are attributed to fiber alignment. While this accounts for some of the difference, another factor is the fact that paper is dried under tension in the machine direction. The ratio of the zero-span tensile strength has been used as an indicator of fiber alignment, but this method is flawed because the strength of individual fibers increases when dried under a stress. Methods relying on the speed of sound waves do not measure fiber alignment. The speed of sound waves is proportional to the stiffness and the square root of density. Although fibers are stiffer in the longitudinal direction, fibers that dry under stress have a higher stiffness too. The effect of each variable cannot be ascertained by a single number.

Work by Jentzen (1964) shows that the strength and stiffness of individual fibers increases when they are dried under tension. Others have verified this effect. However, Kim et al. (1975) found that certain fibers would not increase in strength when dried under tension, including predried kraft fibers and fibers where the hemicellulose has been removed by alkali extraction. The workers hypothesized that fibers would increase in strength if the fibrils of the fibers could flow when shear forces are applied. In short, individual papermaking fibers can be expected to increase in strength in the machine direction.

Effect of Fiber Strength and Bonding on Paper Properties

Van den Akker et al. (1958) studied the effect of fiber strength on sheet strength. They showed that if the orientation of fibers is random in the sheet, the zero-span tensile strength is 3/8 (37.5%) of the load if all of the fibers were aligned in the direction of loading. Their laboratory work verified that the zero-span tensile strength is an important measure of fiber strength. This fact is useful to determine the amount of fiber strength loss that occurs during various methods of refining. The ideal refining method should cause fibrillation with a minimum of fiber strength loss. For example, high consistency refining in disc refiners does this more effectively than low consistency refining in Jordan refiners.

Investigators have studied fiber bonding. For example, Skowronski and Bichard (1987) developed a technique to measure bond strength in papers. The method is based on the energy of delamination.

21.11 ANNOTATED BIBLIOGRAPHY

Bleaching

Giertz HW (1951). Delignification with bleaching agents. In: Hägglund, E. (Ed.), Chemistry of Wood: Academic Press. New York, 631 p.

Giertz, HW., *Svensk Papperstidn.* 46:152(1943).
Schmidt, E., *Ber.* 54:1860(1921); ibid., 56: 25(1923).

Freeness

Biermann, CJ. and JL. Hull, Replacement of the Canadian Standard freeness temperature and consistency correction tables with equations suited to computer use, *Tappi J.* 75(10):245–246(1992).
Sundrani, RS., JL. Hull, and CJ. Biermann, Consistency and temperature correction for Canadian Standard freeness with chemical pulps, *Tappi J.,* In press. (1993).

Fiber Flocculation

Kerekes, RJ., Pulp flocculation in decaying turbulence: A literature review, *J. Pulp Paper Sci.* 9(3):TR86–TR91(1983).
Mason, SG., Fibre motions and flocculation, *Pulp Paper Mag. Can.* 55(13, Dec.): 96–102(1954).
Jokinen, O. and K. Ebeling, Flocculation tendency of papermaking fibres, *Paperi ja Puu- Popper och Tra* 67(5):317–325(1985).
Kerekes, RJ. and CJ. Schell Characterization of fibre flocculation regimes by a crowding factor, *J. Pulp Paper Sci.* 18(1):J32–J38(1992).
Gorres, J., T. Cresson, and P. Luner, Sheet formation from flocculated structures, *J. Pulp Paper Sci.* 15(2):J55–J59(1989).
Smith, MK., Formation potential of west coast kraft pulps, *Pulp Paper Can.* 87(10): T387–T394(1986).

Forces in Wet Fiber Mats

Lyne, LM. and W. Gallay, Studies in fundamentals of wet web strength, *TAPPI* 37(12):698–704(1954).
Swanson, JA., The science of chemical additives in papermaking, *Tappi* 44(1): 142–181 A(1961).

Fiber Physics

Jentzen, CA., The effect of stress applied during drying on some of the properties of individual pulp fibers, *Tappi* 47(7): 412–418(1964). The article was reprinted in *For. Prod. J.* (9):387–392(1967).
Kim, CY., DH. Page, F. El-Hosseiny, and APS. Lancaster, The mechanical properties of single wood pulp fibers. III. The effect of drying stress on strength, *J. Appl. Polym. Sci.* 19:1549–1561(1975).
Van den Akker, JA., AL. Lathrop, MH. Voelker, and LR. Dearth, Importance of fiber strength to sheet strength, *TAPPI* 41(8): 416–425(1958).
Skowronski, J. and W. Bichard, Fibre-to-fibre bonds in paper. Part I. Measurement of bond strength and specific bond strength, *J. Pulp Paper Sci.* 13(5):J165–J169(1987).

General Interest on Pulp Slurries

Wahren, D (1980). In: Bonano, E.J. (Ed.), Paper Technology, Part 1:Fundamentals: Institute of Paper Chemistry. Appleton, Wisconsin. pp. 199–250.

This work includes mathematical development of flow through pipes, properties of fiber suspensions, critical volume concentrations for fiber flocculation, network flow, turbulence, and colloidal flocculation.

EXERCISES

Bleaching

1. From the point of view of pollution abatement, why is ClO_2 preferable to Cl_2? What are the number of electrons transferred in the redox reactions per mole of CI in each?
2. Write the reaction of hypochlorite with iodide.

3. A 50.0 mL aliquot of ClO_2 solution consumed 19.96 mL of 0.152 *N* thiosulfate solution. What is the concentration of ClO_2 in g/L?

4. In the Solvay process for making ClO_2, how much methanol is theoretically required per ton of sodium chlorate?

5. A softwood, unbleached kraft pulp has a Kappa number of 34. During the bleaching process, all of the lignin and 2% of the carbohydrates are removed, what is the pulp yield of the bleach plant? If the yield from the pulp plant is 46%, what is the overall bleached pulp yield from wood?

6. Describe how to prepare and standardize 5 gallons of $KMnO_4$ solution of 0.1000 *N* to be used in the pulp mill for quality control. The laboratory has 2 *M* H_2SO_4, 1 *N* H_2SO_4, 2 *M* KI, 0.1000 *N* $Na_2S_2O_4$, and starch indicator solution.

Paper Machine Calculations

7. A paper machine with a width of 2.5 m has a speed of 10 m/s and produces a paper with a basis weight of 50 g/m^2. Calculate the weight of paper produced per second. From this and assuming a consistency of 0.5% in the headbox, calculate the volumetric flow rate necessary through the headbox. Because one knows the width of the slice and the length per second going through the slice, you should be able to easily solve the slice height. Assume this is an open headbox with 100% efficiency of conversion of potential energy to kinetic energy (unlikely in the first case; impossible in the second case). Calculate the height of the water above the slice from the equations for potential energy ($PE = mgh$, $g = 9.8\ m/s^2$) and kinetic energy ($KE = 0.5\ mv^2$) to obtain the equation.

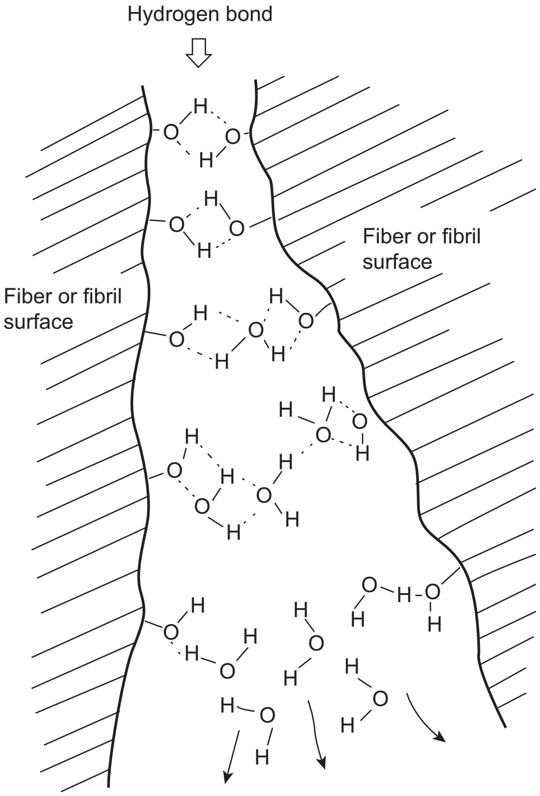
8. A paper machine operates at 20 m/sec and is 10 m wide. Calculate the required equivalent height of water in the headbox assuming all of the potential energy of water is converted to kinetic energy. For paper of basis weight 50 g/m^2, what is the required slice height? (The headbox consistency is 0.5%.) What is the maximum annual production in tons?

9. A paper machine has a speed of 5 m/s with a basis weight of 100 g/m^2 and stock consistency of 0.6% at the headbox. What should the slice height be?

Strength of Wet Fiber Mats

10. In Fig. 21.6, where are the strongest bonds formed between fibers?

As water is removed, it helps draw hydroxy 1 groups together and align them for hydrogen bonding.



As water is removed, it helps draw hydroxyl groups together and align them for hydrogen bonding.

FIGURE 21.6 Hydrogen bonding and water removal. *©1991 James E. Kline. Reprinted from* Paper and Paperboard *with permission.*

CHAPTER

22

Purification of Process Water in Closed-Cycle Mills

22.1 INTRODUCTION

With increasing environmental pressures and stringent new clean-water regulations, the pulp and paper mills are moving toward effluent closure. Depending on specific mill conditions, the advantages of operating a closed water cycle may extend beyond "environmentally benign" to include reduced energy and operating costs in certain process areas, especially the waste treatment plant. The closed-cycle or zero-effluent mill is an attractive concept because it responds to short-term environmental legislation and also future legislation, which could regulate additional effluent parameters and require tertiary effluent treatment systems, extensive testing of effluent contaminations, testing of effects on receiving waters, etc. Purification of industrial wastewaters for process water reuse represents a major step in water savings and in closing the chemical processes. In view of the increasingly higher demands on the quality of mill effluent discharge, it appears advantageous to upgrade the secondary effluent by a suitable tertiary polishing stage and reuse the tertiary effluent in mill operations. This concept of effluent management might lead to complete closure of the effluent cycle in certain mills. The main issues associated with effluent reuse are effects of residual constituents on mill operations, product quality, and corrosion aspects.

Several pulp and paper mills are exploring methods to modify effluent composition and reduce effluent volume. Reduced effluent volume means a closed effluent-free pulp mill operation. The best and lowest-cost closed-cycle configuration is specific to every mill. In all cases, it is necessary to determine the appropriate combination of in-mill and ex-mill measures for achieving zero discharge at minimum cost. The ultimate goal of a closed-cycle mill is to have minimal impact on the environment.

22.2 MEASURES TO ACHIEVE CLOSE CYCLE

The only way of reducing the amount of effluent is to replace fresh water by already used so-called "white water" treated or not. The reuse of process water is, in most cases, possible without any treatment, and this kind of recycling is a normal routine in all pulp and paper mills.

The base for selection of an adequate treatment system is good knowledge of the process and also the raw materials and their effect on

https://doi.org/10.1016/B978-0-12-814240-0.00022-7

the water to be treated. In addition, the result of the treatment has to be defined clearly taking into account how the different components react to different treatment methods and which components are necessary to separate from the water to make it reusable.

The water treatment method has to be selected based on the quality demands of the treated water. For example, is it necessary to remove suspended solids, suspended solids and colloids, or all components? A coarse treatment classification can be made from the kind of treatment result achieved. These are the separation of fiber, leaving pigments and other fines in the water; suspended solids, giving clear water; colloidal substances; dissolved substances; and inorganic salts.

The water treatment methods available for achieving the desired objectives are as follows:

1. Mechanical separation, which can be amplified by using chemical coagulation and flocculation
2. Biological treatment
3. Membrane filtration
4. Evaporation, distillation, crystallization (freeze concentration)

Internal treatment of white water was originally introduced to retain otherwise lost fiber and filler, which had a positive effect on the process economy. Later on, the separation of the solids from the water resulted in high-quality clear filtrate, which could be used in showers on the wire part of the paper machine. In the case of several paper machines in a mill, the water savings can be significant. Energy is also saved as the temperature is maintained. However, one has to be careful. Clear white water contains organic substances that act as carbon sources for bacterial growth. Elimination of primary suspended solids does not eliminate the possibility of secondary suspended solids. The bacterial growth can be very harmful, as it can cause spray nozzles to become plugged. Slime problem can be taken care of by using chemicals, biocides, dispersants, etc. It can also be controlled by increasing the temperature of the system to higher than 50°C or maintaining a pH of 8.5–9, but both these methods are not possible in many cases.

Internal white water treatment has to be economically feasible. Earlier, the recovery of valuable solids justified a simple so-called save-all treatment. But now, the price of water has increased because stringent rules and limitations are applied on effluent quality and the demand on freshwater quality has increased. Water used for cooling and sealing purposes should be kept clean, but the situation is often the opposite. White water is allowed to intrude the system, and the water is rejected as waste. In this case, it is easy to find the reason of pollution and take the necessary preventive measures. Clean cooling water can be reused. The retention disturbing compounds should not be allowed to enter the paper machine system. To restrict the amount of disturbing components such as anionic trash in the paper machine system in combination with low freshwater usage, it is necessary to isolate the pulping department from the paper mill. This can be achieved by high consistency pulp transfer in combination with indirect heat transfer. The filtrate from pulp dewatering is treated for efficient removal of dissolved and dispersed substances in the first place. The countercurrent principle needs to be applied, which means that the clean (or treated) water is used on the paper machine and that excess, preferably clarified water is pumped to the pulping department. The pulp is transferred to the paper machine at high consistency (15%–35%) to reduce the transportation of disturbing agents. The most polluted water should be collected at the pulping department and if so decided, treated biologically for reuse. While implementing this scheme, it is important to take care of the energy distribution through the production line. Pulp at high consistency does not transfer heat but water does. The even distribution of energy has to be taken care of by heat exchangers, making it possible to maintain the correct temperature on the paper machine.

In cases, when water has to be free from suspended solids (SS), both particle size and concentration have to be defined as according to the definition, all particles above the size of 1–5 μm are SS. Separation of SS is dependent on the technique used. Screening is used when coarse material has to be separated, whereas clarification is used when small particles are also to be separated. Sedimentation is a widely used clarification method. However, care has to be taken not to overload the system. Particles settle according to Stoke's law in the gravity field at a certain velocity depending on their size and density. To achieve good results, flocculation aids are used. Flotation is feasible if the solids to be separated have a lower density than water or when small amounts of oil-like droplets have to be eliminated from the water. Clarification by flotation is achieved by the rising force of air bubbles attached to the particles.

Water containing suspended solids can be filtered using a well-defined mesh or fine screen. The filtrate quality depends on the mat of fibers formed, and usually water of different degrees of clarity is obtained from a drum filter or disc filter. By utilizing a bed of sand or a combination of different materials of different particle sizes, it is possible to effectively separate suspended solids from water. But, this kind of filtration needs backwashing because the capacity of this type of systems for solid accumulation is limited. Sometimes, the use of semipermeable membranes, especially the microfilters, is helpful in separating very fine suspended particles.

One of the methods is chemical precipitation. By applying certain polyvalent metal ions, such as Fe^{2+}, Fe^{3+}, Al^{3+}, Ca^{2+}, Mg^{2+}, it is possible to destabilize a part of the colloids and achieve coagulation, which leads to adsorption on solids. Formation of metal hydroxide enhances the separation, and resulting solids are separated in conventional ways. The efficiency is dependent on the process behind the water to be treated. Lignin and fat-type colloids are partially separated, but carbohydrates remain in solution. Efficiency, measured by Chemical oxygen demand (COD) or Biological oxygen demand (BOD), shows great variations. The application of metallic cations for coagulation is disturbed by complexing agents such as Ethylenediaminetetraacetic acid (EDTA) or Diethylenetriamine pentaacetic acid (DTPA) used in the bleaching process.

Colloidal and dissolved substances can partially be removed from wastewater by membrane filtration, known as micro-, nano-, and ultrafiltration (UF). The efficiency, measured as COD and total organic carbon (TOC) removal, depends on the membrane quality (its material and openness) and volume reduction factor, among other parameters. The general observations about the performance of membrane filtration processes are presented in Table 22.1.

Membrane filtration appears to be feasible as part of an internal water treatment system. UF has been successfully implemented for the recovery of pigment and binder in connection with coating of board and paper. Several types of white water and effluent have been studied on a pilot plant in connection with the Eureka project on "Improved water reuse in pulp and paper industry."

TABLE 22.1 Membrane Filtration Processes

Typical flux for ultrafiltration (UF) is 5–10 m^3/m^2/day at a pressure of 1–5 bar and for nanofiltration (NF) is 1.5–2.5 m^3/m^2/day at 10–15 bar.
Reductions of dissolved COD by UF is 10%–50%, depending on the source of white water or effluent; the corresponding TOC reductions are 15%–50%.
Applying NF on the UF permeate, the reductions in COD and TOC are 65%–95% and 70%–90%, respectively, of the original values.
NF, also called "loose reverse osmosis," removes inorganics, which is indicated by a reduction of specific conductance in the range of 40%–85%.

Based on Bajpai (2012).

Biological treatment of white water improves the clarification significantly. The reason for the same is that the organic compounds stabilizing the fines in suspension are consumed by the bacteria present in the bioreactor. The primary carbon sources are the carbohydrates and extractives. These are responsible for poor first-pass retention, poor dewatering on the wire, and bad smell in the product. The introduction of internal biological treatment will improve the efficiency of conventional wastewater treatment systems. In addition, it will eliminate the possibility of secondary solids, as the carbon source is consumed in the bioreactor. However, the clear filtrate from the pulping has to be cooled before biological treatment if the temperature exceeds 30−35°C, supplemented with phosphorous and nitrogen, and the pH has to be adjusted to neutral (7.0 ± 0.5). Several types of bioreactors and methods are available, and the selection of optimum technology (aerobic or anaerobic) will depend on a case-by-case evaluation. In many mills, biological effluent treatment is already implemented, which can be used for the same.

For making the biologically treated water useful in the process replacing fresh water, suspended solids and possible color have to be removed. This is most efficiently obtained by UF. Flux through the UF membrane increases considerably compared with water before biological treatment, which enables higher capacity for a given filtration area at constant pressure drop and temperature. The bacterial biomass partially binds chlorides, which has been shown by the fact that the amount of chloride in dry matter was found to be 1500−3000 ppm for biomass grown in a white water where the chloride concentration was 20−40 ppm. However, in the conditions prevailing in biological treatment, heavy metals are normally precipitated as hydroxides, provided that the complexing additives such as DTPA and EDTA are not used in excess. The biodegradability of these substances still remains questionable, which can be evaluated using the existing bioreactors.

With the combination of biological and efficient after-treatment (membrane or chemical precipitation), it is possible to replace fresh water in the process. However, there are few important requirements that should be considered mentioned below:

1. Bioprocesses need nutrients in the form of nitrogen and phosphorous. These elements have to be added before the biological treatment in such a manner that the concentration in the treated water is lower than the incoming wastewater.
2. Biological process takes place at neutral pH.
3. The after-treatment is required to separate secondary suspended solids (bacterial cells). With proper operation, the treated water will be free from components causing biological activity, retention, and dewatering disturbances and thus be of acceptable quality for recycling.

The above referred treatments do not remove inorganics from the water, and the overall salt content, measured as specific conductivity, has to be kept at or below an acceptable limit by extracting part of the treated water as effluent. If waste heat of sufficient temperature is available, partial evaporation at low pressure can be feasible. The resulting salt solution has, of course, to be disposed off in an acceptable way. Alternately, the inorganic-rich stream may be cooled to crystallize out the salts.

22.3 MILL CLOSURE PROCESSES

Kraft Mills

Several kraft pulp mills throughout the world are actively involved in the development of closed-cycle technology. Complete closure, however, is difficult with chlorine-based sequences because the resulting bleach liquor chloride level is a threat to the recovery boiler. No bleach plants at paper grade bleached kraft mills are known to be operating effluent-free on a continuous basis. Mills with oxygen delignification and a low chlorine dioxide charge may be able to close the bleach plant if chloride levels in the recovery cycle are monitored carefully. Fiberline and bleach plant process changes that reduce elemental chlorine demand, such as extended cooking, oxygen delignification, and high chlorine dioxide substitution, have been used for several years, but lower adsorbable organic halides (AOX) limits, changing markets surrounding the use of chlorine chemicals, and the drive for bleach plant closure to reduce COD emissions have focused interest on totally chlorine-free (TCF) bleaching. The TCF bleach plant uses no chlorine-based bleaching chemicals, eliminating concerns about dioxins and furans and the more general measurement of chlorinated organic compounds. An added benefit of TCF processes is the high potential for complete reuse of bleach plant filtrates in the recovery cycle. Partial closure of the bleach plant and other mill systems leads to increased concentrations of organics (dissolved wood compounds) and inorganics, often called nonprocess elements (NPEs). Consequences of these are listed in Tables 22.2 and 22.3.

Therefore, before implementing a closure strategy, the consequences for mill operations such as mill uptime; construction materials; mill personnel safety, and pulp quality have to be analyzed. Kraft mill bleach plant effluent flows usually range from 10 to 30 m^3/ADt in modern mills. Many European mills have flows between 15 and 25 m^3/ADt. Few mills have bleach plant effluent flows under 10 m^3/ADt. There are still many mills having bleach plant effluent flows above 30 m^3/ADt. The two main strategies for bleach plant closure are presented in Table 22.4.

Any of these two methods reduces the emissions in terms of AOX, COD, and other environmental parameters on a mass basis (e.g., kg/ADt). The freshwater consumption and effluent flow may also decrease but not necessarily. Currently, elemental chlorine-free (ECF) effluents cannot be easily recycled to chemical recovery

TABLE 22.2 Effects of Partial Closure of the Bleach Plant

Leads to increased concentrations of organic and inorganic compounds, also including nonprocess element, resulting in increased corrosion, scaling, and deposition within the bleach plant and other mill areas
The accumulation of dissolved solids causes a considerable increase in the consumption of bleaching chemicals
Difficulty in reaching target brightness
Variable pulp quality
pH adjustments with sulfuric acid and sodium hydroxide may be costly because of the considerable buffer capacity of the pulp; the sodium–sulfur balance of the mill may, therefore, be disrupted
Large buffer storage capacity for filtrates is necessary to absorb transient and upset conditions, whose frequency increases with the degree of closure
Precipitation of calcium oxalate, calcium carbonate, and barium sulfate; precipitates of calcium oxalate are dominant at pH values lower than 8, while calcium carbonate precipitates at pH 8–12; barium sulfate precipitates over the entire technically interesting pH 2–12
A control strategy for water management in the plant has to be developed and implemented
Additional evaporation plant capacity and additional recovery boiler capacity may have to be installed

Based on AMEC and Beca AMEC (2006).

TABLE 22.3 Impact of Nonprocess Elements

Increased corrosion in digesters, evaporators, and recovery boilers
Depression of recovery boiler capacity and efficiency
Scaling and deposits in bleach plants, digesters, and evaporators
Increased consumption of chemicals
Variable pulp quality
Efficiency of a Q stage in removing transition metal ions is reduced by extensive system closure due to the inhibition created by the Donnan effect

Based on AMEC and Beca AMEC (2006).

TABLE 22.4 Strategies for Bleach Plant Closure

Increased recycle of filtrates within the bleach plant It results in reduced freshwater consumption and bleach plant effluent flows and does not lead to a reduction of specific emissions such as AOX and COD on a mass basis (e.g., kg/ADt).
Recycle of bleach plant filtrates to the recovery system Only alkaline bleach plant filtrate is recycled generally, but a few mills also recycle acidic filtrate. The filtrate can be used as partial replacement of wash liquid in the fiberline brown stock washing or directly recycled to the recovery area.

Based on AMEC and Beca AMEC (2006).

because of the build-up of chloride ions and in some cases potassium and scaling/deposition of organic and inorganic compounds. The COD loads of Bleached Eucalyptus Kraft Pulp (BEKP) mill bleach plant effluents are about 20–30 kg/ADt for ECF bleaching and 20–35 kg/ADt for TCF bleaching at a Kappa number of 8–12 to the bleach plant and with no recovery of bleach plant filtrates. Partial recovery of bleach plant filtrates has the potential to reduce COD emissions by up to 30%. The harmful effects of partial bleach plant closure are presented below. A number of mills are currently practicing of bleaching filtrate recovery. Table 22.5 shows the list of paper grade kraft mills practicing recovery of bleach plant filtrate.

TABLE 22.5 Kraft Paper Mills Practicing Bleach Plant Filtrate Recovery

Metsä-Botnia—Rauma, Finland
UPM-Kymmene Wisaforest—Pietarsaari, Finland
Blue Ridge Paper—Canton, North Carolina
International Paper—Franklin
Samoa-Pacific—Samoa, California
Södra Cell—Mörrum, Sweden
Sweden Värö—Sweden
M-Real Sverige AB—Husum, Sweden
Aspa Bruk—Munksjo, Sweden
SCA—Östrand, Sweden
Stora Enso—Skoghall, Sweden

Based on Beca AMC (2004, 2006).

In all cases the filtrates are recovered via the pulp washing line. Filtrates are recovered from both ECF and TCF bleach plants, and the challenges of closure are to a great degree the same for all bleach plants. Apart from the mills, shown in the table, there may be other mills practicing filtrate recovery. The original intent for many of these mills was to completely eliminate bleach plant effluents. Mills have generally found that as the degree of closure increases, incremental benefits decrease and technical challenges increase. Complete closure appears to be significantly more difficult to achieve than expected. Most mills have found that operations can be sustained only under partially closed conditions. Furthermore, several of the mills in Sweden have concluded that partial closure coupled with secondary treatment of the remaining effluent represents a more optimal solution than full closure. To reduce operating problems, several mills have decided to decrease the degree of bleach plant closure. There are three essentially closed-cycle bleach plants in operation in Swedish mills that bleach a portion of their total pulp production in addition to the mills presented in Table 22.5. In these mills, a small bleach plant was added to an existing brown paper and board mill to produce white top liner. Alkaline filtrates from bleaching are recycled countercurrently to brown stock washing. The neutral or acidic filtrate is returned for washing brown stock in two of the mills, and in the third mill it is concentrated in a low temperature evaporation stage; the concentrate is added to the black liquor concentrators. The bleached pulp production represents only 20% of production in SCA Munksund and Kappa Kraftliner Piteå mill, and in AssiDomän Frövi, 40% of production is bleached. The small capacity of these bleach plants relative to the total capacity of the brown stock system and chemical recovery facilities provides conducive conditions for recovering of bleaching filtrates compared with paper grade bleached kraft mills where all of the pulp is bleached. There are no bleach plants at paper grade bleached kraft mills that operate fully closed on a continuous basis. A number of relatively "closed" new bleaching lines using presses have been built or are under construction. Some perform with bleaching effluent flows from 6 to 9 m^3/ADt, including Advance Agro in Thailand, Stora Enso Skoghall and SCA Östrand in Sweden, and ZP Rosenthal in Germany. Several mills practice recovery of alkaline filtrates via the postoxygen or brown stock washers. A few mills are recovering acidic bleaching filtrates, and few linerboard mills have small bleach plants for top liner production from which all of the filtrates are recycled to associated base liner brown stock systems.

Fig. 22.1 shows an overview of the Champion Bleach Filtrate Recycling (BFR) TM process; Fig. 22.2 shows Union Camp Franklin Fiberline; Fig. 22.3 shows Weyerhaeuser's minimum impact mill model; and Fig. 22.4 shows Louisiana-Pacific bleach plant filtrate recycle.

Process closure in general and particularly bleaching wastewater recovery can lead to increased concentrations of so-called NPEs, which can cause several problems as mentioned before if allowed to accumulate in mill process streams. The degree to which filtrate recovery can be practiced is limited by the availability of means to effectively manage these and other impacts. Important sources of NPEs are raw materials, especially wood, water, and makeup chemicals. Kraft pulp mills operating in a continual manner at a high degree of system closure (for example, with water consumption of approximately 15 m^3/ton of pulp or less) have to use special techniques for separation and to purge the disturbing nonprocess

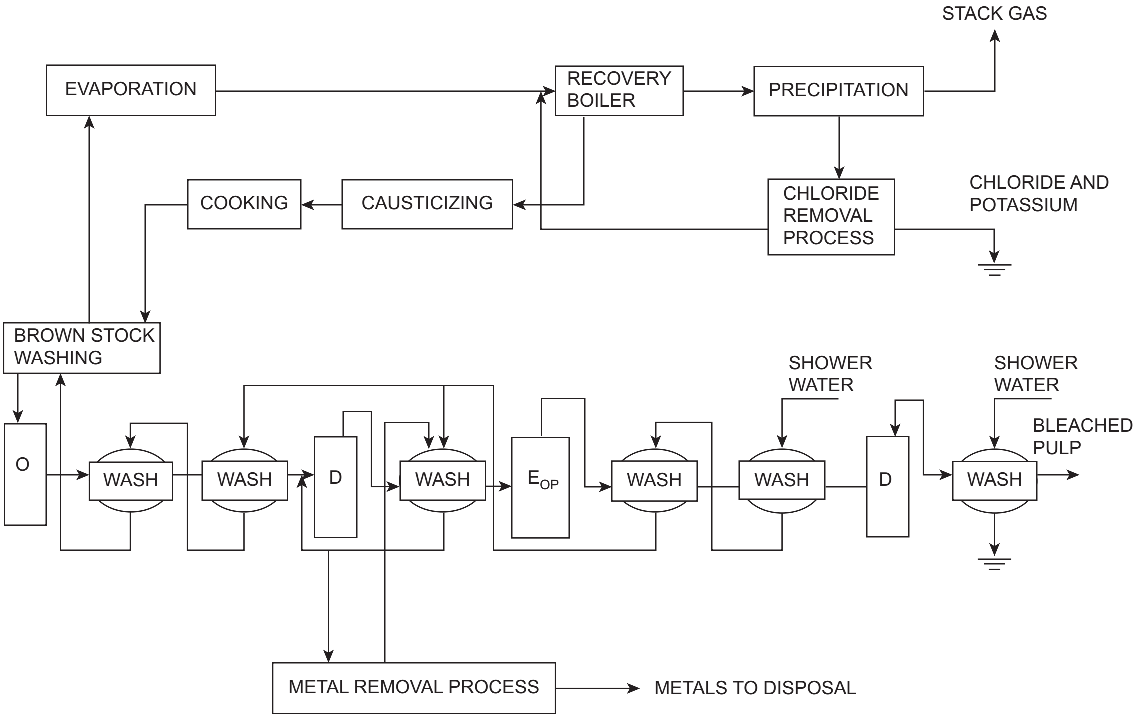


FIGURE 22.1 Overview of the Champion BFR TM process. *Reproduced with permission from Canovas and Maples (1997).*

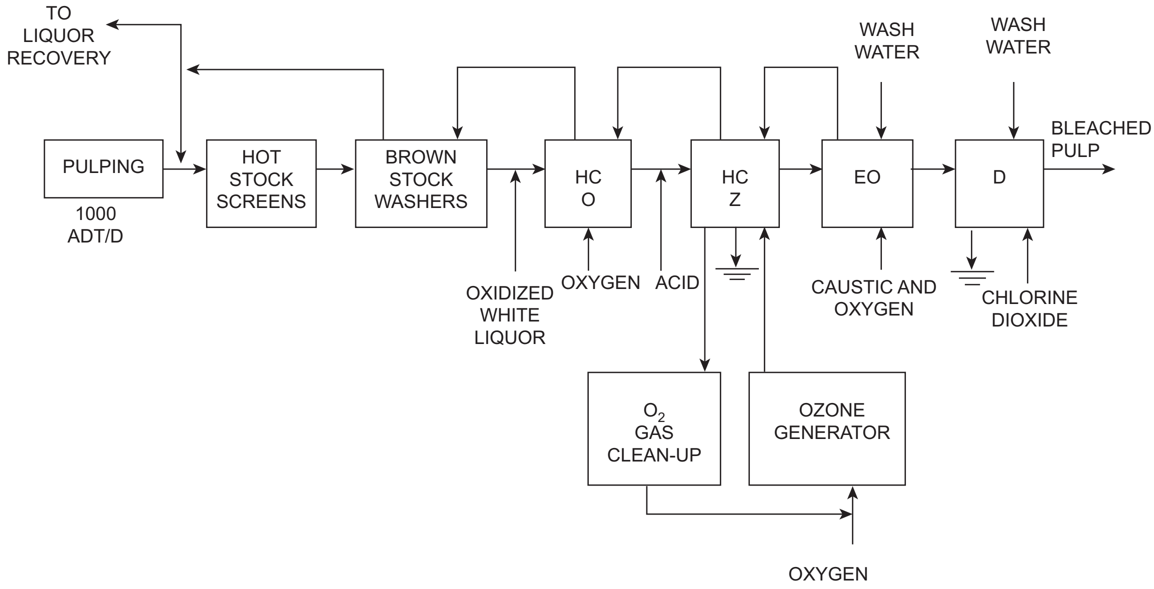


FIGURE 22.2 Union Camp Franklin Fiberline. *Reproduced with permission from Johnson et al. (1996).*

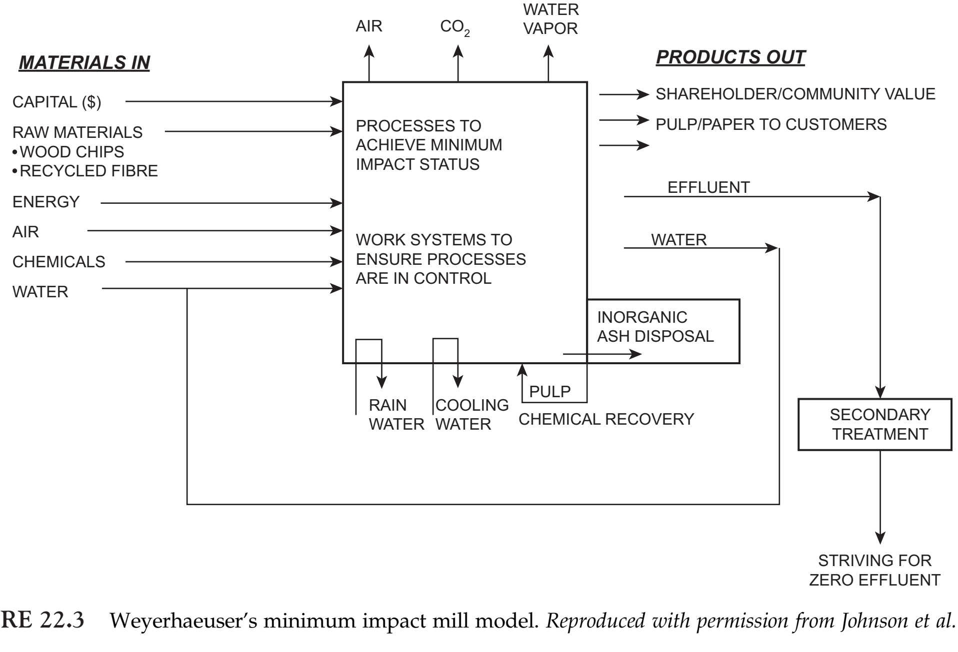


FIGURE 22.3 Weyerhaeuser's minimum impact mill model. *Reproduced with permission from Johnson et al. (1996).*

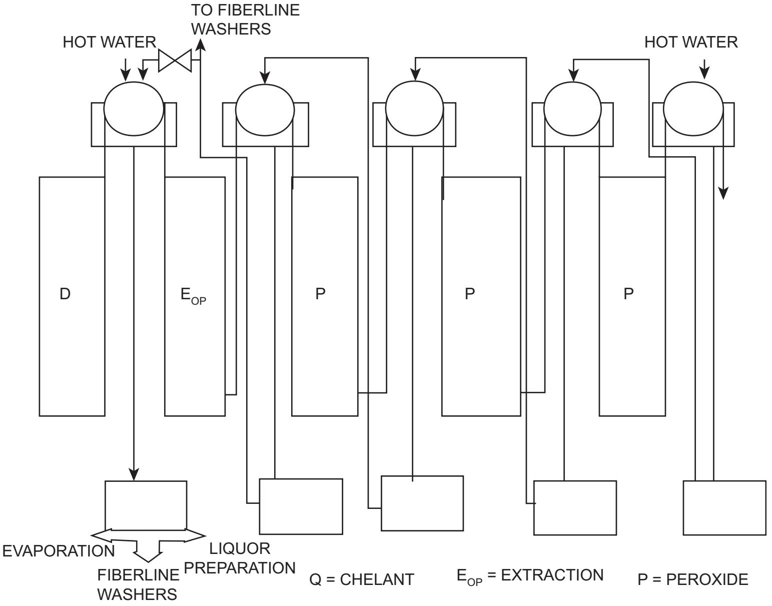


FIGURE 22.4 Louisiana-Pacific bleach plant filtrate recycle. *Reproduced with permission from Johnson et al. (1996).*

substances. NPEs can be classified according to the kinds and locations of impacts they have (Table 22.6).

Methods are available to manage the impacts of NPEs. There are potentially significant impacts associated with certain transition metal ions, including Mn^{+2}, Fe^{+3}, and Cu^{+2} that catalyze the decomposition of peroxide. In ozone bleaching, Fe^{+3} and Cu^{+2} can result in significant degradation of cellulose. This can be attributed to free radical species produced by reactions involving these ions. To limit the impact of transition metals in ozone and peroxide stages, provisions are made to sequester and/or remove these ions. Chelating agents, especially EDTA, are used in a Q stage just before the peroxide stage. The chelating agent affects their removal from the pulp and chemically isolates them in a dissolved state; they are subsequently washed from the pulp and discharged with the Q stage filtrate. Wood chips are normally the main source of most NPEs in a kraft pulp mill. A significant part of these ballast substances can be removed from the wood by leaching the chips with an acidic solution at 80–100°C before the cooking stage. The results of the studies using different leaching liquors (water, acid, chelating compounds, and magnesium sulfate solutions)

TABLE 22.6 Classification of Nonprocess Elements

Chlorine, which exists almost exclusively as chloride ion in mill liquor streams and potassium, have adverse impacts on recovery furnace operation
Calcium and barium can form scale deposits in the bleach plant and at locations where acidic bleaching filtrates are recovered
Manganese, iron, and copper consume certain bleaching chemicals, and the subsequent degradation products can cause pulp strength losses
Silicon and aluminum form scale deposits on heat transfer surfaces

Based on Stratton and Gleadow (2003).

show the possibilities of removing various NPEs from industrial pine chips. Acid leaching using diluted sulfuric acid, which appeared to be the most effective, was shown to decrease the content of most of the metal ions. The content of K was decreased by approximately 75%; Ca, Mn, and Mg by approximately 70%; Al, Ba, Cd, Co, Cu, Ni, and Zn in the range of 50%–65%. The potential for implementation is good. The basic requirements of such a process have been largely clarified, and the process is ready for industrial testing.

Green liquor sludge separation and removal has been considered the important kidney for a number of NPEs in the kraft pulp process. But it is well known that the traditional way of separation by sedimentation is difficult and not sufficiently effective, especially in the case of an increased degree of recirculation of process streams. Much better separation results are possible by the application of filtration techniques. In the framework of the research program KAM2, filtration properties of green liquor sludge have been studied, and processes to improve this inherently difficult separation step have been suggested. The addition of aluminum and calcium ions improves the filtration properties as does the addition of lime mud to the green liquor sludge.

The main purpose for lignin separation from black liquor is to recover surplus energy in the form of a solid biofuel. But, as a side effect, NPEs are removed from the pulp mill liquor cycle together with the lignin. In the framework of the Ecocyclic pulp mill project, the following processes have been studied: precipitation of lignin by acidification, separation of precipitated lignin by filtration, and washing of the lignin. Favorable conditions for precipitation from black liquor of about 30% Dry solids (DS) have been established, as well as the dewatering and washing properties of the precipitated lignin. Important parameters are the precipitation temperature, the ionic strength, and the pH. The method is ready for testing on a pilot scale.

The studies have shown that it is possible to successfully fractionate and concentrate black liquor by UF with polymeric and ceramic membranes. Ceramic membranes maintain favorable properties at high temperatures and high alkalinities. An attractive option is to remove lignin from the digester circulation, which might increase the pulping and bleaching performance.

Internal bleach plant closure to reduce water consumption by a countercurrent recycling of filtrate leads to an increase in water temperature and the concentration of inorganic and organic compounds in the bleach plant. The proposed solution is to introduce new kidneys to the bleach plant to avoid potential process problems. For the D stage filtrate and filtrates from other acidic stages the “Champion’s process concept” can be applied. It includes the removal of multivalent metal ions (Ca^{2+}, Mg^{2+}, Mn^{2+}, etc.) using a cation exchange process. The purified filtrate can be recycled to the bleach plant. Another method used to purify acidic or almost neutral bleach plant filtrates, rich in dissolved NPEs, is to adjust the pH of the filtrate to about 11 (at 60°C) using lime mud, lime, or white liquor. A large number of metal ions will then form slightly soluble compounds that can be separated by filtration or flotation. Neutral and alkaline filtrates can be purified (mainly from organic substances) with the methods of ultra- and nanofiltration. The application of these techniques is, so far, at the stage of laboratory-scale investigations. Different techniques, which are already used in some pulp mills, could also be considered NPE kidneys. Electrodialysis technique is promising for the pulp industry not only for ESP dust treatment but also for removal of chlorides from bleaching filtrates.

Sulfite Mills

Not much information is available on closed-cycle activities in sulfite mills. MoDo paper mill and Stora Enso Nymölla in Sweden, Lenzing AG in Austria, and PWA Waldhof Mannheim

Pulp and Paper mill in Germany are adopting closed-cycle technology. PWA Waldhof Mannheim Pulp and Paper mill has been able to achieve close cycle by using a single-stage bleaching process—OPMgO (hydrogen peroxide–reinforced oxygen delignification with magnesium oxide). The main features of this process are: (1) dissolved organic compounds are returned to the recovery cycle, (2) magnesium oxide is recycled into the process and partly replaces the demand for makeup magnesium oxide, and (3) dissolved lignin and other organics are used to produce combustion energy. With this novel system, the mill was able to reduce significantly the effluent load from the bleaching plant in terms of COD (Fig. 22.5).

Domsjö has operated closed-loop TCF bleaching (Extraction -Oxygen -Hydrogen peroxide, EOP) at its sulfite mill in Örnsköldsvik since 1985. The mill was previously owned by MoDo. Wood is pulped using an acid sulfite process followed by screening and washing. The mill first experienced pitch deposition problems when recycling alkaline bleach plant filtrate to the acidic washing system. This was solved initially through use of UF and now more cost-effectively through chemical flocculation and removal in a dissolved air flotation (DAF) unit. In an acid sulfite system, metal and scale forming materials (such as calcium) are dissolved in the liquor and washed from the pulp before bleaching. However, pitch and oily extractive materials are largely insoluble at low pH, carrying through to the bleach plant where they become dissolved in the alkaline bleaching filtrates. The primary limitation to recycle of bleaching filtrates is the deposition of this material when it is returned to the redstock system. MoDo and Kemira developed a combination of pulp and filtrate treatment techniques to act as a "kidney" for removal of the extractive material. A press is used as the final brown stock wash stage, which facilitates removal of finely suspended globular pitch material, followed by mechanical kneading and mixing with a frota-pulper. The filtrate is treated in a DAF unit to which polyethylene oxide (PEO) is added as a flocculent. The PEO binds to pitch material to form a sludge, which is separated and burned. More than 90% of the extractives are removed in this manner.

Stora Enso's Nymölla mill produces paper grade pulp and uncoated fine papers. The pulp is produced from softwood (from pine and spruce) and hardwood (beech). A magnesium

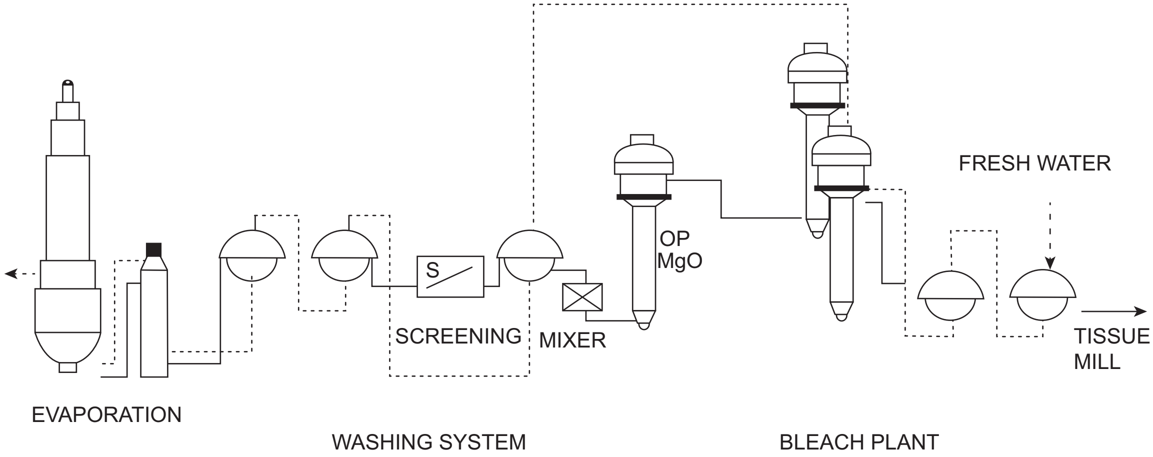


FIGURE 22.5 Flowsheet of Kamyr line at PWA Waldholf. *OPMgO*, hydrogen peroxide–reinforced oxygen delignification with magnesium oxide. *Reproduced with permission from Nimmerfroh et al. (1995).*

bisulfite (magnefite) process is used for pulping. Liquor is recovered in the magnesium-based recovery process. Pulping is followed by delignification and bleaching using oxygen, peroxide, and sodium hydroxide. Because they cause plugging in the furnace, sodium and potassium cannot be recovered into the magnesium-based pulping liquor recovery. To reduce effluent loads, particularly COD, Nymölla installed an UF plant for treating oxygen stage filtrates. The UF plant removes 50% of the COD into a small (2% of original flow), concentrated stream. The concentrate is combusted in the bark boiler. UF is effective at removing high-molecular-weight compounds that tend to be resistant to biodegradation, so the combination of UF and activated sludge treatment has resulted in efficient COD removal.

Lenzing AG in Austria has produced sulfite viscose pulp using ozone and peroxide. Most of the effluent from the bleach plant is now completely recycled, and the mill has run several trials in the fully closed-cycle mode. Lenzing AB produces dissolving pulp from beech using a magnesium bisulfite cook and a TCF ((EOP)ZP) bleaching sequence. The pulp is converted to viscose fiber on site. Lenzing has been a pioneer in the application of oxygen and ozone in bleaching and the implementation of effluent-free bleaching. Its principal motivation in working toward process closure was to minimize the impact on the small receiving stream. A chemical recovery system was installed in 1963 as a first step in closing up the mill. This was followed in 1973 with a spent liquor collection system and in 1983 with a extraction plant for removing acetic acid and furfural from evaporator condensates, enabling condensate reuse in the chemical recovery process for raw acid production. The acetic acid and furfural are purified and sold as commercial by-products of the process. In 1979 the bleaching sequence was converted from CEHH to EPHP, and then in 1984 to (EOP)HP. Medium consistency ozone stages were added to the small and large bleaching lines. The first and most significant step was taken toward making the bleach plant effluent free with the installation of a separate concentrate and burn process for extraction stage filtrate. The EOP filtrate, containing about 2% dry solids, is concentrated to 52% dry solids in a multiple-effect evaporation plant. The concentrated liquor is burned in a specially designed soda recovery furnace, recovering sodium carbonate as a smelt. The sodium carbonate is used for effluent neutralization, with consideration given to installing a causticizing plant and converting the sodium carbonate to sodium hydroxide using purchased lime. The by-product calcium carbonate would be used to neutralize effluent. A new sulfite recovery furnace was installed and with it a magnesium sulfite decomposition plant. Mill trials have been carried out in which the filtrates from the Z and P stages were used on the red liquor washers, confirming the feasibility of eliminating effluent from the bleach plant.

Fig. 22.6 shows simplified flow scheme of the Lenzing bleach plant showing current liquor management, and Fig. 22.7 shows simplified flow scheme of the Lenzing bleach plant showing closed operation mode.

Mechanical Pulp Mills

Mechanical pulp mills using the chemithermomechanical pulping (CTMP) process produce effluents with much higher levels of BOD and COD and that are much more toxic to aquatic organisms. Effluents from CTMP mills are also much higher in BOD, COD, and toxicity than those from mechanical pulp mills using older mechanical pulping processes such as thermomechanical pulping (TMP) and stone groundwood. There is a strong correlation between the load of pollutants in the effluent and the yield of pulp from wood because, unlike chemical pulping, mechanical pulping has no chemical recovery process and therefore any material dissolved out of the wood during the processing of mechanical pulp probably ends up in the

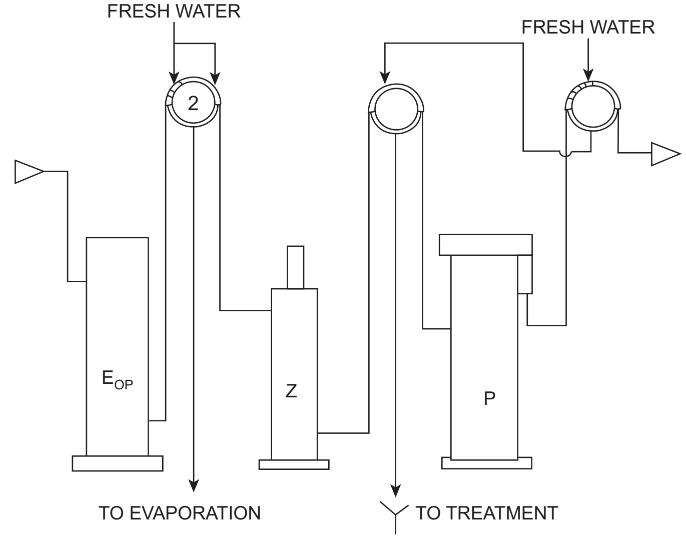


FIGURE 22.6 Simplified flow scheme of the Lenzing bleach plant showing current liquor management. *Reproduced with permission from Krotscheck (1994).*

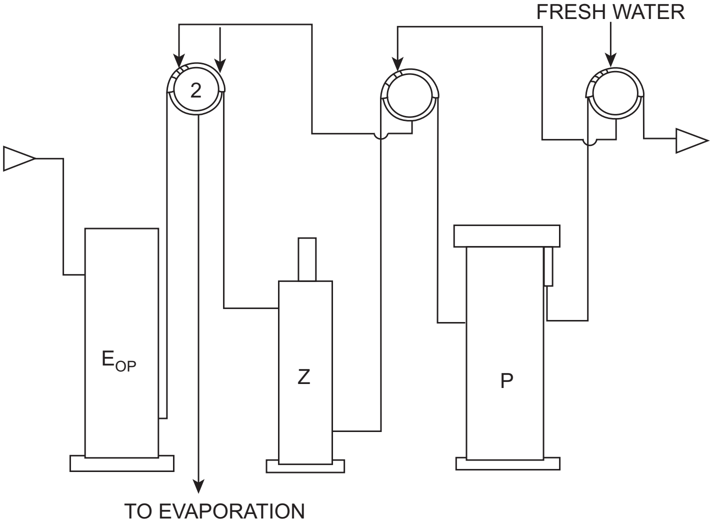


FIGURE 22.7 Simplified flow scheme of the Lenzing bleach plant showing closed operation mode . *Reproduced with permission from Krotscheck (1994).*

effluent. If the pulp is brightened, the additional pollution load from the chemical brightening operation is roughly related to the amount of brightening chemicals used. Most mechanical pulp mills use primary and secondary biological effluent treatment to reduce the impact of their discharges on receiving waters. This treatment would normally include sedimentation to remove suspended solids followed by aerobic or anaerobic biological treatment. Effluent treatment of this nature usually removes in excess of 95% of the BOD and produces a nontoxic effluent. The characteristics of the treated effluent will generally satisfy the regulatory requirements of most jurisdictions. However, in recent years a number of new mechanical pulp mills have been built in areas where water supplies are limited or where receiving waters are not suitable for the introduction of treated effluents. In such situations, mills designed to operate with no effluent discharges may be the only alternative. To achieve zero discharge status, contaminants must be removed from the effluent, producing clean water suitable for reuse in the process. Processes with potential applications include various concentration and separation processes such as freeze crystallization, evaporation, UF, flotation, distillation, and reverse osmosis to separate contaminants from the water. These are commercial technologies, but their application to effluents from mechanical pulp mills was relatively unproven until the 1990s. Two basic approaches have been tried to achieve zero discharge. In one approach, steam driven evaporation is used to concentrate contaminants, which are then incinerated. The other approach uses freeze crystallization as the primary technology, followed by evaporation. Processes are described in more detail herein. Currently, all zero discharge mills utilize evaporation as the primary separation method. Few zero-effluent bleached chemi-refiner mechanical pulp mills started up in Canada in the early 1990s: Louisiana-Pacific Canada Ltd. (purchased by Tembec Ltd.), Chetwynd, British Columbia (June 1991); and Millar Western Pulp Ltd., Meadow Lake, Saskatchewan (February 1992). There are a number of other mechanical pulp mills that are using or have used evaporation technology to reduce or eliminate effluents, including AFI in Myrtleford, Australia; the Stora Enso CTMP mill at Fors, Sweden; Inpacel at Arapoti, Brazil (operating as a TMP mill); and Stora Enso at Kotka, Finland (TMP).

Recycled Fiber Paper Mills

Many recycled fiber paperboard mills consider closure of their process water circuit as a cost-effective investment to meet effluent regulations. The concept of zero discharge mill is attractive both from the standpoint of biological treatment plant savings and the complete elimination of environmental impact because of the mill effluent. Paperboard and roofing felt mills using recycled fiber as furnish are good candidates for zero discharge operation because they typically do not have extensive treatment facilities already in place and their product quality standards are less demanding than for many other paper products.

Most Canadian recycled paperboard mills have already implemented extensive water and energy conservation techniques, such as segregation of clean water from white water, alkaline paperboard-making that enables the reuse of white water for vacuum seals, and good heat exchange networks. These measures have helped to reduce the effluent discharge to about 6 m^3 of effluent/ADt of board. A large fraction of white water is recycled and reused. Fresh water is needed for preparation and dilution of chemicals, selected high pressure showers, and gland seals. Because paperboard mills often change from white top liner to fully brown board, two white water systems are used. When the mill reverts from the fully brown stock to white top liner stock, a substantial amount of brown white water has to be purged and fresh water added for starting the white liner.

There are several references in the literature on closed white water systems in recycled paperboard mills. Green Bay Packaging Inc. implemented a closed-cycle system in the 1970s using reverse osmosis as the method for purging inorganic matter. However, the mill is now operating in a closed-cycle mode without reverse osmosis or any other expensive technology. The mill has achieved system closure primarily by extensively replacing fresh water with process water and a proper selection of chemical additives. The Haltown Paperboard Company mill has used a similar approach for mill system closure. Several paperboard mills in the United

States operate with relatively low-effluent discharge (mean = 18 m^3/ADt and the minimum = 0.4 m^3/ADt). However, details on the technologies selected, choice of water reuse locations, effluent discharge conditions and effects of system closure on production are not available. Little evidence exists for why a particular method of water reuse was successful or unsuccessful. In cases where high degrees of system closure were achieved corrosion and bacterial growth in the paper machine area were observed. Several mills are currently attempting to achieve complete closure by treating the effluent as the freshwater source.

Reuse of white water for dilution of wet-end chemicals and cleaning felts was investigated, and successful strategies were implemented at a recycled paperboard mill. White water was successfully used for the second stage dilution of starch and bentonite clay before addition to the headbox stock. Screened white water (400 mesh) was found to be suitable for cleaning felts at high pressure. The implementation of screened white water reuse in a board mill enabled the mill to reduce its daily minimum effluent discharge from 5.5 m^3/ADt to about 2.3 m^3/ADt of board without affecting the production. The mill's average effluent discharge was reduced by about 40% from 8.5 to 5.1 m^3/ADt.

St. Laurent Paperboard Inc., a corrugated medium mill, situated at Matane, QC, Canada, has successfully undertaken and attained zero process effluent discharge. The process effluent flow was steadily decreased from 6000 m^3/day to 0 in October 1995. The mill meets all present and future environmental regulations. Although the chemical dosages have increased, the incremental costs are just a fraction of what it could cost to operate a secondary treatment plant. Also, zero effluent has resulted in an old corrugated containerboard (OCC) yield that increased from 85% to 92% and related to the higher overall retention of fines/clay into the paper. The reuse process water also resulted in energy saving of about 5%.

Typical process modifications that are required to implement zero discharge operation at paperboard mills have been reviewed. The process equipment items used to achieve this are not sophisticated and generally include primary treatment, adequate water storage, stainless steel metallurgy, and often a segregated cooling water system. Chemical programs must achieve consistently high first-pass retention of fines, clays, size, and colloidal contaminants such as pitch. Recycled water must replace fresh water for most applications, including gland water and paper machine shower water.

Increased white water recycling results in a build-up of organic and inorganic contaminants. The effects of these white water contaminants on the strength properties of paper produced from secondary fiber have been examined. Eight contaminant types were evaluated at three concentrations. The effects of the contaminants grouped as organic and inorganic were measured first, followed by separately determining the effect of individual contaminants. As a group, the organic contaminants had a greater effect in reducing sheet tensile index. For both groups, as concentration increased, sheet tensile index decreased. Taken individually, the organic contaminants, water-soluble wood extractives, neutral sulfite semichemical (NSSC) lignosulfonate, kraft lignin, and defoamer adversely affect sheet tensile index. Of the inorganic contaminants, sodium, calcium, iron, and alum, only iron had a large adverse effect on sheet tensile index.

22.4 PRACTICAL AND ECONOMIC CONSIDERATION

The closed-cycle mill will never be completely closed. A "zero discharge" mill is in fact a technical impossibility because there will always be the need for a continuous purge of dissolved solids and also conventional solid wastes such as ash, dregs, and slaker grits. Even a zero liquid discharge mill will present serious technical challenges to prevent a build-up of undesirables, which would encourage corrosion or deposition. Process upsets will occur in a closed-cycle facility just as surely as they do in a conventional mill. To be a truly closed cycle, the mill must have the capability for containment and storage of all process spills, as well as the means for either returning the liquor or filtrate to the process or sending it on to waste treatment. State-of-the-art process controls and information systems will be mandatory for proper monitoring of critical process variables in a closed-cycle mill. Although there is still considerable debate over the most cost-effective and reliable process design for closed-cycle facilities, particularly for non-TCF bleached kraft mills, most of the studies indicate that there is no significant increase in the capital cost associated with designing a new facility for full-scale closure. This is mainly due to offsetting the cost of additional evaporation, cooling, and spill protection/surge capacity with savings resulting from considerably downsized water and wastewater treatment systems. However, 7%–9% higher capital costs for the closed-cycle mills (1500 tons/day bleached eucalyptus kraft mill) have been estimated. These estimates assume an ideal location adjacent to a source of water, both for the mill and to disperse effluent. If water supply dams and water or effluent pipelines are required, the closed-cycle case would incur lower off-site costs. For a severe site, this may result in similar overall project capital costs. These mills may have a competitive disadvantage compared with those better located. For example, capital costs for a 1000 ton/day bleached kraft pulp mill (BKPM) are estimated to be $40 million less for a TCF/effluent-free BKPM than for a new ECF BKPM. Principal incremental savings arise from elimination of the waste treatment plant and chlorine dioxide plant. Principal incremental costs arise from the larger evaporator system and cooling tower. With regard to the operating costs, the picture is not quite clear although it appears that a closed-cycle mill may offer some manufacturing cost advantages. These costs are very site-specific and need to be evaluated on a case-by-case basis.

There are indications that the costs are similar for both open and closed cycle. No conclusions regarding the costs of ECF compared with TCF bleaching can be drawn, as the plantation wood has different yields and chemical requirements and consequently different equipment requirements than those for mature wood. Operating costs are reported to be $35 per ton pulp less for a TCF effluent-free BKPM than for a new ECF BKPM. Principal savings are for bleaching chemicals, makeup cooking chemicals, and the effluent treatment plant operation. On the other hand, the operating costs of a closed-cycle sulfite mill in Austria, producing dissolving pulp, were reported to be slightly higher ($1.48 per ton pulp) than the open-cycle operation. From a practical standpoint, the greatest hurdle for widespread implementation of closed-cycle technology will be the capital costs associated with closure of existing mills. Estimated capital costs for the retrofit of closed cycle into existing mills are highly variable, depending to a large degree on the capacity and capability of existing equipment and the product qualities being sought. For bleached chemical pulp mills, the cost of conversion is primarily a function of (1) the existing fiberline configuration; (2) the bleach sequence and bleach chemical costs; (3) utility (power and steam) costs; and (4) waste treatment costs. In general, mills faced with high waste treatment costs and low unit costs for steam and power would have most to gain from closure. With any operating cost savings offset by the substantial depreciation costs of the capital expenditures required for closure, it is doubtful that there will be a compelling economic incentive for converting any bleached pulp mill to closed-cycle operation. Some existing mills such as Lenzing in Austria, SAPPI's Ngodwana in South Africa, and Union Camp (at Franklin, Virginia) in the United States have made major strides toward full or partial closure because of extremely tight limits on allowable effluent discharge rates. For these mills, economics were not the primary consideration. Without regulatory or market pressures, however, most existing mills may never convert to closed-cycle operation unless there is a strong economic incentive. The overall economics depend on (1) capital costs of new equipment, (2) impact of nitrate recycling on bleaching, (3) final quality versus bleaching cost, and (4) market reaction.

22.5 ANNOTATED BIBLIOGRAPHY

AMEC and Beca AMEC, (2006). Review of ECF and TCF Bleaching Processes and Specific Issues Raised in the WWF Report on Arauco Valdivia. Prepared for Resource Planning and Development Commission, Tasmania, Australia.

The Beca AMEC report is a review of ECF and TCF bleaching processes and specific issues raised in the WWF report on Arauco Valdivia and is based on the scientific evidence available to its authors as of May 2006.

Bajpai (2012). Environmentally Benign Approaches for Pulp Bleaching 2nd Edition. Elsevier Inc. USA.

This book focuses on environmentally friendly technologies that can help solve some of the problems associated with conventional bleaching technologies.

Barton DA, Stuart PR, Lagace P, Miner R (1995). Experience with water system closure at recycled paperboard mills. Tappi J.; 79(3): 191–197.

A number of mills producing recycled paperboard operate zero discharge water cycles. This paper discusses experience with water system closure at recycled paper mills.

Beca AMEC (2004) Study report: independent advice on the development of environmental guidelinesfor any new Bleached Eucalypt Kraft Pulp Mill in Tasmania, prepared for the Resource Planning and Development Commission, Tasmania, Australia.

Beca AMEC (2006) Review of ECF and TCF bleaching processes and specific issues raised in the WWF report on Arauco Valdivia. Prepared for Resource Planning and Development Commission, Tasmania, Australia. May 2006.

Brooks TR, Edwards LL, Nepote JC, Caldwell MR (1994). Bleach plant closeup and conversion to TCF: a case study using mill data and computer simulation. Tappi J; 77(11): 83–92.

Process simulation and mill data from Louisiana-Pacific's Samoa, CA, market pulp mill have been used to evaluate the conversion of a conventional oxygen-delignified softwood bleach plant to totally chlorine-free (TCF) bleaching based on hydrogen peroxide. An economic evaluation comparing the TCF process, conventional chlorine bleaching, and 100% ClO_2 substitution is presented.

Canovas RV, Maples G (1997). Champions BFR Process Opens Door to Kraft Bleach Plant Closure. In: Patrick, K.L. (Ed.), Advances in Bleaching Technology. Miller Freeman Books, Calif, p. 141.

Continuing investigations of the bleach filtrate recycle process of Champion International Corporation is presented. Difficulties of bleach plant effluent closure using elemental chlorine-free (ECF) versus totally chlorine-fee (TCF) bleaching technologies are also analyzed.

Evans J (1981). Century-old board mill operates with zero effluent discharge. Pulp Pap. 55(17): 98–103.

The operation of century-old board mill with zero-effluent discharge is discussed in this paper.

Gerbasi B, Stuart PR, Arsenault F, Zaloum R (1993). Techno-economic assessment of several closed cycle technology alternatives for an existing TMP-newsprint mill. Pulp & Paper Canada; 94(12): 123–128.

Techno-economic assessment of several closed-cycle technology alternatives for TMP-newsprint mill is presented.

Jantunen E, Lindholm G, Lindroos C-M, Paavola A, Parkkonen U, Pusa R, Söderström M (1992). The effluent-free newsprint mill. Paperi Ja Puu-Paper and Timber; 74(1): 41–44.

This paper reports that it is possible to build an effluent-free newsprint mill. There is no difference in capital costs and only a minor difference in operating costs between noneffluent mill and a conventional mill. The treatment facilities include biological treatment, flocking with chemicals, and filtering through a sand bed filter and ultrafiltration for other process waters.

Johnson T, Gleadow P, Hastings C (1996). Pulping technologies for the 21st century- A North American view. Part four-emerging technologies and mill closure. Appita; 49(2): 76–82.

This excellent paper focuses on pulping technologies for the 21st century. Emerging technologies and mill closure are discussed.

Kenny R, Naumov A, Babinskiy GA, Yampolsky MD, Volsky O, Goncharov A (1995). Tappi J, 78(3): 191–196.

Russians have developed tertiary treatment systems to minimize the impact of effluent on receiving waters. Experience with three Russian mills is presented. Tertiary treatment is effective in removing suspended solids and BOD.

Kenny R, Yampolsky M, Goncharov A (1995). An overview of a Russian zero discharge unbleached kraft pulp and paper mill-Selenga Pulp & Paper Company. Pulp and Paper Canada 1995; 96(5): T155–T157.

The Selenga Pulp & Paper Company in partnership with Sibgiprobum developed the closed-cycle system. The regulatory history and treatment plant design are reviewed in this paper.

Krotscheck, AW, Sixta H, Peter, W, Gerzer, T (1994). Effect of Bleach Plant Closure—Laboratory Bleaching. In: Proceedings of Int. Non-chlorine Bleaching Conf. Amelia Island, Fla, p. 13.

The effect of bleach plant closure in sulfite dissolving pulp mill is presented.

Lagace P, Stuart PR, Kubes GJ (1996). Development of a physical-chemical zero discharge process for a TMP-newsprint mill. Pulp & Paper Canada 1996; 97(11): T414–T419.

The physical-chemical process for treating the effluent of a thermomechanical pulping (TMP) newsprint mill, so that the mill could operate without any effluent discharge, is discussed. This process shows promise as part of a closed-cycle treatment scheme for TMP-newsprint mills.

Lindholm G, Jantunen E (1996). Treatment and reuse of process water in pulp and paper industry, steps towards effluent free operation. In: Proceedings of Tappi Minimum Effluent Mill Symposium, Tappi Press, Atlanta, USA: 195–208.

This paper discusses the possibilities of removing a majority of dissolved and dispersed substances in an economically effective way to produce water that can replace the use of fresh water without endangering production efficiency or product quality. The proposed solution consists of biological water treatment in combination with countercurrent water-fiber flow and total removal of suspended solids.

Mannisto H, Mannisto E, Winter P (1995). Technical and economic implications of converting bleached-kraft mills to low-effluent operation. Tappi J, 78(1): 65–73.

A study of technical and economic consequences of the conversion of a bleached kraft mill to low-effluent concepts was carried out. This study also included an evaluation of the environmental impacts and the

assessment of the risks involved in implementing the low-effluent concepts. Low-effluent concepts involving the recovery of bleach plant effluent are not cost-effective for existing mills.

Maple GE, Ambady R, Caron JR, Stralton SC, Vega Canovas RE (1994). BFR-A new process toward bleach plant closure. Tappi J, 77(11): 71−80.

A Champion-International Corporation paper mill has commercialized bleach filtrate recycle (BFR) technology—a new process with the potential to significantly reduce waste effluents produced in bleaching pulp. The BFR process dramatically reduces the discharge of dissolved organic compounds to unprecedented levels and, ultimately, helps eliminate them altogether.

Nimmerfroh N, Suss HU, Bottcher HP, Luttgen W, Geisenheiner A (1995). The German approach to the closed cycle sulphite mill development and implementation. Pulp and Paper Canada; 96(12): T414−420.

TCF bleaching of sulfite pulp has been state of the art in Germany for some years. A fundamental step in the AOX-driven discussion was the installation of oxygen delignification stages. The paper shows the effects of switching from NaOH to MgO on pulp and effluent characteristics.

Prasad B, Kirkman A, Jameel H, Gratzl J, Magnotta V (1996). Mill closure with high-kappa pulping and extended oxygen delignification. Tappi J; 79(9): 144−152.

High-kappa kraft pulping coupled with multiple oxygen stages and TCF bleaching can be used to close a pulp mill without overloading the recovery system and with a production increase, under certain circumstances. This study also demonstrates the use of process simulation for determining optimal solutions to complex process problems.

Ramamurthy P, Dorica J, Rollin Y: Reduction in effluent discharge from recycled paperboard mills. In: Proc. Tappi Minimum Effluent mill Symp. Tappi Press, Atlanta, USA 1996; 335−340.

Reuse of white water for dilution of wet-end chemicals and cleaning felts was investigated, and successful strategies were implemented at a recycled paperboard mill. The mill's average effluent discharge was reduced by about 40%.

Reeve DW, Rowlandson G, Kramer JD, Rapson HW (1979). The closed-cycle bleached kraft pulp mill-1978. Tappi J 1979; 62(8): 51−54.

The closed-cycle or zero-effluent mill concept is discussed. It responds to short-term environmental legislation and future legislation that could regulate additional effluent parameters and require tertiary effluent treatment systems, extensive testing of effluent contaminations, testing of effects on receiving waters, and so on.

Reeve DW (1984). The effluent-free bleached kraft mill Part XIII. The second fifteen years of development. Pulp Paper Canada 1984; 85(2): T27−T30.

Reeve has outlined some of the developments required to eliminate discharge of effluent from a bleached kraft pulp mill.

Ricketts JD (1994). Considerations for the closed-cycle mill. Tappi J; 77(11): 43−49.

This paper discusses impact of closure strategies on mill costs and operation.

Rousseau S, Doiron B (1996). Zero Process effluent discharge attained at St.-Laurent Paperboard Inc., Matane, Quebec. Pulp & Paper Canada, 97(9): T302−T305.

Zero Process effluent discharge attained at St. Laurent Paperboard Inc., Matane, Quebec, is discussed in this paper. At zero-effluent discharge rates, the overall solids content dissolved in the manufacturing water reached its equilibrium at about 12,000 mg/L, while the conductivity stabilized around 6000 μS/cm.

Shenassa R, Reeve DW, Dick PD, Costa ML (1996). Chloride and potassium control in

closed kraft mill liquor cycles. Pulp and Paper Canada; 97(5): T173–179.
Chloride and potassium accumulation in the kraft pulping cycle is a growing problem for many pulp mills. This paper discusses the control of chloride and potassium in closed kraft mill liquor cycles.
Stratton SC, Gleadow P (2003). A review of global technology developments and mill experiences in the 1990s TECHNICAL BULLETIN NO. 860.
This report provides a summary of the pollution prevention and effluent minimization (so-called "process closure") technologies developed and implemented during the 1990s whose impacts have been to reduce the generation and discharge of waste materials from pulp manufacturing operations. It focuses primarily on bleached kraft pulp mills but includes information on mechanical and sulfite pulping processes.
Stuart P, Lagace P (1996). Review of process modifications for implementation of zero discharge at recycled fiber board mills. In: Proc. Tappi Minimum Effluent mill Symp. Tappi Press, Atlanta, USA, 327–333.
This paper reviews the process modifications for implementation of zero discharge at recycled fiber board mills.
Vendries E., Pfromm PH (1998). Influence of closure on the white water dissolved solids and the physical properties of recycled linerboard. Tappi J, 81(9): 206–213.
The effect of closing the white water system on the physical properties of linerboard produced from recycled fiber under acid rosin sizing conditions was investigated in this study.
Welkener U, Hassler T, McDermott M (1993). The effect of furnish components on depositability of pitch and stickies. Nordic Pulp Paper Res J, 8: 223–225, 232.
The effects of three different white water and TMP water fractions on the deposition of pitch and stickies have been investigated. Variations in the amount of pitch deposition could be observed depending on the type of pitch and on the TMP water or white water fraction used.
Young J (1994). Chetwynd pioneers innovations in zero-effluent pulp production. Pulp & Paper 1994; March: 73–75.
Louisiana-Pacific at Chetwynd, British Columbia, a Canadian bleached chemithermomechanical pulp mill, is operating zero-effluent discharge.
Young J (1994). Green Bay packaging begins third year with closed water system. Pulp Pap. 1994; 68(11): 105–111.
Green Bay Packaging Inc. implemented a closed-cycle system in the 1970s using reverse osmosis as the method for purging inorganic matter. However, the mill is now operating in a closed-cycle mode without reverse osmosis or any other expensive technology. The mill has achieved system closure primarily by extensively replacing fresh water with process water and a proper selection of chemical additives.
Young, J (1994). Meadow Lake enters third year of zero-effluent pulp production. Pulp & Paper 1994; March: 56–61.
Millar Western at Meadow Lake, Saskatchewan, a Canadian bleached chemithermomechanical pulp mill, has entered third year of zero-effluent pulp production.

CHAPTER

23

Fiber From Recycled Paper and Utilization

23.1 INTRODUCTION

Paper recycling in an increasingly environmentally conscious world is gaining importance. Recycled fibers play a very important role today in the global paper industry as a substitute for virgin pulps. Paper recovery rates continue to increase year after year in North America and Europe. A lot of the increase in paper recovery can be attributed to the increase in easy residential and commercial recycling through single-stream recovery systems, as 87% of Americans now have access to curbside or drop-off paper recycling programs.

In Oct. 20, 2016, the European Recovered Paper Council (ERPC) announced that the paper recycling rate in Europe reached an impressive 71.5% in 2015. According to ERPC's final monitoring report for 2015, compared to 2010, collection and recycling has increased by almost 1 million tons of paper. The 2015 European paper recycling rate of 71.5% is 1.5% higher than the target set by the ERPC in the third European Declaration on Paper Recycling for the period 2010−15.

Obtaining fiber from recycled paper is a matter of separating impurities from the usable fiber. This involves extensive systems for removing foreign materials, including skimmers to remove floating items, removing heavy items at the bottom of a repulper, and removing stringy items such as rope and wet strength papers. Coarse screening is used for further cleaning before using fine screens. Vortex cleaners, through-flow cleaners, and, for printing and tissue grades, deinking systems are used. The steps used in recovering fiber can be accomplished in a wide variety of different orders.

Recycled or Secondary Fiber

The source of recycled fiber is recycled paper or paperboard arising outside of the mill. It is distinguished from *broke*, which is off-specification paper produced at the mill and reused within the mill. There may be similar considerations, however, when using broke in a mill. It is very important to have "pure" sources of paper from which to recover high quality fiber. Newspapers should not be mixed with magazines, brown paper, or boxes. Office papers should not be contaminated with newsprint or brown papers.

The product with the largest recovery by amount and percentage in the United States is old corrugated containers (OCCs). Over 50% of OCC is recovered in the United States. One reason is that large amounts of OCC are generated at specific sites, such as grocery stores and other retail outlets. Newspapers and other post-consumer wastes are much more expensive to collect and tend to be highly contaminated with unusable papers and trash. Still, 33% of newsprint is recovered, but only one-third of this ends up in new newsprint.

Biermann's Handbook of Pulp and Paper: Raw Material and Pulp Making
https://doi.org/10.1016/B978-0-12-814240-0.00023-9

Old newsprint (ONP) is used in OCCs. This allows a higher level of postconsumer waste to be included in OCCs, which is important for some classifications of paper. The strength of ONP can be increased by chemical treatment (such as with NaOH), refining, the use of starch adhesives, and fiber fractionation.

Many US states, however, have enacted (or are working on) legislation that demands large amounts of recycled fiber (10%–50%) in newsprint. The Garden State Paper Co. New Jersey was the first US company to use deinked newsprint in newsprint. They started with a 90 ton/day facility using a washing process in the 1960s.

Use of Recycled Paper

About 80% of all wastepaper comes from three sources: corrugated boxes, newspapers, and office papers. Less than 20% of wastepaper is deinked to be used in newsprint, tissue, or other bright grades. Most wastepaper is used in paperboards, chipboard, and roofing materials where color is not important. The percentage of deinked newsprint and other grades is expected to increase considerably over the next few years.

Shrinkage

Shrinkage represents the loss of material from the original feedstock to the recovered product. A plant that recovers 90 lb of dry fiber for every 100 lb of dry paper has a shrinkage of 10%. A plant recovering OCC may have a shrinkage of about 8%. A plant recovering newsprint for use in newsprint (news to news) may have a shrinkage of 15%–20% for flotation deinking and up to 30% using combined flotation and washing deinking. A plant recovering office paper and producing pulp of high brightness (above 85%) may have shrinkage of 35%. Shrinkage represents the loss of fillers, fines, plastics, dirt, ink, and useful fiber.

23.2 STATISTICS

The importance of recovered paper as a raw material in the paper industry has increased dramatically during the last decade. The US paper recovery rate rose to an all-time high of 67.2% in 2016—up from 66.8% in 2015 (Table 23.1). Consumption of recovered paper at US paper and paperboard mills was stable at 30.8 million tons in 2016—down just 0.1% compared with the 2015 level—whereas exports rose from 1.3% to 21.8 million tons. There are also some domestic uses of recovered paper outside the paper industry, including as base materials for insulation and molded pulp products. The paper recovery rate measured 33.5% back in 1990, which was the base year against which the American Forest & Paper Association began setting its recovery goals. Member companies of AF&PA have set a goal to increase the US paper recovery rate to more than 70% by 2020. The 2016 data show continued progress toward meeting the goal.

In 2016, 33.7% of the paper and paperboard recovered in the United States was used to produce containerboard, which is the material used for corrugated boxes, and 11.8% was used to produce boxboard, which includes base stock for folding boxes and gypsum wallboard facings. Net exports of recovered paper to China and other countries accounted for 40% of the paper collected for recycling in the United States in 2016 (Table 23.2).

The latest data on recovery rate for printing-writing papers is shown in Table 23.3. An estimated 58.6% of printing-writing papers were recovered for recycling in 2015, which is higher from 53.0% in 2013 to 57.7% in 2014. The actual tonnage of printing-writing papers

TABLE 23.1 Paper and Paperboard Recovery Rate

Year	Recovery Rate (%)
1990	33.5
1991	36.7
1992	38.5
1993	38.7
1994	41.5
1995	44.0
1996	45.6
1997	44.2
1998	44.6
1999	44.5
2000	46.0
2001	48.3
2002	48.2
2003	50.3
2004	49.3
2005	51.5
2006	53.0
2007	56.0
2008	57.7
2009	63.6
2010	63.5
2011	66.8
2012	65.1
2013	63.6
2014	65.2
2015	66.8
2016	67.2

Based on www.paperrecycles.org.

recovered for recycling dropped 3.3% in 2015, but domestic purchases of these papers (i.e., new supply) dropped by a more substantial 4.9%, which resulted in an increase in the recovery rate.

TABLE 23.2 Uses of Recovered Paper

Packaging Type	Share of Total (%)
Newsprint	3.0
Tissue	8.0
Containerboard	31
Boxboard	12.0
Other	5.0
Net Exports	41.0
Total	100

Based on www.paperrecycles.org.

The recovery rate for OCC/unbleached kraft papers was approximately stable in 2016 at 92.7%. Domestic consumption of OCC increased 0.3% in 2016, whereas exports increased 1.7%. However, these gains were offset by higher domestic containerboard consumption, leading to an almost stable recovery rate (Table 23.4).

In 2016, total recovery of newsprint/mechanical papers reduced by 6.3%. However, new supply of these grades (domestic production plus imports less exports) reduced by an even more substantial 7.0%, which resulted in an increase in the recovery rate for newsprint/mechanical papers from 71.6% in 2015 to 72.2% in 2016 (Table 23.5).

Data published by the US Environmental Protection Agency for the year 2014 show that paper and paperboard packaging accounts for nearly three-quarters of packaging materials recovered for recycling in the United States (Table 23.6).

The amount of paper going to landfills is reduced by more than half since 2003. This was partly due to an increase in the paper recovery rate from 55% in 2003 to over 67% in 2016. In addition to recycling, some paper is diverted from landfills as it is disposed of in other ways, such as via incineration with energy recovery or in the case of bathroom tissue, via the sewer system (Table 23.7).

TABLE 23.3 Recovery of Printing-Writing Papers

Year	Recovery Rate (%)
1994	34.2
1995	36.4
1996	36.1
1997	34.8
1998	37.7
1999	38.9
2000	42.1
2001	39.6
2002	38.0
2003	40.5
2004	42.6
2005	44.1
2006	48.4
2007	53.5
2008	54.7
2009	61.0
2010	54.6
2011	56.8
2012	54.5
2013	53.0
2014	57.7
2015	58.6

Based on www.paperrecycles.org.

TABLE 23.4 Recovery of Old Corrugated Containers

Year	Recovery Rate (%)
1993	54.5
1994	58.8
1995	65.0
1996	68.5
1997	67.7
1998	67.6
1999	65.7
2000	68.7
2001	70.2
2002	69.9
2003	72.8
2004	70.0
2005	73.5
2006	73.6
2007	75.0
2008	77.6
2009	82.0
2010	85.1
2011	91.2
2012	91.0
2013	89.4
2014	89.2
2015	92.9
2016	92.7

Based on www.paperrecycles.org.

23.3 RECYCLED FIBER PREPARATION

The Nature of the Contaminants and Their Removal

One of the biggest obstacles to using recycled or secondary fiber is effective contaminant removal. Recycling of paper is a process of removing contaminants from the useful fiber. It is useful to compare various steps used for contaminant removal by diagrams such as that in Fig. 23.1. The efficiency of a process is the percentage of rejects removed. The reject rate is the percentage of useful fiber that is discharged with the rejects. Consider a simple pipe split with equal flows to rejects and accepts; 50% of the

TABLE 23.5 Recovery of Old Newsprint/Mechanical Papers[a]

Year	Recovery Rate (%)
1993	46.8
1994	49.8
1995	50.7
1996	49.1
1997	48.4
1998	49.5
1999	49.8
2000	52.3
2001	58.9
2002	60.1
2003	63.9
2004	62.3
2005	64.4
2006	70.0
2007	68.8
2008	69.2
2009	70.3
2010	72.0
2011	73.0
2012	70.4
2013	67.5
2014	69.2
2015	71.6
2016	72.2

[a] *Includes newsprint, uncoated mechanical papers, and coated newspaper inserts.*

Based on www.paperrecycles.org.

contaminants are removed (50% efficiency), but with a fiber reject rate of 50%, nothing has been accomplished. In Fig. 23.1, two hypothetical systems are presented, "A" and "B." It should be apparent that system "A" is superior because it can be run at the same efficiency for a lower fiber reject rate or can be run at a higher efficiency with the same fiber reject rate compared with "B." For any given system, this diagram shows the trade-offs between improved efficiency and fiber reject rates that one will encounter with cleaning, screening, deinking, and other processes.

TABLE 23.6 Packaging Recovery

Packaging Type	Share of Total (%)
Paper and Paperboard	74.8
Glass	7.6
Metal	5.8
Plastic	5.4
All Other	6.4
Total	100

Based on www.paperrecycles.org.

Contaminants can be classified according to their source. *Stickies* are a diverse group of materials that are tacky to the touch. They may enter the process through the polymeric contaminants of secondary fiber, including hot melt adhesives (typically consisting of ethylene vinyl acetate-wax-hydrogenated resin acid combinations), wax and polyethylene from coated boxes, contact adhesives (polybutylene, natural rubber, etc.), pressure-sensitive adhesives (styrene-butadiene rubber [SBR], carboxylated polybutadiene, and vinyl acrylates), polystyrene, and so forth. Some of these structures are shown in Fig. 23.2. Stickies may also arise on the paper machine from wood extractives that polymerize during pulping and, especially, bleaching; additives used within the mill such as fatty acids and other defoamers; rosin and synthetic sizing agents; and polymers used within the mill, such as natural rubber splicing tapes. They tend to be soluble in nonpolar solvents such as diethyl ether, toluene, or methylene chloride,

TABLE 23.7 Paper Landfilled

Year	Paper Landfilled (million tons)
1993	38.4
1994	37.9
1995	36.3
1996	34.4
1997	37.3
1998	38.4
1999	41.4
2000	40.0
2001	36.6
2002	37.7
2003	36.6
2004	39.9
2005	37.8
2006	36.9
2007	32.9
2008	28.1
2009	19.3
2010	20.3
2011	18.4
2012	23.1
2013	23.2
2014	22.4
2015	21.1
2016	20.9

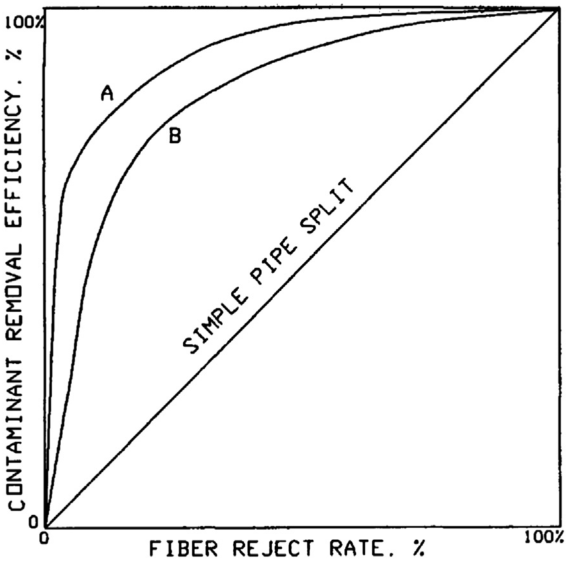


FIGURE 23.1 Contaminant removal efficiency and fiber reject rate.

have a tacky feel to them, and are very difficult to remove from the process.

Stickies are designated as either micro or macro because these two classes behave differently during the papermaking process. Microstickies are smaller than 150 μm and will pass through a 0.006 in. slotted screen. A second classification is passing through a 200 mesh screen (<76 μm). Microstickies are determined by tests such as those of Buckman (plastic bottle), Berol (polypropylene film), Doshi (microfoam), and PIRA (paper machine wire). Talc and zirconium are used for the control of microstickies.

Macrostickies are determined by making handsheets that are then hotpressed and dried. The stickies are determined by counting with the needle nest, counting specks with the Tappi method, or dying the fibers with a water-soluble black dye. Another method that requires standards dyes the stickies with a water-insoluble dye. Some manufacturers say talc and related materials remove macrostickies by increasing their density and allowing their removal in forward cleaners, but this is probably not true. Twin-wire machines seem to have more difficulty with stickies (wire plugging) than Fourdrinier machines. In addition to talc, zirconium compounds are also used for stickies control.

Sticky control agents should be added after the refiners, but as far upstream as possible to allow them ample time to work. Control agents

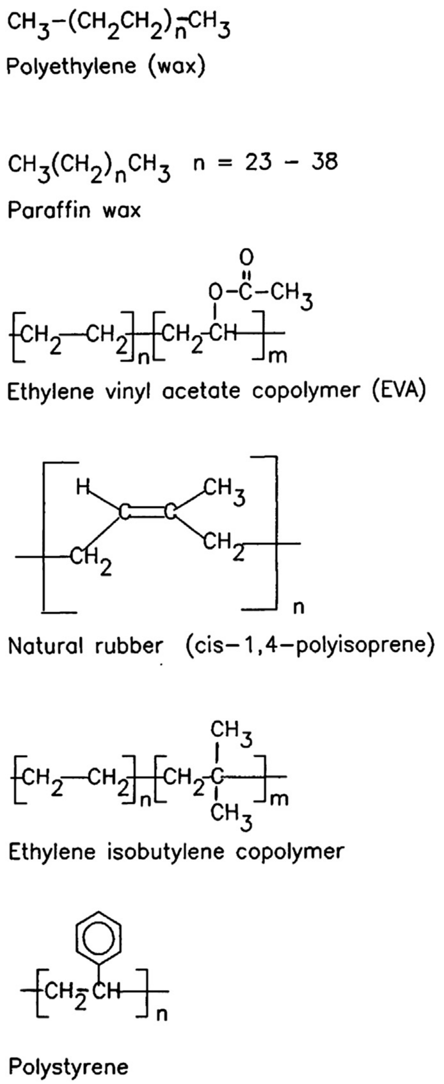


FIGURE 23.2 Several wastepaper contaminants.

include talc (used at 0.6%—2% on pulp), dispersants, zirconium compounds (0.1% on pulp), and alum sequestering agents (to prevent agglomeration of stickies). Synthetic fibers were used at one time (0.1% on pulp), but this method is no longer used. Several mills report that the use of 0.006 in. slotted screens has appreciably decreased the problems associated with stickies in recycled pulp.

Fillers include calcium carbonate, which can interfere with rosin/alum sizing, clays, and titanium dioxide. *Films and laminates* include polyethylene, aluminum foil, etc. *High density materials* include materials such as glass, grit, sand, and metallic objects. *Other materials* include small amounts of unbleachable dyes, wet strength resins, and stringy materials such as carpets.

Ink consists of pigments, such as carbon black or titanium dioxide, to supply color and opacity and a vehicle to carry the pigment and bind it to the paper. The vehicle consists of solvent and resin to bind the pigment to the paper. Traditionally the vehicle was vegetable oil. This is significant as vegetable oil is easily saponifiable with alkali, allowing the ink to be dispersed during deinking. Saponification converts the triglyceride plant oil to glycerol and the salts of the three constituent fatty acids (see Fig. 2.31, Vol. 1).

The type of resin depends on the type of ink and how it attaches to the paper. Inks may "set" on the paper by one of several mechanisms according to Horacek (1978).

1. *Absorption* of the hydrocarbon vehicle into the paper substrate; this type of ink is used in newsprint and tends to smudge.
2. *Evaporation* of the ink vehicle; this is used in magazine and catalog grades using letterpress or offset printing with rosin esters and metal binders.
3. *Oxidation* of a drying oil with multifunctional carboxylic acids and alcohols left on the paper surface after the vehicle is absorbed into the paper.
4. *Ultraviolet* (*UV*) *or electron beam radiation curing* of monomers or prepolymers in the vehicle into polymers such as acrylics.

Infrared hardening, *precipitation* of binders, *gelation*, and *cooling* of hot thermoplastic inks used in electrostatic printing (photocopy and laser printers) are other mechanisms used less often but are increasing.

The first two types of ink are readily dispersible by emulsification. Oxidation-cured inks are often saponified by alkali, but radiation-cured inks do not easily break into pieces smaller than 50−100 μm. The vehicles of inks that dry consist of mineral oils, waxes, alkyd resins, and other hydrocarbon resins; inks which cure by infrared or UV radiation are made with epoxy, urethane, vinyl, or polyol acrylates; xerographic inks contain SBR, polyesters, and acrylates. Latex binders are SBR, carboxylated butadiene, polyvinyl acetate, etc. As ink, and the paper to which it is attached, ages, it becomes more difficult to remove. This should be kept in mind when deciding how to handle wastepaper inventory. Also, the size of the ink particles is very important; typically, newsprint ink has very small particles, on the order of 1−10 μm, ledger has large particles, on the order of 50−1000 μm, and mixed news/magazine grades have intermediate particle sizes on the order of 1−50 μm.

Aside from being classified by their source, contaminants are often classified by their method of removal. Some examples are large, dense materials; small, dense materials; "ultradense" materials; fibrous, light materials; small, light flakes; and so on until you are sick. Such classification schemes identify categories by density, size, composition, shape, etc. As these classifications are arbitrary and the contaminants change as the fiber is processed, they are not mentioned here. Keep in mind, however, what types of contaminants each process removes, to what degree each is removed, and how the process alters the contaminants so that they may or may not be removed in subsequent steps. For example, too much agitation will break stickies apart so that they may not be removed by screening; however, remaining stickies are sometimes deliberately dispersed so that they will have limited impact during papermaking.

One way to limit the amount of contaminants in the secondary fiber is to pay close attention to the wastepaper coming to the mill. The Paper Stock Institute of America circular PS-83 specifies that newspapers for recycling should be almost as clean as when they were delivered to the consumer. Newspapers that are wrapped in plastic (even strappings) or kraft paper or that have more than 2% rejects should be rejected. Ideally, little useful fiber should be removed with the contaminants when processing wastepaper.

23.4 RECYCLED FIBER RECOVERY

Introduction

Recycling fiber is the process of separating useful fiber from the contaminants of wastepaper. A series of processes can be used to accomplish this task. There are also many possible ways of arranging these steps. Each mill has its own needs, its own hypotheses about the best method, and its own operating experiences. In this section we will consider many of the processes available and how they work.

Crow and Secor (1987) list 10 steps for deinking, including pulping, prewashing heat and chemical loop, screening (coarse and fine), through-flow and reverse cleaning, washing, flotation, dispersion, bleaching, and water recirculation and makeup, with brief descriptions of each of these processes. While other methods are available, these represent most of the tools available for fiber recovery from wastepaper. Not all steps are used in all recycled fiber plants.

Continuous Pulper

Recycled fiber recovery begins at the pulper, Figs. 23.3 and 23.4, which is nothing more than a large blender to disperse pulp into an aqueous slurry. Pulping may be done at high or low consistencies using different rotors. Fig. 23.3 shows a high consistency pulper and Fig. 23.4 shows a low consistency pulper with trash removal.

During pulping, some of the gross contaminants are removed. A *ragger* is a chain which is pulled out slowly over a long period of time (perhaps a meter every few hours). The ragger

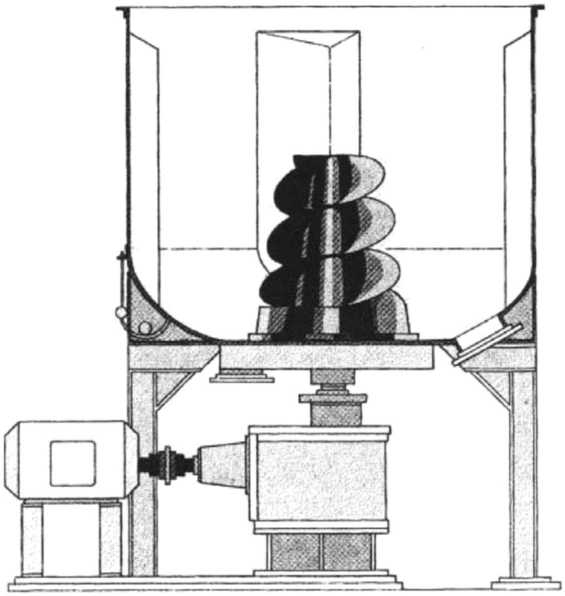


FIGURE 23.3 HI-CON high consistency pulper. *Courtesy of Black Clawson, Shartle Division.*

catches baling wire, wires, plastic sheeting, stringy materials, tapes, wet strength paper, and other long materials that wrap around it as the stock rotates in the pulper. The accumulated material forms a *rag rope* that is over a foot in diameter upon removal. Fig. 23.5 shows a diagram of a ragger with cutter.

Relatively large heavy contaminants such as nuts, bolts, rocks, pipe fittings, and other material do not pass through the holes of the pulper and are eventually forced outward to *the junk chute* at the lower periphery of the pulper. This material is removed by one of several possible means. A *junk tower* is a long tube with an overhead grapple that is used to manually remove debris that accumulates at the bottom of the tower. A *continuous junk remover* is an enclosed bucket conveyer used to automatically remove heavy and floating debris on a continuous basis (Fig. 23.6). It has often been used when processing OCCs. Because of the high maintenance due to chain breakage and inability to keep the pulper clean, bucket and chain trash-removing configurations are no longer used in new equipment. The *junk trap* consists of a vertical tube with valves on the top and bottom to isolate it from the pulper. The top valve is normally open to allow junk to enter, and the bottom valve is closed to retain the contents. The junk trap is emptied by closing the top valve and opening

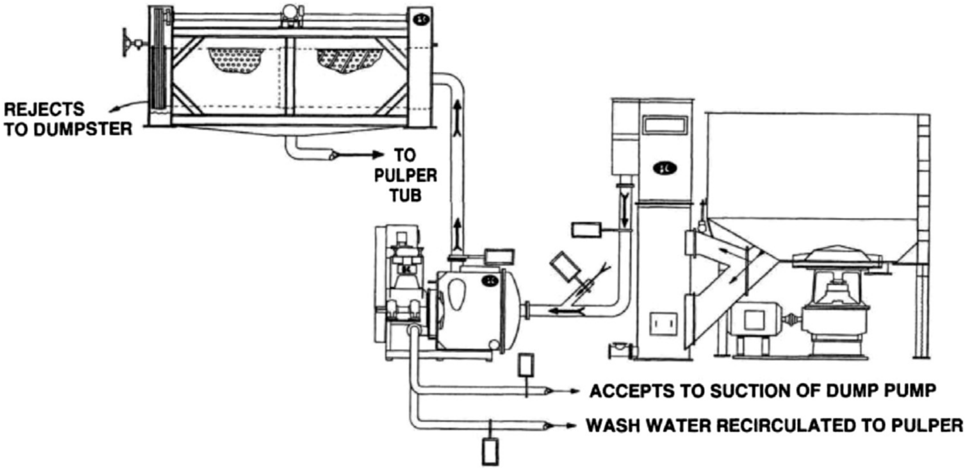


FIGURE 23.4 Hydrapurge detrashing system. *Courtesy of Black Clawson, Shartle Division.*

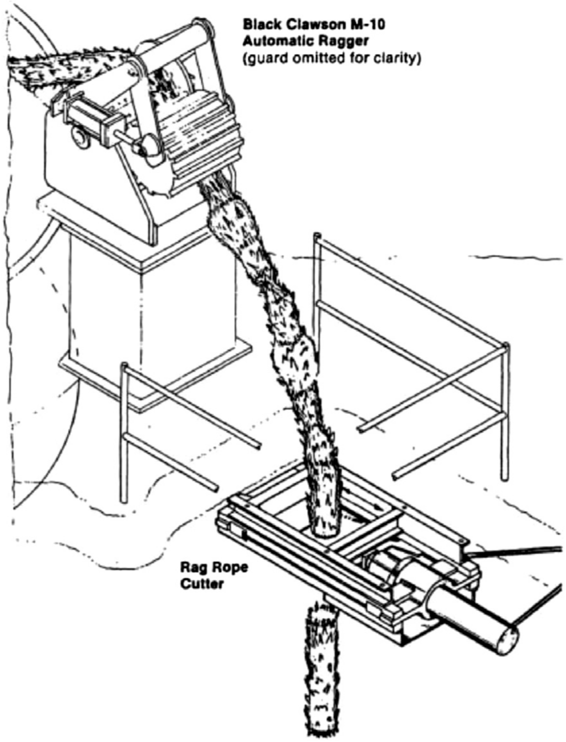


FIGURE 23.5 Rag rope cutter. *Courtesy of Black Clawson, Shartle Division.*

the bottom valve to let the debris out. The bottom valve is then closed, the top valve opened, and the processes repeated as necessary.

On the order of 18 kWh/t (1 hp-day/ton) is required to disperse the fibers, and about the same amount is used for cleaning and screening. The pulp from the pulper then usually goes to pressure screens and high density centrifugal cleaners.

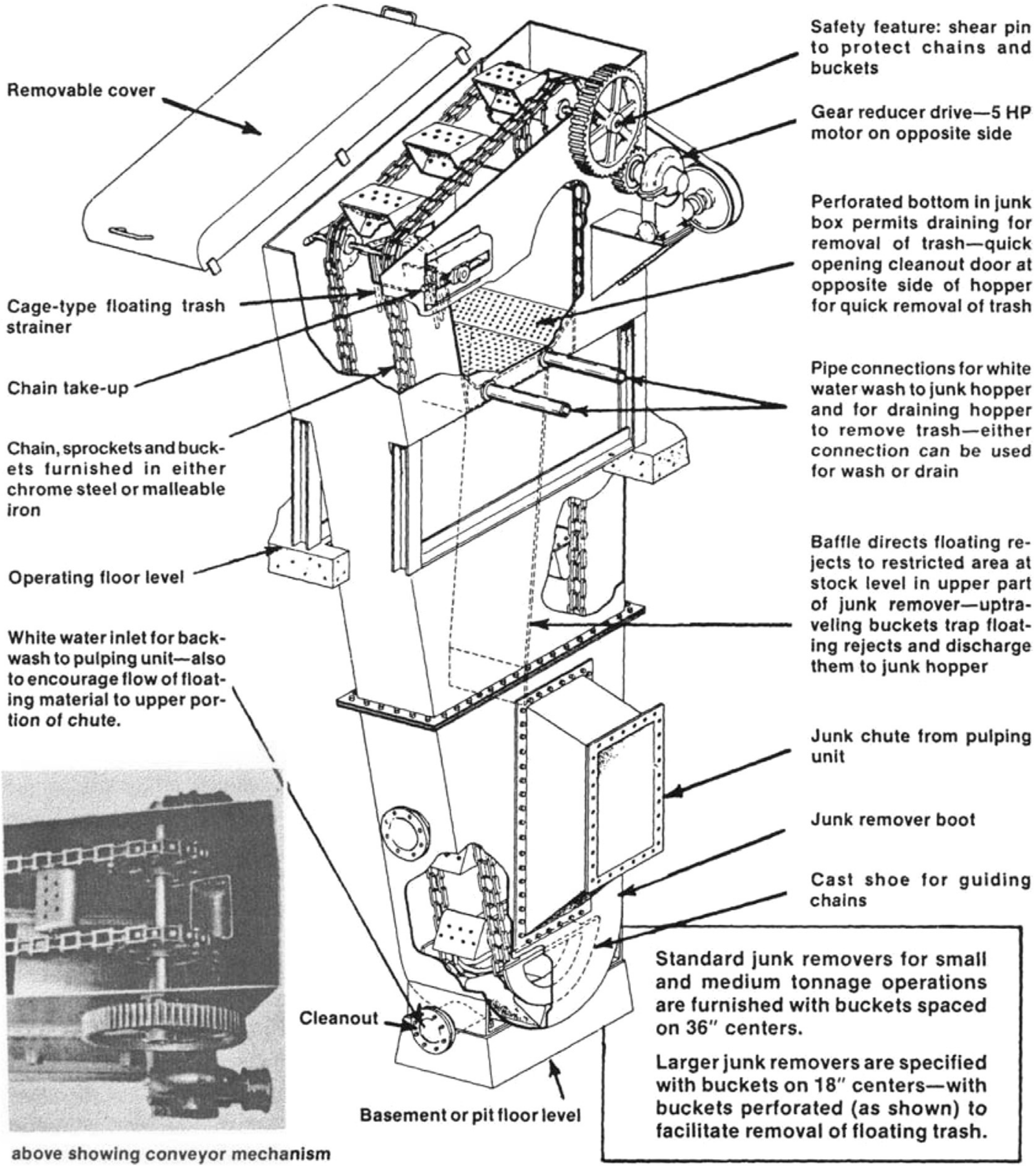
Sometimes high temperatures and agitation in the pulper might break up contaminants into very small particles and must be avoided. These conditions would be avoided if fine screening is the only subsequent method of contaminant removal. These conditions might also be avoided if ink flotation is being used. In other cases, as with ink washing, these conditions might be desirable.

Most deinking plants operate their pulpers in batch mode. Deinking conditions in the pulper are typically 6%–15% consistency, 40–70°C, pH 9–11 (generally below 10 for groundwood pulps to limit yellowing), for 1 h. The trend is toward higher consistency pulping, which has the advantages of enhanced ink separation, reduced pulping time, and lower specific energy consumption.

Pulping at high consistency requires dilution of the pulp to about 5% consistency before it will pass through the extraction plate at the bottom of the pulper (Plate 23.1) or other coarse screening devices (6–16 mm [1/4—5/8 in.] hole size). A tub extension on the pulper is used so dilution water can be added, or the pulper contents are dumped into a stock chest. Typically, white ledger paper is pulped at 15%–20% consistency, newsprint at 10%–50%, the primary screen rejects are often sent to 12% consistency, and OCC at 4%–5% consistency.

Screening

The stock is then sent to a screening system. Because primary screen rejects may be as high as 50%, the primary screen rejects are often sent to a secondary screen to recover usable fiber. Pressure screens are coming into widespread use for this purpose. The basket has a life of 6–12 months for deinking grades and 2–4 months for nondeinking grades, which tend to have more abrasive particles in them. Wear occurs at the rejects end where the consistency is higher and water does not lubricate as well. The trend is toward modular assembly of pressure screens so that the reject end section can be replaced while reusing most of the basket. Fiberprep uses an inward-flow design and claims that centrifugal force keeps the heavy debris away from the screen and thereby reduces screen basket wear and increases throughput. More information on pressure screens may be found in Chapter 3, Volume 2.



Standard junk removers for small and medium tonnage operations are furnished with buckets spaced on 36″ centers.

Larger junk removers are specified with buckets on 18″ centers—with buckets perforated (as shown) to facilitate removal of floating trash.

FIGURE 23.6 Junk remover. *Courtesy of Black Clawson, Shartle Division.*

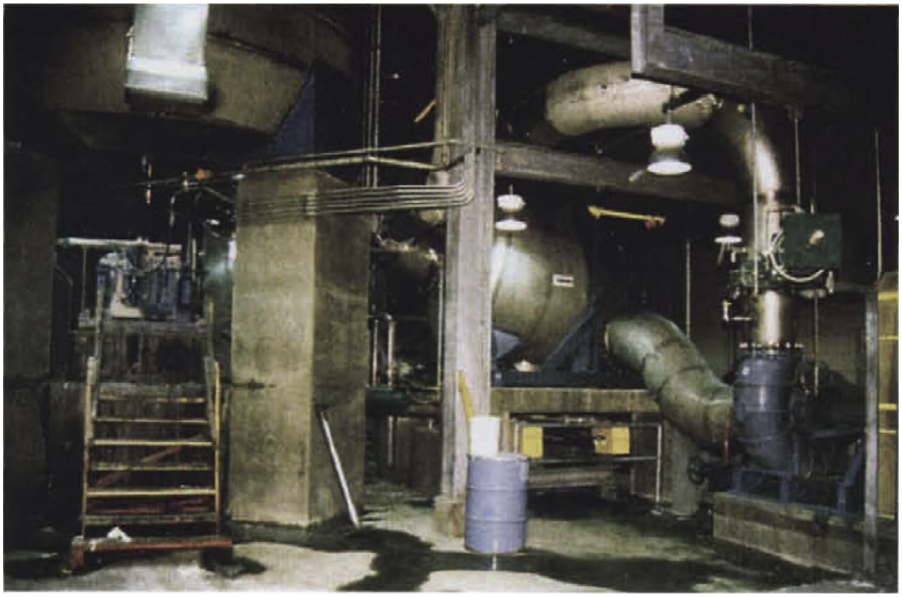


PLATE 23.1 The bottom view of a 60 m^3 batch pulper, with dilution water addition, and an 8 mm round hole screen.

Centrifugal, Vortex, or Cyclone Cleaners

The basic principles of low density vortex cleaners for cleaning pulp before the paper machine are described in Chapter 3, Volume 2. In forward cleaners, a tangential input flow causes a vortex to form inside the cleaner; heavy particles move to the outside of the vortex and eventually drop to the bottom of the cleaner with the rejects while the pulp accepts move to the center of the vortex where they are removed at lower pressure. By this means, small heavy debris such as sand, glass, and metal fragments are removed.

Medium (1%–3%) and high (2%–5%) density centrifugal cleaners are used at 2%–5% consistency and low pressure drops, 70–210 kPa (10–25 psi), to remove heavy contaminants of particle size 50–1000 μm (0.002–0.040 in.) that escape with the pulp through the pulper coarse screen and other screens. Fig 23.7 shows two high density cleaners used in a 500 ton/day secondary fiber mill. Fig. 23.8 shows a diagram of a high density cleaner and its operation. Rejects consist of small pieces of tramp metal, glass, and stones. Reject rates are below 1%. Water (10–40 gal/min) may be used in the throat of the cleaner to decrease the consistency in this region and help the heavy particles settle. These cleaners are typically about 2.5–6 m (8–20 ft) tall (although low profile cleaners are available) with a diameter of 0.20–0.65 m (8–26 in.) at the wide portion. The reject trap consists of a pair of valves that are manually or automatically operated. The top valve is left open to collect debris, whereas the bottom valve remains closed. When the trap gets full, the top valve is closed and the bottom valve is opened to remove debris. The bottom valve is then closed, and the top valve is then opened. A single high density cleaner can process several hundred tons of pulp per day.

If very fine grit remains, a low density cleaning system is used that operates below 1% consistency (high pressure, 200–275 kPa or 30–40 psi) as described in (Chapter 3, Volume 2).

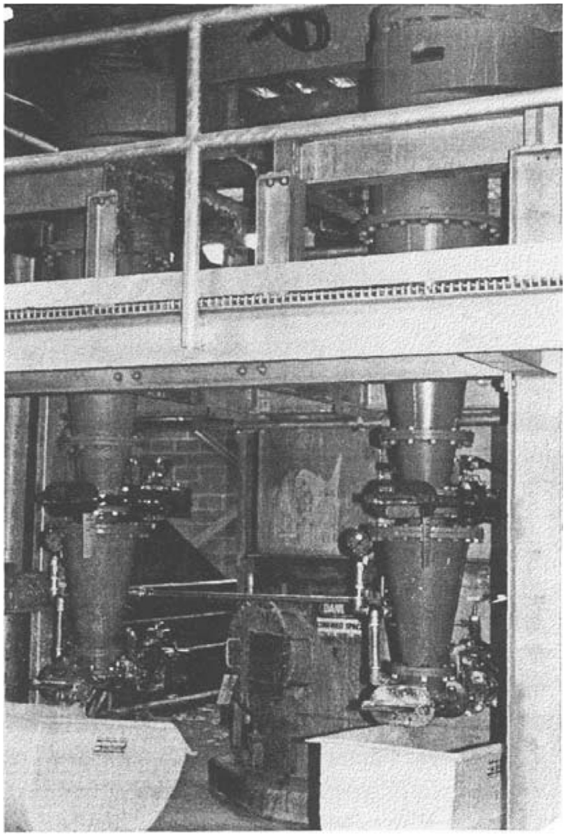


FIGURE 23.7 Two high density cleaners.

Black Clawson's trademark for high and medium density cleaners is the Ruffclone. The high density cleaners use 5–10 kWh/t (0.3–0.5 hp/day/t) pulp. Their fine paper forward cleaners are Ultra-clones that use about 30–80 kWh/t (1.7–4.5 hp/day/t).

Reverse Cleaners, Through or Parallel Flow Cleaners

Lightweight contaminants were first removed by *reverse cleaners*, where normal forward cleaners were used and merely operated in reverse. These cleaners required very large pressure drops on the order of 500 kPa (70 psi) and used large amounts of energy. Recent developments allow both the rejects and the accepts to be removed at the bottom. Such cleaners, while called reverse cleaners, are better termed *through* or *parallel flow* cleaners. The reject rates have been reduced from 20% to 30% for the original reverse cleaners to 2%–3% for modern designs. This means that numerous stages are not required. Fig. 23.9 shows the operation of a through flow cleaner. Beloit (LeBlanc and McCool, 1988) has developed a number of centrifugal cleaners that are examples of recent improvements.

Beloit developed these cleaners using image analysis to track contaminants in the isolated fiber, transparent cleaners with high-speed video cameras to observe the separation process, and analysis of the internal flow patterns. The Uniflow cleaner, which appeared in 1982, is a *through-flow cleaner* that removes lighter-than-water contaminants, such as plastics and other polymers, stickies, and pitch. The feed of the cleaner is at the top, and both the rejects and accepts flow through the cleaner and out the bottom, hence the term uniflow. An internal core with a small annulus around the air core collects the rejects. This circumvents the upward moving, inward spiral flow that interfered with lightweight reject separation and led to high reject rates in earlier reverse flow cleaners. These changes were claimed to reduce the rejects from 20% to 1%–2% with a twofold improvement in lightweight contaminant removal.

Black Clawson's through-flow cleaners are the 3 in. X-Clone cleaners were first operational at the Stone Container mill in Florence, South Carolina, in May of 1984 and have been described by Bliss (1986). These cleaners use 1% consistency pulp with a 60–100 kPa (10–15 psi) pressure drop. The power requirements are 6–10 kWh/t (0.3–0.5 hp/day/t). The reject rate is normally 1%–4% at a consistency

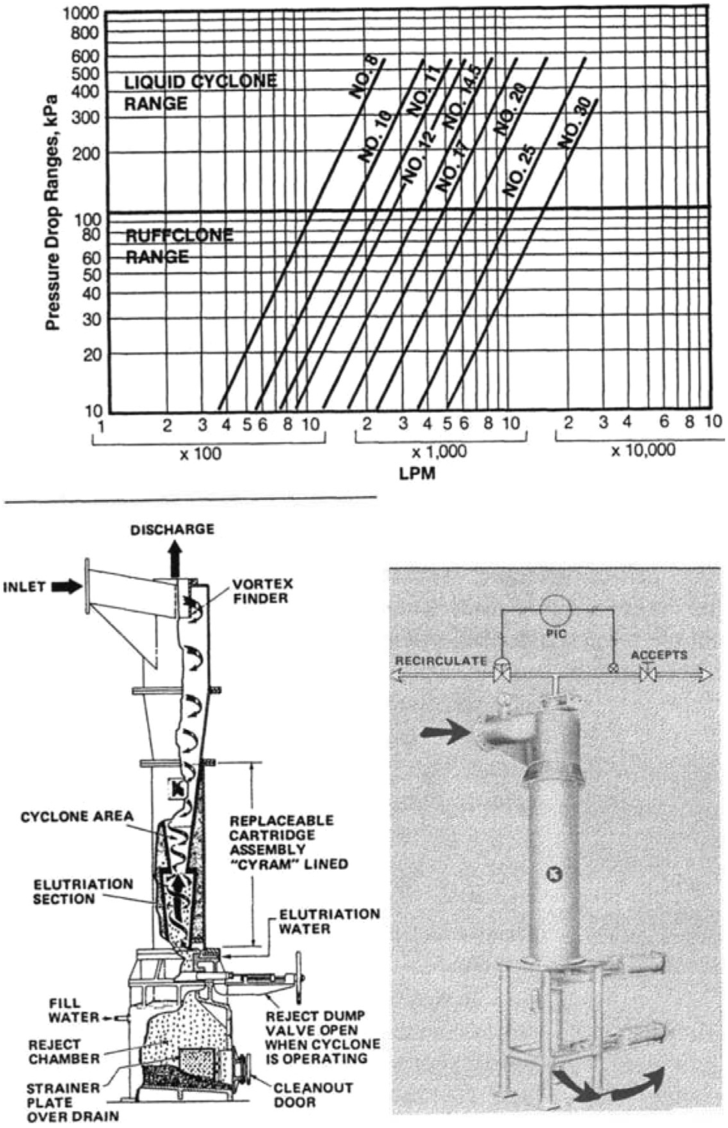


FIGURE 23.8 Ruffclone and Liquid Cyclone high density cleaners with capacity chart and recirculation loop for constant discharge pressure. *Courtesy of Black Clawson, Shartle Division.*

of 0.1%—0.4%. High stock temperatures improve the efficiency. Two banks of primary cleaners in series may be used, and the rejects from the primary bank are sometimes treated in secondary cleaners. The Beloit Posiflow centrifugal cleaner, introduced in 1986, is an *SL forward cleaner* that removes heavier-than-water contaminants. It is claimed that in some systems the conventional three-stage cleaning systems are replaced with a single stage.

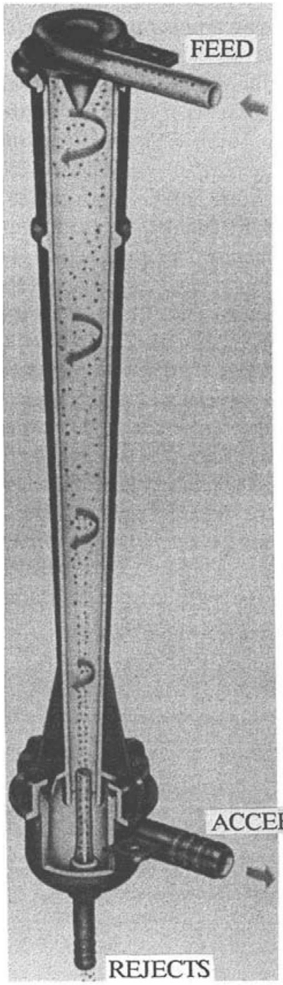


FIGURE 23.9 A through-flow cleaner designed to remove low density contaminants. *Courtesy of Beloit.*

Gyroclean

An alternative to reverse cleaners is the Gyroclean of Fiberprep shown in Fig. 23.10. The unit was developed by Lamort and Centre Technique du Papeterie in France. The manufacturer claims the unit can operate at up to 2% consistency. Fiber loss is said to be minimal, and no secondary units are required. Units are available to process 70–520 m^3/h (300–2300 gal/min). The acceleration experienced by the stock is said to be up to 700 times normal gravity.

Deinking Chemistry

Less than 20% of secondary fiber is deinked in the United States. In addition to high wood costs, recent legislation will change this picture as many states will require recycled fiber in new newsprint as a means of reducing the large quantities of material sent to landfills, of which about 40% is paper. The ink is about 0.5%–2% of the mass of the wastepaper to be deinked.

The overall deinking process from the point of view of the fiber can be broken down into four steps:

1. repulping with concomitant ink removal from the fibers
2. cleaning and screening operations to remove the bulk of the ink from the stock
3. separation of residual ink contaminants from the fiber stock
4. bleaching, if necessary

Other steps are necessary for the process, such as recovering the wastes from the effluents to allow water reuse.

A variety of chemicals are used in ink removal, including the sodium salts of hydroxide (for fiber swelling, saponification of ester-containing resins, and ink dispersion), carbonate (as a buffering agent), silicate (peroxide stabilizer via metal ion sequestering, wetting agent, pH buffer, and ink dispersant), polyphosphate (0.2%–1% on pulp as a metal ion sequestering agent and ink dispersant), peroxide or hydrosulfite, fatty acid soaps, nonionic surfactants, and other materials. The nonionic surfactants are usually alkyl phenol or linear alcohol ethylene oxides (as described in Chapter 4, Volume 2). Petroleum ether, a mixture of C6–C10 alkanes, is sometimes used in small amounts to soften the ink vehicle. If any of these materials carry over into the papermaking system, there may be difficulties with foaming, scale formation, wet end chemistry, or surface sizing at the size press.

There are two commonly used methods of ink removal: *ink washing* and *ink flotation or froth flotation.* Ink can also be removed by *solvent extraction*

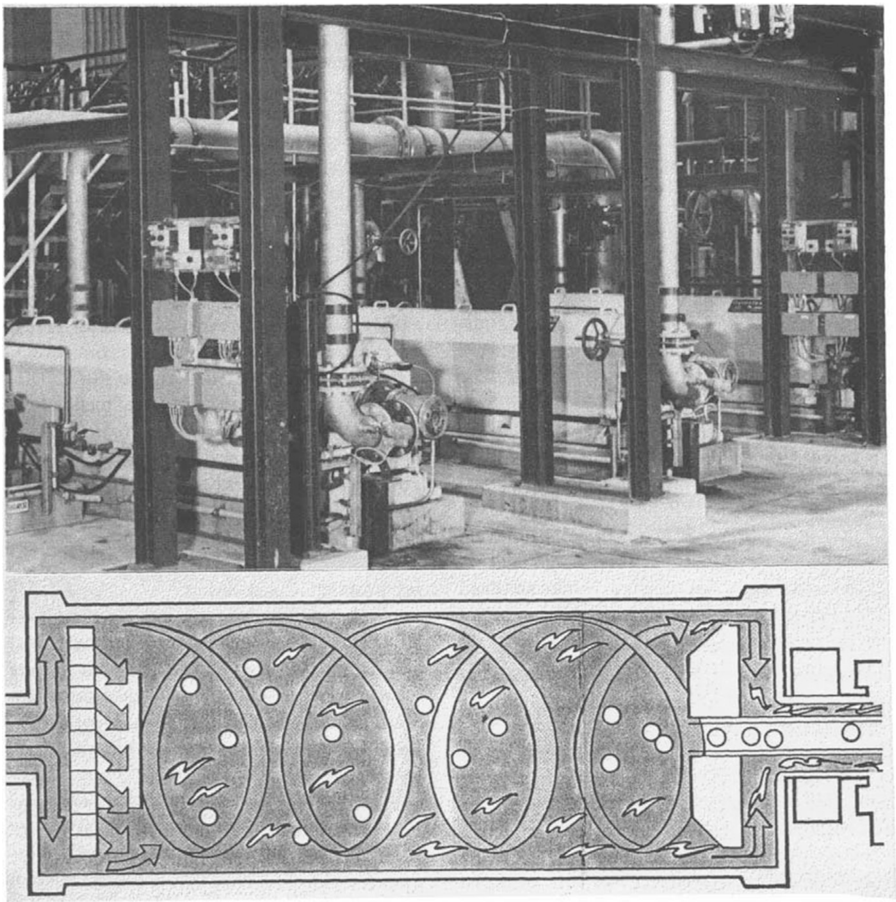


FIGURE 23.10 Gyroclean system for removal of lightweight contaminants. Three units in service (top) and the operating principle (bottom) are shown. *Courtesy of Fiberprep.*

in a process that resembles dry-cleaning, but it is too expensive to have widespread use.

Ink Washing

Ink washing involves ink removal by washing it from the fiber using sodium hydroxide, sodium silicate, and hydrogen peroxide with a suitable dispersant in the pulper. Often the dispersant is stearic acid, and micelle formation occurs in the classic mechanism by which soap is able to make grease and oils water "soluble." A water-ink emulsion system is formed with particle sizes averaging below 1 μm. The emulsion is washed from the pulp, and the ink is removed from the wash water by flocculation so the wash water may be reused. Hard water should not be used during ink washing as this will precipitate the soap and the complex will not be water soluble. The clarified water is then reused to wash more pulp. This general method has been used since the nineteenth century. It is suitable for traditional inks with vegetable oil vehicles that are readily saponifiable and dispersible.

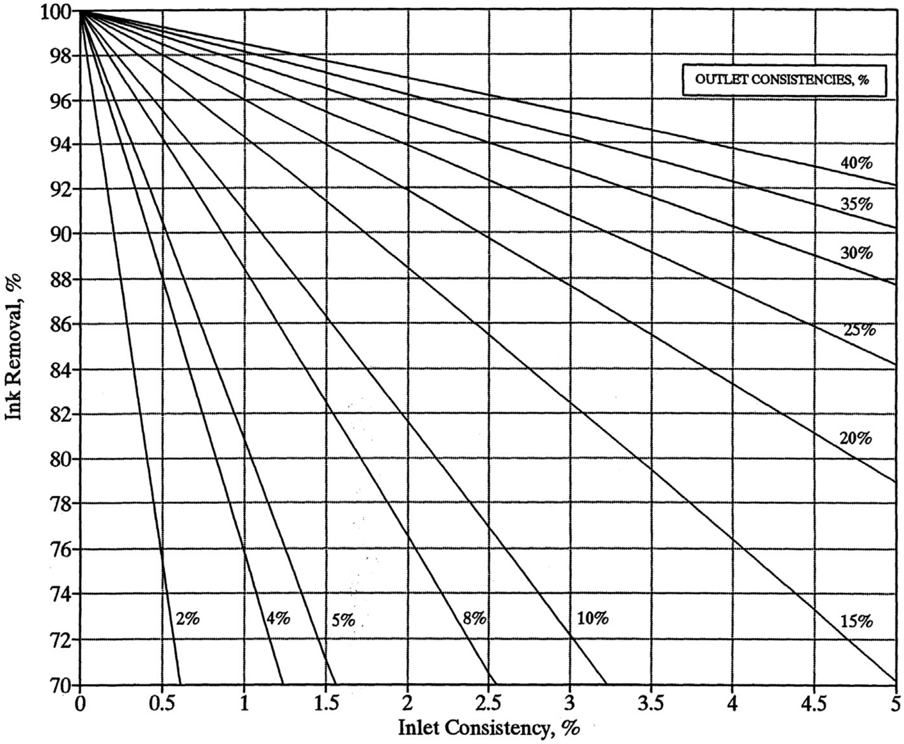


FIGURE 23.11 Theoretical washing efficiency based on inlet and outlet consistencies.

Fig. 23.11 shows the theoretical ink removal for a washing system. This graph indicates the percentage of water removed in a single stage of washing based on the water going in and the water going out. For example, consider 100 lb of a pulp slurry with an inlet consistency of 3% and an outlet consistency of 12%. There are 3 lb of fiber and 97 lb of water going in. The 3 lb of fiber corresponds to 25 lb of slurry at 12% outlet consistency or 22 lb of water going out. This means that 75 lb of the original 97 lb were removed to give a washing efficiency of 77.3%.

In fact, this is only true for materials that are water soluble and have no affinity for the fibers. Ink particles of finite size will be trapped by fiber networks that form as the slurry is concentrated on a screen. Larger ink particles are more easily retained by this mechanism. Washing equipment may take on a variety of forms, such as rotary vacuum washers and double belt washers discussed in brown stock washing. Some manufacturers have specific products for this task, such as Black Clawson's DNT belt washer (Gilkey and McCarthy, 1988). This washer uses an endless synthetic wire with headbox, breast roll, and couch roll to dewater and thicken pulp up to 15% consistency.

Ink Flotation

Ink flotation borrows from technology developed by the metallurgy industry for mining, which started being used to deink paper in the 1960s. *Perry's Chemical Engineer's Handbook, sixth edition* is a good reference for the basic principles of this process. Flotation has been used extensively in Japan and Europe but only recently came into widespread use in the United States. Flotation is a process that separates materials based on the property of wettability. Under appropriate conditions, nonpolar (hydrophobic) materials are able to adhere to air bubbles and rise to the surface.

The process is carried out in ink flotation cells (several cells may be used in series) using sodium hydroxide, sodium silicate, and hydrogen peroxide with a *collector system* consisting of a surfactant. With ink flotation, large ink particle sizes are desired (at least 5 μm, but 10–50 μm is ideal) so the ink can agglomerate and be skimmed from the slurry. Many new inks and inks on office papers incorporate cross-linked resins and flake off the fibers in relatively large particles, making flotation the preferred method. As the ink is already flocculated, it is fairly easily separated from the process water.

Ink flotation can be divided into three phases: collision of ink particles with air bubbles, attachment of ink particles to air bubbles, and separation of the ink particle–air bubble complex from the pulp. The reject rate of any system depends on how the ink–foam complex is removed. The fate of the collector chemical seems to be of great importance in some paper grades. The amount of deinking chemical in the pulp accepts is called the *carryover*. Ideally very little collector must leave with the stock accepts. Flotation deinking is done at lower consistency than washing and is done at about 1% consistency.

One type of flotation cell is shown in Fig. 23.12 and Plate 23.2. In this system, water and air are pumped into various points of the cell. The surface is skimmed to remove the ink. In 1988, Beloit introduced pressurized ink flotation (Fig. 23.13) with the claim that it removes more ink over a wider particle size range. Details of this method are found in Carroll and McCool (1990).

The collector system is based on fatty acids, such as stearic acid with calcium or nonpolar surfactants. Occasionally, cationic or ampholytic compounds have been used. In the first system, fatty acid salts (0.5%–5% on pulp with a known degree of unsaturation, that is, number of double bonds as determined by the iodine number) and calcium ions are used. Calcium (like taking a shower in hard water) causes the fatty acids to precipitate, thereby supplying a hydrocarbon nucleus upon which the nonpolar ink particles can collect. Calcium is used at about 200 ppm as $CaCO_3$. The nonionic collector systems use an alkyl (C-9 is common) phenol or relatively large primary alcohols linked to oligomers (6–16 monomers) of ethylene oxide. The presence of inorganic fillers such as clay or talc assists in the ink flotation method and thus they are usually used. Without the use of inorganic fillers, additional, larger bubbles may be required, lower rise distance should be used, and larger flotation cell capacity may be needed. However, most of the filler will not be removed by flotation.

Flotation methods are also used to recover the water from wastewater streams. This is described below.

Hybrid Deinking Processes

New deinking mills may use combined ink flotation and washing, especially for recovery of bleached chemical pulps. The bulk of the ink is removed by flotation, and residual ink is removed by washing. In this system, the dispersants are added after the pulper but before washing, so that residual ink that is not removed by ink flotation is emulsified and removed during the washing process. This process is the best of both worlds and is particularly useful for paper wastes that contain many different types of ink formulations. As ink formulations become more difficult to disperse by saponification and emulsification, such as radiation-cured resins, ink flotation is necessary, but removal of residual ink during washing is best accomplished by emulsification.

Trends in ink formulations to decrease their impact on the environment and make printed

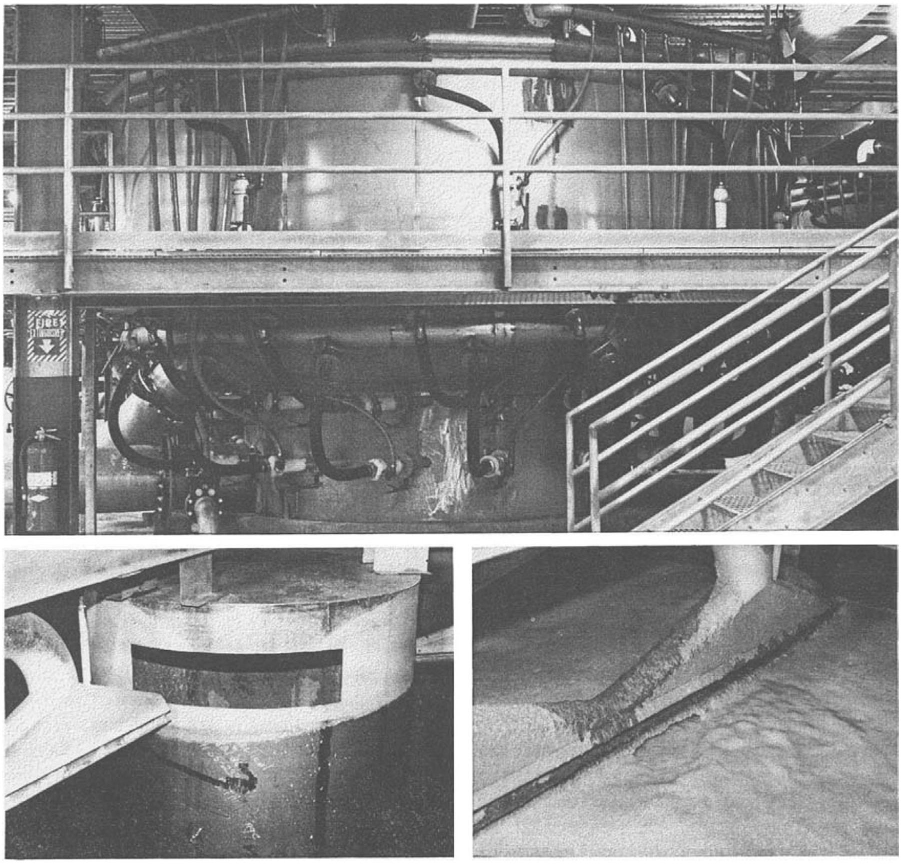


FIGURE 23.12 Vertical deinking flotation cell. Air and water are introduced under pressure. The inserts show the skimmer and water inlet holes (an empty cell on the left). *Courtesy of Fiberprep.*

papers easier to recycle include the decrease in the use of volatile organic compounds (VOCs, i.e., hydrocarbon and other solvents). Corrugated flexo inks recently were 10%–20% VOC but now range from 0% to 2%. The use of appreciable amounts of heavy metals in inks is under attack. Reductions in lead, chromium, copper, and, to a lesser extent, barium have begun to occur.

Mills in Europe and Japan even use flotation-wash-flotation systems. About 10%–20% of mills using a dual system use washing followed by ink flotation. This method has the disadvantage that many large ink particles that might have been removed by flotation would be dispersed before flotation but has the advantage of more favorable treatment of various washing solutions in some mills.

Posttreatment processes are developing as well for even further ink removal. One method is to use disk dispersion above 20% consistency with about 80–140 kWh/t (4–6 hp-day/ton) to reduce particle sizes from several hundred microns to less than 50 microns so they are not visible as individual specks to the eye. This is followed by additional washing or flotation. Another approach is acidification of the pulp slurry followed by additional treatment of

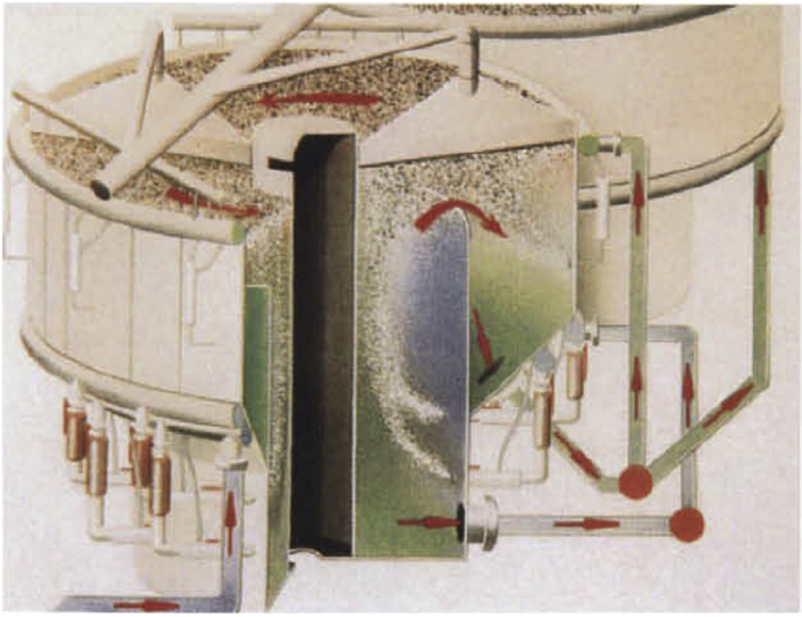


PLATE 23.2 VerticeF flotation deinking system with two levels of aeration. *Courtesy of Fiberprep.*

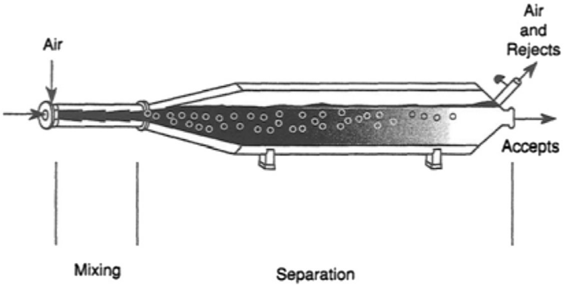


FIGURE 23.13 Pressure deinking module. *Redrawn from a photograph supplied courtesy of Beloit.*

cleaning, very fine screening, etc. The state of the art for deinking newsprint is 92%–95% or higher ink removal.

Solvent Extraction of Ink

At the risk of confusing the issue, there is a third method for ink removal, but it is generally uneconomical. The method is solvent extraction by use of nonpolar solvents (Hiraoka, 1990). The process resembles dry cleaning of clothing and was used, although not fundamentally for deinking, by Riverside Paper Co. in the United States and Tagonoura Sangyo in Fuji City, Japan, for recovery of waxed paper, milk carton grades, etc. where both the paper and polyethylene resin is reusable. Riverside recovered 99% of its trichloroethylene solvent, and Tagonoura recovers 90% of its hexane solvent.

Water Recycling and Sludge Recovery

The water containing the ink particles that have been removed from the fiber must be cleaned for reuse in the mill. One method of doing this is to use a flotation method similar to that used in flotation deinking.

Krofta Engineering Corp. is one manufacturer of a device that does this (Fig. 23.14). The raw liquid is pressurized with air under 60–80 psig pressure. When the raw liquid is introduced

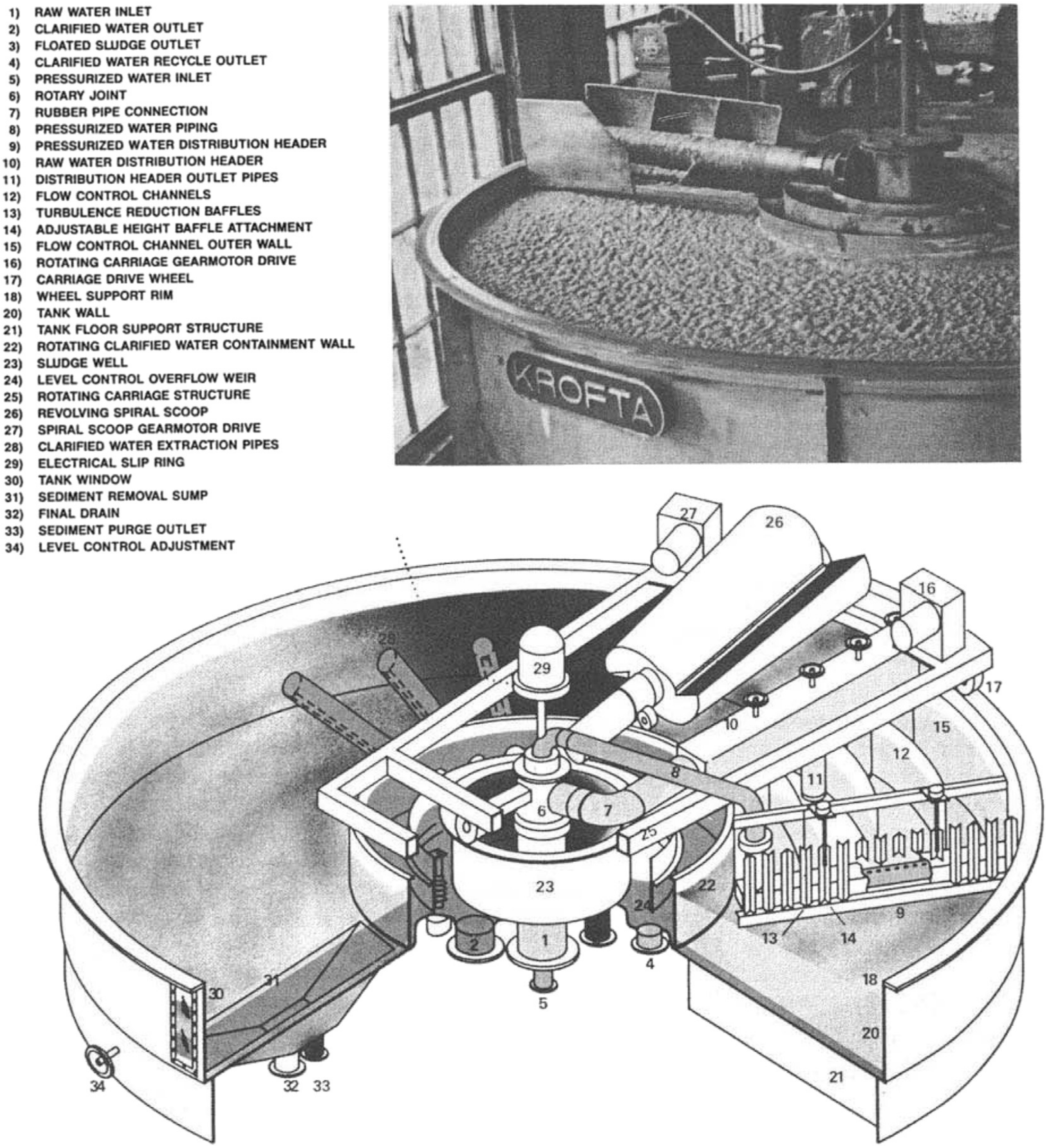


FIGURE 23.14 Dissolved air flotation deinking effluent clarification. *Courtesy of Krofta Eng. Corp.*

into the tank, it goes to ambient pressure so that small air bubbles are formed that attach to the suspended solids to be removed. The lightweight sludge then floats to the surface. As the air was dissolved in the water, the process is called *dissolved air flotation.* The retention time is typically 3—4 min.

Polymer systems are used to help the separation. The sludge is skimmed from the top by the rotating skimmer and collected in the middle for removal. The treated water escapes underneath. The sludge collector rotates around the cleaner in this continuous process. The sludge that is obtained from the water to be recycled must be pressed to remove much of the water so that the sludge can be sent to a landfill or disposed of otherwise. Fig. 23.15 shows a sludge press.

Some problems with recycling paper are mentioned by Hoekstra (1991). For example, using 210 t/day old magazine (OMG) paper to produce 150 t/day secondary fiber generates 3001 of waste at 21% solids content. With high tipping fees at the landfill, this is quite a problem. Burning of the sludge gives 6.5 t ash if 22% of the solids are ash. Analysis of sludge from five deinking plants gave the following level of heavy metals (parts per million): cadmium, <0.2; chromium, 16–118; copper, 31–400; lead, 3–210; manganese, 31–880; nickel, 1–25; and zinc, 36–1200. These were generally below those of municipal sludge. Also, the printing industry is accepting new ink formulations without heavy metals. Biological oxygen demand (BOD) load is about 15–30 kg/t (30–60 lb/ton) pulp and total suspended solids (TSS) is about 10–50 kg/t (20–100 lb/ton) for deinked grades, with washing methods producing more than flotation methods. Effluent volume is about 5 m^3/t.

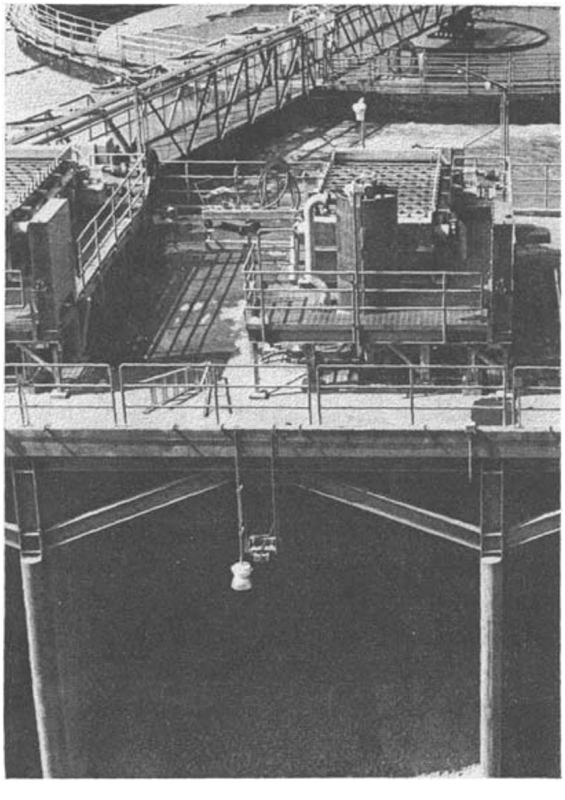


FIGURE 23.15 A sludge press in the foreground. The mill's primary and secondary effluent treatment is in the background.

Flotation and Washing for Deinking

A comparison of flotation and washing methods for deinking is presented in Table 23.8. Paper containing water-based flexographic inks often uses an acid bath for its removal; therefore the overall process may be an acid flotation–base flotation method. Flotation deinking is mostly for newspapers and magazines. Newsprint alone (which is essentially unfilled in the United States) must be deinked by washing (and water-based inks must be absent), but mixtures of newsprint and magazines (or magazines alone) are usually deinked by flotation.

Evaluation of the Deinking Process

The process of deinking may be evaluated by brightness or ink speck counts of the pulp or handsheets from the pulp. Solvent extraction of deinked pulp gives a quantitative method of ink content, provided interfering compounds are not present; however, appropriate selection of spectroscopic methods of analysis (IR, UV, VIS, NMR, etc.) of the extract could easily give accurate ink determinations.

Brightness alone cannot be used to quantify ink as brightness depends on a variety of factors, including the distribution of the ink on the fibers.

TABLE 23.8 Comparison of Washing and Flotation Methods of Deinking Paper

Washing (Like Washing Machine for Clothes)	**Flotation**
NaOH: fiber swelling, breaks up esters (e.g., soy bean oil); colloidally separates ink from fiber	NaOH: fiber swelling, breaks up esters (e.g., soy bean oil); colloidally separates ink from fiber
Sodium silicate: "buffer" and sequestering agent to protect peroxide	Sodium silicate: "buffer" and sequestering agent to protect peroxide
Hydrogen peroxide: prevents mechanical pulps from yellowing above pH of 10; bleaching	Hydrogen peroxide: prevents mechanical pulps from yellowing above a pH of 10; bleaching
Dispersant: sodium salt of stearic acid (i.e., soap; do not use calcium, just as one avoids hard water to wash one's body or clothes) or low-foaming (low number of C atoms in alkyl chain), nonionic alkylphenol ethoxylates or linear alcohol ethoxylates	Collector system: fatty acid (0.5%—5%, usually 1%) and calcium (200 ppm) to make fatty acid water insoluble, forming large particles; nonpolar surfactant, especially C-9 alkyl phenol; or large primary alcohol linked to 6—16 monomers of ethylene oxide; the large nonpolar particles 30—60 μm adhere to air bubbles
Fillers and fines: largely removed in the process	Fillers: 8%—14% (clay) help process, but only 25%—30% is removed, so often old magazine is added when old newsprint is treated by flotation but this has problems (heavy metals that are a disposal concern, inks that are harder to remove, bale-to-bale variability in ash composition)
General notes: emulsion particles of about 1 μm are formed; hydrophilic particles more easily removed; process from 1800s; only small particles (less than 5 μm) removed; limited to only a few types of paper; low consistency with high reject volume using 10,000 or more gallons of water per ton pulp; long pulping times; high brightness; low yield	General notes: new method (1960s) from metal ore technology; required for modern polymeric inks that do not disperse well; many choices of paper grade; 1%—2% consistency; 3000 gallons of water per ton pulp; low brightness; high yield
CHEMICALS USED IN ONE OR BOTH PROCESSES	
Alkylphenol ethoxylate	
$CH_3(CH_2)_n(C_6H_4)(OCH_2CH_2)_mOH$	
Linear alcohol ethoxylate	
$CH_3(CH_2)_n(OCH_2CH_2)_mOH$	Finely divided solids (fillers, alumina, fines, and other colloids) contribute to foam problems by surrounding air bubbles to decrease the surface tension.
Fatty acid soap	
$CH_3(CH_2)_nCOO^-Na^+$	
Fatty acid ethoxylate	
$CH_3(CH_2)_n(CO)(OCH_2CH_2)_mOH$	

Miscellaneous notes:

Postdeinking fiber treatment may use dispersion to break large particles into pieces the eye cannot detect individually, but pulp brightness decreases. Carryover of calcium can cause scaling and corrosion problems, whereas carryover of surfactants can interfere with the wet end chemistry and surface sizing operations. Combined flotation/washing systems provide some difficulties because washing requires a good dispersant that would prevent large particles from forming during flotation. Dispersant collectors called *displectors* have been developed. These are often ethoxylated derivatives of fatty acids. Mixtures of various surfactants are also used commercially. If one uses paper machine white water in the secondary fiber plant, alum may help the ink bind to the fiber.

The effluent must be clarified of the ink so the water can be reused. Two chemical treatments may be used, including a primary flocculent which is a low molecular weight cationic polymer or alum and a secondary flocculent of high molecular weight anionic polymer. Water-soluble flexo inks have a large amount of dispersant in their formulation and typically high levels of flocculent to clarify the water.

Small particle sizes decrease brightness much more than large particle sizes of the same amount of ink. This is due to the increased surface area to volume ratio of smaller objects. This also accounts for the decrease in brightness often observed to occur with mechanical disintegration. Still, the overall pulp brightness gives a good indication of deinking effectiveness but does little to indicate the source of trouble should the brightness go down if the system is not operating well. Furthermore, one should not allow any sort of washing of the pulp during formation of the brightness pad. Finally, brightness does not indicate the presence of ink specks visible to the unaided eye, i.e., larger than 50–70 μm (about 0.003 in.) in diameter, which may alone be unacceptable.

Image analysis techniques offer a good method to observe the deinking process. Modem image analysis systems controlled by computers offer a reproducible method for characterizing deinked furnish without undue operator time and bias, which can be quite significant in an otherwise quite time-consuming and subjective procedure. Not only can ink speck counts be made, but ink speck size distributions can also be determined so that information on the degree of emulsion or flocculation in the deinking process can be gathered over a period of time at a given mill. Fig. 23.16 shows an automated system used in a mill for quality control.

Image analysis systems are available that require very little theoretical knowledge on their operation. Earlier models are not as automatic and require attention to the light source which must not vary in intensity and spectral composition. Image analysis has also been used in several studies (Hacker, 1991) to measure lightweight contaminants. Here it is necessary to dye the paper with a water-based black ink (such as Parker Super Quink Ink) to enhance contrast by leaving the lightweight (nonpolar) contaminants amber in color while the paper turns black.

Slurry Concentration

After deinking and cleaning, the dilute pulp slurry must be concentrated for further processing and storage. Fig. 23.17 shows a large disc filter used to concentrate a pulp slurry from 0.6% to 10% consistency at a mill that recovers 500 tons/day of secondary fiber.

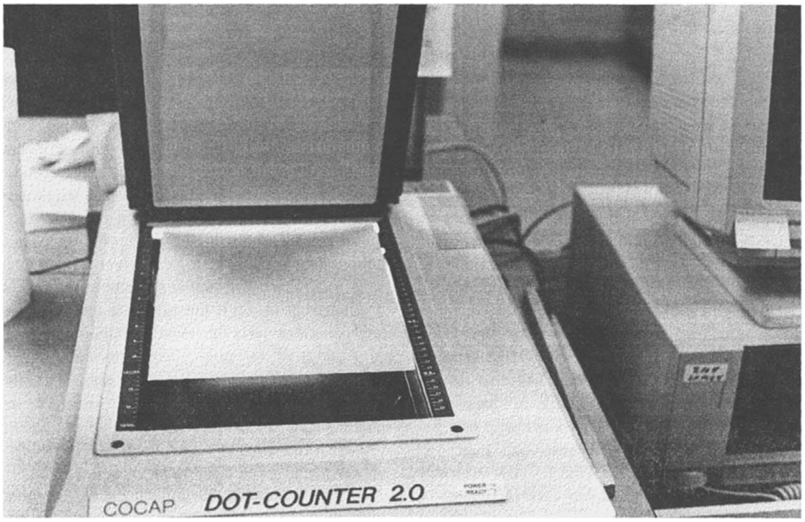


FIGURE 23.16 An automated counter at a deinking mill for determining ink spot size distributions.

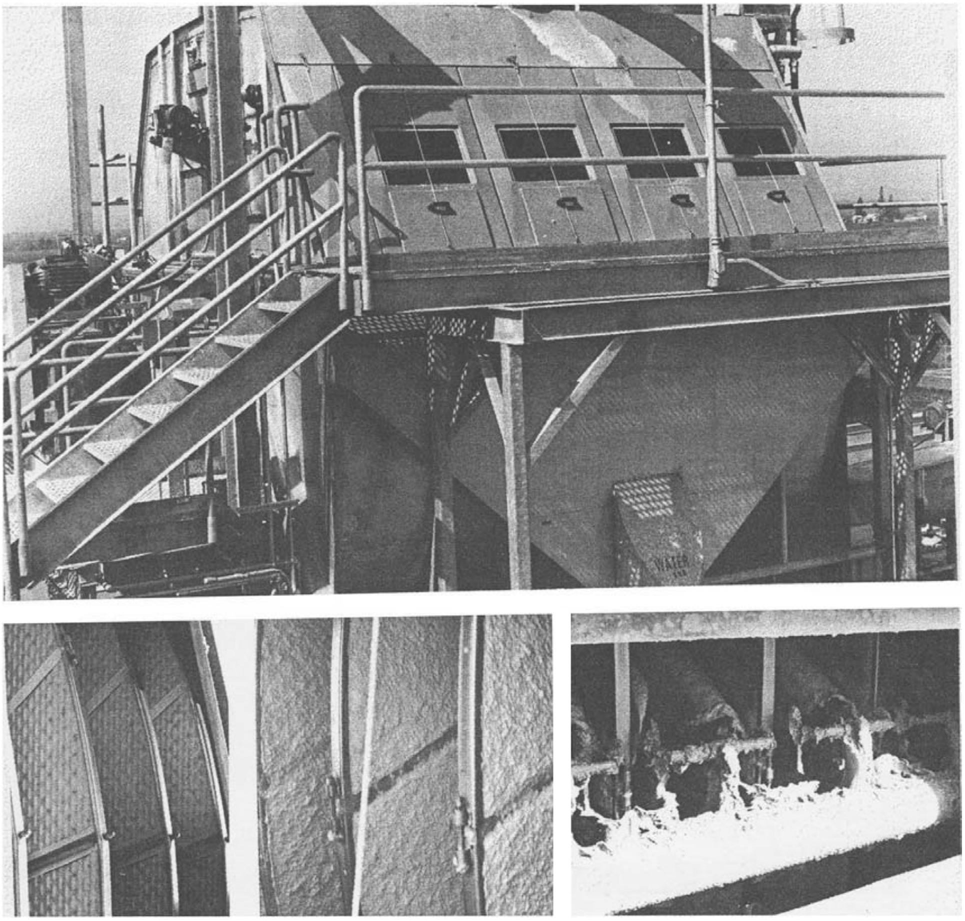


FIGURE 23.17 A large disk filter for concentrating the pulp slurry at a deinking mill (500 t/day). Inserts show the filter discs when cleaned, with fiber, and with fiber removal.

23.5 BLEACHING OF SECONDARY FIBER

The quality and brightness of the recycled fiber furnish will dictate its end use. The removal of colored complexes, such as dyes and other unwanted materials (i.e., ink and stickies), is an important operation to produce a recycled pulp with good properties, including good optical properties. Chlorine-based chemicals, such as hypochlorite, were used to bleach recycled fibers. However, growing public concerns about the negative environmental impact of organochlorine compounds generated in these processes have led to the adoption of more environmentally friendly processes in the mill. Totally chlorine-free (TCF) processes using non—chlorine-containing chemicals are some of the technologies. The common TCF bleaching chemicals for recycled fibers are oxygen (O), ozone (Z), and hydrogen peroxide (P), which are oxidative chemicals, and sodium hydrosulfite (Y) and formamidine sulfinic acid FAS (F), which are reductive chemicals.

Bleaching With Hydrogen Peroxide

Hydrogen peroxide is attractive as a bleaching agent for secondary fibers. Hydrogen peroxide is the most frequently used chemical for high-yield pulp bleaching when high levels of brightness are required. For a mixed waste-paper furnish of ONP and OMGs, bleaching has some similarity to mechanical pulp bleaching. However, most of the secondary fibers have been bleached before and so they will not necessarily respond in the same way to the bleaching stage as virgin pulps.

Hydrogen peroxide is found to be very effective in bleaching recycled pulp. It can be performed in a pulper, or a bleaching tower, or a disperser. The bleaching liquor usually contains hydrogen peroxide, caustic soda, Diethylenetriamine Pentaacetic Acid (DTPA) and/or sodium silicate, and/or other peroxide stabilizers. If it is applied to the pulper, a soap or surfactant may be added to help in ink removal. In most cases, for the same hydrogen peroxide charge, the brightness of the resulting recycled pulps is usually lower than the bleached mechanical pulp. This is due to the fact that the recycled furnish contains some residual ink particles. Peroxide bleaching of recycled pulp could take place in a disc-type disperser; the time is very short; however, the temperature is high (90−95°C) and the pulp consistency is also very high (30%−35%). This method effectively minimizes the brightness loss because of break up of the ink particles and improves the efficiency of the subsequent flotation operation. Bleaching results are significantly affected by the process parameters: stock consistency, temperature, reaction time, and chemicals used.

Brightness is higher at higher pulp consistency. When the pulp consistency is above 30%, mixing problems are encountered. The bleaching chemicals do not mix homogeneously into the pulp without the use of highly effective mixing methods. This results in a leveling of brightness increases. For this reason, the consistency is mainly limited to 25% in separate bleaching stages. Because hydrogen peroxide is also used in other stages of secondary fiber processing, such as during slushing, the application cannot always occur under optimum conditions. The consistency at bleaching usually is in the range of 10%−25%. No practical or acceptable alternatives to high consistencies exist for economic reasons. However, temperature, reaction time, and alkalinity can optimize the reaction.

Bleaching With Ozone

Ozone is an excellent bleaching chemical for recycled pulps containing minimal amount of mechanical pulp fibers. Ozone is well known as a powerful oxidizer. It is also the only oxygen-based bleaching chemical able to destroy optical brighteners that enter the secondary fiber pulp primarily via wood-free writing and printing papers. Ozone transforms dyes into colorless compounds as a result of its high reactivity toward conjugated bonds. Ozone bleaching of secondary fibers has been extensively studied. A 2-year cooperation between Ponderosa Fibers and Air Liquide has resulted in the first commercial application of ozone for bleaching of secondary fibers (Muguet and Sundar, 1996). This proprietary bleaching process was started about 2 decades ago.

Ozone is a powerful oxidizer, second only to fluorine (oxidative potential O_3: 2.07 V, F_2: 3.03 V and CI_2: 1.36 V). It oxidizes organic compounds containing mainly $>C{=}C<$ linkages which are oxidized to carbonyl groups $>C = 0$. Ozone also attacks the aromatic groups. Ozone is a very strong oxidizing agent, and owing to its mesomeric nature, oxygen can react with different ionic mechanisms. The heterolytic decomposition of ozone in which different polyoxide stages occur results in the splitting of $C{=}C$ bonds. The carboxyl and carbonyl groups are formed simultaneously. Oxygen and hydrogen peroxide are formed in situ as part of this process. Aromatic and especially phenolic structures are also attacked by ozone and are decomposed into simple aliphatic acids. These reactions are not selective and last only a few seconds. Ozone has a limited stability in aqueous systems that lead to homolytic decomposition. This is one of its drawbacks.

Decomposition of ozone is catalyzed by the presence of even the negligible amounts of transition metal compounds, heavy metals or base ($pH > 3$). The radical reactions also result in degradation of carbohydrate structures, which are not desirable besides forming hydrogen peroxide and oxygen.

Ozone is usually generated by corona discharge in pulp and paper applications. Ozone bleaching is commonly carried out at high consistency. Medium consistency can be an alternative. Castillo et al. (1995) has studied the effect of several process variables on bleaching. Brightness depended linearly on ozone charge and pulp consistency. Low consistency decreased the final brightness because of the reaction of ozone with water. Temperature had no effect. Usually, acidic conditions are used for ozone bleaching of virgin fibers as metals ions accelerate ozone decomposition and a pH of 2.5 helps to solubilize and remove these ions. Chelating agents can also be used for inactivation of the detrimental ions. Ozone can efficiently remove the dyes under neutral or alkaline pH too (Kogan et al., 1994). The radical reactions of the ozone caused by the increased concentration of OH ions can also lead to color stripping of dyes although less effectively than at a low pH. Acidic conditions actually have many disadvantages, such as the need for an acid, pH shock inducing stickies problems, risk of $CaSO_4$ deposits, loss of $CaCO_3$, etc (Muguet and Sundar, 1996). But in case of bleaching pulp for tissues, acidic conditions can be justified because low levels of ash are required for tissues. The highest increase in brightness was observed in case of fiber furnish containing either unbleached or semibleached chemical fibers.

Very little or no bleaching effect was observed in case of secondary fibers containing high content of mechanical fibers. However, improvement of mechanical properties was noted (Gangolli, 1982). Treatment of mechanical pulp with ozone affects the optical properties through both the light adsorption and light scattering abilities. Ozone bleaching is greatly affected by the composition of the deinked pulp. Improvement of mechanical or optical properties depends on the composition of wastepapers. Higher content of mechanical fibers exceeding 20% prevent any optical gain. Higher brightness is obtained when ozone is used in combination with hydrogen peroxide. Ozone is able to destroy fluorescence. Brightness increases (UV excluded or UV included) with increasing ozone dosage but fluorescence decreases, and 80% of the fluorescence is found to be removed at 1% ozone on a mixed white/colored paper.

Air Liquide has developed the Redoxal process, which is an ozone-based reductive/oxidative process combining Z, P, and Y or FAS. ZP is found to be effective in bleaching a large range of furnish. Excellent optical properties, high color removal, and acceptable yield are obtained. Hydrogen peroxide is used after ozone without washing to stabilize the previously achieved brightness, protecting the pulp from the brightness reversion.

Ozone treatment allows almost complete destruction of optical brighteners. This is particularly important for using deinked pulps in papers used for food applications.

Formamidine Sulfinic Acid

FAS, ($CH_4N_2O_2S$) sometimes also called thiourea dioxide, can be used either alone or in sequence to bleach recycled pulps. FAS is a strong reducing agent and is thus effective in removing dyes. In such application, FAS is more effective than sodium hydrosulfite. FAS has become a key chemical used for the brightening and color stripping of secondary fibers. The ability of FAS to effectively color strip results in a significant reduction in the filtrate color as well. FAS contains thiocarbamide sulfur dioxide according to the X-ray structure analysis. The material forms at low temperatures under acidic to neutral pH conditions in a reaction from two hydrogen peroxide molecules and one thiocarbamide molecule.

FAS is used in a pulper, bleaching tower, or disperser (Kronis, 1997). It is a low-odor, crystalline-reducing agent and can be used on all types of wastepaper. Its use is particularly recommended when using a furnish containing dyed paper. Its use as bleaching agent was first proposed in the textile industry. Process patented by Süss and Krüger (1983) proposes bleaching conditions for mechanical pulp and secondary fiber pulp that can apply in a single-stage and a two-stage process with other bleaching chemicals. FAS is a white to slightly yellow powder, odorless, and nonflammable.

FAS is oxidized by atmospheric oxygen like all reducing bleaching chemicals, but it is significantly less prone compared with dithionite. This allows a wider range of application possibilities for bleaching not only as a separate bleaching stage but also in combination with other stages of the stock processing operation. FAS also has a lower sulfur content compared with dithionite. This has a positive effect on the sulfate load of the white-water loop. The sulfate level in the bleaching effluent can be reduced by as much as 75%. As a result, the corrosion susceptibility of the equipment and instruments is lower. Also, the production of unpleasant odors due to hydrogen sulfide is lower.

FAS is only slightly soluble in water, and under alkaline conditions the solubility increases. Only about 27 g/L enter the solution as sulfinate, the solubility under alkaline conditions increases up to 100 g/L. The alkaline solutions of FAS have a higher solubility, but its aqueous solution decomposes very rapidly. Because of this reason, alkaline bleaching solutions are prepared only shortly before their addition in a continuous process. Consumption must then occur as soon as possible. FAS hydrolyzes to the sulfinate anion and urea under heat and alkaline conditions.

The sulfinate anion has a high negative redox potential and is responsible for reductive bleaching (Fallon, 1994). Compared with dithionite, FAS has a slightly higher reductive potential when both chemicals are under alkaline conditions. Important parameters for FAS bleaching are: temperature, time, alkalinity, consistency.

Consistency, in the case of FAS, is important only to the extent of the increased possibility of air entrapment in the pulp at the higher consistencies that would decrease the efficiency of FAS. Also of prime importance in determining the feasibility of using FAS is the furnish type and the degree of brightening or color stripping required. In regard to the furnish, factors include the type of paper and the amount of wood-containing fibers; the amount of colored grades used; the amount of ink blanketing on the fiber; and the nature of the dyes present. Sodium hydroxide is commonly used as an alkaline source.

The most important process parameter of FAS bleaching is the reaction temperature, which is the most effective means of controlling the bleaching reaction.

When both hydrogen peroxide and FAS are used in a deinking line, it is important to recognize that a residual of hydrogen peroxide will consume FAS and vice versa (Kronis, 1997). This is particularly important if FAS treatment immediately follows a hydrogen peroxide bleaching stage because of the significant hydrogen peroxide residual that normally results and the more expensive FAS that could be consumed. Conversely, a residual of FAS before the hydrogen peroxide stage is normally not of concern because of the low levels of FAS applied and the negligible amounts remaining at the end of a FAS stage.

It is important to destroy or reduce the residual hydrogen peroxide before the FAS treatment. Thought should be given to having a postflotation stage between the hydrogen peroxide and FAS.

Hydrosulfite

Sodium hydrosulfite is also very effective in bleaching recycled pulp because sodium hydrosulfite is a strong reducing agent and can effectively react with the dyes in the pulp. Also, most recycled furnish usually contains some mechanical pulps that can be bleached by sodium hydrosulfite. The bleaching conditions for recycled pulp by sodium hydrosulfite are very similar to those for mechanical pulps. If the furnish, such as mixed office waste, contains mainly chemical pulps, significant brightness gain could be achieved by performing a hydrosulfite (Y) stage at a much higher temperature, 80−100°C and at pH of 7.0.

Sodium dithionite is a reductive bleaching chemical. It is also known as sodium hydrosulfite. Reductive bleaching is especially essential not only for bleaching but also for removing color from colored recovered paper and carbonless paper (Hache et al., 1994, 2001). Many dyes used to color paper can be effectively destroyed by reductive bleaching chemicals. Sodium dithionite is known to be effective for color stripping and can remove many types of dyes. Most of the acidic and direct dyes are permanently decolorized by sodium dithionite because it breaks the azo groups. Some of the basic dyes are temporarily decolorized. Dithionite is sometimes used in combination with an oxidizing agent, as some dyes which are not reactive with oxidizing chemicals can react with some reducing agents.

Sodium dithionite decomposes rapidly when exposed to air. When exposed to water, the solid form liberates sulfur gases which are corrosive to equipment and buildings. The aqueous solution is typically stored in closed tanks with a nitrogen pad. Sodium dithionite is generally supplied as dry powder. These commercial products may contain stabilizers, buffers (phosphates, carbonates), and chelates.

Dithionite was produced for the first time in 1906 by BASF in Germany in powder form. Initially, the product was obtained by the zinc dust process. Zinc is first converted into zinc dithionite in an aqueous solution with sulfur dioxide and then by sodium hydroxide to sodium dithionite and zinc oxide. Later on, a process was developed which uses the sodium amalgam from the mercury cell electrolysis of sodium chloride solution and converts this directly to sodium dithionite with sulfur dioxide. This process produces a material which is free of heavy metals and therefore stable. Chlorine-alkali electrolysis in Europe is changing from the amalgam process to the diaphragm process due to the mercury content of the wastewater. BASF later developed the formate process in which sodium formate is converted with bisulfite to sodium dithionite. Sodium formate is produced from carbon monoxide and sodium hydroxide.

Dithionite was used for the first time for bleaching of mechanical pulp in the 1930s. Initially, sodium dithionite was used in small amounts as a powder. The bleaching effect was limited because the bleaching time and the temperatures were too low. Good results were obtained when atmospheric oxygen was excluded. With the introduction of continuous bleaching processes such as tower bleaching, the use of solutions of dithionite proprietary blends became necessary to ensure their homogeneous mixing with stock. Another option is the use of cooled, alkalized solutions of sodium dithionite. At temperatures below 10°C, these solutions are so stable that they can be stored for long periods. This eliminates the complicated process of dissolving the powder.

23.6 USES OF RECOVERED PAPER OTHER THAN PAPERMAKING

Some of the recovered paper is utilized outside the paper industry for construction purposes, insulation, mailing bags, and other end uses. In most countries, no accurate data are available to estimate the recovered paper utilization for applications other than the paper industry. In addition to the paper industry use, over 8% of collected paper is used in other applications—construction material, animal beddings, composting, and energy. Recycling is considered better than composting in the materials management hierarchy.

Concepts of recycled fiber biorefineries have not been studied much. In the recycled fiber biorefinery concept, the biomass raw material is essentially fibers from recovered paper, with some other biomass such as starch mainly from corrugated board as well as some nonrenewable organic materials such as plastics entering the paper recycling chain with the collection of packaging paper and board. Most of the large paper recycling and deinking mills already produce some bioenergy and other bioproducts, but not yet liquid biofuels or biochemicals, from their rejects. Coarse rejects can be incinerated to produce energy onsite or secondary solid fuel, for example, with the Rofire and FoxFire processes (Verhaevert, 2007), which are being used in Dutch mills. FoxFire is a Dutch company. It is turning paper mill waste into an energy product for the cement industry. Coarse rejects can also be used to produce various composite materials (Christmas, 2002). Deinking sludge incineration produces, despite the high ash content, some excess heat used on-site. Deinking sludge is commonly used in the production of bricks and cement (Hanecker, 2007). A special incineration process treating sludge from different mills to produce cement has been reported in the Netherlands. Sludge can also be used to produce panelboard for the building industry (Valtonen et al., 2000). Biogas is generated at the anaerobic effluent treatment plant from the RP soluble biomass fraction. The biomethane produced in packaging paper recycling mills can lead to significant savings on the gas consumption (Clumpkens, 2008). In addition to recycling and deinking rejects, RP sorting rejects should be included in the recycled fiber biorefinery domain.

Recovered paper can be also used for insulation in constructions. The insulation is made from a composite of recycled paper consisting of newspaper, cardboard, and telephone directories. Fibrous insulation can be used for building, renovation, and reinsulation projects. These are more environmentally friendly than conventional fiberglass insulation and are also denser and good for both sound reduction and increased airflow.

Recycled newspaper are also being used in construction and manufacturing. In asphalt road surfaces, development of traditional "tarmac" road coverings use old newspaper fibers to act as a thickener, which holds the liquid bitumen in place around the aggregate of the asphalt. Without it, the bitumen would drain away, allowing the aggregate to be more easily dislodged by traffic.

In concrete repair, recycled newspaper fibers are used as a carrier for an electrolyte solution, which enables concrete steel–reinforced structures to be realkalized or desalinated, both responsible for the corrosion of the steel reinforcement.

More and more homes are being built using recycled fibers as wall and loft/roof insulation, providing levels of insulation far and above that of traditional houses.

Recycled paperboard and newsprint are also used to produce molded paper, which is considered as one of the most sustainable packaging materials available today. It has enjoyed a renaissance because of the excellent environmental credentials of paper. Molded pulp is produced from 100% recovered paper, with the process being tolerant of some contamination, typically more than a conventional sheet or board product. The method involves dispersing 100% recovered paper in water to form a homogeneous fiber suspension. This mixture is pumped into a vat containing a large revolving drum. Packaging molds are mounted onto the surface of the drum. The liquid pulp is sucked into the molds by means of a vacuum and water is simultaneously extracted. The wet packaging is then pressed and dried. The final product is subsequently postpressed and printed or labeled.

With the increase of paper consumption, more wastepaper of poor quality is entering the solid wastes circuit. For wastepaper, a better solution other than fiber recovery is its incineration (Gavrilescu, 2008). Although these residues are still largely dumped on landfill sites, a trend toward thermal processing is considered. Mixed recycled paper represents a valuable source of energy. Recovered paper has also been used in art and handicraft.

Example of a Process

To summarize this chapter, a recycling plant is presented in Fig. 23.18. This is a news plant using 70% news and 30% magazine for the feedstock. Numerous plant layouts are possible; this represents one choice.

23.7 ANNOTATED BIBLIOGRAPHY

General Deinking

Woodward, T.W. Deinking chemistry Notes *1991 Chemical Processing Aids Short Course*, Tappi Press, pp 85–105.
This is an excellent, highly recommended reference on deinking chemistry with 85 literature citations that includes information on inks, printing, deinking chemistry, and bleaching.
Crow, D.R. and R.F. Secor, The 10 steps of deinking, *Tappi J*, 70(7):101–106(1987).
Shrinath, A., J.T. Szewczak, and L.J. Bowen, A review of ink-removal techniques incurrent deinking technology, *Tappi J*, 74(7):85–93 (1991).
The information in this reference is better presented in the articles it cites or those cited in this chapter. The article's strong point is the

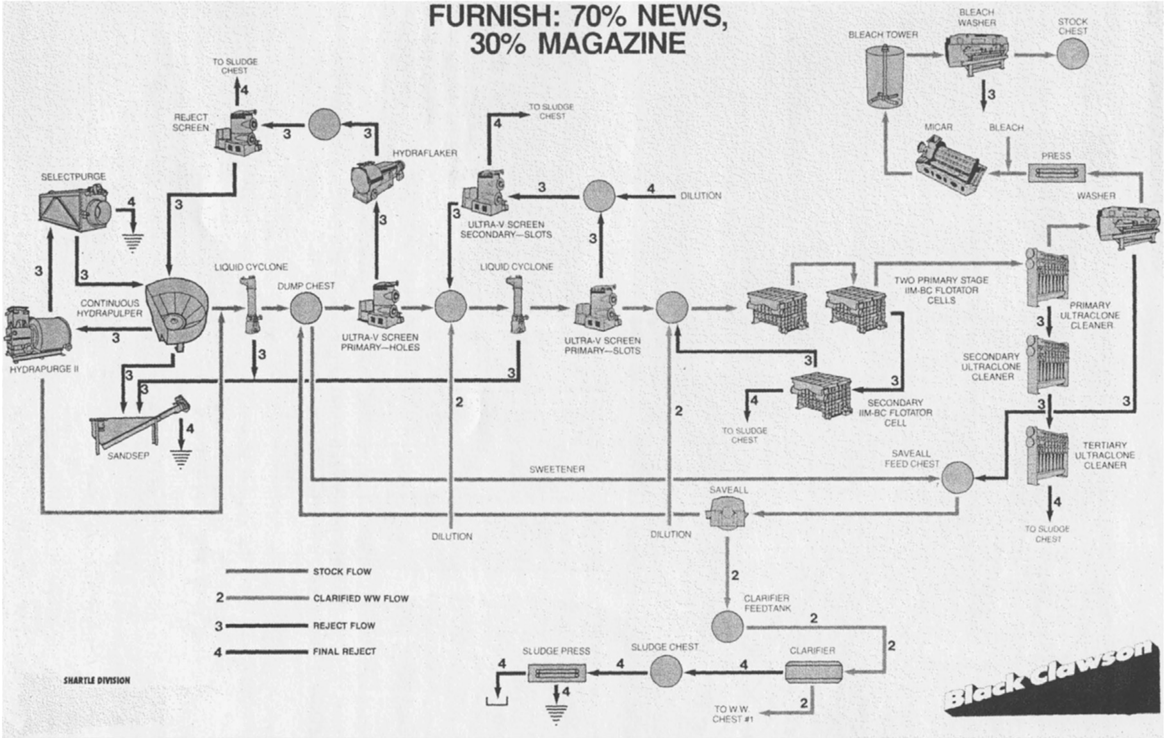


FIGURE 23.18 Layout of a newsprint to newsprint plant. *Courtesy of Black Clawson, Shartle Division.*

coverage of printing processes and ink removal strategies for specific types of ink.

Bobalek, J.F. and M. Chaturvedi, The effects of recycling on the physical properties of handsheets with respect to specific wood species, *Tappi J.* 72(6):123–125(1989). Ibid., *Tappi Proceedings, 1988 Pulping Conference,* pp 183–187.

Bliss, T., Through-flow cleaners offer good efficiency with low pressure drop, Pulp &. Paper 59(3):61–65(1985).

Commercial bleached kraft loblolly pine, eucalyptus, quaking aspen, and northern pine were subjected to 0–3 cycles of handsheet formation without wet pressing (with light refining), with concomitant strength and other properties reported. It is unclear whether these handsheets were air-dried or ovendried, but these conditions do not seem to duplicate commercial production practices.

Cox, J., Wastepaper growth highlighted in API's capacity survey. *Am. Papermaker* 54(2): 37–40(1990).

lannazzi, F.D. and R. Strauss, Municipal solid waste and the paper industry: the next five years, *Pulp & Paper* 64(3):222–225(March, 1990).

Olkinuora, M., U.S. leads the world in the production and consumption of wastepaper, *Pulp &* Paper 64(3): 130–132 (March, 1989).

This paper gives figures for 1986 when the United States was recovering 27.4% of its wastepaper. By 1990 this figure was over 30% and will most likely continue to rise as pressure mounts to reduce the amount of solid waste going into landfills, of which wastepaper is approximately 50% of domestic waste. Japan recovers about 50% of its paper, which is near the sustainable maximum as fibers lose strength with each use.

Sorenson, D., Environmental concerns, economics drive paper recycling technology. *Pulp & Paper* 64(3)56–57:(March, 1990).

Bajpai, P (2006). *Advances in Recycling and deinking* (180 pp). U.K: Smithers Pira.

Bajpai P (2013). *Recycling and Deinking of Recovered Paper*, Elsevier Insights, USA.

Hanecker, E.: Progress in Paper Recycling, vol.16, n°4: 34-37, August 2007

Contaminants

Horacek, R., Deinking, Beloit (Jones Div.), Dalton, Mass., 1978.

This reference is considered out of date by Beloit and is no longer available from them.

Centrifugal Cleaners

LeBlanc, P.E. and M.A. McCool, Recycling and Separation Technology, *1988 TAPPI Pulping Conf. Proceedings,* pp 661–667.

Bliss, T., Through-flow cleaners offer good efficiency with low pressure drop, *Pulp & Paper* 59(3):61–65(1985).

Ink Washing and Flotation

Gilkey, M.W. and C.E. McCarthy, A new device for high efficiency washing of deink furnishes. *Proceedings, 1988 Pulping Conference,* TAPPI Press, pp 649–654.

Carroll, W.P. and M.A. McCool, Pressurized deinking module. *Proceedings, 1990 TAPPI Pulping Conference,* pp 145–152.

Surfactants

Mah, T., Deinking of waste newspaper, *Tappi J,* 66(10):81–83(1983), no references.

Mill experience is given regarding the deinking of waste newspaper. Paper of 48%–52% brightness was obtained by washing. The two problems were foaming and deinking waste news; both problems are related to the surfactant. The results of several alkyl and alkyl phenol oligoethyleneoxides are presented.

Okada, E., Deinking agent and its research development, *Japan Pulp Paper* 27(4): 45–49(1990).

Deinking surfactants for flotation deinking were studied. Also, the fatty acid method was compared with nonionic surfactants, with the fatty acid method generally working better.

Balos, B, J. Patterson, K. Hornfeck, and M. Liphard, Flotation deinking chemistry, *PaperAge* 106 (Recycl. Annual):15–17(1991).

This study compares classes of surfactants in flotation deinking based on a laboratory setup. Here again, the fatty acid soaps compared well with compounds of six other classes. Water hardness of at least 180 ppm $CaCO_3$ was recommended for complete flotation.

Solvent Extraction of Ink

Hiraoka, M. Latest waste paper treatment process, *Japan Pulp Paper* 27(4):33–42(1990).

Sludge, Environmental Considerations

Hoekstra, P.L., Paper recycling creates its own set of environmental problems, *Amer. Papermak.* 54(4):30,33(1991).

The problems of sludge disposal are considered.

Metals in Ink

Donvito, T.N., T.S. Turan, and J.R. Wilson, Heavy metal analysis of inks: a survey, *Tappi J.* 75(4): 163–170(1992).

Heavy metals in inks are an environmental concern, especially in deinking sludge. This paper investigates methods of determining heavy metals in inks. Many states will require the sum of Pb, Cd, Hg, and Cr to be below 100 ppm by 1994.

Decolorizing Methods

Cheek, M.C., A practical review of paper decolorizing methods - present and future, in *Proceedings, 1991 Papermaker's Conference,* TAPPI Press, pp 71–78.

This is a useful, general reference on paper decolorizing chemicals and processing conditions (i.e., for decoloring broke for reuse within the mill).

Ink Removal Test Methods

McKinney, R.W.J., Evaluation of deinking performance, a review of test methods, *Tappi J.* 71(1):129,431(1988).

A brief evaluation is made of the following test methods: brightness measurement, ink removal-ink speck analysis, yield, and solvent extraction.

Image Analysis

M.P. Hacker, 1991 *Pulping Conference Proceedings,* pp 455–468.

This study measured lightweight contaminants in paper with a water-based black ink (such as Parker Super Quink Ink) to enhance contrast by leaving the lightweight (nonpolar) contaminants amber in color while the paper turns black.

McCool, M.A. and L. Silveri, Removal of specks and nondispersed ink from a deinking furnish, *TappiJ,* 70(11):75–79(1987).

Zabala, J.M. and M.A. McCool, Deinking at Papelera Peninsular and the philosophy of deinking system design, *Tappi J.* 71(8): 62–68(1988).

Klungness, J.H, L.E. Fernandez, and P.L. Plantings, Image analysis for measuring adhesive contaminants in pulp, *Tappi J.* 71(1): 89–93(1989).

Lowe, G., B.H. Licht, and G. Leighton, Deinking plant optimization using image analysis, *Tappi J,* 74(1):125–129(1991).

Dallard, D.H and CM. Brown, *Computer Vision,* Prentice-Hall, Englewood Cliffs, New Jersey, 1982, 523 p.

This is an often-cited general text on image analysis.

Gonzalez, R.C. and P. Wintz, *Digital Image Processing*, second ed., Addison−Wesley, Reading, Mass., 1987, 503 p.
This is an often-cited general text on image analysis.

Flotation Clarification of Effluents

Mahony, L.H., The role of flotation clarification in de-inking and secondary fiber operations, *PaperAge* 107(Recycling Update): 46−47(1991).
This paper describes the Krofta Engineering Corporation dissolved air flotation system.

Screening Stickies

Heise, O., Screening foreign materials and stickies, *Tappi J.* 75(2):78−81(1992).
This article is a review of the current technology. Charts show the screening efficiency versus reject rate, slot velocity, rotor velocity, and screen plate surface.

Flotation and Washing for Deinking

Ferguson, L.D., Deinking chemistry (two parts), *Tappi J.* 75(7):75−83 and 75(8): 49−58(1992).
This is a detailed look at deinking chemistry.

Agglomeration Deinking

Olson, C.R., Richmann, S.K., Sutman, F.J., Letscher, M.B., Deinking of laser—printed stock using chemical densification and forward cleaning, *Tappi J.* 76(1): 136−144(1993).
Snyder, B.A. and J.C. Berg, Liquid bridge agglomeration: a fundamental approach to toner deinking, *Tappi J.* 77(5):79−84(1994).
Agglomeration deinking is a relatively new method of deinking that is applied to office papers printed with laser printing inks. Betz and PPG offer chemistry systems in this area. Surfactants are used to agglomerate small particles of ink into large particles that can be removed by screens or forward hydrocleaners.

Enzymatic Deinking, Biodeinking

Welt, T. and R.J. Dinus, Enzymatic deinking—a review, *Progress Paper Recycling* 4(2):36−47(Feb., 1995), with 81 references.
Enzymatic deinking uses cellulases (to, hypothetically, remove the fibrils from the surface of fibers where the ink anchors itself to the fiber), hemicellulases, pectinases, or, less studied, esterases (lipases), which would saponify inks with triglycerides (soybean oil). The process was not commercial at the time of this article.

Gyrocleaner

Marson, M., New lightweight cleaner units solve mill's plastic problems. *Pulp & Paper* 64(6):93−96(1990).
The development and operation of the Gyrocleaner mentioned and shown on page 271 of this book are described.

Flotation Deinking Versus Flotation Clarification

Doshi, M.R., Flotation deinking versus flotation clarification, *Progress Paper Recycling* 1(2):83(Feb., 1992).
Dispersed air flotation deinking is a separation process where ink is separated from fiber (a selective process). Large bubbles are used, 0.1−1.0 mm in diameter, that quickly rise to the surface, leaving fibers behind; particles must be relatively

large and hydrophobic to be removed. Dissolved air flotation clarification to clean process water, however, is designed to remove all particles (a collective process). Small air bubbles are used, 0.01−0.1 mm, under conditions of relatively low turbulence.

Stickies

Doshi, M.R., Properties and control of stickies. *Progress Paper Recycling* l(l): 54−63(Nov., 1991).

Doshi, M.R., Quantification, control, and retention of depositable stickies, *Progress Paper Recycling* 2(l):83(Nov., 1992).

Dirt Counting

Glowacki, J.J., Ponderosa boosts dirt count accuracy with PC/scanner, *Pulp & Paper* 69(2):93−94(1995).

Dirt counting has come a long way over the last several years. This system uses a standard computer image scanner with software to give a dirt size distribution analysis. These systems are easy to use, highly repeatable, and quick.

Bleaching of Secondary Fibers

Ackerman, Ch Göttsching, L, & Pakarinen, H (2000). Papermaking potential of recycled fiber. In L. Göttsching & H. Pakarinen (Eds.), *Recycled Fiber and Deiking.* Finland: Papermaking Science and Technology. Chapter 10, pp (book 7).

Muguet, M., and Sundar, M. (1996). Ozone bleaching of secondary fibers. *Wastepaper VII.* Chicago, IL, 4−7 June.

Castillo, I., Vidal, T., and Colm, J. F. (1995). Upgrading of recycled paper by ozone. *Eighth international symposium on wood and pulping chemistry* (Vol. 1, p. 353). Helsinki.

Kogan, J., Perkins, A., and Muguet, M. (1994). Ozone bleaching of deinked pulp. *TAPPI recycling symposium proceedings* (p. 237). Boston, MA.

Gangolli, J. (1982). The use of ozone in pulp and paper industry. *Paper Technology and Industry*, *26*(5),152.

Kronis, J. D. (1997). Optimum conditions play major role in recycled fiber bleaching with FAS. In K. L. Patrick (Ed.), *Advances in bleaching technology.* California: Miller Freeman Books. (p. 104).

Süss, H.-U., & Krüger, H.. (1983, March). German Patent DE 3,309,956 C1. Fallon, K. C. (1994). In situ formation of formamidine sulfinic acid: An oxidative/reductive bleaching process for recycled fiber. *TAPPI pulping conference proceedings* (p. 263). San Diego, CA.

Hache, M., Fetterly, N., & Crowley, T. (2001). North American Mill experience with DBI. *87th annual meeting, PAPTAC.* Montreal.

Hache, M. J. A., Brungardt, J. R., Munroe, D. C., & Teodorescu, G. (1994). The color stripping of office wastepaper with sodium hydrosulphite. *Pulp and Paper Canada*, *95*(2),120.

Other Uses of Recovered Paper

Verhaevert, J. (2007). Utilizing the energy potential of paper production by-streams. *KCPK international conference fibre raw material for paper & board*, 21 March, paper 12.

Valtonen, O., Soukka, R., Martilla, E., Hammo, S. (2000). Research Report EN B-135, Lappeenranta University of Technology, August.

Clumpkens, M. (2008). The energy neutral mill. *COST strategic workshop improving energy efficiency in papermaking*, Amsterdam, 9−11 June.

Gavrilescu, D. (2008). Energy from biomass in pulp and paper mills. *Environmental Engineering and Management Journal*, 537−546.

EXERCISES

1. What types of contaminants are encountered in recycled paper?
2. What are some of the tools used to remove contaminants from paper?
3. What is the relationship between contaminant removal and fiber reject rate?
4. What are the two mechanisms of deinking in widespread use?
5. Deinked newsprint generally would not be bleached with sodium hypochlorite. Why not?
6. How do through-flow cleaners operate? What type of contaminants do they remove?

CHAPTER

24

Pulp Bioprocessing

24.1 INTRODUCTION

Biotechnology has the potential to increase the quality and supply of feedstocks for pulp and paper, reduce manufacturing costs, and create high-value products. Because the **pulp** and **paper** industry is capital intensive, with facilities specific to the tasks, new technology must either reduce expenses or fit easily into the existing process design. Biotechnology is defined as the use of biological organisms/systems and processes for practical or commercial purposes. Biotechnology encompasses activities, including fermentation, immobilized cell and enzyme technology, cell and tissue culture, and monoclonal antibody techniques, although in recent years, the term has been increasingly identified with techniques for genetic transfer and DNA manipulation. Biotechnology provides processes/products where nonbiological processes are impractical, increases specificity in reactions, provides less environmentally deleterious process, saves energy, and decreases cost. The raw material in forest-based industries is wood and its components. Thus, possibilities for using biotechnology in these industries are abundant. Biotechnology refers to the use of microorganisms or biological substances to develop new products of industrial, agricultural, or therapeutic interest to improve the quality of human life. Today, enzymes are used for an increasing range of applications. In fact, enzyme-catalyzed processes are gradually replacing chemical processes in many areas of industry because they save energy, water, and chemicals; help to improve product quality; and furthermore, also give valuable environmental benefits. These benefits are becoming more and more important at a time of increasing awareness about sustainable development, green chemistry, climate change, and organic production. Biotechnological methods offer potential opportunities for changing the industry toward more environmentally friendly and efficient operations compared with the traditional methods. Biotechnological processes are environmentally friendly, energy efficient, more specific and can be used in place of nonbiological processes. The use of biotechnological processes in the pulp and paper industry results in increased pulp yield, improved fiber properties, enhanced paper recycling, reduced processing, and environmental problems and energy efficiency. Many applications have approached or are approaching toward commercial reality. Suitable biological treatments in conjunction with less-intensive conventional treatment could help solve many of the problems of currently used processes. Several applications have been successfully transferred to commercial use. This chapter gives updated information on various biotechnological processes useful in pulp processing.

Biermann's Handbook of Pulp and Paper: Raw Material and Pulp Making
https://doi.org/10.1016/B978-0-12-814240-0.00024-0

24.2 PROCESSES

Debarking

Debarking is the first step in all processing of wood. This step consumes a substantial amount of energy. Extensive debarking is required for high-quality mechanical and chemical pulps because even a small amount of bark residue causes the darkening of the product. In addition to its high energy demand, complete debarking leads to losses of raw material because of prolonged treatment in the mechanical drums. The border between the wood and bark is the cambium, which consists of only one layer of cells. This living cell layer produces xylem cells toward the inside of the stem and phloem cells toward the outside. The common characteristics of the cambium include a high content of pectins and the absence or low content of lignin in all the wood species. The content of pectins in cambium cells varies among the wood species but may be as high as 40% dry weight. The content of pectic and hemicellulosic compounds is very high in the phloem. Pectinases are found to be key enzymes in the process, but xylanases may also play a role because of the high hemicellulose content in the phloem of the cambium. Enzymatic treatments cause significant decreases in energy consumption during debarking. The energy consumed in debarking is decreased as much as 80% after pretreatment with pectinolytic enzymes. The enzymatic treatment also results in substantial savings in raw material. Enzymes may be able not only to increase existing debarking capacity, thus saving capital investment, but also available as an aid to be used when debarking is difficult. Finnish researchers used debarking enzymes, specific for the hydrolysis of the cambium and phloem layer, from *Aspergillus niger*. A clear dependence was found between the polygalacturonase activity in the enzyme preparation and reduced energy consumption in debarking (Table 24.1).

In addition to polygalacturonase, the enzyme mixture produced by *A. niger* also contained other pectolytic and hemicellulolytic activities. The amount of energy needed for removal of bark was found to decrease to 20% of the reference value. Birch bark contains large amounts of the extractive betulinole that causes depositions in kraft pulp made from chips contaminated bark. The depositions may form spots in papers, web brakes, and sets off on equipments. The colored bark of pines and spruces may give dark spots in mechanical paper. Efficient debarking is therefore needed. Debarking of logs is, however, not a trivial task, and intensive

TABLE 24.1 Debarking of Spruce With Enzymes

	Enzyme Dose (nkat/mL)				
Enzyme	**Polygalacturonase**	**Polymethoxyl galacturonide lyase**	**Xylanase**	**Endoglucanase**	**Energy Consumption as % of Control**
Pectinex ultra SPL	185	0.6	2.0	5.5	50
Pentosanase	0.2	<0.1	100	1.6	82
Partially purified polygalacturonase	185	<0.1	0.2	<0.1	87
Crude polygalacturonase	185	<0.1	1.1	1.6	77

Based on Ratto et al. (1993).

debarking leads to significant losses of wood yield. Thus, techniques for enhancing debarking are interesting. The innermost layer of the bark, i.e., the phloem and the cambium, has a different chemical composition than the wood log itself. The middle lamellas in this region consist mainly of pectin, which is more susceptible to microbial degradation. Microbial or, potentially, enzymatic removal of pectin could thus be used to weaken the binding of the bark to the log, thus facilitating debarking.

Fig. 24.1 shows the principle for biodebarking. The phloem and cambium layers (inner bark) located between the wood (xylem) and the other bark in wood are only lignified to limited extend and can therefore be degraded by enzymes/molds.

There are different types of fungi that are able to degrade attack this tissue, both white rot fungi, and specialized molds. A problem is that the cambium/phloem is a living tissue and has defense systems against microbial attacks. A few studies with treatment of logs (mainly softwoods) with different types of fungi—the inoculum is added to the stumps of the logs—have shown that barking can be enhanced, but the technique has not been commercialized.

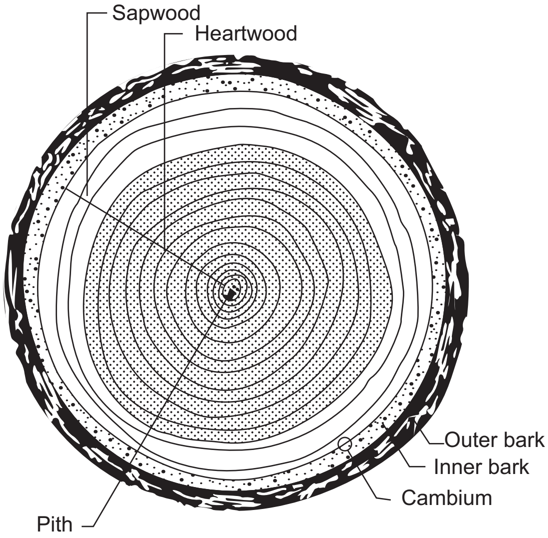


FIGURE 24.1 Principle for biodebarking. The phloem and cambium layers (inner bark) located between the wood (xylem) and the other bark in wood are only lignified to limited extend and can therefore be degraded by enzymes/molds. *Reproduced with permission from Winandy (1994).*

24.3 PULPING

Wood destroying fungi are used for pretreating wood chips for facilitating mechanical, thermomechanical, or chemical pulping. Certain white rot fungi can remove lignin and hemicellulose from the wood cell walls leaving the cellulose. However, the cellulose from wood delignified in this way has normally a low degree of polymerization and thus produce a very weak paper. A shorter treatment with white rot fungi, that do not remove all of the lignin, have, however, been shown to enhance both mechanical and chemical pulping. There are several requirements for a fungus to be able to work commercially in biopulping. These include relatively fast growth rate, preferred activity against hemicellulose and lignin combined with low activity on cellulose, ability to degrade extractives, and ability to grow on both hardwood and softwood.

Several fungi have been tested with promising results (Table 24.2).

Two white rot fungi, *Phanerochaete chrysosporium* and *Ceriporiopsis subvermispora*, have shown good results. *P. chrysosporium* grows according to the “simultaneous rot” strategy and can also degrade cellulose efficiently. Therefore most focuses have been on *C. subvermispora*, a delignifying fungus that fulfills most of the desired criteria. At the University of Wisconsin in Madison, USA, research has been carried out on mainly biomechanical pulping with this organism, and several full-scale trials have been performed. The biopulping processes so far developed are compatible with the operations at a mechanical pulping mill, although positive

TABLE 24.2 Energy Savings From Biomechanical Pulping of Loblolly Pine Chips With Different White Rot Fungi

Fungus	Energy Savings (%)
Ceriporiopsis subvermispora	42
Phlebia tremellosa	36
Phlebia subserialis	32
Phlebia brevispora	28
Hyphodontia setulosa	26
Phanerochaete chrysosporium	14

Incubation with fungi for 4 weeks.
Based on Leatham et al. (1990).

effects have been also observed in connection with chemical pulping. The wood chips are first decontaminated on-site by steaming to remove competing microbes, which can attack cellulose and thus destroy the fiber quality. After a cooling phase, the chips are inoculated with the biopulping fungus. Supply of additional nutrients such as a cheap sugar solution facilitates the fungal colonization process but is not absolutely necessary. The inoculated chips are then piled, and the treatment is allowed to proceed for 1–4 weeks in the optimal temperature and moisture content for fungal growth. Energy savings of 30%–40% in the refining step have been reported for the biopulping compared with untreated control, and the yield loss were insignificant. The paper produced is often also stronger than the control, but the pulp brightness often decrease (in one case from 55% ISO to 40% ISO). It was, however, easy to adjust this brightness loss with hydrogen peroxide bleaching. Although the energy saving is significant, the biopulping with *C. subvermispora* have weaknesses—this fungus is not particularly aggressive against other organisms, and the inoculum is relatively costly, and therefore sterilized by using a quick steam treatment and nutrition addition is necessary. Another biopulping candidate is the white rot fungus, *Phlebiopsis gigantea*, which is very aggressive toward other microorganisms. This organism may also stimulate debarking of logs. The nonselective white rot fungi, *Coriolus hirsutus*, have been modified, so that cellulose degrading enzymes are partly suppressed, and have been shown to enhance kraft pulping of eucalyptus. This fungus is interesting because it grows at higher temperatures in comparison with most other organisms. In spite of intensive research efforts, the exact mechanism of biopulping is not completely known. Microscopic studies have shown that, in some cases, the cell wall morphology is not visibly altered, but the material no longer reacts with lignin stains. In other cases, improvements in pulp properties have been observed with samples with a mass loss of less than 10% during the fungal treatment. It appears that other factors than delignification also contribute to the biopulping process. Gradual penetration of marker proteins has been observed as a function of biopulping time, indicating a generation of pores in the cell wall structure. Because the pores do not seem to be large enough to allow diffusion of ligninolytic enzymes, these effects may be result of action of the lignin-oxidizing intermediates generated by the fungus. The opening of the pores in the cell wall may actually also contribute to easier penetration of pulping chemicals, providing a plausible explanation for the positive effects also noted during chemical pulping. The lignin may off course also be structurally modified although the fungus does not remove it.

Table 24.3 shows properties of mill-refined pulps prepared from eucalyptus wood chips treated with *P. chrysosporium*. Biopulping process can be fitted into an existing mill's wood handling system (Fig. 24.2).

Enzymatic pretreatment of logs and chips has been also explored. At the first glance, enzymatic treatment of native wood does not seem like a good idea because lignification makes the wood

TABLE 24.3 Mill Scale Evaluation of Biopulping of *Eucalyptus grandis* Hill ex Maiden With *Phanerochaete chrysosporium* RP-78 Under Nonaseptic Conditions—Properties of Mill-Refined Pulps

Samples	Consistency, First Disk Refiner (%, w/v)	Shive Content of the Pulps (%, w/w)	Refining Degree (degree SR)	Specific Volume (cm^3/g)	Average Fiber Length (mm)	Tensile Index (Nm/g)	Delamination Strength (kPa)
Control	29.4	0.12	22	2.9	557	25 ± 1	217 ± 19
Fungal treated	22.5	0.04	22	2.5	562	33.6 ± 0.5	295 ± 30

Based on Masarin et al. (2009).

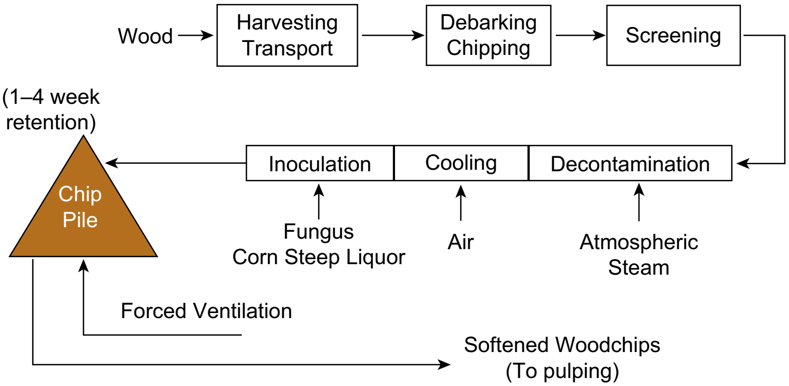


FIGURE 24.2 Biopulping process can be fitted into an existing mill's wood handling system. *Reproduced with permission from Bajpai (2012).*

so compact that the large enzyme molecules cannot penetrate into the cell wall. Despite that enzymatic treatment of wood chips with different enzymes has given positive effects on both mechanical and chemical pulping. Pretreatment of pine chips with the ligninolytic enzyme, laccase, has been shown to reduce the energy consumption of mechanical pulping by 6%–8%. Also pretreatment with manganese peroxidase seems to have similar effects. The mechanism behind this effect is probably depolymerization or modification of lignin structure although no mass loss of the treatment has been found. However, manganese peroxidase is technically more difficult to apply in the process. Pretreatment of wood chips with polysaccharide degrading enzymes (cellulases, xylanases and pectinases) gives some improvements of kraft pulping (reduced reject and increased delignification). The mechanism behind these effects may be that nonlignified portions in the wood, such as boarded pits, are degraded and that this enhances the penetration of the white liquor in the wood chips during pulping. Pulping of nonwoody raw material with enzymes has better possibilities. High-quality pulps of cotton and bast fibers of flax and hemp are made by an intense beating of the raw fibers that make them more flexible and shorten them. This process is energy consuming, but addition of cellulases and—for hemp and flax—pectinases reduce the beating time significantly. The technique has been tested in full scale but is presently not used.

24.4 DEPITCHING

Storage of the wood logs or chips for some time before pulping reduces the pitch content in wood. This is a traditional method used to reduce pitch problems during the papermaking processes and in the equipment. Pitch consists of waxy, hydrophobic extractives, such as triglycerides and steryl esters, and cause a lot of technical problems in especially mechanical pulping; it deposits on equipments and disturbs the fiber—fiber bonding (due to deposits on the fiber surface that disturb hydrogen bonding), thus leading to weaker paper, and larger pitch deposits (that have get lost from equipment) can also cause tearing of the paper sheets in the paper machine, leading to very costly web brakes. However, traditional seasoning offers no control over the microbial species growing on the chips, and the results are therefore highly unpredictable; the formation of color is common (loss of brightness), and strength loss due to attack of soft rot and white rot fungi is not uncommon. Methods for controlled seasoning have thus been developed using microbes that can both effectively remove extractives without causing discolorization or strength loss and suppress the growth of other microbes. An albino strain of the sap stain fungus, *Ophiostoma piliferum*, is commercially available for controlled seasoning under the name Cartapip. It degrades extractives and prevents growth of other microorganisms on the chips if it is applied on fresh chips. This treatment reduces the risks of pigment formation, loss of pulp yield and fiber weakening, and decreases the pitch content in both high- and low-extractive containing wood, although it is mainly used for pines that often have high pitch content. The main targets are the triglycerides, which are the likely key component in pitch deposits. In the case of pine wood, with high content of extractives, the fungal treatment also improves the fiber properties in mechanical pulp and even seems to lower the energy consumption in refining. This might be because the fungal treatment open pits in the wood that might improve the steaming pretreatment in mechanical pulping and by an enhanced fiber—fiber interaction. Reduction in resin content and Kappa numbers of spruce chips treated with various fungi after 2 weeks' incubation is shown in Tables 24.4 and 24.5, respectively.

The enzymatic products have been also commercialized to be applied on pulp. Lipases have been available for commercial use for decades and are also used to control pitch problems in mechanical pulp mills especially in Japan and China, relying on oriental tree species with high content of extractives.

TABLE 24.4 Effect of Fungal Treatment[a] on Resin Content of Spruce Chips

Fungus	Resin Content (%)
Control	1.2
Ceriporiopsis subvermispora	0.8
Ophiostoma piliferum	0.9
Phanerochaete chrysosporium	0.9

[a] *Incubation for 2 weeks.*
Based on Fischer et al. (1994).

TABLE 24.5 Effect of Fungal Treatment[a] on Kappa Numbers After Sulfite Cooking

Fungus	Kappa Number
Control	25.9
Ceriporiopsis subvermispora	20.1
Ophiostoma piliferum	25.5
Phanerochaete chrysosporium	23.8

[a] *Incubation for 2 weeks.*
Based on Fischer et al. (1994).

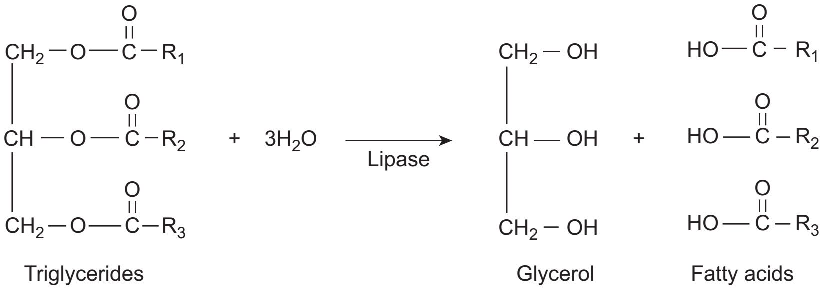


FIGURE 24.3 Hydrolysis of pitch by lipase. *Reproduced with permission from Bajpai (2012).*

By using lipases, the pitch deposits in the paper may be decreased up to 30%, and improved brightness and paper strength are obtained. The effect on paper strength may be due to improved fiber–fiber interaction when the triglycerides deposited on the fiber surfaces are removed. The lipases are normally added directly after the refining and the bleaching.

The enzymatic method for pitch control using lipase was the first successful case of the use of an enzyme as a solution to pitch problems in the papermaking process. Lipases hydrolyze the lipids to their constituent fatty acids and substituted polyol (Fig. 24.3).

Lipases from *Aspergillus oryzae*, *Candida cylindraceae*, and *Pseudomonas* sp. have been mostly used. Few commercial preparations of lipases for pitch removal are available. More than 70% of triglyceride was hydrolyzed at 500 ppm of lipase with a commercial preparation of lipase (Table 24.6).

TABLE 24.6 Effect of Lipase on Hydrolysis of Triglycerides

Lipase Concentration[a] (ppm)	Hydrolysis of Triglycerides (%)
1	12.9
3	50.0
5	74.2

[a] 4% pulp slurry.
Based on Irie and Hata (1990).

Enzymatic pitch control with Resinase A2X reduced triglyceride content. The contents of the surface pitch in groundwood pulp produced from unseasoned wood were 2.6%–2.8% compared with 1.5%–2.2% in groundwood produced from seasoned wood. Triglyceride (TG) content in the surface pitch of the seasoned wood was 7%–9%. On the other hand, they were 18%–25% in unseasoned wood, which was 2.5 times higher. The enzymatic treatment reduced TG content at the inlet of the mixing chest to less than 6% while 50% unseasoned was used. During the entire trial period, the removal frequency was kept at less than 0.3 times per day by the enzymatic treatment. So, the enzyme addition guaranteed a normal and stable operation at the paper machine with a relatively high unseasoned wood mixture. Finally, it was concluded that the enzymatic treatment would reduce woodyard space required for seasoning.

The use of laccase-mediator system for the removal of lipophilic extractives present in pulps has been explored. Laccase from the basidiomycete, *Pycnoporus cinnabarinus*, in the presence of the mediator 1-hydroxybenzotriazole (HBT) was very efficient in removing free and conjugated sterols (95%–100% decrease) from eucalyptus kraft pulp; triglycerides, resin acids, and sterols (65%–100% decrease) from spruce thermomechanical pulp; and fatty alcohols, alkanes, and sterols (40%–100% decrease) from flax soda pulp. The removal of lipids by laccase-HBT

TABLE 24.7 Effect of Laccase Treatment on Removal of Extractives From Mechanical Pulp

Laccase Dose (U/gm)	Remaining Extractives (%)
1	85
5	74
25	73

Based on Paice (2005).

resulted in the formation of several oxidized derivatives that were absent or presented low abundances in the initial pulps. In spite of this, the total lipid content in pulps decreased significantly, and the most problematic compounds were completely removed. About 85% removal of extractives from mechanical pulp by laccase treatment has been reported (Table 24.7).

24.5 RETTING

Retting is a process using the action of microorganisms and moisture on plants to dissolve or rot away much of the cellular tissues and pectins surrounding bast fiber bundles and so facilitating separation of the fiber from the stem. It is used in the production of fiber from plant materials such as flax, hemp, etc. Fibers are obtained from flax stems by the process of retting. Two methods used for retting flax at commercial levels using pectinolytic microorganisms are water-retting and dewretting. Water-retting traditionally depends on anaerobic bacteria that live in lakes, rivers, ponds, and vats to produce pectinases and other enzymes to ret flax. The stench from anaerobic fermentation of the plants, extensive pollution of waterways, high drying costs, and putrid odor of resulting fibers resulted in a move away from anaerobic water-retting in the mid-20th century to dewretting. Dewretting is the result of colonization and partial plant degradation by plant-degrading, aerobic fungi of flax stems, which are harvested and laid out in swaths in fields. The highest quality linen fibers are produced using dewretting but concern exists within this industry about low and inconsistent quality. Enzymes have the potential to provide an improved method to ret flax for textile fibers. Enzymatic-retting produces high and consistent quality fibers of staple length for blending with cotton and other fibers. Enzymatic retting is faster and more reproducible than traditional methods and may provide the spinners with a better quality product. Commercial enzymes are available which produce fibers with good yield and quality. The yield of enzyme-retted fibers was as good or even better than those from high-quality water-retting. A disadvantage, however, was lower fiber strength because of the continued activity of the cellulases in the mixtures. Treatment with an oxidizing agent, such as sodium hypochlorite, or reagents giving a high pH that denatured the enzymes prevented the continuing cellulolytic activity. Research on enzyme retting led to a series of patents and to a semiindustrial scale trial but no commercial system has been developed. Commercial enzymes containing only pectinase resulted in fibers with significantly higher strength than cellulase-containing mixtures (Table 24.8).

24.6 BLEACHING

Xylanases

Xylanases are commercially used in bleaching of kraft pulp. The discovery that xylanases can be used to facilitate pulp bleaching was made in late 1980s, and xylanase-assisted bleaching processes have since become established technology in many countries.

The main enzyme needed for enhancing the delignification of kraft pulp is endo-β-xylanase, but enrichment of xylanase with other hemicellulolytic enzymes improves the effect of

TABLE 24.8 Properties of Fibers From Flax Retted With Different Enzymes

Enzymes	Strength (g/tex)	Fineness (SSI)	Elongation (%)
Control (Unretted)	42.0	5.20	1.9
0.1% Multifect FE + Mayoquest 200	21.6	4.33	1.3
0.2% Multifect FE + Mayoquest 200	17.8	4.12	0.5
2.0% Texazyme BFE + Mayoquest 200	36.7	4.69	1.8
5.0% Texazyme BFE only	34.6	4.27	1.6
0.1% Bioprep only	33.2	3.79	2.0
0.1% Bioprep + Mayoquest 200	34.9	2.95	2.3
0.1% Bioprep + Barapon + Clavodene	34.8	3.55	2.5
0/05% Viscozyme + Mayoquest 200	27.6	3.60	1.4

Based on Foulk et al. (2008).

enzymatic treatment. The use of xylanase enzymes in pulp bleaching was first reported in 1986 by Viikari et al. The Finnish forest companies were the first in the world to start mill scale trials in 1988. In North America, the first mill trials of xylanase were carried out at Port Alberni in 1991 and ongoing usage in some mills started in 1992. Presently, a significant number of European, North American, South American, and Japanese mills are bleaching full time with enzymes. Xylanase use is more common in Canada than the United States because of more stringent adsorbable organic halides (AOX) levels. In the United States, the Cluster rule pressured mills to completely convert to elemental chlorine-free (ECF) bleaching in an economic way. In addition, weak markets for many pulp and paper products have forced mills to reduce their bleaching costs. Fortunately, the use of xylanase enzymes can address both needs. Most full time applications focus on cost reductions using O_2-ECF bleaching. Recent developments involve use of enzymes to eliminate the first chlorine dioxide stage and thereby help reduce water usage.

Enzymatic bleaching has been in commercial operation in North America for many years. Typically, these enzymes have been obtained from fungal sources such as *Trichoderma reesei*. Early enzyme biobleaching applications used blends of natural enzymes that attacked a broad spectrum of materials in the pulp. Most enzyme-assisted bleaching uses xylanases that hydrolyze xylan. Xylanases have been isolated from a number of microorganisms, including eukaryotes and prokaryotes of both filamentous and nonfilamentous varieties. The use of xylanases from fungi in pulp bleaching can be problematic because some species produce cellulases in conjunction with the desired hemicellulases, and even small amounts of cellulase can negatively affect important pulp properties, including yield, viscosity, and strength properties. Other sources of xylanases have been obtained from bacterial *Escherichia coli*. To date, millions of tons of commercial enzyme-treated pulp have been successful produced in North American mills. Enzyme application has resulted in cost savings in 3 and 4 stage bleach plants and in fiberlines with and without oxygen delignification. In Japan, Oji Paper is unique in manufacturing xylanase on-site at its Yonago mill.

Xylanases are sold as concentrated liquids, and the amount required per metric ton of pulp is very low, less than a liter. The cost of enzyme per ton of pulp varies and depends on the dosage required and the supplier. The approximate cost of enzyme treatment is around $1.2−2.0/per ton of pulp (TP). Because of the low enzyme price and low capital costs of enzyme stage, the potential economic benefits of enzyme bleaching are significant.

A survey of mill usage of xylanase revealed that the mills have spent most of its effort in decreasing AOX, followed closely by meeting customer demands (which in many cases was decreasing chlorine usage), and eliminating chlorine gas. These objectives were followed in effort by reducing off-grade pulp, decreasing biological oxygen demand (BOD), and cutting costs. The least effort was devoted to increasing throughput, eliminating dioxin and converting to totally chlorine-free (TCF). The most widely reported benefit of enzyme treatment is a savings in bleaching chemicals. The chemical savings was 8%–15% with an average of 11% of the total chemical across the bleach plant. The other widespread benefits were in improved effluent, including reduction in AOX of 12%–25%, reduction in effluent color, and other improvements to the effluent. Other benefits of enzyme treatment reported increased bleached brightness (1 point gain), tear strength (5% gain), and pulp throughput (10% increase). Xylanase enzymes can cut bleaching related energy usage by 40%. This would result in carbon dioxide emissions savings of between 155,000 and 270,000 tons annually in European paper industry. Table 24.9 shows the results of plant-scale trial with xylanases.

TABLE 24.9 Plant-Scale Trial Results With Xylanase

(A) Effect on Bleaching Chemical Requirement

	No Enzyme	Enzyme
Production rate (a.d. metric tons/day)	796	789
UNBLEACHED PULP		
Soda loss (as Na_2SO_4, kg/ton)	9.7	10.1
Kappa number	31.1	31.4
C_D STAGE		
Active chlorine multiple	0.23	0.21
Chlorine (%)	4.58	3.75
Chlorine dioxide (%)	0.7	0.82
Chlorine dioxide substitution (%)	28.5	36.4
Total equivalent Cl_2 (kg/a.d. metric tons)	64.1	59.0
E_{OP} STAGE		
Hydrogen peroxide (%)	0.4	0.4
Oxygen (%)	0.8	0.8
D_1 STAGE		
Chlorine dioxide, (%)	1.67	1.58
Total equivalent Cl_2 (kg/a.d. metric tons)	43.9	41.7
D_2 STAGE		
Chlorine dioxide (%)	0.23	0.20
Total equivalent Cl_2 (kg/a.d. metric tons)	6.0	5.2
Brightness (% ISO)	89.2	90.3
Overall total equivalent Cl_2 (kg/a.d. metric tons)	114.0	105.8
Total ClO_2 demand (%)	2.6	2.6

(B) Effect on Physical Strength Properties

Parameter	**No Enzyme**	**Enzyme**
PFI revolutions	2280	2333
Tear index, mN·m^2/g	137 ± 7	130 ± 6
Tensile strength, km	9.2 ± 0.4	9.6 ± 0.3
Burst index, kPa·m^2/g	77 ± 4	78 ± 3
Strength factor, km·mN·m^2/g	1260 ± 57	1248 ± 54
Viscosity, cps	23.5 ± 2.3	24.5 ± 2.1

Based on Manji (2006).

Xylanases such as endoxylanases are xylan-specific enzymes. They catalyze the hydrolysis of xylose–xylose bonds within the xylan chain and solubilize only a fraction of the total xylan present. However, the actual enzymatic mechanism in bleaching is not yet well understood. The results from laboratory studies and mill trials show about a 35%–41% reduction in active chlorine at the chlorination stage for hardwoods and 10%–20% for softwoods, whereas the savings in total active chlorine were found to be 20%–25% for hardwoods and 10%–15% for softwoods. In the ECF bleaching sequences, the use of xylanase increases the productivity of the bleaching plant when the production capacity of chlorine dioxide is a limiting factor. This is often the case when the use of chlorine gas has been abandoned. In TCF bleaching sequences, the addition of xylanase increases the final brightness value, which is a key parameter in the marketing of chlorine-free pulps. In addition, the savings in TCF bleaching are important with respect to both costs and the strength properties of the pulp. Xylanase pretreatment leads to reductions in effluent AOX and dioxin concentrations because of reduced amount of chlorine required to achieve a given brightness. The level of AOX in effluent is significantly lower for xylanase-pretreated pulps as compared with conventionally bleached control pulps. The xylanase-treated pulps show unchanged or improved strength properties. Also, these pulps are easier to refine than the control pulps. The viscosity of the pulp is improved as a result of xylanase treatment. However, the viscosity of the pulp is adversely affected when cellulase activity is present.

The most conventional method is to add xylanase to the brown stock pulp before the high density tower. The enzyme reaction takes place in the tower, and the treated pulp then passes into the bleach plant. Xylanase has also been added later in the bleaching sequence rather than to the brown stock pulp. The latest generation of alkali tolerant enzymes requires little, if any, addition of acid to adjust the pH. Earlier generation of enzymes had pH optima ranging from 5 to 6.5 and required acid addition to brown stock pulp. Instances of corrosion problems were seen when acid was incorrectly applied. New xylanases have higher pH optima and function optimally without pH adjustment.

The acid of preference by far has been sulfuric acid. However, with the development of alkaline xylanases, noncorrosive carbon dioxide is an excellent choice and also improves washer performance. Typical site of acidification is indicated in Fig. 24.4.

To optimize and adapt the enzymatic treatment to individual existing mill conditions, detailed laboratory work is generally required. Interestingly, xylanase bleaching has been scaled up directly from laboratory scale to the large industrial scale (1000 TP/day) without intermediate pilot stages. No expensive capital investments have generally been necessary for full scale runs. The most significant requirement is the addition of pH adjustment facilities. Xylanase pretreatment has been shown to be easily applicable with existing industrial equipment, which is a considerable advantage of this technology. Bleaching with xylanase requires proper control of pH, temperature, and retention time. Most of the enzymes are active at acidic or neutral pH although some of them function under alkaline conditions. Mill operations also affect the performance of the xylanase enzyme. The effect of raw material, pulping process, brown stock washing, and bleaching sequence should be assessed by laboratory testing before mill usage of enzymes.

Xylanases may help eliminate the need for increased chlorine dioxide generation capacity because chlorine dioxide charges can be reduced. Similarly, the installation of expensive oxygen delignification facilities may be avoided. The benefit of a xylanase bleach boosting stage can also be taken to shift the degree of substitution toward higher chlorine dioxide levels while maintaining the total dosage of active chlorine.

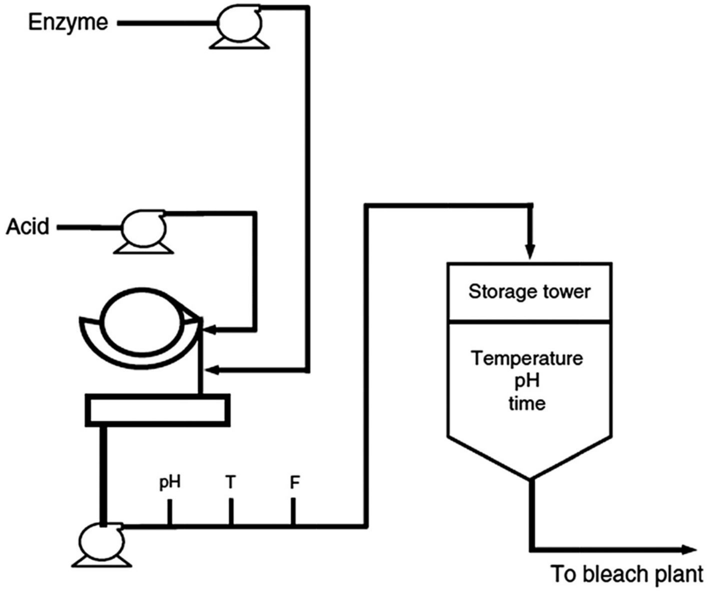


FIGURE 24.4 Typical xylanase and acidification site. *Reproduced with permission from Bajpai (2004).*

This will dramatically reduce the formation of AOX. In TCF-bleaching sequences, the addition of enzymes increases the final brightness value, which is a key parameter in marketing chlorine-free pulp.

Ligninolytic Enzymes

Ligninolytic enzymes have been also explored for pulp bleaching. In contrast to xylanases that act indirectly to remove lignin, bleaching with ligninolytic enzymes would constitute a real delignifying step. However, because of the very complex chemistry of ligninolytic enzyme systems, it was in the end of the 1990s that the first promising results were obtained. Bleaching with ligninolytic enzymes from white rot fungi appears most promising because this class of fungi can perform relatively selective lignin degradation. However, the cellulose always appears to be damaged somewhat, even by "delignifying" white rot fungi. Lignin degradation by white rot fungi is based on oxidations of nonphenolic and phenolic aromates in lignin and by radical attacks of hydroxyl radicals. Some of the ligninolytic systems have, however, a much higher selectivity for lignin than oxygen delignification (that also damages cellulose), and therefore the concept of bleaching with ligninolytic enzymes has gained much interest. However, significant technical problems remain with ligninolytic bleaching techniques, and highly selective bleaching can also be obtained by using chemicals such as for instance chlorine dioxide and peracetic acid. Ligninolytic enzymes generally cooperate with low molecular weight cofactors, redox mediators, and need an oxidant, such as hydrogen peroxide or oxygen. This makes these techniques more complicated than xylanase bleaching, and reasonably realistic bleaching stages have only been presented for two ligninases, manganese peroxidase and laccase. Manganese peroxides depend on hydrogen peroxide and manganese (II) for the bleaching reaction. In the presence of hydrogen peroxide, Mn^{2+} is oxidized to Mn^{3+}. This is the reactive species performing a one-electron oxidation on the lignin to recreate Mn^{2+}. Furthermore, the manganese ion needs a chelator, such as malonate or oxalate. Overdosing of hydrogen peroxide will inactivate the enzyme. A bleaching stage for laboratory use has been developed based on MnP. The Kappa number was found to be lower for the MnP bleached pulp than for the control in all steps, but the largest difference was seen in the final hydrogen peroxide bleaching step.

Laccases are in many ways easier than manganese peroxidases to apply technically because they use molecular oxygen as the oxidant and cannot be inactivated by overdosage. Laccases based bleaching can be performed in bleaching in equipment similar to that in oxygen delignification, and the enzyme can also be produced at relatively moderate cost. However, efficient bleaching by laccases is dependent on the addition of a low molecular weight redox mediator. Although some natural redox mediators have been identified, most research has been focused on finding a synthetic mediator more efficient than the natural mediators. The role of the redox mediator in the laccase system is not only to overcome sterical barriers but the activated mediators also perform different types of reactions on the lignin than the laccase itself; activated mediators can abstract hydrogens from the alpha-carbon leading to depolymerization reactions, whereas laccase mainly oxidizes the phenol, to a stabilized radical, which can decompose and lead to coupling reactions. Most efficient redox mediators contain an NO group that is believed to be oxidized by the laccase to stabilized NO• radicals, which are believed to selectively attack the lignin. In the case of 2,2′-azinobis-(3-ethylbenzthiazoline-6-sulfonate) (ABTS) there are, however, some indications that the active component may be a two-electron oxidized form. It has been shown that efficient delignification of pulp can be achieved by using a combination of a laccase and a mediator. The data show that the laccase step reduces the Kappa number without any reduction in pulp viscosity. On the other hand, the brightness reduces, which may be explained by the formation of quinones in the pulp. The brightness increases, however, quickly in the following extraction and hydrogen peroxide bleaching steps. Table 24.10 presents the results from the pilot plant trial with laccase-mediator system.

Although the laccase bleaching stage is easier to upscale than MnP bleaching, it cannot presently compete with traditional techniques, partly because of the cost of mediators and environmental concerns (many redox mediators are toxic).

24.7 PRODUCTION OF DISSOLVING PULP

Dissolving pulp is a high-grade cellulose pulp, having low contents of hemicellulose, lignin, and resin, and has special properties, such as a high level of brightness and uniform molecular-weight distribution. These are either acidic sulfite pulps or prehydrolyzed kraft pulps and are commonly used for the production of cellulose derivatives and regenerated cellulose. To obtain products of high quality, these pulps must fulfill certain requirements, such as high cellulose content, low hemicellulose content, a uniform molecular weight distribution, and high cellulose reactivity. Xylan degrading enzymes have been explored for selective removal of pentosans in preparing dissolving grade pulp. The complete removal of residual hemicellulose seems unachievable because of the modification of the substrate or to structural barrier. It appears that pentosans in the bleached pulp are well shielded by other pulp components and therefore not susceptible to enzymatic attack. Even with very high enzyme loadings and prolonged incubation periods, xylan hydrolysis is limited. The wood species and the method of their pulping, the accessibility of pentosans and their quantity in pulp, the penetration

TABLE 24.10 Summary of Results From the Pilot Plant Trial With Laccase-Mediator System

Sequence	Pulp	Dosage of Enzyme/ Mediator (kg/TP)	Degree of Delignification (%)	Maximum Brightness (% ISO)
L-E-Q-P	A	2/13	56.6	76.5
L-E-L-E-Q-P	A	2 × 2/2 × 8	50.6/67.7	82.7
L-E-Q-(P)	B	2/8	44.2	

		Conditions		
Parameter	**L Stage**	**E Stage**	**Q Stage**	**P Stage**
Consistency (%)	10	10	5	10
Temperature (°C)	45	60	60	75
pH	4.5	11.5	5	11.2
Residence time (min)	120	60	30	210
Pressure (bar)	2	–	–	–
Dosage	Enzyme: 2 kg/t Mediator: variable	NaOH	0.2% diethylenetriaminepentaacetic acid (DTPA)	3% peroxide

Based on Call and Mücke (1997).

capabilities and substrate specificity of the enzymes, the inhibitory action of bleaching chemicals, and the linkage of xylan to lignin and cellulose by covalent and hydrogen bonds, respectively, may be the factors contributing to the difficulties in removing xylan from the bleached pulp. Xylanase treatment of unbleached pulp appears to be more effective because of the presence at this stage of more hemicellulose accessible for enzymatic degradation. Alkaline extraction in conjunction with enzyme treatment leads to some improvement of the pulp characteristics.

Use of xylanases from *Aureobasidium pullulans* in biobleaching of sulfite pulps for dissolving pulp production reduced the pentosan content by 13% and enrichment of α-cellulose by 1 point, after 1-h enzyme treatment with 15 IU xylanase/g pulp. At the same time, the impact of xylanase treatment on brightness and Kappa number was insignificant (Table 24.11). Bleaching of sulfite pulp with *A. pullulans* xylanases and chemicals in sequence OD1E0D2H resulted in production of a dissolving pulp having the highest α-cellulose content (92.1%–92.4%) as related to control (91.6%) (Table 24.12).

TABLE 24.11 Effect of Xylanase Enzyme From *Aureobasidium pullulans* on Properties of Sulfite Pulp

Pulp Treatment	Kappa Number	α-Cellulose (% w/w)	Pentosan (% w/w)	Brightness (% ISO)
Control	6.7	89.9	3.9	56.0
Xylanase treated	6.5	90.7	3.4	56.5

Based on data from Christov et al. (1995).

TABLE 24.12 Bleaching of Sulfite Pulp With *Aureobasidium pullulans* Xylanase and Reduced Amount of Active Chlorine in OD1EOD2H Sequence

Pulp Treatment	% Total Active Chlorine Reduction	α-Cellulose Content	Pentosan (% w/w)	Brightness (% ISO)
Control	0	91.6	2.4	87.5
Xylanase treated	0	92.4	1.9	88.5
	13	92.2	1.7	88.4
	23	92.2	1.8	89.6
	37	92.1	1.8	88.3

Based on data from Christov et al. (1995).

The reactivity of cellulose is very important for many applications of dissolving pulps. High reactivity saves chemicals and, even more importantly, can give a *more even product*; residues of unreacted cellulose in cellulose derivatives are often regarded as a factor lowering the value. Enzymatic treatments hold great potential for increasing cellulose reactivity in dissolving pulps. A monocomponent endoglucanase with a cellulose-binding domain significantly improves the cellulose reactivity.

24.8 SHIVES REMOVAL

Shives are small bundles of fibers that have not been separated into individual fibers during the pulping process. They appear as splinters that are darker than the pulp. One of the most important quality criteria for bleached kraft pulp is the shive count. It has been found that a novel enzyme formulation, Shivex, containing xylanase activity can be used to increase the efficiency of shive removal by bleaching. By treating brown stock with Shivex, mills can increase the degree of shive removal in the subsequent bleaching by 55%. Depending on the shive level in the incoming brown stock and the desired shive level of the bleaching pulp, this allows a mill to decrease its actual shive count or to increase its margin of safety against shives. The increase in shive removal is accompanied by an increased efficiency in the bleaching of pulp. Therefore, mills can decrease chlorine use in a bleach plant without compromising on shive counts. Shivex is a multicomponent mixture of proteins, some of which are xylanases, but the degree of shive removal by the enzyme is not directly related to the enzymes' xylanase activity or bleach boosting effectiveness. At a given bleached brightness, *Shivex* treatment results in a lower shive count. Xylanase treatment, therefore, helps to remove shives from the pulp beyond the associated gain in the brightness. Removal of shives and ease of pulp bleaching by the use of xylanases also help in reducing the energy requirement.

24.9 EFFLUENT TREATMENT

Every year the pulp and paper industry consumes billions of cubic meters of water and produces huge amounts of highly polluted wastewater that needs to be treated. Conventional techniques of wastewater treatment require a high energy input, and their environmental impact is debatable. Thus, the need to find sustainable, environmentally friendly and efficient treatment techniques is required.

Of the different waste streams, bleach plant effluents are most toxic because of various chlorinated organic compounds generated during the bleaching of pulp. Several different chlorinated organic compounds have been identified. The chloroorganics in wastewater are divided into high-molecular-weight and low-molecular-weight compounds. The low-molecular-weight compounds (mol. wt. < 1000) are major contributors to mutagenicity and bioaccumulation because of their hydrophobicity and excellent ability to penetrate cell membranes. The low-molecular-weight compounds are known to bioaccumulate in the aquatic food chain. Legislation has been introduced to limit the levels of these toxic compounds in effluents. Additionally, during bleaching treatments chromophoric, highly oxidized, polymeric lignin/chlorolignin derivatives are formed that give rise to a dark color in the effluent. The color poses an esthetic problem and contributes to the BOD. Several strategies—internal process modification and external treatment—have been examined for reducing the pollutants. Internal process change is one of the options adopted by the pulp and paper industry to reduce the pollution at the source. Physicochemical methods are not economically viable. Biological methods have the potential to eliminate/reduce the problems associated with physicochemical methods. In secondary treatment processes, activated sludge is the most commonly used process. Aerated lagoons are efficient in removing BOD, chemical oxygen demand (COD), and AOX. Anaerobic contact reactors, anaerobic filters, and fluidized bed reactors are suitable in reducing organic pollutants. White rot fungi are found to be very effective for efficient degradation of the refractory material. High removals are achieved in the case of combination of physicochemical and biological processes. The confirmation of the reported results, their applicability in the real field, and economic evaluations are very important in adopting the process.

Several methods have been attempted for decolorization and detoxification of bleached kraft effluents. Biotechnological methods have the potential to eliminate/reduce the problems associated with physicochemical methods. These methods may be aerobic as well as anaerobic bacterial treatment, fungal treatment, or enzymatic treatment. The bacterial processes are not very effective because of the limitation that they cannot degrade the high-molecular-weight chlorolignin compounds and enzymatic processes are not cost-effective. Among the biological methods tried so far, fungal treatment technology using white rot fungi appears to be the most promising in this regard. One of the drawbacks associated with the fungal treatment has been the requirement of easily metabolizable cosubstrate such as glucose for the growth and development of ligninolytic activity. To make the fungal treatment method economically feasible, there is a need to reduce the requirement of cosubstrate or identify a cheaper cosubstrate. Hence, efforts should be made to identify the strains that show good decolorization with less or no cosubstrate and can utilize industrial waste as a cosubstrate. Efforts should be also made to utilize the spent fungal biomass for preparing the culture medium required in the synthesis of active fungal biomass. If succeeded, the cost of treatment may be further reduced. As lignin degrading system of white rot fungus has a high oxygen requirement, use of oxygen instead of air as fluidizing media should be explored. Increasing the oxygen concentration in the culture atmosphere is expected to have a dual effect: It would lead to an increased titer of the lignin degrading system and to increased stability of the existing system. A quantitative study of extracellular enzymes is also required to gain insight into the possible enzymatic mechanism involved in the degradation of lignin-derived compounds present in the effluents.

Enzymes have been also explored for wastewater treatment in the pulp and paper industry. The advantages are that only catalytic and not stoichiometric amounts of the reagents are needed, and the low organic concentrations and large volumes typical of bleaching effluents are therefore less of a problem. With laccase and peroxidase enzymes, high-removal efficiencies were obtained for chlorinated phenols, guaiacols, vanillins, and catechols. The color removal from effluents at neutral pH by low levels of hydrogen peroxide was enhanced by adding peroxidase. No precipitation occurred during the decolorization process.

24.10 ANNOTATED BIBLIOGRAPHY

Akin D (1998). Enzyme retting of flax for linen fibers: recent developments. In: Book of Papers American Association Textile Chemists and Colorists. American Association Textile Chemists and Colorists, Research Triangle Park, NC, pp. 273–280.
This book chapter presents recent developments in the area of enzyme retting of flax for linen fibers.
Bajpai P (1999). Application of enzymes in pulp & paper industry. Biotechnol. Prog. 15 (2), 147–157.
This article reviews the application of enzymes in the pulp and paper industry. Attention is focused on the recent advances.
Bajpai P (2004). Biological bleaching of chemical pulps. Crit. Rev. Biotechnol. 24 (11), 1–58.
This article presents an overview of developments in the application of hemicellulase enzymes, lignin-oxidizing enzymes, and white rot fungi in bleaching of chemical pulps.
Bajpai P (2009). In: Schaechter, M., Lederberg, J. (Eds.), Xylanases in Encyclopedia of Microbiology, third ed., vol. 4. Academic Press, San Diego, California, USA, pp. 600–612.
This chapter presents properties, production, mode of action, purification, and industrial application of xylanases.
Bajpai P (2012) Biotechnology in Pulp and Paper Processing. Springer Inc., New York, US, pp. 412.
This book presents a comprehensive coverage of all aspects of biotechnology in the pulp and paper industries.
Bajpai P, Bajpai, PK (2001). Development of a process for the production of dissolving kraft pulp using xylanase enzyme. Appita 54 (4), 381–384.
This paper discusses a process for the production of dissolving kraft pulp using an enzymatic pretreatment with xylanase enzyme.
Bajpai P, Bajpai PK, Varadhan R (2005). Production of dissolving grade pulp with hemicellulase enzyme. In: Proceedings International Pulp Bleaching Conference, Stockholm, Sweden, pp. 303–305.
This study reports the feasibility to produce dissolving grade pulp with hemicellulase enzymes.
Bajpai P, Ananad A, Bajpai, PK (2006). Bleaching with lignin oxidizing enzymes. Biotechnol. Annu. Rev. 12, 349–378.
This article presents an overview of the developments in the application of lignin-oxidizing enzymes in bleaching of chemical pulps. The present knowledge of the mechanisms on the action of enzymes as well as the practical results and advantages obtained on the laboratory and industrial scale are discussed.
Bourbonnais R, Paice, MG (1996). Enzymatic delignification of kraft pulp using laccase and a mediator. Tappi J. 79 (6), 199–204.
Enzymatic delignification of kraft pulp using laccase and a mediator 2,2′-azino-bis-(3-ethylbenzthiazoline-6-sulfonate) (ABTS) is presented in this paper. After one-stage treatment followed by alkaline extraction, the extent of delignification was 25%–40% for kraft pulps and over 50% for a sulfite pulp. Repeating the treatment reduced the Kappa number of a softwood kraft pulp by 55%.
Buchert J, Mustranta A, Tamminen T, Spetz P, Holmbom B (2002). Modification of spruce lignans with trametes hirsuta laccase. Holzforschung 56, 579–584.
The effect of *Trametes hirsuta* laccase on isolated spruce wood lignans was evaluated. Lignans were treated with different laccase dosages and treatment times. About half of the phenolic groups present in lignans

remained intact during the treatment. The oxidation of phenolic groups in lignans produced oligomeric structures containing approximately 4—5 lignan units. Precipitation of the formed oligomeric structures probably prevented further polymerization.

Call HP (1991). Laccases in Delignification, Bleaching and Wastewater Treatment. Patent No. DE 4137761.

Laccases have been shown to facilitate bleaching of kraft pulp in conjunction with organic mediators. Laccases have also been used for a long time in detoxifying and decolorizing of waters containing phenolic pollutants. This patent discusses applications of laccases for bleaching and for effluent treatment in the pulp and paper industry.

Call HP, Mücke I (1997). History, overview and applications of mediated lignolytic systems, especially laccase-mediator-systems (Lignozym-process). J Biotechnol 53: 163—202.

This paper presents a general overview about the literature with a special focus on laccase-assisted reactions. The general applicability of the laccase-mediator system is given by a comparison of results obtained with pulps from different sources of wood and from several pulping processes. The technical feasibility of this enzyme-mediator-based technology for delignification of pulps has been demonstrated in a pilot plant trial.

Christov LP, Prior, BA (1993). Xylan removal from dissolving pulp using enzymes of *Aureobasidium pullulans*. Biotechnol. Lett. 15, 1269—1274.

In this article, the ability of a crude enzyme preparation of *Aureobasidium pullulans* to hydrolyze xylan from sulfite dissolving pulp has been examined.

Christov LP, Akhtar M, Prior BA (1995). Biobleaching in dissolving pulp production. In: Proceedings of the sixth international conference on biotechnology in the pulp and paper industry: advances in applied and fundamental research. Vienna, Austria, pp 625—628.

In this article, the biobleachability of industrial sulfite pulp from a dissolving pulp producing mill was studied using two strains of the white rot fungus and the xylanase preparation from the yeast. It was found that the fungus can brighten the pulp very effectively, thus eliminating the need of a second chlorine dioxide stage during ECF-bleaching.

Covarrubias R (2009). Enzymatic Pitch Control. Tissue World. Apr—May, pp. 38—39.

Use of enzyme-based approach for pitch control is discussed in this paper.

Dhiman, SS, Sharma J, Battan, B (2008). Industrial applications and future prospects of microbial xylanases: a review. BioResourses 3 (4), 1377—1402.

This review discusses factors affecting xylanase production and its potential industrial applications in textile, paper, pulp, and other industries.

Dube E, Shareck F, Hurtubise Y, Beauregard M, Daneault C, 3—4 Feb. (2009). Enzyme-Based Approaches for Pitch Control in Thermomechanical Pulping of Softwood and Pitch Removal in Process Water. EXFOR and Annual Meeting 2009, Montreal, QC, Canada, pp. 69—74.

Using enzymatic approach, a pitch control method was developed for use with thermomechanical pulping of softwood and for pitch removal from process water. Combination of a novel biodegradable surfactant and a lipase reduced resin acids, sterols, and triglyceride by 48%, 32%, and 78%, respectively, compared with untreated samples. Using laccase treatment of the process water, the fatty and resin acids were reduced by 42% and the lignans by 60%.

Farrell RL, Hata K, Wall, MB (1997). Solving pitch problems in pulp and paper processes by the use of enzymes or fungi. Adv. Biochem. Eng./Biotechnol. 57, 198—212.

This paper discusses the use of enzymes and fungi for solving pitch problems in pulp and paper processes.

Field JA (1986). Method for Biological Treatment of Waste Waters Containing Nondegradable Phenolic Compounds and Degradable Nonphenolic Compounds. EP Patent 1986; EP 238148.

A method for biological treatment of wastewaters containing nondegradable phenolic compounds and degradable nonphenolic compounds is described in this patent.

Fischer K, Akhtar M, Blanchette RA, Burnes TA, Messner K, Kirk TK (1994). Reduction of resin content in wood chips during experimental biological pulping process. Holzforschung 48, 285−290.

This research examined the ability of two biopulping fungi, *Ceriporiopsis subvermispora* and *Phanerochaete chrysosporium*, to reduce the resin content of wood chips, and the ability of a commercial depitching fungus, *Ophiostoma piliferum*, to biopulp.

Fischer, Messner K (1992). Reducing troublesome pitch in pulp mills by lipolytic enzymes. Tappi J. 75 (2), 130−134.

Use of lipolytic enzymes for reducing troublesome pitch in pulp mills is described in this paper.

Forss K, Jokinen K, Savolainen M, Williamson H (1987). Utilization of enzymes for effluent treatment in the pulp and paper industry. In: Proc 4th International Symposium on Wood and Pulping Chemistry, vol. 1, Paris, France, pp. 179−183.

The use of novel enzymes and rDNA technology in sludge and wastewater treatment is discussed.

Foulk JA, Akin DE, Dodd BR (2008). Pectinolytic enzymes and retting. BioResources 3 (1), 155−169.

Influence of pectinolytic enzymes on retting effectiveness and resultant fiber properties are discussed in this paper.

Fujita Y, Awaji H, Taneda H, Matsukura M, Hata K, Shimoto H, Sharyo M, Sakaguchi H, Gibson K (1992). Recent advances in enzymatic pitch control. Tappi J. 74 (4), 117−122.

Recent advances in enzymatic pitch control are discussed. This method has been continuously applied in the production line for newsprint and wood-containing paper at Japanese mills since May 1990. Better and steady operations and resulting product quality improvement have been achieved by this enzymatic pitch control method.

Gutiérrez A, del Río JC, Rencoret J, Ibarra D, Martínez AT (2006). Main lipophilic extractives in different paper pulp types can be removed using the laccase-mediator system. Appl. Microbiol. Biotechnol. 72, 845−851.

In this work, the appropriateness of an enzymatic treatment using the laccase-mediator system for pitch biocontrol is evaluated.

Irie Y, Hata K (1990). Enzymatic Pitch Control in papermaking system. Proceedings of 1990 Papermaking Conference, Atlanta, pp 1−10.

A new enzymatic pitch control has been developed and proved to be very successful for troublesome pitch problems.

Leatham GF, Myers GC, Wegner TH (1990). Biomechanical pulping of aspen chips: energy savings resulting from different fungal treatments. Tappi J 73(5):197−200.

Energy savings resulting from different fungal treatments during biomechanical pulping of aspen chips is presented in this paper.

Masarin M, Pavan PC, Vicentim MP, Souza-Cruz PB, Loguercio-Leite C and Ferraz, A, (2009). Laboratory and mill scale evaluation of biopulping of *Eucalyptus grandis* Hill ex Maiden with *Phanerochaete chrysosporium* RP-78 under non-aseptic conditions, Holzforschung, **63**, 259−263.

This study presents results of laboratory- and mill-scale evaluation of biopulping of

Eucalyptus grandis with *Phanerochaete chrysosporium* under nonaseptic conditions. About 18.5% net energy saving could be achieved. Biopulps contained lower shive content and had improved strength properties compared with control pulps.

Manji AH (2006) Extended usage of xylanase enzyme to enhance the bleaching of softwood kraft pulp. TAPPI J 5(1):23–26.

This excellent article discusses extended usage of xylanase enzyme to enhance the bleaching of softwood kraft pulp.

Paice M, Zhang X (2005). Enzymes find their niche. Pulp Pap. Can. 106 (6), 17–20.

Paprican researchers have reviewed the status of enzymes in paper and pulp industry.

Paice MG, Jurasek, L (1984). Peroxidase catalyzed color removal from bleach plant effluent. Biotechnol. Bioeng. 26, 477–480.

Use of peroxidase enzyme for color removal from effluent from the caustic extraction stage effluent of a bleach plant has been studied.

Paice M (2005). Enzyme application in pulp and paper manufacturing. Lakehead University Symposium, 27 Sep 2005.

This presentation discusses the status of biotechnology in pulp and paper industry.

Sharma H (1987). Screening of polysaccharide-degrading enzymes for retting flax stem. Int. Biodeterior. 23 (3), 181–186.

This article presents screening of polysaccharide-degrading enzymes for flax retting.

Ratto M, Kantelinen A, Bailey M and Viikari L (1993). Potential of enzymes for debarking. Tappi J. 76(2), 125–128.

In this study, the effect of enzymatic pretreatment on the energy consumption of wood debarking was examined on the laboratory scale using enzymes to degrade the cambial layer.

Tolan JS, Guenette M, Thebault L, Winstanley C (1994). The use of a novel enzyme treatment to improve the efficiency of shive removal by bleaching. Pulp Pap Canada 95(12):T488.

This paper discusses the use of novel enzyme to improve the efficiency of shive removal by bleaching.

Van Sumere, CF (1992). Retting of flax with special reference to enzyme-retting. In: Sharma, HSS, Van Sumere, CF (Eds.), The Biology and Processing of Flax. M Publications, Belfast, Northern Ireland, pp. 157–198.

This paper provides data on retting of flax with enzyme. The processed fibers were characterized.

Viikari L, Kantelinen A, Sundquist J, Linko M (1994). Xylanases in bleaching: from an idea to industry. FEMS Microb. Rev. 13, 335–350.

The utilization of hemicellulases in bleaching of kraft pulp is considered as one of the most important new large-scale industrial applications of enzymes. This method is environmentally safe and has proven to be economically realistic in a short period.

Winandy JE (1994).Wood Properties In: Arntzen, Charles J., ed. Encyclopedia of Agricultural Science. Orlando, FL: Academic Press: 549–561. Vol. 4, October 1994.

CHAPTER 25

Forest Biorefinery

25.1 INTRODUCTION

Biomass, especially lignocellulosic material, represents an abundant renewable carbon source. This is potentially convertible to energy, fuels, and speciality chemicals; their integrated production through advanced technological processes of separation and conversion that reduces carbon cycle impact defines the biorefinery concept. The term "biorefinery" can be defined as a facility that integrates biomass extraction and conversion processes and equipment for producing fuels, heat, power, and value-added products. The forest biorefinery is an opportunity for the pulp and paper industry to diversify its product mix and to generate revenues from new products. Biorefinery units can be integrated in a pulp and paper industry to manufacture bioproducts in addition to core cellulose-based products. This integrated complex is characterized by the sharing of raw materials, by-products, utilities, and infrastructure resulting in significant economic advantages.

Biorefinery offers a wide range of potentially attractive products, from biofuels to specialty chemicals. In addition to the traditional commodities used as transportation fuels, 12 building block chemicals have been identified by the NREL as promising bioproducts that can be obtained from sugars, either through biological or chemical conversions. Those building blocks can be further processed to produce high-value bio-based chemicals or materials. The final products may be used by different industrial sectors such as textiles, housing, health, and hygiene. To be economically viable, the biorefinery must target the most suitable market demand for its product mix. Several examples of biorefinery units integrated in pulp and paper mills have been reported in the literature. Studies have been performed to convert kraft mills into integrated biorefineries, mainly for ethanol production. Additional research was dedicated to gasification-based biorefineries; gasification of black liquor or wood residues has been evaluated as a mean to produce liquid fuels and chemicals. The focus of those studies was either the technoeconomic feasibility or the environmental benefit of developing an integrated forest-based complex. The topic of biorefineries as means of processing industrial material and efficient utilization of renewable products is well known and applied worldwide, in almost every developed and emerging country. The forest products industry's manufacturing facilities are an ideal foundation to develop the Integrated Forest Products Biorefinery (IFPB) (Fig. 25.1).

Those facilities, which today produce pulp, paper, and wood products, also are geared to collect and process biomass. Rather than creating a "greenfield" operation, additional bioconversion or thermochemical processes can be built

Biermann's Handbook of Pulp and Paper: Raw Material and Pulp Making
https://doi.org/10.1016/B978-0-12-814240-0.00025-2

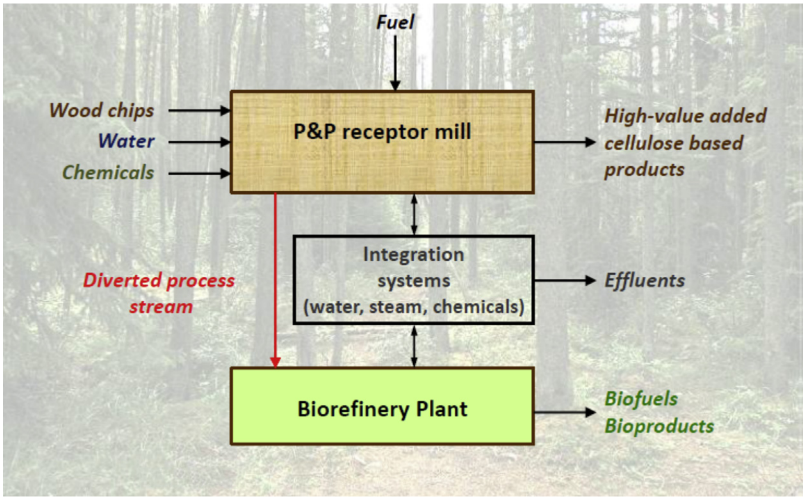


FIGURE 25.1 The concept of integrated forest biorefinery. *Reproduced with permission from Kannangara (2016).*

around existing mills to generate bioenergy or manufacture bioproducts. This presents industry with dramatic potential to increase the productivity and profitability of its manufacturing infrastructure. Possible benefits include: improved efficiency of raw material utilization, protection of traditional product lines, creation of higher skilled and better paying jobs, and access to new domestic and international markets for bioenergy and bioproducts.

The conversion of forestry and agricultural biomass is accomplished by various pathways, offering the opportunity to revitalize the pulp and paper industry. The main biorefinery feedstocks are hemicellulose, cellulose, lignin, and bark, used to generate building block molecules, chemicals, fuels, polymers, or dissolving pulp. The large-scale implementation of the biorefinery will result in profitable and sustainable processes with positive environmental impacts.

In the recent years, there has been great interest in the concept of the forest biorefinery from the forest industry, research community, and policy makers. The concept is attractive because it addresses current concerns around oil prices, finite fossil resources, and Kyoto commitments. Biomass rich nations see an opportunity to utilize their natural bioresources in new ways to achieve maximum value and productivity within the confines of sustainability.

Few of today's pulp and paper mills are already operating as forest biorefineries. By-products from the pulping process are used in boilers to produce heat and power, and in some cases, marketable products such as kerosene, tall oil, and cellulose derivatives are generated in addition to paper products. In the optimized forest biorefinery, advanced technologies would enable more of the wood feedstock to be converted to higher-valued products, including chemicals and more marketable fuels such as ethanol and hydrogen.

The products produced in a biorefinery will mainly be a function of the feedstocks available. Properties of feedstock such as cost, location, composition, moisture content, and availability will determine the appropriate technical options. Feedstock costs can represent a large portion of plant operating costs. One approach is to locate the biorefinery near the feedstock for reducing or eliminating transportation costs. If the feedstock is a waste stream from an existing process, disposal or treatment costs may be counterbalance, resulting in a near zero feedstock cost. About half the organic mass that enters a kraft mill is incinerated. Capturing more useful energy from this organic mass is a main aspect of mill energy efficiency programs. Boiler temperatures and pressures have increased over time to increase power production in steam turbines. However, conventional cogeneration does not represent the ceiling of usefulness for these feedstocks; rather, it represents the floor. In addition to recovery boiler, most of the kraft mills operate a wood waste boiler. Most require this additional steam to operate their process, but there is tremendous opportunity to improve process energy efficiency to eliminate any fossil fuel used to generate steam and to liberate feedstocks for biorefinery opportunities. In addition to available on-site feedstocks, conventional forestry practices leave residuals—branches, foliage, and tree tops—on the forest floor. These represent 15%–20% of the tree mass above the root and are generally not used. In some countries, residuals are collected and used as fuel for large combined heat and power plants. Tax incentives meant to reduce fossil fuel use in response to Kyoto have been a driving force behind these practices. In some countries, wealth of natural resources and inexpensive hydroelectric power have been the main barriers to implementing similar practices. But, this is changing, as demand in regions normally in surplus of hydroelectric power is growing beyond the installed capacity, leading to increased reliance on high cost incremental capacity. Pulp and paper mills are typically the largest industrial infrastructure located near forestry residuals. Despite that, transportation to the mill site has been highlighted as an obstacle to utilize this material. Mobile energy densification technologies have been suggested. These technologies are truck-based pyrolysis units that concentrate these residuals for transport to a utilization site. It may also be attractive to utilize nonforestry biomass waste in some cases.

There is no singular concept of a biorefinery. In fact, there is an infinite amount of concepts depending on the combination of production pathways from the raw material toward the finished products. Of all the platforms considered, the conversion platform is the one that presents more challenges. Several new processes are being developed to answer these new challenges. The main processes are associated to two different technology basis: biochemical platform and thermochemical platform (Table 25.1). Top value-added chemicals that can be produced in a biochemical platform biorefinery have been identified (Table 25.2).

TABLE 25.1 Biorefinery Platforms

BIOCHEMICAL
Laboratory, pilot plant, and commercial scale
Value-added chemicals (both from sugar and lignin), building block chemicals, materials (from lignin or lignocellulose), fuel ethanol, heat, and electricity (from lignin)
THERMOCHEMICAL
Laboratory, large-scale pilot plant
Syngas, pyrolysis oil, value-added chemicals, gaseous or liquid fuels
BIOGAS
Large-scale pilot plant; commercial
Methane and carbon dioxide; value-added products
CARBON-RICH CHAINS (OIL)
Commercial
Fatty acid methyl ester (biodiesel), glycerin, and fatty acids as platform chemicals

Based on Carvalheiro et al. (2008).

TABLE 25.2 Top Value-Added Chemicals From Biochemical Platform Biorefinery

Aspartic acid
Glutamic acid
Succinic acid
Fumaric acid
Malic acid
Itaconic acid
Levulinic acid
Glucaric acid
2,5-Furandicarboxylic acid
3-Hydroxy butyrolactone
Glycerol
Arabitol
Xylitol
Sorbitol

Based on Werpy and Petersen (2004).

25.2 OPPORTUNITIES IN THE PULP AND PAPER INDUSTRY

Pulp and paper mills are ideal sites for biorefineries because of the following reasons:

- Paper and forest products companies are efficient growers, harvesters, transporters, and processors of biomass
- Pulp and paper mills are located near numerous sources of biomass, such as forest and agricultural residuals, and energy crops, and have existing infrastructure to ship finished product

Paper mills use over several million tons of dry wood per year as a raw material. These mills have ready access to a roughly equal amount of forest residuals and an even greater amount of agricultural waste and energy crops. Pulp and paper mills are familiar with producing power from biomass: Currently they produce 60% of their power from wood residuals and spent liquors. Pulp and paper mills also have a highly trained workforce capable of operating energy and biorefinery systems. Pulp and paper companies are considering following general biorefinery configurations: In the simplest case, biorefinery configurations try to transform biomass into biofuels replacing bunker carbon or natural gas currently consumed in the pulp and paper manufacturing processes, potentially benefitting from an improved carbon footprint and carbon credits. Greenfield biorefineries versus those implemented in retrofit to operating pulp and paper mills, versus brownfield biorefineries that are developed around pulp and paper mill closures. Biorefineries that try to capitalize from the emerging huge biofuels market via ethanol production versus biorefineries seeking to focus more on smaller volume bioproducts potentially having a higher added value. And in the most complex, and potentially most value-generating one for the forest products industry, is to try to establish a fully integrated forest biorefinery along with the proven and needed pulp and paper manufacturing operations. In this case, the aggregate benefits of operating and management synergies will emerge across time.

By integrating forest biorefinery activities at an existing plant, pulp and paper mills have the opportunity to produce significant amounts of bioenergy and bioproducts and to drastically increase their revenues while continuing to produce wood, pulp, and paper products (Figs. 25.2 and 25.3).

Manufacturing new value-added byproducts from biomass represents for some forestry companies an unprecedented opportunity for revenue diversification. The biorefinery builds on the same principles as the petrochemical refinery. In a petrochemical refinery the raw material is normally crude oil, whereas in the forest biorefinery the raw material is wood/biomass. The raw material is fractionated into

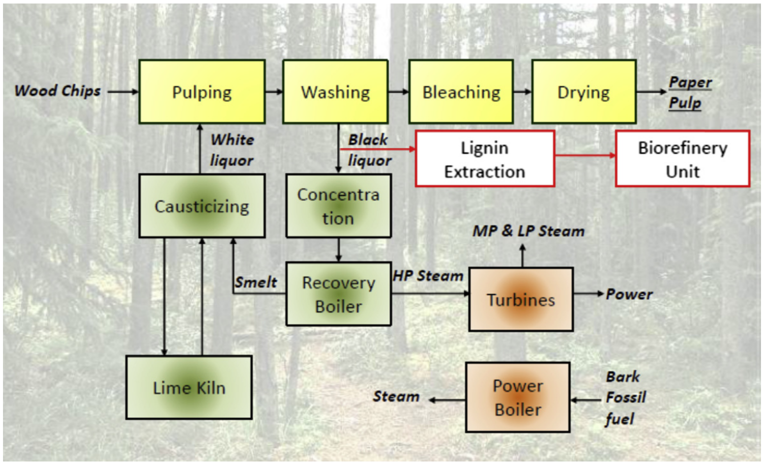


FIGURE 25.2 From kraft pulp mill to lignin biorefinery. *HP*, high pressure; *LP*, low pressure; *MP*, medium pressure. *Reproduced with permission from Kannangara (2016).*

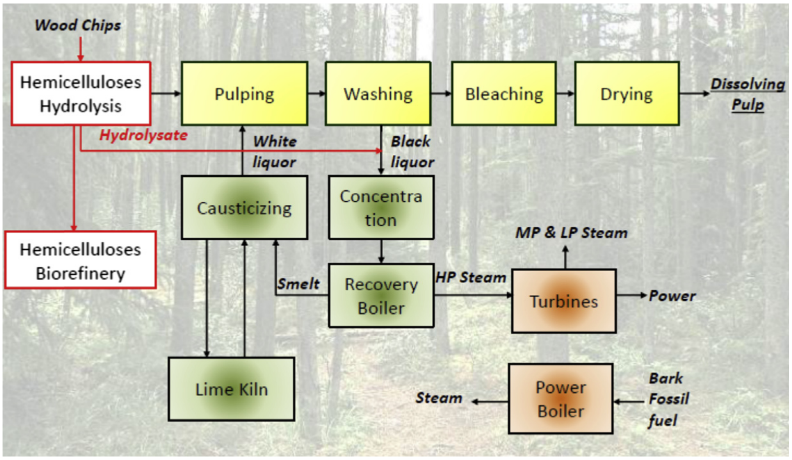


FIGURE 25.3 From dissolving pulp mill to hemicelluloses biorefinery. *HP*, high pressure; *LP*, low pressure; *MP*, medium pressure. *Reproduced with permission from Kannangara (2016).*

several product streams. The products can be a final product or a raw material for another process. New technology is being developed that could be integrated into an existing pulp and paper mill, transforming it into a forest biorefinery. There are still significant challenges associated with these new technologies, but several of them look promising. Research is focused on biorefinery technology development in North America and around the world. But, these process technology development activities alone do not address most of the significant risks associated with implementing this technology.

25.3 BIOREFINERY OPTIONS

For implementation of biorefinery in a pulp and paper mill, several process alternatives should be considered. These are recovering more of the biomass left in the forest, removing lignin from the black liquor in the digester, pyrolysis of bark, etc. In one of the biorefinery workshop, one important consensus reached was that before mills can implement the forest biorefinery, they need to increase its energy efficiency, eliminate fossil fuels from their operations, and maximize carbon availability for the forest biorefinery. This appears to be a valid point because many of the activities today regarding the forest biorefinery are motivated by the Kyoto Protocol.

The biorefinery technologies currently under development are typically characterized as biochemical and thermochemical processes:

- Biochemical processes use steam, dilute acid, concentrated acid, and/or enzyme hydrolysis to convert the hemicellulose and cellulose of biomass into simpler pentoses and glucose.
- Thermochemical processes use slow- or medium-temperature gasification or higher temperature pyrolysis to create a high hydrogen content synthetic gas (syngas) that can be used for electricity generation or catalytically converted into liquid biofuels.

Emerging biorefining technologies are presented in Table 25.3.

TABLE 25.3 Emerging Biorefining Technologies

Technology
Hemicellulose preextraction *Low yield, Medium Capital cost*
Black liquor gasification *High yield, High Capital cost*
Removal of lignin from black liquor *Low/High yield, Low/High Capital cost*
Tall oil extraction *Low yield, Low Capital cost*

Based on Wising and Staurt (2006).

Black liquor gasification technology is thermochemical, whereas hemicellulose preextraction, lignin precipitation, tall oil extraction are biochemical. The choice of biorefinery technology will depend firstly on the choice of appropriate products, as they relate to markets and the supply chain. Depending on the choice of technologies implemented, the yield, the impact on the pulp and paper process and the capital cost will vary. Because the processes in a pulp and paper mill are strongly linked, it is difficult to foresee the impact implementing these different technologies might have on the entire mill. In addition, adding two or more technologies to one mill will result in process issues that are even complex to anticipate.

One of the key criteria for forest biorefinery options is that the processes are adaptable. For many of the products that could be produced in a forest biorefinery follows different value cycles. If these products could be changed the most profitable product could be produced at a time where the value of said product is the highest. By developing a concept of adaptable forest biorefinery, the mill would be less economically vulnerable because the product produced could change over time.

Preextraction of Hemicellulose

This concept has been most extensively investigated. The building blocks of hemicelluloses are hexoses (glucose, mannose, and galactose) and pentoses (xylose and arabinose), which exist in a pyranose and furanose forms. The removal and recovery of hemicellulose is a main step of pretreatment processes for biological conversion to ethanol or other products. A variety of pretreatment methods to hydrolyze and fractionate hemicellulose components have been studied in detail. During kraft pulping, hemicelluloses are degraded into low molecular weight isosaccharinic acids and end up in the black liquor, with degraded lignin. To prevent an environmental impact and recover energy, black liquors are concentrated and burned. As the heating value of hemicelluloses is considerably lower than that of lignin, extracting the hemicelluloses before the pulping stage for generation of high-value products has the potential to improve overall economics. Hemicelluloses can be used directly in polymeric form for novel industrial applications, such as biopolymers, hydrogels, or thermoplastic xylan derivatives; source of sugars for fermentation to fuels, such as ethanol; or chemicals, such as 1,2,4-butanetriol, a less hazardous alternative to nitroglycerine.

The cosmetics industry uses hemicelluloses as emulsifiers to prepare water and oil emulsions. Also hemicelluloses as immunomodulators or those properties that fight infections have been explored. The building blocks of hemicelluloses also include sugars with interesting physiological effects. Mannose has been shown to help combat certain stomach infections. Conversion of xylose into xylitol and mannose into mannitol has been studied. These sugars are packed with potential. If hemicelluloses are broken down into smaller pieces or so-called oligomers, these pieces are highly bioactive. Also, they promote tree growth or function as growth hormones. Hemicellulose can also be used as a dietary fiber. These sugars are slow carbohydrates, which help balance blood sugar levels and promote weight loss. Table 25.4 presents use of hemicelluloses as papermaking additives, and Table 25.5 presents some of the most important current and potential applications of xylan in the pulp and paper, pharmaceutical, chemical, food, and fermentation industries.

Removal of hemicelluloses from wood as a pretreatment step is presently being practiced commercially in the production of dissolving pulps. The hemicelluloses are removed to allow the production of pure cellulose. Dissolving pulps are processed into products such as cellulose nitrate, cellulose xanthate (rayon fibers), and cellulose acetate. Preextraction of hemicellulose can provide a totally new feedstock for biofuel production, thus increasing the total revenue stream for the pulp and paper industry. Development of a pretreatment process can solubilize hemicellulose sugars with minimal formation of fermentation inhibitors, while preserving the fiber integrity is required.

Preextraction of these waste hemicelluloses before the kraft pulping could improve pulp mill operations to a great extent. It will reduce the cooking time; enhance kraft cooking liquor impregnation; improve the pulp properties and the pulp production capacity for kraft pulp mills that are recovery-furnace limited. These process benefits and biofuels possibilities are strong drivers for the development of wood hemicellulose preextraction technologies for kraft pulp mills. An important consideration that should be taken into account with any preextraction of wood chips before kraft pulping is the need to develop a system that is readily integrated with modern pulping operations and will not have any adverse effect on the quality of kraft pulps. A key parameter in the production of many grades of paper is the strength of the final paper sheet. If the degree of polymerization (DP) of cellulose is decreased beyond its normal ~1600 postpulping to ~700 after bleaching, the strength properties of the sheet are degraded. This relationship is due to the fact that cellulose is the primary load-bearing element in a lignocellulosic fiber and has a direct relationship to the fiber strength, which contributes to paper strength. Hence, any hemicellulose preextraction technology used before the kraft pulping needs to reduce the hydrolysis of cellulose. Hemicellulose content is related to paper bond strength. This has been attributed to the adhesive properties of hemicellulose. For kraft pulps with an α-cellulose content higher than ~80%, a reduction in paper sheet strength properties occurs. This product specification defines a limit for hemicellulose preextraction technologies. In an

TABLE 25.4 Major Applications of Xylan

Food	Xylose
	Xylitol
	Biodegradable polymers—plastics, films
	Coatings with increased hydrophobicity and water resistance (acetyl xylans)
Pulp and paper	Beater additive
	Improved swelling
	Porosity
	Drainage
	Strength
	Fiber coating
	Wood resin stabilizer
Chemical	Thermoplastic material
	Polypropylene Filler
	Paint formulations
	Gel-forming material
	Chiral polymer building blocks
Pharmaceutical	Anticoagulant
	Anticancer agent
	Cholesterol reducing agent
	Wound treatment agent
	HIV inhibitor
Fermentation	Enzymes
	Xylanase
	Xylose isomerize
	Biopolymers
	Polyhydroxy alkanoates

Based on Christopher (2012).

TABLE 25.5 Hemicelluloses as Papermaking Additives

DRY-STRENGTH
Positive effect of spruce hemicelluloses on mechanical properties However, moderate compared with cationic starch Little effect of birch hemicelluloses But neutralization of anionic charge of birch hemicelluloses (carried by the xylan fraction) • improves adsorption on pulp • contributes to development of mechanical properties Bleaching required for white grades
ANTIHORNIFICATION
Spruce hemicellulose • improves mechanical properties at first addition (good dry strength aid) but does not maintain mechanical properties after multiple drying cycles (not so good antihornification aid) Birch hemicellulose • helps maintain mechanical properties over multiple recycling
SURFACE SIZING (OLD CORRUGATED CONTAINER, OCC)
Relevant size uptake achieved with all additives Interesting development of mechanical properties when replacing starch with hemicelluloses Birch hemicelluloses Gains of Burst index (+10%), breaking length (+5%), CMT_A index (+5%–10%) Brownish color brought by birch hemicellulose is close to desired "kraft" color for testliner Tear cross direction (CD) index slightly decreases with all additives

Based on Perez et al. (2011).

ideal situation, if 15%–20% hemicellulose could be extracted before pulping and get the same pulp yield as obtained before, it will be possible to keep the same pulp mill production level without increasing the wood demand and would also reduce black liquor solids going to the recovery boiler. Removing the recovery boiler bottleneck may allow the manufacturing of more tonnage. This will further improve the profitability of the kraft mill.

The most common commercial procedures for extracting hemicellulose are presteaming to release natural wood acids followed by water extraction or acid hydrolysis with small amounts of mineral acids. The use of water as prehydrolysis stage relies on the in situ hydrolysis of acetate groups on the hemicellulose chains yielding acetic acid. The liberated acid lowers the solution pH to a range of 3–4. This results in the hydrolysis and solubilization of hemicelluloses. Control of the prehydrolysis parameters is an important consideration, as more severe conditions will degrade the fiber. Pretreatments of lignocellulosic materials by water or steam are referred to as autohydrolysis, hydrothermolysis or hydrothermal pretreatment, aqueous liquefaction or extraction. Microwave heat-fractionation of wood has been recently used to extract hemicelluloses. This method requires a treatment temperature of 180–200°C for 2–5 min. Other methods for hemicellulose extraction include mild alkaline solutions with and without addition of cations such as Na, K, Li and borate at low temperatures; organosolv fractionation; supercritical carbon dioxide; ionic liquids. Organosolv fractionation technology developed by National Renewable Energy Laboratory utilizes a ternary mixture of methyl isobutyl ketone, ethanol, and water in the presence of low concentrations of sulfuric acid to effect a separation of cellulose, hemicellulose, and lignin. The method typically requires a treatment temperature of 140°C for 1 h. This approach fractionates hardwoods, yielding high purity cellulose and selectively dissolving lignin and hemicellulose. However, the method proves difficult with softwoods, requiring more acid, higher temperatures, and longer retention times, resulting in poor cellulose pulps. For integration into a kraft biorefinery, the organosolv extraction method would need to be studied further.

Water prehydrolysis is found to be more effective at removing hemicelluloses than steam prehydrolysis, especially for softwoods. All prehydrolysis treatments also extract low levels of lignin and extractives. A key consideration for extracting hemicelluloses before kraft pulping for nondissolving grades of paper is the need to yield a wood furnish that still yields excellent physical strength pulp properties. This will undoubtedly require an optimization of hemicellulose preextraction technologies providing optimal removal of hemicelluloses for biofuel production and sufficient retention of select hemicelluloses for the production of high-quality kraft pulps.

The concept of hemicellulose preextraction before pulping has been funded by a consortium of large pulp and paper manufacturers and is being operated under the auspices of Agenda 2020. In the United States, wood chip preextraction technologies could make available to the biofuels industry about 14 million tons of hemicelluloses annually while at the same time enhancing the production of kraft pulps. These extractable hemicelluloses could provide a valuable, high-volume resource of sugars for bioethanol production generating ~20–40 million gallons ethanol/year/mill. Potential annual production of ethanol from preextraction of hemicellulose could approach 2 billion gallons of ethanol/year. Extracting the hemicellulose from the wood chips before pulping and depositing the oligomer portion onto the pulp stream after the digester could increase pulp yield by 2%, resulting in approximately $600 million a year in extra pulp production.

The viability of extracting hemicelluloses from wood chips before kraft pulping for dissolving pulps has been established (Fig. 25.3). The challenge for the biofuels and forest products industries is to develop optimized preextraction technologies that provide a hemicellulose stream for biofuels production and a lignocellulosics stream for pulp production. This vision will, undoubtedly, require a cooperative research program with multipartner stakeholders. These efforts would give significant benefits to all interested parties.

Ethanol From Hemicelluloses

For conversion to ethanol, hemicelluloses are first converted to sugars. This is done by using acidic hydrolysis process or enzymatic hydrolysis process. In these processes, monosaccharides are produced that are converted to ethanol using fermentation. Depending on what technologies are optimized for the preextraction of hemicelluloses from wood chips, an acid hydrolysis of polysaccharides to hexoses and pentoses may be preferred. The pentose sugar xylose is the major carbohydrate component of hemicellulose in a wide variety of lignocellulosic biomass species. Consequently, the ability to ferment xylose is an important characteristic.

The enzymatic hydrolysis of pretreated cellulosic biomass has been commercialized for the processing of wheat straw to bioethanol and is being actively pursued for other agricultural waste resources. An important consideration for hemicellulose preextraction and depolymerization treatment protocol is to reduce by-products that are inhibitors of the fermentation of sugars to ethanol, such as furans, carboxylic acids, and phenolic compounds. Some inhibitors are present in the raw material, but others can be formed during the hydrolysis process. The nature, composition, and concentration of these compounds are dependent on the hydrolysis conditions and may have a significant impact on the fermentation production rate of biofuels from the hydrolysate. There are several strategies for dealing with the inhibitors in hydrolysates. First, the hydrolysis conditions may be optimized not only with respect to maximal sugar yields but also to generating reduced amounts of inhibitor compounds. Detoxification before fermentation is another option, including alkali, sulfite, evaporation, anion exchange, or enzymatic treatments. The hydrolyzed hemicellulose sugar solution will finally need to undergo fermentation for the production of ethanol. The microorganisms that are able to ferment sugars to ethanol can be either yeasts or bacteria. Recent advances in genetic engineering, forced evolution, and mutation and selection strategies have enhanced the biological utilization of hexoses and pentoses for the biological production of ethanol. The well-documented fermentation of wood hydrolysates to ethanol provides a strong technical basis from which practical fermentation technologies can be designed for the conversion of preextracted wood hemicelluloses to ethanol. The fermentation of dilute acid hydrolysates from aspen, birch, willow, pine, and spruce using *Saccharomyces cerevisiae* has been reported. These wood hydrolysates contained varying amounts of xylose, glucose, and mannose, and the efficiency of fermentation varied substantially, depending on wood species employed. The use of other yeasts and fungi for the production of ethanol from wood hydrolysates has also been reported, and their efficiencies and cost-performance properties continue to be enhanced.

Chemicals and Materials

Similar to a petrochemical refinery, several chemicals and materials may potentially be produced in an IFPB. This number may be reduced significantly when guided by a department of energy (DOE) study that identifies the top 12 building blocks that may be produced from sugars. Itaconic acid is one of the 12 building block chemicals identified by DOE. Itaconic acid can be produced by fermentation from C5 and C6 monomers. Subsequently, itaconic acid can be converted into polymers. Conversion of hemicelluloses into polymers of itaconic acid presents a great economic opportunity for an integrated forest biorefinery (IFBR).

Another example is the production of carbon fibers using lignin precipitated from alkaline hardwood black liquor. Carbon fibers can be made from hardwood kraft lignin when mixed with commercial polymers such as polyesters, polyolefins, and polyethylene oxide. A major requirement for lignin processing is that it contains a minimum of volatile compounds, sugars, and ash. Because the actual spinning of the fibers occurs at a temperature of about 220°C, a minimal amount of gaseous components should release at this temperature to avoid bubbles in the fibers and thus lower physical properties and avoid spinning problems. Thus filtration to remove particulates, carbohydrate stripping, and washing of (almost) sulfur-free lignin will be required to obtain a suitable feedstock for carbon fiber production.

Removal of Lignin From Black Liquor

A new and cost-effective process for extracting high-quality lignin from kraft black liquor has been developed by STFI-Packforsk. This process is named LignoBoost. Carbon dioxide is used to precipitate lignin. It is then dewatered in the first stage and dewatered/washed in a second washing stage. Washing is done countercurrently. This reduces the risk for lignin dissolution, which is a main disadvantage in the conventional one-stage process. Compared with the one-stage process the water use is lower, lignin is cleaner with respect to ash and sodium, and the capacity is significantly higher. The lignin has very good properties, including 65%–70% dry solids content, ash content of 0.1%–0.5%, sodium 0.01%–0.4%, and heating value of 26 GJ/t. It can be used as biofuel, replacing coal and oil, i.e., in pulp mill's power generation or in lime kilns. LignoBoost gives customers the possibility to increase the capacity of a pulp mill and turn pulp mills into significant energy suppliers. At the same time, the extracted lignin is also of interest for other process industries as a raw material for plastics, coal fibers, and chemicals. There are four key operations in the LignoBoost process. These are precipitation, dewatering, resuspension, and final washing.

The LignoBoost process enables the fast production of high-quality lignin at a low cost. Low filtration resistances can be maintained throughout the process, and an even lignin filter cake that is easy to wash and finally dewater is formed in the second filtration/washing stage. Using the novel process, the specific filtration resistance is one to two orders of magnitude lower compared with the separation and washing made in a single filtration step. The separation of the pH and the ion strength reduction in two different steps result in the lignin becoming much more stable in all process stages with only a small amount of lignin dissolved during the final displacement washing.

The LignoBoost technology has proven its technical maturity over several years of research and laboratory testing and during operation in an industrial-size demonstration plant integrated into the pulping process of Nordic Paper—Bäckhammar, Kristinehamn, Sweden. For production of lignin, acid precipitation was selected as the most potentially promising route. For production of xylan, membrane fractionation was selected as the most promising route. These two methods can be successfully combined.

Metso has patented the LignoBoost technology and has supplied the world's first commercial installation of LignoBoost technology to Domtar in North America. The equipment has been integrated with the Plymouth North Carolina pulp mill. The LignoBoost process separates and collects lignin from the pulping liquor. Separation of a portion of the mill's total lignin production off-loads the recovery boiler and permits an increase in pulp production capacity. The recovered lignin will be used for several applications. This project will allow pulp mills to have a new more profitable value stream from a product that was traditionally burned in the recovery boiler. Domtar's production of lignin started in February 2013 with a targeted rate of 75 t/day (www.valmet.com). A wide range of applications and markets for BioChoice lignin are being developed. These include fuels, resins, and thermoplastics. Having lignin available in large quantities and high-quality from the Domtar plant will help develop the future lignin market for the industry. Another LignoBoost plant started up in 2015 at Stora Enso's Sunila mill in Finland (www.valmet.com). This mill produces 370,000 air-dried metric tons (ADMT) of bleached softwood kraft pulp. The raw materials used are pine and spruce. The annual capacity of the lignin plant is 50,000 MT. The existing kraft lignin market has grown significantly with the start-up of lignin production sites at Domtar's Plymouth North Carolina mill in the United States and Stora Enso's Sunila mill in Finland. Refined lignin can be utilized for producing adhesives, bioplastics, and chemicals such as phenol or BTX or replacing fossil-based fuel. Other interesting areas where it could be used are in carbon fiber production and as precursor to "green carbon" products such as activated carbon or reinforcement filler.

Other Products

Extractives such as rosin and fatty acids are sometimes removed from the spent pulping liquor and processed into crude tall oil. In Canada, most crude tall oil is currently incinerated as fuel in the lime kilns of pulp mills to displace fossil fuel. In the south eastern United States, where extractive content of the wood is much higher, tall oil plants fractionate the crude tall oil into value-added components. Processes have also been proposed to convert both the fatty and rosin acid components of the crude tall oil into green diesel fuel. The processing of tall oil into a high-quality diesel additive has been researched in the laboratory and pilot scale. The later studies included promising road tests by Canada Post Corporation. Given that many kraft pulp mills already collect these extractives, their future utilization for fuels will be based on competing economic considerations. Fatty acids can be directly esterified by alcohols into diesel fuel, whereas the rosin acids can be converted by the "Super Cetane" hydrogenation process developed in Canada. Turpentine recovered from process condensates in Canadian mills is generally incinerated as fuel in one of the on-site boilers. Processing it into consumer grade products is possible but, in many cases, it is more valuable as a fuel.

The average 1000-tons-per-day softwood kraft mill has approximately 7 tons per day of methanol in its foul condensate streams. Most mills use steam strippers to concentrate the methanol to about half its volume before incineration. Some mills use air strippers, which do not remove methanol effectively or simply send foul condensates to effluent treatment where the methanol is consumed by biological activity. It is possible to purify this methanol for alternative uses, either on-site or for sale. One pilot project has used the catalytic conversion process for converting the methanol to formaldehyde. Waste organics sent to effluent treatment at pulp and paper mills are unique compared with municipal organic wastes, which have a very high carbon-to-nitrogen ratio. Certain bacteria in activated sludge treatment systems under such conditions accumulate poly-3-hydroxybutyric acid (PHB), a potential building block for biopolymers. Extraction of PHB remains the significant hurdle to this process. Pulp and paper waste treatment sludge is typically buried in landfills, incinerated or spread on land as a nutrient enhancer. Research is under way to improve the performance of microbes in the conversion of nutrients in effluents to PHB and other fermentation products.

The US pulp and paper industry processes 108 million tons pulpwood per annum. At least 14 million tons of hemicellulose (2 billion gallons ethanol; 600 million gallons acetic acid; $3.3 billion net cash flow), 5 million tons of paper mill sludge (feedstock for ethanol; no pretreatment), and 700 million liters of turpentine and tall oil (feedstock for biodiesel) per annum is available.

Black Liquor Gasification

Please see Chapter 18, Volume 1.

25.4 ENVIRONMENTAL IMPACTS

A key component of the forest biorefinery concept is sustainable forestry. The forest biorefinery concept utilizes advanced technologies to convert sustainable woody biomass to electricity and other valuable products and would support the sustainable management of forest lands. In addition, the forest biorefinery offers a productive value-added use for renewable resources such as wood thinnings and forestry residues, as well as urban wood waste.

Forest biorefineries could produce fewer emissions. The overall environmental implications and life cycle of the forest biorefinery are still being studied. However, there could be a number of positive environmental impacts. For example, a forest biorefinery utilizing gasification (in a black liquor gasification combined cycle configuration [BLGCC]) rather than a Tomlinson boiler is predicted to produce significantly fewer pollutant emissions because of the intrinsic characteristics of the BLGCC technology. Syngas clean-up conditioning removes a considerable amount of contaminants, and gas turbine combustion is more efficient and complete than boiler combustion. There could also be reductions in pollutant emissions and hazardous wastes resulting from cleaner production of chemicals and fuels that are now manufactured using fossil energy resources. In addition, it is generally accepted that production of power, fuels, chemicals, and other products from biomass resources creates a net zero generation of carbon dioxide (a greenhouse gas), as plants are renewable carbon sinks.

25.5 ANNOTATED BIBLIOGRAPHY

Bajpai P (2012). Biotechnology in Pulp and Paper Processing. Springer-Verlag Inc., New York, NY.
This book presents a comprehensive coverage of all aspects of biotechnology in the pulp and paper industries.
Bajpai P (2016). Pretreatment of Lignocellulosic Biomass for Biofuel Production SpringerBriefs in Molecular science Green Chemistry for Sustainability.
This book provides comprehensive and in-depth coverage of the pretreatment of lignocellulosic biomass for production of biofuel and value-added products.
Bajpai P, (2017). Carbon Fibre from Lignin (SpringerBriefs in Materials) 1st ed.
This book reviews in detail major recent advances in the production of carbon fiber from lignin.
Bajpai P (2013). Biorefinery in the Pulp and Paper Industry. Elsevier Inc.
To remain viable, the traditional producers need to increase revenue by producing bioenergy and biomaterials in addition to wood, pulp, and paper products. Integrated Products Biorefineries present the forest products industry with a unique opportunity to increase revenues and improve environmental sustainability.
Carvalheiro F, Duarte LC, Gírio FM (2008). Hemicellulose biorefineries: a review on biomass pretreatments. Journal of Scientific and Industrial Research, 67:849–864.
This review provides biomass pretreatments assuming that hemicellulose stream should be integrated in lignocellulose feedstock-based biorefinery as a primary fraction for converting into value-added compounds other than bioethanol. Different lignocellulosic material treatments are analyzed foreseeing bio-based products possible to obtain from hemicellulose path.
Chambost V, Mcnutt J, Stuart PR (2008). Guided Tour: Implementing the Forest Biorefinery (FBR) at Existing Pulp and Paper Mills, Pulp and Paper Canada, 109 (7–8): 19–27.
A hypothetical “guided tour” is given for the biorefinery implementation for the production of ethanol, in which a phased approach is proposed, and key issues that a given mill should consider for implementing the FBR are highlighted.
Chambost V, Eamer B, Stuart PR (2007). Forest Biorefinery: Getting On With the Job, Pulp and Paper Canada, 108(2): 19–20, 22.
Forest biorefineries can be utilized effectively to create additional economies from forest products used in pulp and paper mills of Canada. The development of biorefinery products, organic chemicals, or bioextractives needs to be supported by R&D measures. The right biorefinery configuration is helpful in process and product design of the paper and pulp mill.

Christopher L (2012). Adding Value Prior to Pulping: Bioproducts from Hemicellulose. Global Perspectives on Sustainable Forest Management book edited by Okia Clement Akais ISBN 978-953-51-0569-5 DOI: 10.5772/36849.

This chapter focuses on adding value before pulping. The bioproducts from hemicelluloses are discussed.

Gonzalez J, Cruz JM, Dominguez H, Parajo JC (2004). Production of antioxidants from *Eucalyptus globulus* wood by solvent extraction of hemicellulose hydrolyzates, Food Chem. 84, 243–251.

Production of antioxidants from *Eucalyptus globulus* wood by solvent extraction of hemicellulose hydrolyzates is discussed.

Kannangara M, Marinova M, Perrier M, and Jean Paris J (2016). The integrated forest biorefinery, an example of green engineering in “5th International Congress on Green Process Engineering (GPE 2016)”, Franco Berruti, Western University, Canada, Cedric Briens, Western University, Canada Eds, ECI Symposium Series, (2016). http://dc.engconfintl.org/gpe2016/12.

This paper reports that Integrated Forest Biorefinery is an attractive means to diversify the pulp and paper industry and generate new profits.

Marinova M, Mateos-Espejel E and Paris J. (2010), From kraft mill to forest biorefinery: an energy and water perspective 11. Case study Cellulose Chem. Technol., 44 (1–3), 21–26.

Hemicellulose extraction from wood chips before pulping and its transformation into high-value products is the biorefining technology identified for integration into the existing pulp mills. A Canadian hardwood kraft pulp mill was selected as a biorefinery acceptor. Hemicellulose, used as a feedstock for promising products, has been analyzed. Issues related to the corresponding energy requirements of the biorefinery and to its sustainability have been investigated.

Menon V, Prakash G, Rao M (2010). Value-added products from hemicelluloses: Biotechnological perspective Global Journal of Biochemistry, Volume 1, Issue 1, 3.

The enzymatic and fermentation routes for the conversion of hemicellulose into useful products are described in this paper.

Perez, DD, Huber P, Petit-Conil, M (2011). Extraction of hemicelluloses from wood chips and some examples of usage in the papermaking process. Colloque Inter fibres. September 6–8, 2011, Bordeaux, France.

This paper focuses on extraction of hemicelluloses from wood chips and presents some examples of usage in the papermaking process.

Ragaukas AJ (2006). The path forward for biofuels and biomaterials. Science 311(1): 484–489.

Advances in genetics, biotechnology, process chemistry, and engineering are leading to a new manufacturing concept for converting renewable biomass to valuable fuels and products, referred to as the biorefinery. The integration of agroenergy crops and biorefinery manufacturing technologies offers the potential for the development of sustainable biopower and biomaterials that will lead to a new manufacturing paradigm.

Ragauskas A J, Nagy M, Kim D H, Eckert C A, Hallett J P, Liotta C L (2006). From wood to fuels: integrating biofuels and pulp production. Indus. Biotech. 2(1): 55–65.

This review highlights the chemical resources available from wood and summarizes which biomaterials are needed for pulp production and which could be utilized for biofuels, with a special emphasis on select hemicelluloses that are currently degraded during kraft pulping that could be utilized for bioethanol production.

Towers M, Browne T, Kerekes R, Paris J and Tran H (2007). Biorefinery opportunities for the Canadian pulp and paper industry, Pulp and Paper Canada 108:6, 26–29.

The Canadian pulp and paper industry must identify new value-added products to compete. One potential pathway is the forest biorefinery. This paper reviews feedstock availability, novel products easily produced in existing facilities, and existing or emerging technologies.

Werpy T, Petersen G (2004). Top Value-Added Chemicals from Biomass, Volume I: Results of Screening for Potential Candidates from Sugars and Synthesis Gas, Pacific NorthProduct west National Laboratory, August 2004 http://www.eere.energy.gov/biomass/pdfs/35523.pdf.

This paper identifies top value-added chemicals that can be produced in a biochemical platform biorefinery.

Wising U, Stuart PR (2006). Identifying the Canadian Forest Biorefinery, Pulp & Paper Canada, 107:6, 25–30.

This paper presents an overview of certain emerging biorefinery process options and highlights the complex and ambiguous decision-making challenges that mills will face who would like to consider implementing the biorefinery.

Yunqiao P, Zhang D, Singh P, and Ragauskas A (2008). The new forestry biofuels sector. Biofuels, Bioproducts & Biorefining. 2(1), 58–73.

This review examines the major chemical constituents of biomass and the recent advances in their conversion to biofuels, with a special emphasis on the forest residues and woody-energy crops to bioethanol.

Index

'*Note:* Page numbers followed by "f" indicate figures, "t" indicate tables.'