Nonwood Plant Fibers for Pulp and Paper

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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

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

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

ISBN: 978-0-12-821800-6

For Information on all Elsevier publications
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Publisher: Susan Dennis
Acquisitions Editor: Kostas KI Marinakis
Editorial Project Manager: Samantha Allard
Production Project Manager: Kumar Anbazhagan
Cover Designer: Vicky Pearson Esser

Typeset by MPS Limited, Chennai, India

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Contents

Preface .... ***ix***
Acknowledgments .... ***xi***
List of Figures .... ***xiii***
List of Tables .... ***xv***

Chapter 1: Introduction ***1***
- 1.1 General Background 1
- 1.2 Taxonomy 12
- 1.3 Monocots (monocotyledons) 12
- 1.4 Dicots (dicotyledons) 12
- 1.5 Anatomy 12
- 1.6 Useful fibers 14
- 1.7 Nonwood fiber identification 15
- 1.8 Straw morphology considerations 15
- 1.9 Depithing 16
- References 16
- Further reading 18
- Relevant websites 18

Chapter 2: Considerations for use of nonwood fiber ***19***
- References 23
- Relevant websites 24

Chapter 3: Worldwide pulping capacity of nonwood fibers ***25***
- References 30
- Relevant websites 31

Chapter 4: Categories of nonwood raw materials ***33***
- 4.1 Categories of nonwood raw materials 33

4.2 Agricultural residues 36
    4.2.1 Sugarcane bagasse (*Saccharum officinarum*) 37
    4.2.2 Corn stalks (*Zea mays*) 40
    4.2.3 Cotton stalks (*Goossypium*) 41
    4.2.4 Rice straw (*Oryza sativa*) 43
    4.2.5 Wheat straw (*Triticum aestivum*) 44
    4.2.6 Cereal straw 45
4.3 Natural growing plants 46
    4.3.1 Bamboo (*Dendrocalamus strictus*) 46
    4.3.2 Esparto (*Stipa tenacissima*) 50
    4.3.3 Reeds (*Phragmites communis* Trinius) 51
    4.3.4 Papyrus (*Cyperus papyrus*) 56
4.4 Nonwood crops grown mainly for their fiber content 57
    4.4.1 Bast fibers 57
    4.4.2 Leaf fibers 66
    4.4.3 Seed hair fibers 71
References 73
Further reading 80
Relevant websites 80

Chapter 5: Problems associated with the use of nonwood fibers and how they are approached 83

5.1 Storage and handling 84
5.2 Pulping 89
5.3 Bleaching 90
5.4 Papermaking 91
5.5 Chemical recovery 92
References 94
Further reading 97
Relevant websites 97

Chapter 6: Handling, storage, and preparation of nonwood raw materials for pulping 99

References 104
Further reading 106
Relevant websites 106

Chapter 7: Pulping properties/pulping 107

7.1 Pulping properties of nonwoody raw materials 107
    7.1.1 Gramineous fiber materials 108

7.2 Pulping of nonwoody raw materials 111
    7.2.1 Alkaline pulping 114
    7.2.2 Sulfite pulping 120
    7.2.3 Organosolv pulping 123
    7.2.4 Chemimechanical pulping and other pulping methods 130
7.3 Washing, screening, and purification of nonwood pulp 135
References 138
Further reading 144
Relevant websites 145

Chapter 8: Bleaching 147

8.1 General background 147
8.2 Bleaching of nonwood pulps 155
References 162
Relevant websites 166

Chapter 9: Chemical recovery 167

9.1 The chemistry of silica 170
    9.1.1 Mineral composition, especially silica 170
9.2 Desilication of black liquor 171
    9.2.1 Partial desilication by raw material cleaning 171
    9.2.2 Spontaneous partial desilication of black liquor by storing (ageing) 172
    9.2.3 Desilication of black liquor by lime addition 173
    9.2.4 Desilication by black liquor by carbonation 173
9.3 Desilication of green liquor 177
9.4 Soda recovery 178
9.5 Alternative recovery processes 181
    9.5.1 Direct alkali recovery system 181
References 184
Further reading 186
Relevant websites 186

Chapter 10: Beating/refining and papermaking 187

10.1 Beating/refining characteristics of nonwood pulp 187
10.2 The papermaking performance of nonwood pulp 196
    10.2.1 The strength properties of wet paper 196
    10.2.2 The adhesion properties of wet paper 197
    10.2.3 Drainage properties of nonwood pulps 197

References 198
Relevant websites 201

Chapter 11: Use of nonwood plant fibers in specific paper and paperboard grades 203

References 209
Further reading 210
Relevant websites 210

Chapter 12: Advantages and disadvantages of using nonwood fiber for papermaking 211

References 214
Further reading 215
Relevant websites 215

Chapter 13: The future 217

References 221
Relevant websites 221

Index 223

Preface

In recent years, the three major problems that are continuing to puzzle the development of the paper industry are the shortage of resources, contamination of environment, and the level of technical equipment. The most dominating factor is the shortage of raw material resources, which is largely due to the contradiction between the structure of the raw material and the structure of the fiber resources. Thereby nonwood fibers possess a rich variety of excellent properties in physical and optical aspects, which could be used to improve their products. However, throughout the world, nonwood fiber accounts for only a small fraction of the raw material of paper and paperboard. But in some developing countries, about 60% of the cellulose fiber comes from nonwood materials, such as bagasse, corn straw, bamboo, reed, grass, jute, flax, and sisal. Particularly in China and India, 70% of the raw materials used in the pulp industry come from nonwood plants including cereal straw and bagasse, and these two countries own 80% of the total nonwood pulp production. Around the world, multitudinous nonwood fibers are used in the field of pulp and papermaking, which include annual agricultural waste and natural growth or artificial cultivation grass and so on.

This book examines the background to use of nonwood plant fibers for pulp and papermaking; worldwide pulping capacity of nonwood fibers; categories of nonwoody raw materials; problems associated with the utilization of nonwood fibers and how they are approached; pulping, bleaching, chemical recovery, and papermaking of nonwood raw materials; use of nonwood plant fibers in specific paper and paperboard grades; and advantages and drawbacks of using nonwood fiber for papermaking and future prospects. 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 and paper making from nonwoods.

Acknowledgments

I am grateful for the help of many people, companies, and publishers for providing information and granting permission to use their material. Deepest appreciation is extended to Elsevier, Springer, Wiley VCH, Appita, Hindawi, MDPI, Intech, and other open-access Journals and publications. My special thanks to Robert W. Hurter, President, HurterConsult Incorporated for providing information on use of nonwood plant fibers in specific paper and paperboard grades.

List of Figures

Figure 1.1 World paper and paperboard production and consumption (10,000 tons). 2
Figure 1.2 Portions of a typical monocot stem (left) and herbaceous dicot stem (right, 50 ×). 13
Figure 1.3 Stem cross sections of *Cannabis* (left, 100 ×) and *Linum* (right, 40 ×). 13
Figure 1.4 Fibers of bamboo (left, with parenchyma, 60 ×), linen (center, 150 ×), and cotton seed hairs (right, 150 ×). 14
Figure 1.5 Stem cross section of wheat (with part of a leaf, 50 ×). 15
Figure 4.1 SEM images of bagasse samples: (A) whole bagasse, (B) fiber, and (C) pith. 38
Figure 4.2 SEM of corn stalk fiber (with different magnification). 41
Figure 4.3 SEM image of cotton stalk. 42
Figure 4.4 Rice straw fiber. 43
Figure 4.5 SEM image of wheat straw fiber. 45
Figure 4.6 SEM image of rye straw. 46
Figure 4.7 SEM of bamboo fiber. 47
Figure 4.8 Scanning electron micrographs of esparto grass fibers. 50
Figure 4.9 Morphology of reed fibers under optical microscope. 53
Figure 4.10 Cross-sectional image of Sabai grass fiber. 55
Figure 4.11 Surface image of Sabai grass fiber. 55
Figure 4.12 (A) Longitudinal view (5000 × magnification) and (B) cross-section (180 × magnification) of jute fiber. 58
Figure 4.13 (A) Longitudinal view and (B) cross-section (100 × magnification) of ramie fiber. 60
Figure 4.14 SEM of Sunn hemp fiber. 60
Figure 4.15 (A) Longitudinal view (10,000 × magnification) of hemp fiber (Smole et al., 2013). (B) Cross-section (200 × magnification) of hemp fiber. 61
Figure 4.16 Scanning electron micrograph of kenaf bast fiber. 64
Figure 4.17 (A) Longitudinal view (10,000 × magnification) and (B) cross-section (30 × magnification) of flax fiber. 65
Figure 4.18 Manila Hemp/Abaca. 69
Figure 4.19 SEM image of Sisal fiber. 70
Figure 4.20 (A) Longitudinal view (5000 × magnification) and (B) cross-section of cotton fiber. 71
Figure 4.21 SEM images of cotton linters. 72

Figure 7.1 Process flow diagram for pulp and paper production. 112
Figure 7.2 Structures of anthraquinone and soluble Anthraquinone. 116
Figure 7.3 Cyclic action of anthraquinone. 117
Figure 7.4 Side view diagram of the pulping extruder. 134
Figure 8.1 Reaction between phenolic lignin units and chlorine dioxide. 154

List of Tables

Table 1.1 Chemical composition of hardwood and softwood. 4
Table 1.2 Percentage of types of nonwood pulp used in paper production. 5
Table 1.3 Comparison of nonwood and wood resources for pulp and papermaking. 6
Table 1.4 Users of nonwood fibers in papermaking. 8
Table 1.5 Average pulp yields of different papermaking raw materials. 9
Table 1.6 Fiber properties of some nonwood fibers. 10
Table 1.7 Fiber properties of some woody raw materials. 10
Table 1.8 Chemical properties of nonwood fibers and their comparison with woody raw materials. 11
Table 1.9 Chemical composition (%) of cereal straws. 11
Table 2.1 Reasons for use of nonwood fibers. 20
Table 3.1 Distribution of nonwood pulp production in the world. 26
Table 3.2 Estimated production of nonwood pulp in different parts of the world. 27
Table 3.3 Availability of nonwood fibers in different parts of the world. 28
Table 3.4 Production/consumption of nonwood pulp. 28
Table 3.5 Imports/exports of nonwood pulp. 28
Table 3.6 Nonwood fibers production in China (Million tons). 29
Table 4.1 Estimated annual collectable yields of various nonwood raw materials. 34
Table 4.2 Length and width of some common nonwood fibers. 34
Table 4.3 Chemical composition of some common nonwood fibers and comparison with wood fibers. 35
Table 4.4 Categories of nonwood raw materials. 36
Table 4.5 Uses of abaca fiber. 68
Table 5.1 Dry matter yields for nonwood fiber crops. 84
Table 5.2 Deterioration during storage of wood and some nonwoods. 85
Table 5.3 Problems in wet depithing. 87
Table 5.4 Generation of pollutants in wet depithing. 88
Table 5.5 Short-period continuous pulping of different raw materials. 89
Table 5.6 Typical paper machine speeds for different furnishes. 91
Table 5.7 Size of nonwood pulp mills. 93
Table 5.8 Reduction in pollution load after implementation of waste minimization measures. 93

Table 6.1 Soda pulping of wheat straw with *C. subvermispora* Strains 1 and 2 at reduced alkali charges. 102
Table 6.2 Effect of cooking time on soda pulping of *C. subvermispora* treated wheat straw. 102
Table 7.1 Delignification stages of straw and softwood. 109
Table 7.2 Reasons for faster solubilization of lignin in gramineous straw materials. 109
Table 7.3 Pulping methods for nonwoody plants. 113
Table 7.4 Properties of pulp produced with different alkaline pulping methods. 115
Table 7.5 Properties of pulp produced with different sulfite pulping methods. 122
Table 7.6 Solvents used in Organosolv pulping. 123
Table 7.7 Advantages of Organosolv process. 124
Table 7.8 Properties of pulp produced with different alcohol pulping methods. 128
Table 7.9 Properties of pulp produced with different organic acids. 130
Table 7.10 Properties of pulp produced with different chemi-mechanical pulping methods. 131
Table 7.11 Benefits from pulp washing. 136
Table 8.1 Chemicals used in bleaching processes. 148
Table 8.2 Functions of different bleaching agents. 149
Table 8.3 Advantages and disadvantages of different bleaching agents. 150
Table 8.4 Classification of bleaching chemicals. 151
Table 8.5 Physical strength properties of bleached wheat straw pulps by an OQPo sequence. 158
Table 8.6 Properties of wheat straw pulps from different stages. 158
Table 8.7 ECF bleaching of nonwood pulps. 160
Table 8.8 TCF bleaching sequences used for wheat straw pulp. 161
Table 9.1 Environmental and economic benefits of chemical recovery process. 167
Table 9.2 Presence of lignin and silica in main nonwoody raw materials in percentage. 168
Table 9.3 Problems associated with the presence of silicate ions in black liquor. 168
Table 9.4 Effect of storage on desilication of black liquor. 172
Table 9.5 Desilication of black liquor at different temperatures. 175
Table 9.6 Desilication of black liquor of various raw materials. 175
Table 9.7 Advantages of desilication of green liquor with lime. 178
Table 9.8 Effect of two-stage causticization of green liquor. 178
Table 9.9 Advantages of fluidized bed reactor. 180
Table 9.10 Cost comparison of the cost of conventional and ferrite recovery processes. 183
Table 9.11 Solubility of silica in regenerated alkali. 183
Table 10.1 Response of fibers during beating and refining. 189
Table 10.2 Factors affecting refining. 190

Table 10.3 Major effects of refining. 191
Table 10.4 Factors influencing the response of pulp fibers to refining. 191
Table 10.5 PFI-refining of enzyme-treated and control (no enzyme treatment) LF-3 pulps. 194
Table 10.6 The wet strength properties of nonwood pulps. 197
Table 11.1 Paper produced from nonwood pulps. 204
Table 11.2 Paper produced from Bagasse. 205
Table 11.3 Paper produced from Straw (cereal and rice). 206
Table 11.4 Paper produced from *Phragmites* communis Reeds. 206
Table 11.5 Paper produced from Bamboo. 206
Table 11.6 Paper produced from Kenaf (whole stalk). 207
Table 11.7 Paper produced from Kenaf (bast fiber). 207
Table 11.8 Paper produced from Esparto. 207
Table 11.9 Paper produced from Flax (bast fiber). 208
Table 11.10 Paper produced from true Hemp (bast fiber). 208
Table 11.11 Paper produced from Jute (bast fiber). 208
Table 11.12 Paper produced from Sisal. 208
Table 11.13 Paper produced from Abaca. 209
Table 11.14 Paper produced from Cotton. 209
Table 11.15 Paper produced from Ekara, Knagra & Nal grass mixed. 209
Table 12.1 Advantages of using nonwood fiber. 212
Table 13.1 Interest in the use of agricultural residues for papermaking. 219

CHAPTER 1

Introduction

Chapter outline

1.1 General Background 1
1.2 Taxonomy 12
1.3 Monocots (monocotyledons) 12
1.4 Dicots (dicotyledons) 12
1.5 Anatomy 12
1.6 Useful fibers 14
1.7 Nonwood fiber identification 15
1.8 Straw morphology considerations 15
1.9 Depithing 16
References 16
Further reading 18
Relevant websites 18

1.1 General Background

The pulp and paper industry is one of the largest industrial sectors in the world. It is supplying globally to more than 5000 million people. In the beginning, pulp and papermaking was a slow and required a large expenditure of labor. However, nowadays these processes are driven by capital intensive equipment and sophisticated paper machines running at high speed. This sector includes products such as office and catalog paper, glossy paper, tissue, and packaging paper, using more than 40% of all industrial wood traded worldwide. United States is currently one of the largest paper consumers in the world.

North American, Northern European, and East Asian companies are dominating the pulp and paper industry. In Australasia and Latin America also, there are large number of pulp and paper mills. China and India will become major players in the industry in the next few years. The worldwide production of paper and board was about 407 million metric tons in 2015 (Fig. 1.1). It is forecast to grow to 467 million tonnes by 2030 (https://www.poyry.com/news/world-fibre-outlook-2030-global-consumption-papermaking-fibre-and-specialty-pulps-has-grown-125).

> One third of the production was attributable to graphic paper and more than half of that production was attributable to packaging paper. Global paper consumption in 2020 is expected to amount to 500 million tons. The largest paper producing countries in the world are China, the United States, and Japan and account for half of the total paper

Nonwood Plant Fibers for Pulp and Paper.
DOI: https://doi.org/10.1016/B978-0-12-821800-6.00001-6

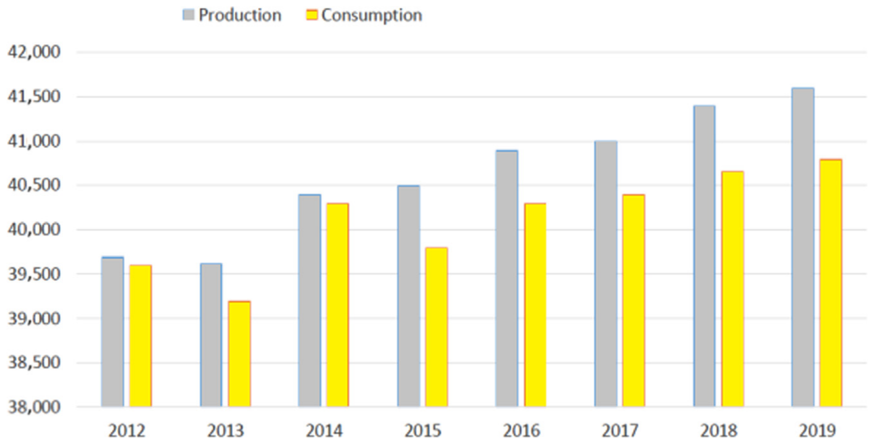

Figure 1.1

World paper and paperboard production and consumption (10,000 tons). *Source: Food and Agriculture Organization of the United Nations. From http://en.dagongcrg.com/uploadfile/2018/0211/20180211113719767.pdf*

> production in the world. Germany and the United States are the leading paper importing and exporting countries. China's production of processed paper and cardboard had ranged at about 10.68 million tons in April 2018. With some 407.5 million metric tons of paper consumed globally in 2014, the world's paper consumption is roughly equal to the amount of paper produced annually. China is the world's largest paper and paperboard consumer in the world, using more than 103 million metric tons yearly, followed by the U.S. with a consumption rate of more than 71 million metric tons. North America, however, has world's highest per capita consumption of paper of any region, consuming 221 kilograms per capita, which is given context when compared to the world average per capita consumption of paper of just 57 kilograms per year.
>
> ***Bajpai (2018a)***

Over the past 40 years, the global demand for paper has increased at an average rate of 4.7% annually. Although future growth is expected to reduce to 2%–3%, the existing woody raw materials may not be sufficient for meeting this growing requirement for paper particularly in the Eastern Europe and Asia Pacific region. Furthermore logging is coming under growing pressure from environmental organizations worried about habitat devastation and other long-term effects of forest harvesting. So, it is important to consider other type of fiber sources for meeting the possible deficit of wood fibers for producing paper. Appropriate nonwood fibers are available in abundance in several countries and are the main source of fiber for producing paper in few developing countries (www.tandfonline.com).

In actual fact, paper producers have been using nonwood fibers since paper was invented in the 1st century AD China. By the end of 19th century, wood became the major raw material for all but very special papers; and in the 20th century, nonwood fibers were utilized continuously.

Now several papers are available which need certain mechanical properties and attributes: some dielectric and electrolytic papers, casing papers used by meat processors, liquid filtration media, and several others which demand a certain appearance and/or organoleptic properties which use pulps from sisal, abaca, and flax for achieving the sought-after objectives. Moreover, with the development and growth of wet-laid (and other) nonwovens technologies commencing in the 1950s and 1960s, fibers such as jute, sisal, abaca, flax, and others such as kenaf and "true hemp" have been considered and used (paper360.tappi.org).

Generally, nonwood fibers are any type of plant material which is not classified as a tree and utilized for producing pulp and paper. There is a broad variety in the physical nature of diverse nonwood fibers delivered to the pulp mill and in the fiber properties of the pulp produced. The dissimilarity between fibers may have an effect on the mill design, selection of equipment, and the quality of pulp.

Wheat straw is generally harvested one time in a year after 6–8 weeks, so baled straw should be stockpiled for the requirement of whole year. Preparation of wood chips differs considerably. Horizontal tube digesters are typically used for nonwoods, whereas for wood Kamyr-type digesters are used. Cooking time in case of straw is shorter and the use of chemicals is lesser. The soda pulping process is generally used. Chemical recovery is quite difficult because of silica, and the drainage of straw pulp is slow, therefore a long wet end in paper machine is required. In contrast, the chipping of bamboo and giant reed can be conducted just like wood and processed in the same mill processing wood. Specialty nonwood fibers have other problems and requirements that will also vary depending on the specific fiber (paper360.tappi.org).

In general, fibers for pulp and paper are obtained from trees or agricultural crops. These include the following:

- Plant materials—wood, straw, and bamboo—obtained directly from the land.
- Plant material by-products or residual from other manufacturing processes. Examples, wood chips from sawmills, bagasse from sugar mill, and cotton linter.
- Fiber recovered from recycled paper or paperboard (Ince, 2004).

> Forest resources have important value in producing a range of different wood resources for pulp and paper-based industries. Wood resources are divided into two types which are softwood (such as spruce, pine, fir, larch and hemlock) and hardwood (such as eucalyptus and birch). Huge majority of wood resources (more than 90–92% of fibres) are used for pulp and paper production globally. These wood resources are used in many kinds of paper grades due to its smooth surface area and strong strength.
>
> ***Holik (2006), Dick et al. (2006), Jiménez et al. (2009), Sridach (2010a)***

Table 1.1 shows the comparison of chemical composition between hardwood and softwood

Wood contains largely cellulose, hemicellulose, lignin, extractives, and ash. The chemical composition varies from species to species (Henricson, 2004). Generally, hardwoods have higher cellulose lower lignin and extractives contents in comparison to softwoods. In hardwoods, the cellulose, lignin, and extractives are 43%–47%, 16%–24%, and 3%–8%, respectively, whereas in softwoods the cellulose, lignin, and extractives are 40%–44%, 25%–31%, and 10%–15%, respectively.

> Trees used to meet virgin wood fibre demand of the forest product industry are already growing except for the new fast growing plantations. Therefore, in global term, there will not be a long-term fibre shortage. However, fibre supplies within and across particular regions will tighten. These regional imbalances are already significant and will continue to grow. Asia is presently the largest fibre deficit region, followed by Western Europe. At the same time, Asia is the focus of fibre demand growth for pulp and paper. If this assessment is accurate, pulp and paper industry's dependence on virgin fibres must be reduced by expansion in the use of recovered paper and growth in the use of nonwood plant fibre in Asia.
>
> ***Chandra (1998), He and Barr (2004)***

These days, in paper industry, the environmental issues are bringing forward the requirement for clean or green technology where the new nonwoody raw materials have been introduced for replacing conventional resources such as woody raw materials with nonwoody raw materials. The cleaner technology is used for achieving higher production with smallest effect particularly on the environment and reduce the dumping expenses, steadiness hazards, and resource cost resulting in a reduced burden on the natural environment and also increase the revenues in pulp and paper industries (Sridach, 2010b). The abundance of nonwood resources in some countries made them responsible for its use in pulp and paper industry. This is considered the best method and more advantageous for nonwood fibers to be used as alternative fibers in pulp and paper industry.

Table 1.1: Chemical composition of hardwood and softwood.

	Wood types Hardwood	Softwood
Cellulose (w/w %)	43–47	40–44
Hemicellulose (w/w %)	23–35	25–29
Lignin (w/w %)	16–24	25–31
Extractives (w/w %)	3–8	10–25
Ash (w/w %)	0.2–0.8	0.2–0.4

Source: Based on Henricson, K., 2004. Wood structure and fibers. <https://noppa.lut.fi/noppa/opintojakso/bj60a1400/materiaali/2-wood-structure-and-fibers.pdf> and Koch, G., 2006. Raw material for pulp. In: Sixta, H. (Ed.), Handbook of Pulp. Wiley-VCH Verlag GmbH and Co. KGaA, Germany, pp. 21–68.

> Some nonwood fibers are used for papermaking due to their fine paper making properties but most of nonwood fibers is used for overcoming the shortage of wood fibers. The use of nonwood fibers is more common in countries with shortage of wood.
>
> *Bajpai (2018a,b)*

Several studies have been conducted on the ability of nonwood raw materials that are tobacco stalks, wheat straw, giant reed, canola straw, Tunisian alfa, vine stems, etc. as a good raw material for replacing the wood in pulp and paper industry (Gominho et al., 2001; Shakhes et al., 2011; Jiménez et al., 2002a; Shatalov and Pereira, 2006; Hosseinpour et al., 2010; Marrakchi et al., 2011; Mansouri et al., 2012; Mossello et al., 2010).

Table 1.2 represents the percentage of types of nonwood pulp used in paper production.

In Asia, the production of nonwood pulp for paper production mainly takes place in the countries that are lacking wood supply particularly China, where it is producing approximately more than two-thirds of the nonwood pulp globally for the production of paper and board (Hammett et al., 2001). Vietnam and Bangladesh are using nonwood particularly jute and bamboo as other fibers in pulp and paper industry for replacing origin wood fiber and increasing their paper production (Bay, 2001; Jahan et al., 2009).

Additionally, United States and Europe are also using nonwoody raw materials such as agricultural residues (hemp and wheat straw) for producing pulp and paper because it prevents the requirement for dumping, which is presently escalating the cost of farming and environmental worsening through pollution, fires, and pests (Chandra, 1998). Additionally, oil palm fibers (WanRosli and Law, 2011), kenaf (Ibrahim et al., 2011; Mossello et al., 2010), and banana stem fiber (Abd Rahman and Azahari, 2012) are examples of nonwood raw materials that are being explored for pulp and paper industry in Malaysia due to the copious sources, for diminishing dumping into landfill and for stopping deforestation activities. Heavy market demands and also the environmental problems due to the large use of wood supply in pulp and paper industry have increased the interest to explore nonwood fiber resources as substitution fiber which is also *environment-friendly* (González-García et al., 2010; Jiménez et al., 2002a). Thus the use of nonwood fiber is a superior option for producing pulp and paper for reducing deforestation of rain forests or primitive forests in the world including Malaysia. Nonwood plants are also the raw materials for the production

Table 1.2: Percentage of types of nonwood pulp used in paper production.

Straw	44%
Bagasse	18%
Reeds	14%
Bamboo	3%
Others	21%

Source: Based on Sridach, W., 2010b. The environmentally benign pulping process of non-wood fibers. Suranaree J. Sci. Technol. 17 (2), 105–123.

of specialty papers of higher quality (Gominho et al., 2001; WanRosli et al., 2004). Nonwoody plants have shown several advantages (Table 1.3).

> Moreover, an additional benefit for these fibre resources is it can give additional income to the farmers for food crop-waste such as straw, bagasse and grasses. Apart from the above reasons, some nonwood plant fibres are in demand for pulp and paper-making due to the special properties that make them better than wood fibre. For example, abaca is an excellent raw material for manufacturing of specialty paper, for its long fibre length and high strength properties such as tear, burst and tensile indices. In addition, sisal can be made into strong products whereas cotton linters are used for premium quality letterhead paper, currency paper, dissolving pulp and other specialty products. Moreover, bagasse and straw are best at contributing excellent formation to papers and can replace hardwood chemical pulps for printing and writing paper.
>
> ***Salmela et al. (2008), Peralta (1996), Chandra (1998), Shi et al. (2010), Sridach (2010b)***

Based on the availability, generally, nonwood fibers can be roughly divided into agricultural residues, natural growing plants (annual plants), and nonwood crops grown mainly for their fiber (Sridach, 2010b; Navaee-Ardeh et al., 2004; Jiménez et al., 2002b; Flandez et al., 2010; Hemmasi et al., 2011; Madakadze et al., 2010; Chandra, 1998).

First, agricultural residues have a lower price and the quality is moderate. These are available in abundance after harvesting season. Examples are rice and wheat straw, corn stalk, and sugarcane bagasse.

The naturally growing plants consist of bamboo (*Dendrocalamus strictus*), reeds (*Phragmites communis* Trinius), sabai grass (*Euaiopsis binata*), papyrus (*Cyperus papyrus*), and elephant or napier grass.

Table 1.3: Comparison of nonwood and wood resources for pulp and papermaking.

Growth cycle	Wood Long growth cycle	Nonwood Short growth cycle
Cellulose content	Higher cellulose content	Lower cellulose content depends on the types of nonwood
Lignin content	Contain higher lignin content	Contain lower lignin content
Chemical uses	Use a large volume of chemical during pulping process	Use a small amount of the chemical in pulping process
Pulping time	Need long time for pulping process	Shorten time for pulping process
Operation cost	Expensive due to the limitation resources	Cheaper cost because the abundance resources
Environmental impact	Increase environmental problem such as global warming and soil erosion	Reduce environmental impact which reduces the deforestation problem and improves sustainable forestry

Source: Based on Rousu P., Päivi R., Anttila J., 2002. Sustainable pulp production from agricultural waste. Resour. Conserv. Recycl. 32 (1), 85–103; Kissinger, S., Gerard, G., Victoria, M., Nicole, R., Ford, J., Kelly, S., et al., 2007. Wood and nonwood pulp production comparative ecological footprinting on the Canadian prairies. Ecol. Econ. 62, 552–558.

The third class of nonwood fiber are fiber from bast fiber, jute (*Corchorus capsularis*), ramie (*Boehmeria nivea*), leaf fibers, abaca (*Musa textiles*), seed hair fiber, cotton fiber, rags and linters, and kenaf (*Hibiscus cannabinus*). This class of nonwood fiber is the most important resource in the manufacturing of pulp and paper.

In agricultural residues, cellulose content is high and lignin content is lower in comparison to annual plants and nonwood crops. These contents in general provide the higher mechanical properties of handsheet. The chemical and physical properties of nonwood fibers also have an effect on their mechanical properties. For instance, elephant grass, in annual plants has lower lignin content and short fiber length which impart high strength properties.

The unit operations in papermaking from nonwood fibers are the same as used in the case of wood fibers. Nonwood fibers are harvested, delivered to the pulp and paper mill, stored for a certain period of time, prepared for pulping, pulped, and then brown stock is subjected to washing, screening, and cleaning. This is followed by bleaching and then papermaking. There can be significant differences depending on the type of nonwood fiber.

> 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.
>
> ***Bajpai (2018b)***

Due to environmental considerations, utilization of nonwood resources for pulp and papermaking is currently showing an increasing trend in the countries having enough supply of wood. Earlier it was found in countries having limited wood supply (Table 1.4). With time, this trend should grow further. The future of nonwood plant fibers as pulping and papermaking raw material appears promising.

> The demand for nonwood plant fibers for papermaking is expected to increase in the highly industrialized nations of Europe and North America due to the environmental concerns like 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.
>
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Three sources for nonwood fibers—agroindustrial residue, dedicated fiber crops, and naturally occurring fibers—are in general recognized.

Table 1.4: Users of nonwood fibers in papermaking.

China
India
Pakistan
Mexico
Peru
Indonesia
Colombia
Thailand
Brazil
Venezuela
United States
Greece
Spain

Source: Based on Atchison, J.E., 1995. Twenty-five years of global progress in non-wood plant fibre pulping Historical highlights, present status and future prospects. In: Pulping Conference, 1–5 October 1995, Chicago, IL. Tappi Proceedings, Book 1. Tappi Press, Atlanta, GA, pp. 91–101 and FAO, 1997. Provisional Outlook for Global Forest Products Consumption, Production and Trade to 2010. Forestry Department, Rome.

> Corn stalks and cobs, wheat and cereal straws, sugar cane bagasse, and other fibers remaining from agricultural production have economic value for production of commodity pulps on a larger scale and also for bio-energy fuels, fiberboard, and other uses. The emergence of crop residue as a valuable resource has evolved to the point where there are competing uses for it—this must be understood when considering the medium- to long-term viability of a given resource for the paper industry. Fiber crops—including abaca, bamboo, sunn hemp, kenaf, ramie, false yucca, and switchgrass, to name a few—offer the potential to develop materials to meet specific requirements. Some of these crops, such as bamboo, may be abundant and naturally occurring; however, due to their growing importance for industrial applications, they are now being cultivated as alternative agricultural crops. But there are issues to consider regarding environmental impacts of the introduction of large-scale monocultures. Naturally occurring fibers that could be used for papermaking have region-specific availability, and there are many variables depending on local conditions. The large-scale use of any of the materials obtained from these sources implies the need for development of an infrastructure, from field or processing facility forward.
>
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Like wood, the chemical and physical properties are dissimilar within the different groups depending on the nonwood fiber resources. The existing uses of nonwood pulps include almost every grade of paper-Printing and writing papers, Linerboard, Corrugating medium, Newsprint, Tissue and Specialty papers (Hurter, 2001).

Table 1.5 shows the annual yields of different papermaking raw materials.

> In general, common nonwood pulps or hardwood substitutes are produced in integrated pulp and paper mills, and softwood kraft or sulfite pulp is added for providing

Table 1.5: Average pulp yields of different papermaking raw materials.

Raw material	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

Source: Based on Pierce, B., 1991. Recycled how many times? Timber Proaucer 1991 (April), 18–21.

> the strength to the paper. Specialty nonwood pulp can be also used instead of softwood kraft or sulfite pulp thereby producing a paper having 100% nonwood. And, in few cases, waste paper pulp may be added in the furnish. The nonwood portion in the furnish usually varies from 20 to 90% and can reach up to 100% depending on the paper grade and the desired paper quality. The possible combinations are infinite and can be adjusted for meeting market needs. Moreover, it is possible to blend small amounts (up to 20–30%) of common nonwood pulps to mainly wood pulp-based papers without affecting paper properties or runnability of paper machine. This provides wood-based mills lacking 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 for adding on their fiber requirements.
>
> *Bajpai (2018b)*

> 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 ultralight weight 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.
>
> *Bajpai (2018a,b)*.

Tables 1.6 and 1.7 present the fiber properties of some nonwoody and woody fibers. Table 1.8 shows the comparison of chemical properties of nonwood fibers with those of woody raw materials. Table 1.9 shows the chemical composition of cereal straws.

Table 1.6: Fiber properties of some nonwood fibers.

Fiber source	Average length (mm)	Average diameter (μm)
Nonwood		
Wheat straw	1.5	15
Rice straw	0.5–1.0	8–10
Rye straw	1.5	13
Oat straw	1.5	13
Abaca	6.0	24
Bagasse	1.0–1.5	20
Bamboo	2.7–4	15
Crotalaria	3.7	25
Corn stalks and sorghum	1.0–1.5	20
Cotton fibers	25	20
Cotton stalks	0.6–0.8	20–30
Esparto	1.5	12
Flax straw	30	20
Hemp	20	22
Kenaf bast fiber	2.6	20
Kenaf core material	0.6	30
Jute	2.0–2.5	20
Rags	25	20
Reeds	1.0–1.8	10–20
Elephant grass/miscanthus	1.2	20
Switch grass	1.4	13
Papyrus	1.5	12
Sisal	3.0	20
Sorghum stalk	1.0–1.7	20–47

Source: Based on Atchison, J.E., McGovern, J.N., 1993. History of paper and the importance of non-wood plant fibres. In: Hamilton, F., Leopold, B. (Eds.), Paper and Paper Manufacture, Vol. 3—Secondary Fibres and Non-Wood Pulping. Tappi Press, Atlanta, GA, p. 3 and Chandra, M., 1998. Use of nonwood plant fibres for pulp and paper industry in Asia: potential in China (master's thesis). Virginia Polytechnic Institute and State University.

Table 1.7: Fiber properties of some woody raw materials.

Raw material	Average length (mm)	Average diameter (μm)
Coniferous wood	2.7–4.6	32–43
Hardwoods	0.7–1.6	20–40
Mixed tropical hardwoods	0.7–3.0	20–40
Gmelina	0.8–1.3	25–35
Eucalyptus	0.7–1.3	20–30

Source: Based on Atchison, J.E., McGovern, J.N., 1993. History of paper and the importance of non-wood plant fibres. In: Hamilton, F., Leopold, B. (Eds.), Paper and Paper Manufacture, Vol. 3—Secondary Fibres and Non-Wood Pulping. Tappi Press, Atlanta, GA, p. 3 and Chandra, M., 1998. Use of nonwood plant fibres for pulp and paper industry in Asia: potential in China (master's thesis). Virginia Polytechnic Institute and State University.

Table 1.8: Chemical properties[a] of nonwood fibers and their comparison with woody raw materials.

	Kenaf	Straw	Bagasse	Bamboo	Eucalyptus	Birch	Spruce
Holocellulose (%)	76.5	78.1	77.8	76.6[b]	74[b]	81[b]	71[b]
Hemicellulose (%)	32.6	24.1	27.9	19.5[b]	18[b]	40[b]	27[b]
Lignin (%)	16.2	18.4	20.8	23.4[b]	26[b]	19[b]	29[b]

[a] Expressed on dry matter.
[b] Extractive free basis.
Source: Based on Ashori (2006).

Table 1.9: Chemical composition (%) of cereal straws.

	Rice	Barley	Wheat	Rye	Oat
Alpha-cellulose	36.2	33.8	39.9	37.4	39.4
Pentosans	24.5	24.7	28.2	30.5	27.1
Lignin	11.9	14.5	16.7	19.0	17.5
Ash	16.1	6.4	6.6	4.3	7.2
Nitrogen	0.6	1.1	0.4	0.7	0.5
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

Source: Based on Aronovsky, S.I., Nelson, G.H., Lathrop, E.G., 1943. Pap. Trade J. 117 (25), 38—48.

> The size of nonwood fibers are between those of hardwoods and softwoods. The cellulose content of most of nonwoods is comparable to that of woods generally used for papermaking, whereas the lignin content is much lower in comparison to woods. Hence, the delignification of nonwoods is relatively easy and consumes less chemicals.
>
> ***Ashori (2006)***

International fiber consultants HurterConsult Incorporated have made an analysis of some possible candidates for Northern Bleached Softwood Kraft (NBSK) replacement (www.hurterconsult.com). Hurter (2013) has presented these candidates, along with comments about the possible opportunities and challenges for each.

Some possible nonwood substitutes for Bleached Eucalyptus Kraft pulp (BEKP) are wheat straw, bagasse, corn stalks, sorghum stalks, bamboo etc. (Byrd and Hurter, 2013). Wheat straw is available in large volume. Silica content may be a problem. New desilication processes are available. Sugarcane bagasse requires depithing and competes as a fuel source. Corn stalks is available in very large volume at a reasonable cost. Sorghum stalks are available in moderately large volume. Several thousand species of bamboo are available and can be processed in wood pulp mill. Some species have fiber length similar to BEK. Giant reed can be processed in wood pulp mill and is considered an invasive species in the

United States. Wheat straw, Corn stalk, and Sorghum stalk are harvested in 6–8 weeks and should be stored until use (Byrd and Hurter, 2013).

1.2 Taxonomy

All seed plants are members of the phylum Spermaphyta and are divided into two subphyla:

- Gymnospermae (gymnosperms have bare seeds) and
- Angiospermae (angiosperms have seeds and are placed inside the ovary of the flower).

Angiospermae are divided into two groups:

1.3 Monocots (monocotyledons)

Monocots possess one leaf in the seed. A seed leaf is a cotyledon; a peanut contains two cotyledons having a small embryo in the middle therefore peanuts are dicotyledons and consist mainly herbaceous plants. These comprise grasses, palms, lilies, and corn. A few plants having a wood-like, stem-like bamboo which are used to make pulp and paper belong to this class. Monocotyledons have parallel venation; the veins run straight across the length of the leaf without converging.

1.4 Dicots (dicotyledons)

Dicotyledoneae possess two leaves in the seed. These include kenaf, hemp, flax, and the hardwoods. There are further division into subclasses, orders, suborder, families, and few subfamilies. Branching veins are seen in the leaves of dicotyledons.

1.5 Anatomy

The primary vascular tissue comprising of xylem and phloem is present in small bundles (Fig. 1.2). The phloem is composed of several specialized cells termed sieve tubes, companion cells, phloem fibers, and phloem parenchyma cells.

In monocot stems the vascular bundles are scattered, whereas in dicot stems vascular bundles are arranged in a ring. There is no pith region in monocots. Dicot stems comprise bundles in a ring surrounding parenchyma cells in a pith region (Fig. 1.3). The scattering of the xylem remains in those monocots which experience secondary growth.

> The outer layer of cells is the epidermis. The layer inside the epidermis is the cortex. The layer inside the cortex but outside the vascular tissue is the pericycle. A cortex is an outer layer of a stem or root in a plant, lying below the epidermis but outside the vascular bundles. The cortex is composed mostly of large thin-walled parenchyma cells of the

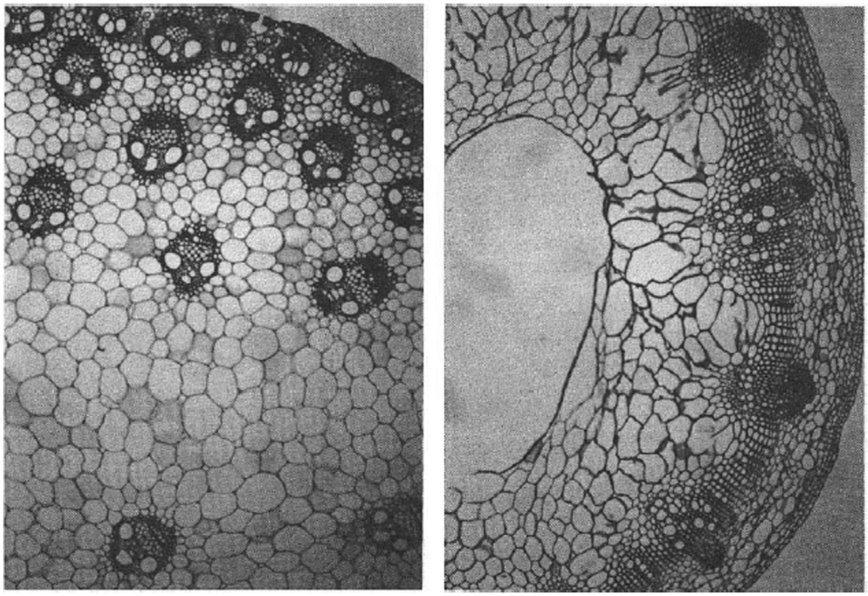

Figure 1.2
Portions of a typical monocot stem (left) and herbaceous dicot stem (right, 50 ×). *Source: Reproduced with permission from Bajpai, P., 2018b. Handbook of Pulp and Paper. Vol. 1: Raw Material and Pulp Making. Elsevier, Amsterdam.*

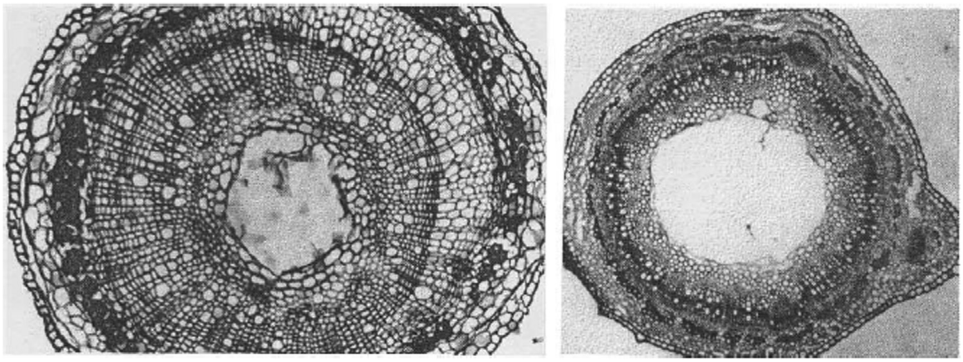

Figure 1.3
Stem cross sections of *Cannabis* (left, 100 ×) and *Linum* (right, 40 ×). *Source: Reproduced with permission from Bajpai, P., 2018b. Handbook of Pulp and Paper. Vol. 1: Raw Material and Pulp Making. Elsevier, Amsterdam.*

ground tissue system and shows little to no structural differentiation. Epidermal cells have sinuous or toothed margins and may have projections in cells termed trichomes which aid in identifying the samples.

1.6 Useful fibers

Useful fiber imparts strength to paper produced from the pulp. These are obtained from the vascular tissue of monocots of barley, *Hordeum* spp.; rice, *Oryza* spp.; esparto, *Stipa tenacissima*; wheat, *Triticum* spp.; bamboo, *Phyllostachys* (Fig. 1.4); sugarcane, *Saccharum officinarum*; and others.

Bast, fibers from the phloem of dicotyledons, is obtained from hemp, *Cannabis sativa*; kenaf, *H. cannabinus*; flax, *Linum usitatissimum* (Fig. 1.4); and others. Fibers are obtained from the pericycle or cortex of some dicotyledons. Cotton is the seed hair of the cotton plant (Fig. 1.4). Fiber from the vascular tissue of leafs is obtained from sisal (*Agave sisalina*) and manila hemp (*M. textilis*).

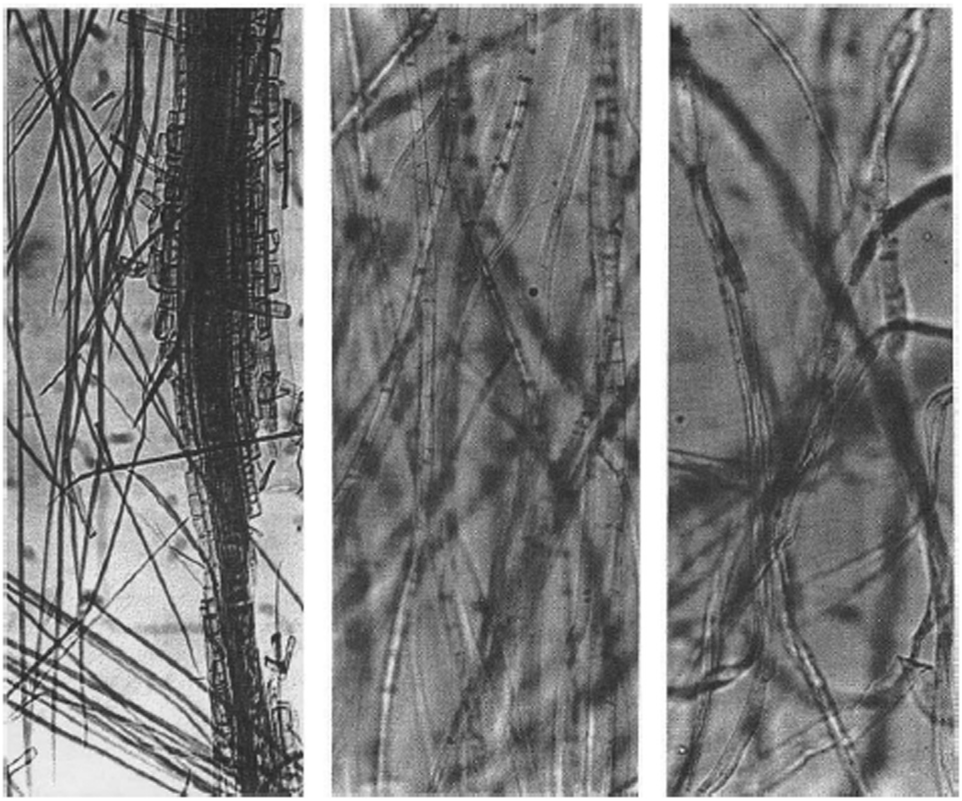

Figure 1.4

Fibers of bamboo (left, with parenchyma, 60 ×), linen (center, 150 ×), and cotton seed hairs (right, 150 ×). *Source: Reproduced with permission from Bajpai, P., 2018b. Handbook of Pulp and Paper. Vol. 1: Raw Material and Pulp Making. Elsevier, Amsterdam.*

1.7 Nonwood fiber identification

Several nonwood fibers can be identified by using several specialized stains. For instance, many stains are available for hemp and flax. Acidified potassium dichromate swells flax quicker in comparison to hemp. Cyanine stains these materials in a different manner. Other separations exist for cotton, linen, and wood; jute and hemp; animal and plant fibers; etc. (Standard T 401 and others).

1.8 Straw morphology considerations

The cross section of the straw stem is shown in Fig. 1.5. The usable fibers are the dark fibers near the edge of the stem containing phloem and other tissues.

In wheat straw parenchyma cells occupy 38% based on the cross-sectional area of the stem, therefore the mass percentage can be lesser. The size of the cells is small and cells have thin wall. These cells contribute to reduced freeness of pulp and do not have much impact on the strength properties of paper. The cooking is slower in comparison with the fiber cells and the requirement of cooking chemicals is high. The composition of the various cell types is very similar (Huamin, 1988; Bajpai, 2018b).

The alpha-cellulose content of the internode of straw of four grains is 37%–42%, whereas the leaves have only 28%–30% alpha-cellulose. The fibers are about 15%–20% longer in the nodes in comparison with the leaves. Whole straw should not be pulped

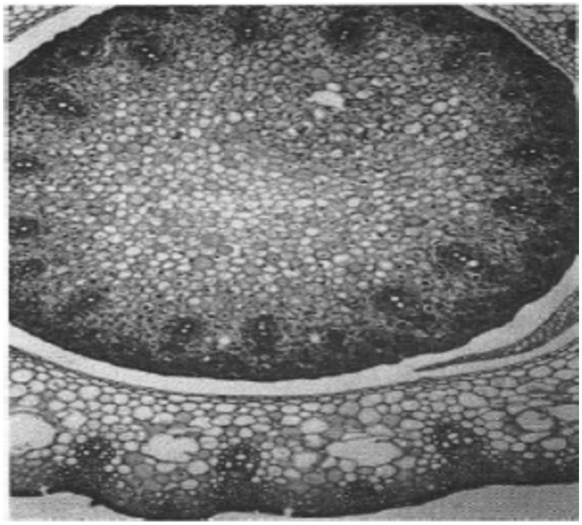

Figure 1.5
Stem cross section of wheat (with part of a leaf, 50 ×). Source: *Reproduced with permission from Bajpai, P., 2018b. Handbook of Pulp and Paper. Vol. 1: Raw Material and Pulp Making. Elsevier, Amsterdam.*

anymore than one would pulp trees with leaves and all. The internode is 35% of orchard grass (including the inflorescence) and 43%−48% of several other types of grasses (Petersen, 1991; Bajpai, 2018b).

1.9 Depithing

In bagasse, and few other nonwood fibers, the pith should be removed before use. The pith consists of small cells (parenchyma) which do not impart strength to the pulp and decreases the freeness significantly (Bajpai, 2018b).

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CHAPTER 2

Considerations for use of nonwood fiber

Chapter outline

References 23
Relevant websites 24

Nonwood fibers are being used as a raw material for papermaking for a long time (Leponiemi, 2011). In 105 AD, paper was first produced in China (Clark, 1985, Atchison and McGovern 1987). It was made from grass, wastes generated from textile industry, old rags, used fishing nets, and mulberry bark (Clark, 1985; Atchison and McGovern, 1987). Nonwoods were used for producing paper for the following 1700 years. During the second half of the 19th century the supply of annual plant fiber raw materials and textile rags was not enough for fulfilling the fiber demand in the United States and the Europe. This scarcity resulted in the development of various techniques of producing paper fibers from wood. The first pulp mill using the soda pulping process was established in the United States in 1860. Many paper mills were also built in Europe in the 1860s and 1870s. Wood was rapidly established as the major fiber source for producing paper (Gullichsen, 2000). Nonwood pulp accounts for about 10% of the world-wide pulp production for producing paper (FAOSTAT Forestry, 2010; Kneer, 2019). China is producing more than two-third of the nonwood pulp worldwide, while nonwood pulp production is fairly meager in Europe, United States, and Africa. The most extensively used nonwoods for producing paper are straw, reed, bamboo, and bagasse (Atchison, 1987, 1996; Pöyry, 2006). According to FAO statistics (FAOSTAT Forestry, 2010), "in 2009 the total worldwide production of the other fiber pulp was 19.1 million tonnes, while total pulp production for paper totaled 178.1 million tonnes." Other fiber pulp is mainly nonwood pulp, but some data collection systems may report recycled pulp as "other fiber pulp" (aaltodoc.aalto.fi). This appears to be the case when reviewing European figures as there is only one operating nonwood pulp mill in Europe. The Dunacell mill, located in Dunaújváros, Hungary, produces 23,000 ton/annum bleached flax and straw sulfate. The consumption of fibers for producing papers is predicted to grow by 1.9% in the long term. Furthermore, nonwood-based pulp produced using sustainable and environment friendly methods will hold its position as an important fiber source in Asia (Pöyry, 2010; Kuusisto, 2010). There are several reasons for use of nonwood fibers (Table 2.1).

Nonwood Plant Fibers for Pulp and Paper.
DOI: https://doi.org/10.1016/B978-0-12-821800-6.00002-8

Table 2.1: Reasons for use of nonwood fibers.

Shortage of wood fibers
Surplus of nonwood plant fibers
Fast annual growing fiber resource having smaller content of lignin than wood
Nonwood pulp can be produced at low temperatures with lower dosage of chemicals
Nonwood fiber pulping can bring additional economic benefits from the food crops
Special papermaking properties of selected nonwood plant fibers
Nonwood fiber raw materials offer a huge fiber resource globally and in North America
Nonwood fiber raw materials offer both hardwood substitutes and softwood substitutes
Virtually any grade of paper can be produced using combinations of nonwood fiber pulps
Nonwood fiber pulps can be used in combination with virgin wood pulp and recycled post consumer pulp thus stretching wood resources
Technology exists for producing pulp and paper from nonwood fiber raw materials technology
Opportunities for developing nonwood projects are endless and depend only on the nonwood raw materials available and end-products

Source: Based on Chandra, M.,1998. Use of Nonwood Plant Fibres for Pulp and Paper Industry in Asia: Potential in China. State University, Master's Thesis.

> Trees needed to meet virgin wood fiber demand of the forest products industry are already growing except for the new fast growing plantations. Therefore, in global terms, there will not be a long-term fiber shortage. However, fiber supplies within and across particular regions will tighten. These regional imbalances are already significant and will continue to grow. Asia is presently the largest fiber deficit region, followed by Western Europe. At the same time, Asia is the focus of fiber demand growth for pulp and paper, housing, and wood for fuel. If this assessment is accurate, pulp and paper industry's dependence on virgin fibers must be reduced by expansion in the use of recovered paper and growth in the use of nonwood plant fibers in Asia.
>
> *McNutt and Rennel (1997); Chandra (1998)*

Although the environmental impact of wood fiber paper production has very much improved over the last 40 years, climate change matters and sustainability have stimulated interest for nonwood pulp products. Some industrial companies visualized a chance about 20 years ago and started importing paper produced from nonwood fiber and molded products into United States and Canada. Eventually some main companies joined the campaign for serving what once was a niche market. Nowadays, millennials are driving the market for nonwood products even greater. The fastest growing market for nonwoods are represented by molded fiber products such as plates, bowls, cups, and clam shells. Whereas most is still being imported, some is now being produced in the United States using nonwood fiber products, and more is expected in the coming future. This is likely due to smaller mill capacities and reduced capital requirements. Nevertheless, it is just a matter of time before someone builds a large scale nonwood fiber pulp mill or integrated mill for satisfying the mounting need. According to Hurter, nonwoods will not replace trees as the primary material for worldwide production of pulp and paper, but they foresee that they will play an important role in the fiber mix over the next 10 or 20 years (paper360.tappi.org).

To begin with, the growth in the use of nonwood fibers will be in the fiber molded products industry. Pulp mills likely will be 100–150 tons/day or less and will need to be creatively designed to be profitable and environmental friendly. It is already happening in the United States; for instance, Aloterra in Ohio State is already producing miscanthus pulp and molded products. Other states are exploring sugarcane bagasse, industrial hemp, wheat straw, corn stover, and other nonwood fibers (paper360.tappi.org).

Eventually a few nonwood market pulp mills dotted across the United States and Canada can be seen in sites where the nonwood resources are available in abundance, either crop residues or intentionally cultivated fiber crops. These mills likely will be in the 300–500 tons/day range, producing high yield unbleached pulp suitable for packaging paper and board grades, molded products and perhaps some tissue products for instance, Columbia Pulp's proposed 400 tons/day wheat straw pulp mill in Washington State (paper360.tappi.org).

According to Hurter,

> woody nonwoods such as bamboo and giant reed offer interesting opportunities for the United States Southeast since these can be chipped and processed using existing mill infrastructures. With more than 1200 bamboo species identified worldwide, one can tailor the farm to provide a range of fiber types—softwood substitutes, hardwood substitutes or somewhere in between—depending on what you want to accomplish. In addition, it is possible to cocook bamboo or Arundo with certain species of wood. This is where I believe the first large scale use of nonwoods in the industry will occur (paper360.tappi.org).

In India, forest-based resources are rapidly diminishing whereas the demand for paper is increasing. For resolving this situation, the Indian government is providing concessions and relief for stimulating use of cellulose raw materials based on agriculture. Consequently use of forest-based raw materials has diminished and use of agricultural residues has increased. Several mills are using agricultural residues (Chandra, 1998; Gupta, 1994).

> Use of nonwood plant fibers for pulp production in China is actually becoming a matter of necessity. China is not having much wood resources. The forests are limited in size and area available for future plantation. Its total forest area is about 119 million hectares, which covers only 12% of the total land area and represents 0.12 hectares per capita in comparison to the world average of 1.1 hectares per capita. Planted forests account for about one quarter of all forested area and contribute to the raw material supply. This area under plantation is further expected to increase as the demand for wood increases. Even after expansion of the national forest, nonwood plant fibers will constitute a major source of fiber for pulp.
>
> ***Al-Simaani et al. (1992); Chandra (1998)***

> Quality trees, such as spruce, for papermaking are difficult to find. Only 7%–8% of total harvested wood, is going to the paper industry, while the amount being burned for fuel is 50–60 million m^3/year. Adding to the problem is the decades old dispute over what should be the primary raw material for the Chinese paper industry, straw, or wood.
>
> ***Xing (1995, 1996)***

> The abundance of nonwood fibers in some countries is also responsible for its use in papermaking. Sometimes, the use in papermaking is considered the best way to dispose of nonwood fibers. Jute has a long historical role in socio-economic development in Bangladesh. In recent years, jute has faced stiff competition from synthetics. As a result, demand for jute in local and overseas markets has shrunk. The situation is further aggravated by a comparatively high growth of low quality jute, from 46% to 54%, from 1977 to 1986. About 200,000 metric tons of jute, with an additional 45,000 metric tons of jute cuttings, remain as surplus in Bangladesh. The Bangladesh government is therefore exploring other possible uses of jute. Use in papermaking is one option being considered.
>
> ***Chandra (1998)***

In Vietnam, excess of bamboo led to the establishment of a pulp and paper mill. However, the availability of bamboo over the years has reduced as the percentage of land under forestation reduced significantly. Therefore, the mill used eucalyptus as additional raw material (Hamilton, 1989).

In Europe and United States, the use of agricultural residues in pulping has a further benefit as it prevents the requirement for dumping, which increases the farming cost of farming and environmental worsening through pollution, fires, and pests (Alcaide et al., 1991, 1993).

Aside from the above reasons, some nonwood plant fibers are in demand for producing paper because of very special properties which makes them better than wood fibers for producing specialty papers. Abaca is a very good fiber resource for manufacturing specialty paper. It has longer fiber length and very good strength properties which make it a better quality material for the production of thin lightweight papers having higher porosity and superb tear, burst, and tensile strengths (Peralta, 1996). It is used for making strong products such as tea bags, cigarette and filter paper, large sausage casings, currency paper, and specialty products which need higher wet strength along with high porosity.

Kenaf has many natural benefits in comparison to wood pulp. The plant is 14-foot high and grows rapidly. It allows two harvests in a year in some areas. In comparison to soft and fibrous, kenaf needs lesser energy for pulping in comparison to wood. Because lignin is absent, kenaf is naturally bright. It does not require chemical pulping or peroxide bleaching. Kenaf newsprint does not turn yellow on aging and exposure to light as that produced from wood (Rosenberg Jim, 1996).

Sisal can be converted into stronger products. Cotton linters are utilized for finest quality letterhead paper, currency paper, dissolving pulp, and other specialty papers. Bagasse and straw are found to be excellent raw materials providing superb formation to papers and are able to replace hardwood chemical pulps for writing and printing paper.

Nonwood fibers can deliver special properties to papermakers which are normally not available from wood-based fiber. For instance, fiber properties of bamboo fibers range from short, fibers of hardwood type to long, and fibers of softwood type. For tissue producers, some variety of bamboo in between these two extremes are able to produce greater softness (usually attained from imported eucalyptus pulp) and strength (usually attained from Canadian softwoods). This would make simpler the papermaking process and permit the producer of premium tissue without relying upon a 100% imported supply of fiber.

> Fiber length is another important property. Some nonwoods—most particularly hemp and flax—have incredibly long fiber length, in some cases up to 10 times greater than that of wood fibers. While such length makes traditional papermaking problematic, these fibers could act as sustainable, biodegradable reinforcing fibers for paperboard composites and other structures (paper360.tappi.org).

In several cases, addition of 10% or 20% nonwood pulp to the furnish will not have any effect on paper machine runnability, but even this apparently small percentage in the furnish will open new marketing opportunity. With the large variety of nonwoods and the several tree species, the possible combinations are almost endless. In the end, it will be all about providing a viable product with the correct specifications and fiber components which meet consumer needs.

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CHAPTER 3

Worldwide pulping capacity of nonwood fibers

Chapter outline

References 30
Relevant websites 31

The pulp and paper industry around the world has been growing rapidly. As a result there has been a huge demand for pulp and papermaking raw material. Recent years have seen a spurt in use of nonwood pulp being used as a raw material for this purpose (Ashori et al., 2004; Mossello et al., 2010). Nonwood pulp including agricultural residues (wheat/rice straw, etc.) and annual plants could be an effective source to produce pulp and paper with acceptable properties (Chandra, 1998; Madakadze et al., 2010, Rosa et al., 1999; Sridach, 2010a,b), especially in countries with insufficient forest resources, for example, China (Zhuang et al., 2005; He and Barr, 2004). The region that has invested the most time and resources into the pulping of nonwoods is Asia and the Pacific. In particular, China is the leader in the utilization of nonwoods pulp for papermaking in terms of volume (Zhan, 2010).

China has a long tradition for using nonwood raw materials for pulp and paper due to its limited forest resources and rich supply of agricultural residues and nonwood plants (Stafford, 2007). Besides, China is the biggest market of using nonwood fibers in paper, board and tissue products (Haizheng et al., 2006). However, the total production and consumption of nonwood fibers are declined with more commercial pulp mills have been built and imports from other countries (Hammett et al., 2001). It is interesting to note that some tissue mills (for household and sanitary paper production) have begun to use nonwood fibers in their products as a way to preserve the natural forests (Shi et al., 2010).

China and Rest of Asia account for around 88% of total nonwood pulp in paper and packaging, but their share has been slowly declining. Total production in 2017 was 10.4 MM tones. China accounts for over half the production of nonwood pulp and India accounts for an additional 23%. Combined, a total of 80% of the total nonwood pulp production. Latin America accounts for 5%. Table 3.1 shows the distribution of nonwood pulp production in the world in 2014 (Lyua et al., 2017).

Renewed interest in nonwood raw materials is driven by Good availability, increasing environmental consciousness/search for positive environmental image, and development of new technologies for processing these fibers.

Nonwood Plant Fibers for Pulp and Paper.
DOI: https://doi.org/10.1016/B978-0-12-821800-6.00003-X

Table 3.1: Distribution of nonwood pulp production in the world.

China	57%
Asia	22%
Europe	14%
America	5%
Africa	2%

Source: Based on Lyua, Z., Chengb, Y., Suna, H., Jianga, B., Chena, C., Lyua, Z., 2017. Cleaner production technology and cleaner production evaluation for nonwood pulping in China. In: Proceedings of International Workshop on Nonwood Pulping and Papermaking Technology. ISBN: 978-602-17761-5-5.

World production of nonwood pulp for papermaking is expected to decline from 10.4 million tonnes in 2017 to 8.1 million tonnes by 2030. China accounts for 57% of the world nonwood pulp production. Production in China forecast to decline due to tightening environmental regulations and closing down of old nonwood pulp mills. Production in Rest of Asia, North America, other regions forecast to grow.

Nonwood raw materials include a wide range of both long and short fiber raw materials. Short fibers dominate, with 93% of production. Short fiber include straw (wheat, rice), reed, bagasse, bamboo, esparto grass, oil palm bunch, coconut husks, etc. Long fiber include abaca (Manila hemp), cotton linters/combers, flax, hemp, jute, kenaf (bast), and sisal (Chandra, 1998; Pande and Roy, 1996).

Examples of novel nonwood raw material applications include Bamboo in tissue and dissolving pulp. Bagasse in nonwovens and food service boards and straw and grass fiber in tissue, packaging and molded fiber products.

Nonwood pulp is available, especially in Asia, but there is opportunity in other regions. Availability of nonwood fiber raw material is not a major limitation for expanded use. Straw might be the most important source of nonwood fiber for the pulp industry. The availability of straw is estimated at 1.3 billion BDMT/year. The global availability of other nonwood fibers amounts to another 1.3 billion BDMT (https://www.imfa.org/wp-content/uploads/2019/03/Kathren-Kneer.pdf).

Closures continue, but new capacity could eventually tip the balance the other way.

Older nonwood fiber mills are often not environmentally friendly, are small and have inadequate facilities or capital to deal with chemical and energy recovery. High capital costs required per ton of capacity for building new, medium scale, environmentally friendly wood pulp mills is making nonwood pulp more popular. New mills using nonwood fibers are generally less capital intensive and more environmentally friendly.

Nonwood raw materials include a wide range of both long and short fiber raw materials.

Short fibers dominate, with 93% of production:

- Short fiber: straw (wheat, rice), reed, bagasse, bamboo, esparto grass, oil palm bunch, coconut husks, etc.
- Long fiber: abaca (Manila hemp), cotton linters/combers, flax, hemp, jute, kenaf (bast) and sisal
- Examples of novel nonwood raw material applications are given below:
  Bamboo in tissue and dissolving pulp
  Bagasse in nonwovens and food service boards
  Straw and grass fiber in tissue, packaging, and molded fiber products

Nonwood pulp is available, especially in Asia, but there is opportunity in other regions. Availability of nonwood fiber raw material is not a major limitation for expanded use. Straw might be the most important source of nonwood fiber for the pulp industry. The availability of straw is estimated at 1.3 billion BDMT/year. The global availability of other nonwood fibers amounts to another 1.3 billion BDMT.

Estimated Production of Nonwood pulp in different regions is shown in Table 3.2 and Availability of nonwood fibers in different region is shown in Table 3.3.

Tables 3.4 and 3.5 lists the production/consumption/imports/exports of nonwood pulp.

Table 3.2: Estimated production of nonwood pulp in different parts of the world.

Abaca	0.1 Millions of tonnes/year	Philippine
Bamboo	2.6 Millions of tonnes/year	India, P.R. China
Bagasse	2.7 Millions of tonnes/year	India, P.R. China. Latin America, Africa
Cotton linters and Combers	0.3 Millions of tonnes/year	United States, Canada, Europe, P.R. China
Hemp, Flax	0.1 Millions of tonnes/year	United States, Canada, Europe, India, P.R. China
Reed	0.7 Millions of tonnes/year	P.R. China
Straw	3.6 Millions of tonnes/year	India, P.R. China, Pakistan

Source: Based on Kneer, K., 2019. Nonwood fibers: a global and regional perspective. <https://www.imfa.org/wp-content/uploads/2019/03/Kathren-Kneer.pdf>.

Table 3.3: Availability of nonwood fibers in different parts of the world.

Asia	*Straw, Reed, Bamboo, Bagasse, Cotton Linters, Flax, Hemp, Abaca*
Africa	*Bagasse*
Europe	*Flax, Hemp, Grass*
Latin America	*Bagasse*
United States and Canada	*Straw, Bagasse, Cotton Linters, Flax, Hemp*

Source: Based on Kneer, K., 2019. Nonwood fibers: a global and regional perspective. <https://www.imfa.org/wp-content/uploads/2019/03/Kathren-Kneer.pdf>.

Table 3.4: Production/consumption of nonwood pulp.

		1000 MT				
		2010	2011	2012	2013	2014
Production	World	18,284	17,718	16,015	13,927	13,189
	Asia	15,964	15,416	13,727	11,276	10,521
	China	12,970	12,400	10,738	8285	7549
	Indonesia	105	105	105	105	105
Consumption	World	18,306	17,598	16,072	13,963	13,174
	Asia	15,956	15,391	13,775	11,311	10,538
	China	12,952	12,405	10,735	8270	7520
	Indonesia	122	118	133	116	120
Imports	World	516	463	484	437	409
	Asia	183	198	222	211	205
	China	56	85	68	63	64
	Indonesia	17	14	28	12	15
Exports	World	494	582	427	401	424
	Asia	190	222	175	175	187
	China	74	81	71	78	93
	Indonesia	0	0	1	1	1

Source: Based on FAO (2014). http://www.fao.org/forestry/44134-01f63334f207ac6e086bfe48fe7c7e986.pdf; Liu, H., An, X., 2017. Current status and new development of nonwood pulp. In: China Proceedings of International Workshop on Nonwood Pulping and Papermaking Technology. Published by Center for Pulp and Paper, Ministry of Industry, Indonesia. ISBN: 978-602-17761-5-5.

Table 3.5: Imports/exports of nonwood pulp.

		1000 MT				
		2010	2011	2012	2013	2014
Imports	World	516	463	484	437	409
	Asia	183	198	222	211	205
	China	56	85	68	63	64
	Indonesia	17	14	28	12	15
Exports	World	494	582	427	401	424
	Asia	190	222	175	175	187
	China	74	81	71	78	93
	Indonesia	0	0	1	1	1

Source: Based on FAO (2014). http://www.fao.org/forestry/44134-01f63334f207ac6e086bfe48fe7c7e986.pdf; Liu, H., An, X., 2017. Current status and new development of nonwood pulp. In: China Proceedings of International Workshop on Nonwood Pulping and Papermaking Technology. Published by Center for Pulp and Paper, Ministry of Industry, Indonesia. ISBN: 978-602-17761-5-5.

Table 3.6: Nonwood fibers production in China (Million tons).

Fiber type	2010	2011	2012	2013	2014	2015
Wheat straw	7.19	6.60	5.92	4.01	3.36	3.03
Bagasse	1.17	1.21	0.90	0.97	1.11	0.96
Bamboo	1.94	1.92	1.75	1.37	1.54	1.43
Reed	1.56	1.58	1.43	1.26	1.13	1.0
Total	11.86	11.31	10.0	7.61	7.14	6.8

Source: Based on FAO (2014). http://www.fao.org/forestry/44134-01f63334f207ac6e086bfe48fe7c7e986.pdf; Liu, H., An, X., 2017. Current status and new development of nonwood pulp. In: China Proceedings of International Workshop on Nonwood Pulping and Papermaking Technology. Published by Center for Pulp and Paper, Ministry of Industry, Indonesia. ISBN: 978-602-17761-5-5.

(FAO, 2014) and Table 3.6 show the nonwood fibers production in China (Zhan, 2010).

> In 1970, the total worldwide capacity for production of nonwood fibers papermaking pulp was only 7 million metric tons. However, since that time there has been a dramatic increase in nonwood fibers pulping capacity. From 1970 to 1996, nonwood fiber pulping capacity on a global basis increased 2–3 faster than the capacity for production papermaking wood pulp. There is scope for 10%–15% of wood pulp being replaced by nonwood pulp without significantly affecting strength, optical, and surface properties of most paper grades. The percentage annual increase in the nonwood plant fiber pulp capacity is more than double the average annual increase in the wood pulp capacity, that is, 4.7% versus 2.0%.
>
> ***Ashori et al. (2004); www.tandfonline.com.***

> Straw was used for the first time as a raw material for paper in 1800, and in 1827 the first commercial pulp mill began operations in the United States using straw.
>
> ***Atchison and McGovern (1989)***

> Plant species currently used for papermaking belong to the botanical division Spermatophyta (seed plants), which is divided into two divisions, Angiospermae (seeds enclosed within the fruit) and Gymnospermae (naked seeds), the latter including the class Coniferae. Angiospermae include two classes, Monocotyledonae and Dicotyledonae. The most common plant species used for papermaking are coniferous trees of the Gymnospermae and deciduous trees of the Dicotyledonae. Nonwood papermaking plants, such as grasses and leaf fiber plants, belong to the class Monocotyledonae and bast fiber and fruit fiber plants are dicotyledons. Promising new nonwood species for fiber production have been identified in earlier research on the plant families Gramineae, Leguminosae, and Malvaceae. In northern Europe, particular interest has focused on grasses and other monocotyledons. Of several field crops studied, reed canary grass has been one of the most promising species for fine paper production in Finland and Sweden. Other grasses, such as tall fescue (*Festuca arundinacea* Schr.), switchgrass (*Panicum virgatum* L.), and cereal straw can be used for paper production. In central Europe,

elephant grass (*Miscanthus sinensis* Anderss.) has been studied as a raw material for paper and energy production.

Berggren (1989); Paavilainen and Torgilsson (1994); Janson et al. (1996); Radiotis et al. (1996); Atchison (1988); Lönnberg et al. (1996); Olsson (1993); Mela et al. (1994); Nieschlag et al. (1960); Nelson et al. (1966); Ilvessalo-Pfäffli (1995); Saijonkari-Pahkala (2001); Walsh (1997); jukuri.mtt.fi.

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Relevant websites

https://www.imfa.org/wp-content/uploads/2019/03/Kathren-Kneer.pdf

http://www.tandfonline.com

CHAPTER 4

Categories of nonwood raw materials

Chapter outline

4.1 Categories of nonwood raw materials 33
4.2 Agricultural residues 36
  4.2.1 Sugarcane bagasse (*Saccharum officinarum*) 37
  4.2.2 Corn stalks (*Zea mays*) 40
  4.2.3 Cotton stalks (*Goossypium*) 41
  4.2.4 Rice straw (*Oryza sativa*) 43
  4.2.5 Wheat straw (*Triticum aestivum*) 44
  4.2.6 Cereal straw 45
4.3 Natural growing plants 46
  4.3.1 Bamboo (*Dendrocalamus strictus*) 46
  4.3.2 Esparto (*Stipa tenacissima*) 50
  4.3.3 Reeds (*Phragmites communis* Trinius) 51
  4.3.4 Papyrus (*Cyperus papyrus*) 56
4.4 Nonwood crops grown mainly for their fiber content 57
  4.4.1 Bast fibers 57
  4.4.2 Leaf fibers 66
  4.4.3 Seed hair fibers 71
References 73
Further reading 80
Relevant websites 80

4.1 Categories of nonwood raw materials

Several types of plant fibers have been suggested for producing paper, and under test conditions several of them have produced products with acceptable properties (Hurter 1988, 1997, 2001). However, these acceptable properties are not enough for their utilization in the pulp and paper industry. Important qualities are, abundant availability of raw material, all through the year, ability to store without getting deteriorated, geographically concentrated, balanced collection and cost of storage, higher yield of better value fibers, lower cost of pulp production, and enough requirement for the product at a cost that will make certain commercial operation (Maddern and French, 1989). Estimated annual collectible yields of some nonwoody plant fiber resources are presented in Table 4.1. Fiber properties of some nonwood and wood fibers are compared in Table 4.2. Their chemical properties are

Nonwood Plant Fibers for Pulp and Paper.
DOI: https://doi.org/10.1016/B978-0-12-821800-6.00004-1

Table 4.1: Estimated annual collectable yields of various nonwood raw materials.

Raw material	Collectable as raw material*	Equivalent in bleached pulp*
Rice straw	1.4–2.0	0.4–0.6
Wheat straw	2.2–3.0	0.7–1.0
Barley straw	1.4–1.5	0.4–0.5
Rye straw	2.5–3.5	0.8–1.0
Oat straw	1.4–1.5	0.4–0.5
Sugar cane bagasse	5.0–12.4	1.7–4.2
Corn stalks	5.5–7.0	1.55–1.95
Sorghum stalks	5.5–7.0	1.55–1.95
Cotton stalks	1.5–2.0	0.6–0.8
Reeds	5.0–9.9	2.0–4.0
Kenaf, total stem	7.4–24.7	3.0–9.9
Kenaf bast fiber	1.5–6.2	0.7–3.2
Natural bamboo	1.5–2.0	0.6–0.8
Cultivated bamboo	2.5–5.0	1.0–2.1
Crotalaria bast fiber	1.5–5.0	0.7–2.5
Papyrus	20.0–24.7	5.9–7.4
Abaca	0.7–1.5	0.4–0.7
Seed flax straw	1.0–1.5	0.18–0.27
Cotton staple fiber	0.3–0.9	9 0.25–0.86
Second cut cotton linters	0.02–0.07	0.015–0.062

Source: Based on Atchison, J.E., 1989. Data on nonwood plant fibers. In: Kocurek, M.J. (Ed.), Pulp and Paper Manufacture Volume 3—Secondary Fibers and Nonwood Pulping. TAPPI press, Atlanta, pp. 5–16.

*BD metric tons per hectare per year.

Table 4.2: Length and width of some common nonwood fibers.

Common name	Scientific name	Average fiber length (mm)	Average fiber width (mm)
Abaca	*Musa textilis*	6	24
Kenaf	*Hibiscus cannabinus*	5	21
Sidal	*Agave Sisalana*	3	20
Bamboo	*Dendrocalamus arundinacea*	2.7	14
Raphia	*Raphia hookeri*	2.4	30
Sabai	*Eulaliopsis binata*	2.1	9
Common reed	*Phragmites communis*	2.0	16
Jute	*Corchorus caspsularis*	2.0	20
Papyrus	*Cyperus papyrus*	1.8	12
Sugar cane	*Saccharum officinarum*	1.7	20
Corn	*Zea mays*	1.5	18
Rice	*Oryza sativa*	1.4	8
Wheat	*Triticum aestivum*	1.4	15
Esparto	*Stipa tenacissima*	1.2	13
Albardine	*Lygeum spartum*	1.1	12
Ramie	*Boehmeria nivea*	120	50
Flax	*Linum usitatissimum*	33	19
Hemp	*Cannabis sativa*	25	25
Ceiba, kapok tree	*Ceiba pentandra*	19	19
Cotton linter	*Gossypium spp.*	18	20
Paper-mulberry	*Broussonetia papyrifera*	10	30
Sunn	*Crotalaria juncea*	8	30

Source: Based on Han (1998); Han and Rowell (1997); Duan et al., 2017. Analysis of structural changes in jute fibers after peracetic acid treatment. J. Engineered. Fibers Fabr. 12 (1), 33–42. http://www.jeffjournal.org. https://www.fpl.fs.fed.us/documnts/pdf1998/han98a.pdf.

presented in Table 4.3. The minimum fiber length required for producing acceptable paper strength properties depends on several factors, and fiber lengths are not clearly related to strength properties (Young, 1997). Different fiber lengths are required for different properties in paper. For instance, long fiber length is required for strength properties. However, they gather together and consequently do not offer good formation. Conversely with shorter fibers excellent formation is achieved (Chandra, 1998; Orgill, 1997).

Based on availability, nonwood plant fibers presently used in the paper industry can be largely divided into three groups (Table 4.4). These are agricultural residues, naturally growing plants, and nonwood crops grown mainly for their fibers (Subrahmanyam et al., 2004).

Table 4.3: Chemical composition of some common nonwood fibers and comparison with wood fibers.

Type of nonwood fiber	Cellulose (%)	Lignin (%)	Pentosans (%)	Ash (%)	Silica (%)
Bamboo	26–43	21–31	15–26	1.7–5	0.7
Sugarcane bagasse	57–66	21–31	15–26	1.7–5	1.5–3.0
Rice	28–48	12–16	23–28	15–20	9–14
Wheat	29–51	16–21	26–32	4.5–9	3–7
Barley	31–45	14–15	24–29	5–7	3–6
Oat	31–48	14–19	27–38	6–8	4–6.5
Rye	33–50	14–19	27–30	2–5	0.5–4
Esparto	33–38	17–19	27–32	6–8	–
Sabai	54–57	17–22	18–24	5–7	3–4
Switch grass		43	34–36	22–24	1.5–2
Reed (*Phragmites communis*)	44–46	22–24	20	3	2
Arundo donax		21	28–32	4–6	1.1–1.3
Jute sticks (whole jute)	47–57	15–18	–	2–5	–
Seed flax (bast)	43–47	21–23	24–26	5	–
Kenaf (bast)	44–47	15–19	22–23	2–5	–
Jute (bast)	45–63	21–26	18–21	0.5–2	–
Hemp (bast)	57–77	9–13	14–17	0.8	–
Ramie (bast)	87–91	–	5–8	–	–
Kenaf (core)	37–49	15–21	18–24	2–4	–
Jute (core)	41–48	21–24	18–22	0.8	–
Abaca	56–63	7–9	15–17	3	–
Sisal	47–62	7–9	21–24	0.6–l	–
Seed hull (cotton linter)	85–90	0.7–1.6	3–3.3	0.8–2	1
Type of wood	**Cellulose (%)**	**Lignin (%)**	**Pentosans (%)**	**Ash (%)**	**Silica (%)**
Angiosperm (hardwood)	40–45	26–34	7–14	<1	–
Gymnosperm (softwood)	38–49	23–30	19–26	<1	–

Source: Based on Han (1997, 1998). https://www.fpl.fs.fed.us/documnts/pdf1998/han98a.pdf.

Table 4.4: Categories of nonwood raw materials.

Agricultural residues
Sugarcane bagasse (*Saccharum officinarum*)
Corn stalks (*Zea mays*)
Cotton stalks (*Goossypium*)
Rice straw (*Oryza sativa*)
Wheat straw (*Triticum aestivum*)
Cereal straw
Natural growing plants
Bamboo (*Dendrocalamus strictus*)
Esparto (*Stipa tenacissima*)
Reeds (*Phragmites communis* Trinius)
Sabai grass (*Eulaliopsis binata*)
Papyrus (*Cyperus papyrus*)
Nonwood crops grown primarily for their fiber contentBast Fibers
Jute (*Corchorus capsularis*)
Ramie (*Boehmeria nivea*)
Sunn Hemp (*Crotalaria juncea*)
Hemp (*Cannabis sativa*)
Kenaf (*Hibiscus cannabinus*)
Flax tow (*Linum usitatissimum*)
Leaf fibers
Abaca (*Manila hemp*) (*Musa textilis*)
Sisal (*Agave sisalana*)
Seed hair fibers
Cotton fibers
Cotton linters
Cotton rags
Textile wastes of various type

Source: Based on Hammett, A.L., Young, R.L., Sun, X., Chandra, M., 2001. Nonwood fiber as an alternative to wood fiber in China's pulp and paper industry. Holzforschung 55, 219–224. Subrahmanyam, S.V., Godiyal, R., Janbade, V., Sharma, A., 2004. Preparation of monograph of different fibrous raw materials used by Indian paper industry. Central Pulp and Paper Research Institute Saharanpur, UP, India. <www.dcpulppaper.org/gifs/report24>; Chandra (1998). Chandra, M., 1998. Use of Nonwood Plant Fibres for Pulp and Paper Industry in Asia: Potential in China. State University: Master's Thesis.

4.2 Agricultural residues

These are produced as byproducts from harvesting and processing of agricultural crops. Agricultural residues represent an important lignocellulosic biomass category. These contain mainly cellulose, hemicellulose, and lignin.

> These materials may represent both an environmental burden, in areas where field incineration is a traditional practice, and monetary losses, considering the loss of extra-income for farmers. Agricultural wastes are of primary interest as raw materials for pulp and paper production due to their high production yields per hectare, high availability, low costs and low lignin content, which allows pulp processing in totally chlorine free bleaching facilities.
>
> ***www.cellulosechemtechnol.ro***

> These residues include straw, stalks (corn, sorghum, cotton). It is renewable in real time, while the fastest renewal time for commercial pulpwood is seven years. The cost of such plant fibre has already been pre-paid by the production of grain and oilseeds. Existing farm machinery can be used. Crop residues can be used as animal fodder, bedding, soil amendment and as energy source. Agricultural by-products are characterized by a low raw material price and moderate quality.
>
> *Chandra (1998)*

4.2.1 *Sugarcane bagasse (*Saccharum officinarum*)*

Among the several agricultural residues used for producing pulp, sugarcane bagasse shows most promise. Bagasse is the residual fiber which remains after the squeezing of sugarcanes during the production of sugar. Generally bagasse consist of 40%–60% cellulose, 20%–30% hemicellulose, and about 20% lignin. It is easily accessible and available in several countries. Bagasse is mostly found in countries which are producing large quantities of sugar, for example, Brazil, Vietnam, China, or Thailand. Although bagasse is a byproduct, several people consider it as a waste product as in the earlier period, bagasse was mostly utilized as a fuel for the production plants. Even nowadays, some bagasse is still being used for the ovens in factories ovens. However, as people started recycling materials, the value of bagasse is also increasing. These days, it is utilized for producing the packaging materials, disposable tableware and the building materials, The paper industry is now replacing wood fibers with bagasse for producing, toilet paper, cardboards, and napkins.

> Bagasse, being a by-product of the sugar industry, enjoys a unique position among the nonwood fibres for pulp manufacture, mainly due to its availability in large quantities at a central collection point. Its distinct advantage over other nonwood plant fibres is that the costs of collection, crushing, and cleaning the material are borne by the sugar mill. Bagasse is generally used as fuel in the sugar mill.
>
> *www.khartoumspace.uofk.edu*

Major problem in pulping of bagasse is the presence of high pith content of stalks, which is around 30% by weight of the stalk. The pulp is usually comparable to hardwood pulps (Casey, 1980). Bagasse has been a very good source for cogeneration in sugarcane industries and also other sectors. Length of bagasse fiber is 1.0 to 1.5 mm and diameter is ca20 micron which is comparable to hardwoods such as eucalyptus (0.7–1.3 mm length and 20–30 micron diameter) (Covey et al., 2006). Therefore bagasse pulps similar to hardwood pulp quality can be produced with appropriate production processes. In pulp and paper industry, a mill based on bagasse could be developed rapidly without the restrictions relatively to the lead times enforced by a wood based mill (www.pulpandpaper-technology.com).

Bagasse requires different type of treatment in comparison to general processing of wood chips. Bagasse when stored for longer time leads it to biological action which may quickly turn the material to harsh color degradation, deterioration of fiber properties, and yield loss. Therefore special techniques of storage are required. Presence of pith cells in bagasse are in the range of 30%–35%. This makes the material fine, thin walled having lower cellulose. Such fibers are not suitable for producing paper. Pith cells utilize large amount of chemicals, resulting in poor pulp drainage, and reduced scattering in mechanical pulps. But, effective depithing is possible. In bagasse silica content is quite low in comparison to several other nonwood fiber sources. But the amount of silica at 0.5% is 20 times more as compared to eucalyptus and it must be controlled during depithing for preserving the life of refining disks. Silica is a main problem in chemical recovery of bagasse. Chemical, semichemical, and many other types of mechanical pulp in both bleached and unbleached forms can be produced from bagasse.

Several nonwood fibers are comparable to the short fiber hardwoods and other regular pulps are so long that they must be shortened for optimizing their papermaking value. There is a extensive variation in the fiber properties of nonwood fibers in comparison to hardwood pulp for producing paper. The diameter of the fiber is smaller and has lower coarseness. The potential usefulness of these fiber properties provides ideas in pulp and papermaking. Scanning electron micrograph (SEM) images of (A) whole bagasse, (B) fiber, (C) pith are shown in Fig. 4.1 (Chimenez et al., 2013).

> The treated bagasse fiber has lower tensile index and burst index with higher bulk, tear index, and opacity compared to the untreated bagasse. So, the higher bulk and opacity improves paper's printability, while the strength properties were still acceptable when the mass removal was about 10–15%.
>
> ***www.pulpandpaper-technology.com***

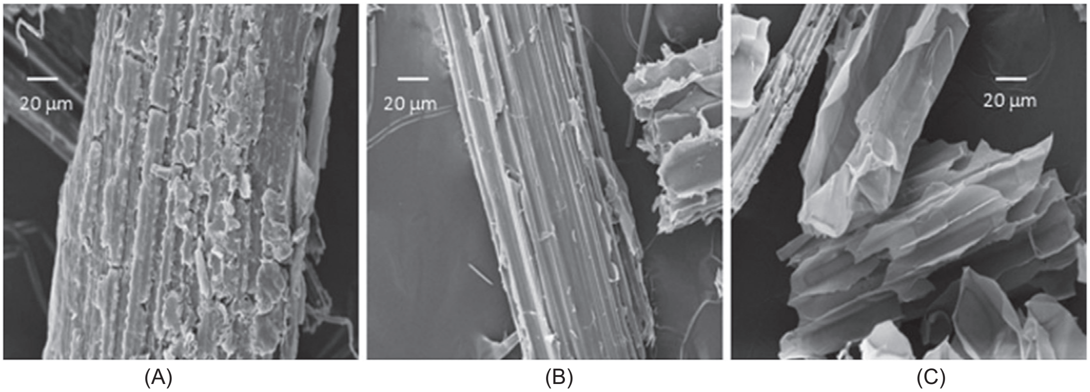


Figure 4.1
SEM images of bagasse samples: (A) whole bagasse, (B) fiber, and (C) pith (Chimenez et al., 2013).
SEM, Scanning electron micrographs.

The viscosity of bagasse is superior to regular pulp and the treated bagasse can be easily pulped to lower kappa number which requires lesser bleaching chemicals. The simplicity of recovery and the presence of lower silica in bagasse makes the process infrastructure requirement simpler and therefore there is no need for a costly recovery boiler and lime kiln.

There is a requirement of highly developed or custom manufacturing infrastructure for processing bagasse fibers. Although, industries are managing the special needs and utilize the same facility during the bagasse season, there is a good scope for developments and the unexploited market in this area.

The special needs for bagasse processing mostly stand at different stages and purposes. Several companies have machinery which can be used for bagasse and other nonwood fibers (www.pulpandpaper-technology.com).

Bagasse pulps are used to produce almost all grades of papers—newsprint, wrapping, printing, toilet, glassine, corrugated medium, linerboard, and bleaching boards. It has been also used for producing all types of reconstituted panel board (Atchison, 1987, 1989).

In Florida Vincent Corporation has been active since long in the areas of fish processing and conversion of bagasse and also forage crops. Its superior technology is keeping the production on throughout the year, by using wood and also nonwood fibers. Voith GmbH has started bagasse paper mill which is the most modern mill running successfully. It produces superior quality graphic paper from bagasse, which is difficult to produce and process. This technology is supplied by Voith Paper; covers both stock preparation and paper making. The plants using this technology for bagasse are operating in several countries—India, Bangladesh, Indonesia, and Pakistan, and Iraq.

> On a Voith Paper line, the Tamil Nadu Newsprint and Papers Ltd. have been commercially producing newsprint from bagasse in India since 1996. In the history of newsprint production, this was the first time that 100% bagasse had ever been used as raw material. Since the starting of Quena project, the full benefit of the experience was obtained in India.
>
> Special storage equipment and techniques are required to make the processed and non-processed bagasse available during the non-season. In order to decrease the disadvantage of seasonality feature and maintain a constant production a large storage capacity must be developed. However, the challenge still lies in managing the storage of bagasse because of its high in volume and low in density when compared with wood. The circumstances that need to be taken in control vary from individual site and the receiving site.
>
> www.pulpandpaper-technology.com

Machines need to be intelligent enough to work with wood and also non wood fibers for avoiding the loss during the processing of nonwood fibers.

> Bioprocess resulted in a 50% saving in energy consumption needed for pulp refining, in comparison to that recorded for refining pulp from bagasse not biologically treated. Another benefit came in the form of a 35% improvement in the paper's mechanical characteristics (tensile strength and tear resistance) without appreciable loss of material. As the traditional pulp resources exhausts, the more demand rises for nonwood fibres.
>
> Storage can be a reason for worry as sugar cane is a seasonal crop and the crushing mills operate for only about half the year, so it is usually important to store large quantities of bagasse for long periods. Unfortunately, bagasse is prone to degradation and therefore special methods of storage are required. Currently it is used as a renewable resource in the manufacture of pulp and paper products and building materials.
>
> *Covey et al. (2006); Poopak and Reza (2012); Jahan et al. (2009); www.greenseal.org*

4.2.2 Corn stalks (Zea mays)

Cornstalk is the most promising source of fiber among the agricultural residues and other nonwood fiber. The utilization of cornstalks for paper has received much publicity, mainly because of the relatively large supply of readily available fibrous material for which the farmer has no profitable use. For many years cornstalks have been proposed as a source of cellulose, and particularly cellulose pulp for paper.

> Corn is a major crop in a number of countries, and as a consequence, the stalks are considered a good fiber source for low grades of paper. The idea of corn stalk usage in papermaking has been considered, reconsidered, and abandoned a number of times due to changes in availability of fibers as raw materials. Applying corn stalks to the paper industry not only can alleviate the shortage of resources, but also make full use of straw resources, greatly reduce the pollution of straw burning.
>
> *Chandra (1998)*

> Cornstalk contains about 27% hemicelluloses, which is higher than most of the hardwoods and nonwood fiber materials. Preservation of hemicelluloses in papermaking fiber is important for increased fiber-to-fiber bonding and pulp yield.
>
> *www.fpl.fs.fed.us*

> Corn stalk offer a promising alternative to hardwood and softwood species in terms of fiber as well as energy under value prior to processing concept. Cornstalk contains more hemicelluloses than wood that can be partially extracted prior to pulping without reducing pulp and paper

Figure 4.2

SEM of corn stalk fiber (with different magnification). *SEM*, Scanning electron micrographs. *Source: Reproduced with permission Cheşca, A.M., Nicu, R., Tofanica, B.M., Puitel, A.C., Vlase, R., Gavrilescu, D., 2018. Pulping of corn stalks—assessment for bio-based packaging materials. Cellul. Chem. Technol. 52 (7–8), 645–653.*

> quality. The hemicelluloses in the form of fermentable sugar were extracted to produce ethanol. The average fiber length of cornstalk pulp is similar or better than hardwood pulp. Cornstalk pulp can serve as an important raw material for printing, writing and specialty grades paper.
>
> ***Ahmed and Zhu (2006); Chesca et al. (2018); www.fpl.fs.fed.us***

The structural features of corn stalks resemble with sugarcane. Average fiber length is 1.5 mm (0.5–2.9 mm) and average fiber width is 0.018 mm (0.014–0.024 mm). Typical fibers are quite narrow, have thick wall and blunt, or pointed ends (Ilvessalo-Pfaffli, 1995). SEMs of corn stalk fiber are shown in Fig. 4.2 (Cheşca et al., 2018).

*4.2.3 Cotton stalks (*Goossypium*)*

The biomass which remains in the field after picking up the seed cotton is called cotton stalk. It is possible to get about three tonnes of stalks per hectare. However, with hybrids the yield is more. Under irrigated conditions the stalk yields are more than in rainfed crop. Cotton is being produced in more than 80 states in the World, which produce the enormous amount of cotton stalk (Wang et al., 2016). The holocellulose content is high in cotton stalk. It contains about 60% holocellulose, 7% lignin, and also 7% ash. The composition is comparable to the most common hardwoods in respect of fibrous structure not like other

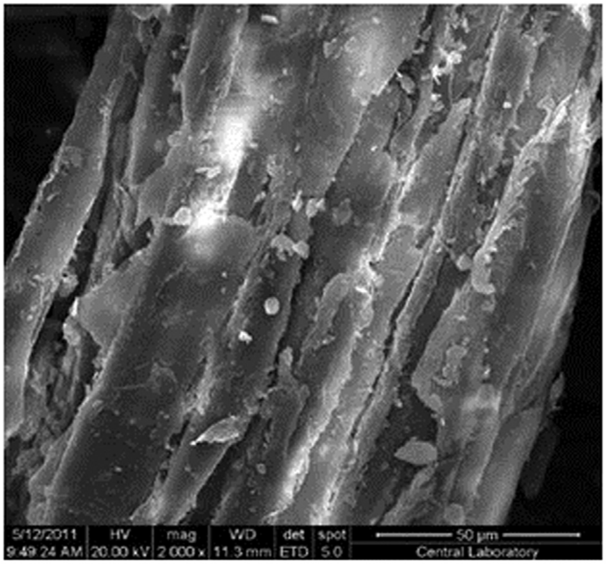


Figure 4.3
SEM image of cotton stalk. *SEM*, Scanning electron micrographs. *Source: Reproduced with permission Haykira, N.I., Bahcegulb, E., Bicakc, N., Bakir, U., 2013. Pretreatment of cotton stalk with ionic liquids including 2-hydroxy ethylammonium formate to enhance biomass digestibility. Ind. Crop. Prod. 41, 430–436.*

agricultural crop residues. SEM image of cotton stalk are shown in Fig. 4.3 (Haykira et al., 2013).

Several studies have been carried out with cotton stalk for producing paper (Jahan et al. 2001, 2002). Good results have been obtained with cotton stalk pulp in combination with other pulps for producing paper of good quality. The average fiber length of cotton stalk fibers is 0.6–0.8 mm and diameter is 0.02–0.03 mm (Alcaide et al., 1991, 1993; Ilvessalo-Pfaffli, 1995).

> Cotton stalks are available in large quantities in several parts of the world. The stalks contain a substantial percentage of pith cells which, together with the dark-colored outer bark, create problems in both pulping and papermaking process. Two major problems have hindered commercial utilization of cotton stalks for production of pulp and paper. The first problem is that of transportation of the raw materials, which are bulky in nature. This problem can be solved to some degree with densification techniques. The second problem is that of debarking, which is made difficult due to the fact that cotton stalks are thinly-branched, bushy plants. The chemical and morphological properties of cotton stalks are comparable to hardwoods. The pulp yield is about 40–45% with kappa number 30–35. The SR number of unbeaten cotton stalks pulp is about 12–15. The tensile strength of cotton stalks pulp is very high but tear index is very low. Blending cotton stalks pulp with jute pulp could increase tear index. The bleachability of cotton stalks pulps is very good in ECF bleaching.
>
> ***www.fao.org***

4.2.4 Rice straw (Oryza sativa)

Rice straw, is available in abundance in countries short of wood such as China, India, Bangladesh, etc. and can be used for producing paper. Rice straw is generated in nearly equal quantities during grain production and can be obtained by paper mills at reduced cost (Yee et al., 2019). But rice straw is expensive to collect and store, and has a very amount of silica. Inspite of these shortcomings, it is a preferred fiber source in countries short of wood, because of its ready availability. Rice straw fiber has an average fiber length of 1.4 mm and the average fiber width is 0.009 mm (Ilvessalo-Pfaffli, 1995). Fig. 4.4 shows the appearance and the SEM image of the rice straw fiber (Ota and Uehira, 2012).

Rice straw is used for producing printing and writing paper, glassine and greaseproof paper, duplex and triplex paper, corrugating medium, strawboard, and "B" grade wrapping paper.

When the rice straw is burnt openly harmful green house gases are generated and released in to the air causing serious problems to global air chemistry and human health. Therefore it is a double benefit option (for farmers as well as industries) for using rice straw for producing paper.

In terms of production share, it is the third most important crop in China, next to wheat straw and corn stover (Shao et al., 2017), and it accounted for approximately 14% of total straw production (including wheat straw, corn stover, sugar cane, cotton stalk, hemp, etc.) in 2008 (Zhou et al., 2011; Li et al., 2012). Part of it is used for livestock, compost, barnyard manure, etc., but the vast majority of it is burned in the field, which is a waste of an important resource and causes increased air pollution (Zhang et al., 2017). It is hoped that the conversion of rice straw into biorefinery products will become commercialized to make full use of the plant, but examples, such as the successful application of a digester mainly from rice straw, remain sparse. Over the last 20 years, it is impressive how much the mass production of pulp from rice straw has grown,

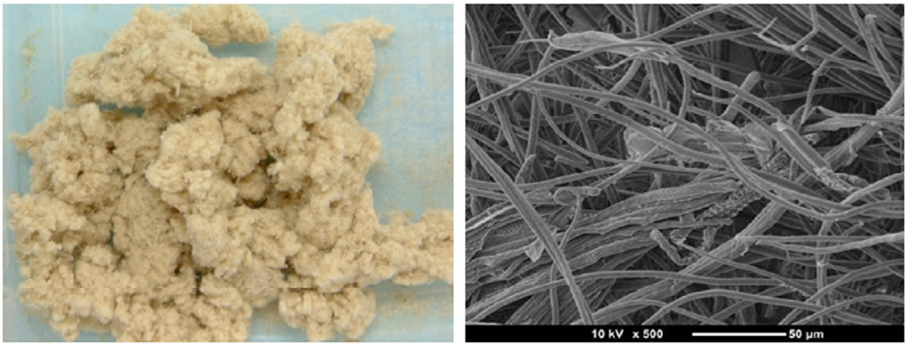


Figure 4.4
Rice straw fiber. *Source: Courtesy of WIT Press from Ota, T., Uehira, A., 2012. Development of green composites using agricultural waste. WIT Transactions on The Built Environment, vol. 124. WIT Press. https://doi.org/10.2495/HPSM120361, ISSN 1743-3509 (on-line). www.witpress.com.*

and this has had a huge impact on the development of the Chinese paper industry due to its compensation for an acute shortage of wood. It is well known for rice straw to have low lignin content, approximately 52 ± 16 g/kg rice straw (Van Soest, 2006). And it is a fibrous material suitable for papermaking, besides the characteristics of its easy pulping, because of its high percentages of cellulose and hemicellulose, in the range of 32%–47% and 19%–27%, respectively (Binod et al., 2010).

*4.2.5 Wheat straw (*Triticum aestivum*)*

Wheat straw is a renewable raw material that is available in abundance in several parts of the world. Wheat straw is nonwood agricultural waste which is serving as an excellent fiberous resource to recycle into quality paper in many parts of the world. Wheat straw is the stalk which is left after wheat grains are harvested. Usually it has been treated as a waste. In few countries, farmers burn it, contributing to air pollution and causing a public health hazard. But, these stalks still have value. Wheat straw has 34%–40% cellulose, 20%–25% hemicellulose, and 20% lignin (Yaqoob et al., 2011). The chemical composition varies according to the wheat straw genetics, geographic conditions, and pulping condition of pulp straw. Other constituents are the silica, ashes, and extractives.

Straw was in-fact an important source of fibers for the paper industry in Europe, Canada, and United States until the wood pulp industry was fully established. Presently straw is being used in areas where wood is in short supply (specifically in Europe, Asia, Africa, and Central and South America). Average length of wheat straw is 1.4 mm (0.4–3.2 mm) and width is 0.015 mm (0.08–0.034 mm). Usually fibers are somewhat narrow, have a thick wall, and possess a blunt or pointed ends (Ilvessalo-Pfaffli, 1995).

SEM image of wheat straw fiber is shown in Fig. 4.5 (Zheng et al., 2018).

It is used for producing printing and writing paper, glassine and greaseproof paper, duplex and triplex paper, corrugating medium, strawboard, and “B” grade wrapping paper.

> India is the second largest producer of wheat in the world, with production hovering around 68 to 75 million tonnes for the past few years. It accounts for approximately 12% of world’s wheat production, and is the second largest wheat consumer after China. The latest estimated demand for wheat production for the year 2020 is approximately 87.5 million tonnes, or about 13 million tonnes more than the record production of 75 million tonnes harvested in the 1999–2000 crop season. In India, three species of wheat are cultivated: Triticum aestivum, Triticum durum, and Triticum dicoccum. Although around 60 varieties are grown by farmers in the various zones, only a few varieties occupy substantial area. Presently, the most dominant variety in India is Triticum aestivum PBW-343, which occupies around 6 million ha.
>
> ***FAO (2004); Nagarajan (2005); Gupta (2004); Joshi et al. (2007); www.ncsu.edu***

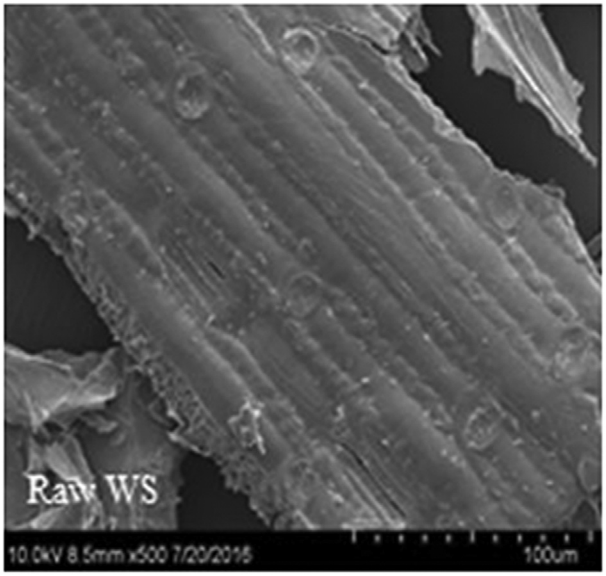


Figure 4.5
SEM image of wheat straw fiber (Zheng et al., 2018). *SEM*, Scanning electron micrographs.

Wheat straw possesses superior quality for papermaking in comparison to other nonwood fibers such as sunflower and cotton stalk, vine shoots, and because of its higher breaking length of paper (Hou et al., 2011, Rudi et al., 2016; Alcaide et al., 1993; Khristova et al., 1998; Ververis et al., 2004; López et al., 2013). The amorphous structure having much lower degree of polymerization (100−200), and reduced lignin content of cereal straw makes its chemical processing comparatively easier, particularly for nonsulfur processes (Jahan et al., 2012; Resalati et al., 2012; Garcia et al., 2013; www.lignocellulose.ir).

4.2.6 Cereal straw

The cellulosic fibers of nonwood species, for instance residues of agricultural and agrifood industries, are very suitable for producing papers with unique characteristics because of their suitable morphology, composition, and heterogeneity (García Hortal, 2007; González-García et al., 2010). Many kinds of cereal straw are utilized including those from rye (*Secale cereale*), oat (*Avena sativa*), and barley (*Hordeum vulgare*). Among these rye is the most appropriate for pulp production because of its availability, and the higher yield and strength properties of its pulp (Chandra, 1998; Hammett et al., 2001). Therefore it is most suitable for pulp production. SEM image of rye straw is shown in Fig. 4.6 (Domanski et al., 2016).

> To date, several residues of agricultural and agri-food industry have been studied (orange tree pruning, vine shoots, cereal straws, palm oil waste (EFB), etc.) Among all these nonwood raw materials, cereal straws are a very important source of raw material.

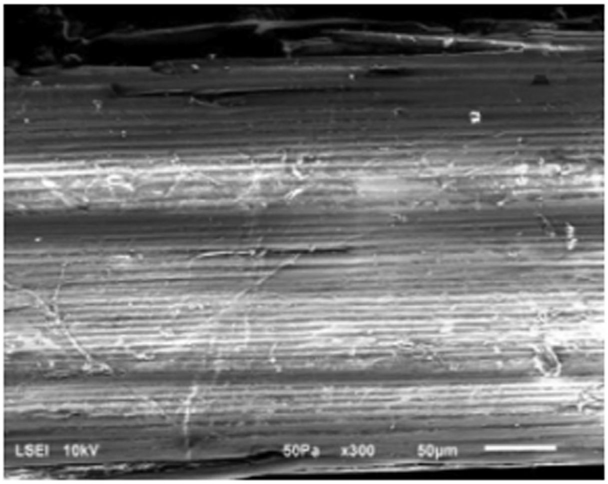


Figure 4.6

SEM image of rye straw. *SEM*, Scanning electron micrographs. *Source: Reproduced with permission Domanski, J., Borowski, S., Marchut-Mikolajczyk, O., Kubacki, P., 2016. Pretreatment of rye straw with aqueous ammonia for conversion to fermentable sugars as a potential substrates in biotechnological processes. Biomass Bioenergy 91, 91–97.*

According to FAO in 2009, the world production of wheat, barley, maize, oats, and rapeseed was 1,742 million tonnes. Considering that one kilogram of cereals generates approximately one kilogram of residue (straws), this agricultural activity creates a large quantity of residue each year. Such materials are used, nowadays, at best and in small quantities, as organic amendment and food for cattle, but mostly they are burned directly in the field, which causes pollution and fire risk.

Berrocal et al. (2004); Navaee-Ardeh et al. (2004); Huang et al. (2006); Rodríguez et al. (2008); Jiménez et al. (2009); Rodríguez et al. (2010); Chen et al. (2011); Ferrer et al. (2011); González et al. (2011); Hou et al. (2011); Fatehi et al. (2010); Vargas et al. (2012); Rodríguez et al. (2010); www.ncsu.edu

4.3 Natural growing plants

4.3.1 Bamboo (Dendrocalamus strictus)

In China paper has been made from bamboo for more than 1500 years. In the recent years, demand has grown significantly as the consumers are looking for environmentally friendly products from sustainable raw materials. In response to this demand, paper producers are introducing new paper products from bamboo to the market having comparable strength properties, brightness, and printability to paper manufactured from wood pulp (www.bamboogrove.com).

Bamboo usually grows in warm tropical weather. Bamboos have not even geographical distribution and are found mainly in the natural vegetation of several parts of the world.

The bamboo pulp is one type of paper pulp such as wood pulp, straw pulp, or reed pulp. The fiber dimension of bamboo is in between wood fiber and straw fiber (Galaleldin Insaf, 2004). SEM of bamboo fiber is shown in Fig. 4.7 (Júnior et al., 2014).

Bamboo is a highly sustainable raw material. Bamboo grows very fast. Some species grow more than a meter a day. In marked contrast to trees which need several years to recover from harvesting, bamboo gets matured in a period of 3–5 years or less. When bamboo is cut, the stem is left in the soil; a new shoot sprouts and the growth process begins again. Bamboo prospers in depleted soil. In areas where rainforests have been unambiguous and burned, bamboo is one of the few plants which grows without problems and starts the process of returning nutrients to the soil. Bamboo is able to grow on hillsides and on sharp slopes where few other bumper crops can. Bamboo helps in reducing soil erosion. The rhizomes of the bamboo plant branch out from the stalk. This helps in securing soil from erosion and hold valuable soil moisture. This also helps in preventing silt from choking rivers and streams and affect aquatic life.

Bamboo grows in two clearly different forms, that is single stemmed or densely clumped. They are able to grow fast, and reach their full height of 15–30 m in 2–4 months by long growth rates of 20–100 cm. The diameter of the stem is generally 5–15 cm. Maturity is

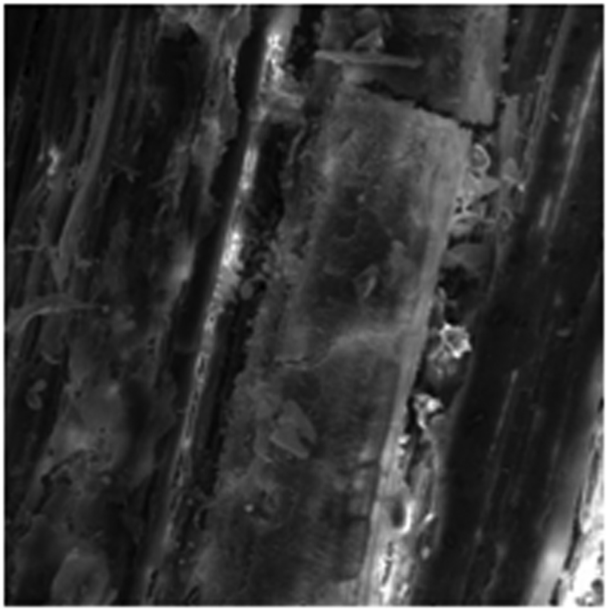


Figure 4.7

SEM of bamboo fiber. *SEM*, Scanning electron micrographs. *Source: Reproduced with permission Júnior Ae, C., Barreto, A.C.H., Rosa, D.S., Maia, F.J.N., Lomonaco, D., Mazzetto, S.E., 2014. Thermal and mechanical properties of biocomposites based on a cashew nut shell liquid matrix reinforced with bamboo fibers. J. Compos. Mater. 49 (18).* http://doi.org/10.1177/0021998314545182.

attained when the culm is 3−4 years old (Ilvessalo-Pfaffli, 1995). There is variation in the fiber length of bamboo from species to species. In some species there is variation from bottom to top and, in some cases, with intermodal length. Average fiber length and average fiber diameter is 2.7−4.0 mm and 0.015 mm, respectively (Ilvessalo-Pfaffli, 1995). Bamboo is used for making printing and writing paper, bristol board, duplex and triplex paper, linerboard, wrapping and bag paper, multiwall sack, and newsprint substitute.

Bamboo pulp is used for making bamboo paper. This paper is strong and has extensive uses (Chen et al., 2019). The bleached bamboo paper is utilized for producing offset paper, typing paper, and high quality culture paper. The unbleached bamboo paper is mostly used in packaging. Apart from this, bamboo pulp and wood pulp are blended and used for producing cable paper, insulation paper, and cement bag paper.

> Bamboo fiber is the best fiber materials for papermaking after the softwood fiber because some kinds of bamboo have long fiber and same features as softwood. Bleached bamboo pulp has better tearing strength and evenness compared to the hardwood pulp. As the cost of bamboo pulp is lower than wood pulp, the need for bamboo pulp increases continuously. In 2010, bamboo pulp takes 0.56% of Chinese pulp capacity. Bamboo pulp has great market potential in China. As for the international market, it is affected by the production or stock of main pulp exporting countries and pulp consumption. The pulp price is changed by the trend of world economic development. Because the bamboo pulp has the similar property with softwood pulp and hardwood, the price of bamboo pulp can reference the price of hardwood pulp.
>
> ***www.paperpulpingmachine.com/applications/bamboo-pulp-making/***

Bamboo is generally found in subtropical and tropical areas. The major areas where bamboo is being produced are the Asian-Pacific Region (I), the Americas Region (II), and Africa (III) (Mera and Xu, 2014). About 80% of bamboo forest lands in the world are in the Asia and Pacific regions. India and China together account for about 70% of the bamboo forest in Asia. Coincidently several developing countries lacking wood have rich bamboo resources.

> From the view of forest conservation or sustainable economic development, bamboo is an important nonwood fiber raw material for pulping and papermaking, especially in these developing countries. In fact, bamboo has been an indispensable fiber raw material for papermaking industry in the India subcontinent and China. Compared with wood, bamboo has the advantages of a short growth cycle (3 to 5 years), self-reproduction, and low cost in maintenance and regeneration. Bamboo is reputed as the second forest. As a fast growing graminaceous plant, bamboo contains 57 to 65 wt% cellulose, 27 to 30 wt% hemicellulose, and 4.9 to 5.0 wt% lignin. Considering its chemical composition, bamboo is a better fiber raw material for pulping and paper making compared with other nonwood fibers such as rice/wheat straw, reed, and bagasse. Bamboo fibers are comparable to hardwood fibers in several fiber characteristics, i.e., the fiber length, aspect ratio, and fibrous cell wall cavity ratio.
>
> ***Wei et al. (2016)***

> Accompanied with the rapid economic development, China has become the largest paper production and consumption country in the world during the last decade. Simultaneously, a great change in the raw material structure of the pulp and paper industry has taken place in China. The proportion of nonwood fibers in the pulp and paper industry of China has exhibited a gradual decrease. However, due to shortage of wood resources, utilization of nonwood fibers remains important in China. The total production capacity of bamboo pulp in China reached 2,400,000 tons in 2017, and most of the bamboo pulps (about 80%) are for the production of household paper grades. It is worth noting that household paper grades prepared from unbleached bamboo pulp have become a welcomed product for customers and have achieved encouraging commercial success in China.
>
> ***www.bioresources.cnr.ncsu.edu***

For promoting use of bamboo for production of pulp, local governments are providing support in China for plantation of bamboo and improving the transport conditions. A special subcommittee of Bamboo Pulp Working Committee was formed in 2016 under the China Paper Association for accelerating the development of bamboo pulping technology and enhancing the cooperation between paper mills and research institutes.

Bamboo has become a very important reinforcing fiber in Asian countries, particularly in India and China, on the one hand, because of its large availability and on the other hand due to its shortage of softwood in these regions.

> Two large pulp and paper mills in India are producing about 200,000 t/year paper pulp exclusively from bamboo. A new bamboo based pulp mill has been installed in China with a capacity of 200,000 tons per year bleached pulp production using the TCF bleaching sequence. A pulp mill in Thailand is reported to produce 210,000 ton per year, making pulp largely from bamboo by the SuperBatch cooking system, oxygen delignification, followed by ECF bleaching sequence. There are over 1,000 species of bamboo throughout the world, growing in a wide range of climates and regions. Morphological properties and pulping behavior of different bamboo species have been studied and wide variation in fiber dimensions has been reported among the species, but no significant differences in the chemical composition of bamboo chips or pulps have been found, nor in the amount of alkali consumed during pulping. The chemical properties of different species of bamboo, viz. Bambusa vulgaris, Bambusa stenostachya Hackle, Neosinocalamus affinis and Bambusa balcooa, have been analyzed and reported.
>
> ***Tian et al. (2010); Mittal and Maheshwari (1999); Singh et al. (1976); Alves et al. (2010); Chang et al. (2013); Zhang et al. (2016); Vena et al. (2010); www.cellulosechemtechnol.ro***

> Bamboo provides jobs and economic development. In economically depressed areas where unemployment and lack of income foster civic unrest, bamboo offers farmers a viable cash crop and jobs in bamboo paper mills give residents a chance to provide a higher standard

> of living for their families. The exportation of bamboo paper products also allows poor countries a chance to build their economies and provide better roads and services.
>
> *www.bamboogrove.com/bamboo-paper.html*

4.3.2 *Esparto (*Stipa tenacissima*)*

Esparto is also called Esparto grass. It is one of two types of gray-green needle grass (*Lygeum Spartum* and *Stipa Tenacissima*). It is a perennial grass grown in northwest Africa and the southern part of the Iberian Peninsula used for crafts (cords, baskets, espadrilles, etc.). It is native to southern Spain and northern Africa. It can withstand desert conditions and is able to live by the coast. It has stiffer, rush-like leaves, and can grow in rocky soil on high plains. It is able to grow up to three or four feet in height. Its stems are cylindrical and grow in clusters. The plants are young they serve as forage but when they get matured they possess a lot of strength and flexibility. For several years the grass has been used in several different crafts for making ropes, sandals, baskets, mats, and other useful things. Esparto leaves are also used in producing paper.

The fiber produces a better quality paper often used in producing books. Fig. 4.8 shows the SEMs of esparto grass fibers (Maghchiche et al., 2013).

It was first used in Great Britain in 1850 and is being widely used there and in Europe, but it is seldom found in the United States due to the cost of transport. It is generally blended with 5%–10% wood pulp. The “Spanish” grade is generally considered as the better-quality, whereas the “Tripoli” grade, from Africa, is the lesser in quality. The fibers are

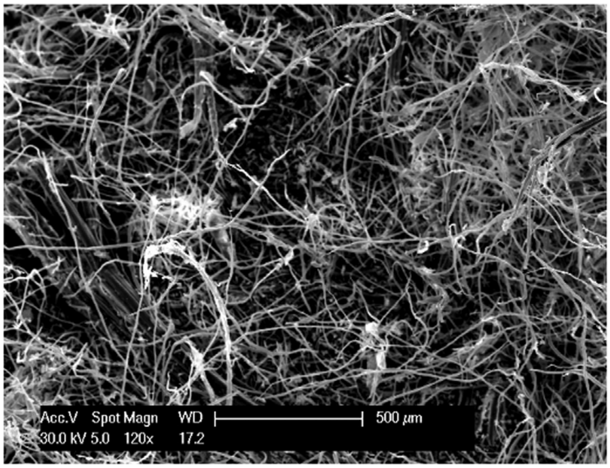


Figure 4.8

Scanning electron micrographs of esparto grass fibers. *Source: Reproduced with Permission Maghchiche, A., Haouam, A., Immirzi, B., 2013. Extraction and characterization of Algerian Alfa grass short fibers (Stipa tenacissima). Chem. Chem. Technol. 7, 339–344.*

somewhat shorter in relation to their width; but do not produce large amount of dust. Due to the shorter fiber length, the tensile strength of the paper is lesser in comparison to those of several other papers, but its resistance to shrinkage and stretching is greater, and the paper is a well-filled, dense paper with superb inking qualities and folding properties.

Esparto grass grows wildly in United States, Canada, and in the Mediterranean steppe areas of southern Spain.

> The grass is usually grayish green in color, occurs as long rolled up leaves reaching lengths of 1 m. It is coarse and strong and grows in bunches about 3 m in diameter. Where growth is prolific, the clumps tend to merge into one great mass for covering several square miles. About 12 to 15 years is needed for establishing esparto from seed to a form appropriate for harvesting.
>
> *Chandra (1998)*

> The quantity of cellulose contained in this plant, the flexibility, the smoothness and the mechanical resistance of its fibres confer to it the very required properties in papermaking; qualities recognized since a long time. The esparto grass is a resistant plant to much branched rhizome, forming initially the compact stocks then becoming circular with the deterioration of the old branches. Esparto grass resists at the great variation of temperature (−19 °C) in Rogassa region in the Algerian western south, while supporting the very hot summers (+40 °C). The optimal photosynthetic activity of the esparto takes place at the temperatures ranging between 15 and 25 °C. The relatively low temperatures lower than 4°C, slow down the assimilation and delay germination.
>
> *www.chem.asu.ru/chemwood/volume11*

Beginning in the middle of the last century, esparto grass is grown in Algeria and parts of southern Spain. It became a very important resource for producing fine papers. The fiber are obtained from the leaf of the plant. In hot weather, leaves roll into tubes as they get ripened, giving a superficially solid look. They are pulled out in bunches and compressed into bales for shipping. Not like the stems, the leaves do not have nodes and are comparatively easier to pulp, which is generally conducted with the soda pulping process (McDonald, 1969).

Fibers of esparto are slim and round. The diameter is around 0.01 and the length is over one mm. They have very small canal or lumen and so are very springy. These fibers are fine and short, and produce a bulky, smooth, well formed paper which is outstanding as the major ingredient for fine printing and lithographic paper (Clark, 1985).

*4.3.3 Reeds (*Phragmites communis *Trinius)*

Reed is one of the most commonly distributed wetland plant genera in the world.

> The most commonly used reed is a tall perennial grass, which grows generally in marshes. Reeds grow abundantly in swamplands, river bottoms lands and delta areas of

> Russia, Romania, Egypt, northern China, North Korea and Spain. Depending on conditions, such as soil characteristics, hydrologic condition, amount of nutrients, and pH, the diameter will vary from 9 to 22 mm and the height from 2.5 to 5 meters. The plant is mature by the end of September the beginning of October, but it is necessary to allow an additional 4–6 weeks to complete the food accumulation in the root stock, which will ensure the following year's reproduction. In April, the young stalks contain as much as 80% moisture. By July, this moisture content is down to 60–65% and as low as 26–27% in December. The decrease in moisture content helps control the degradation of reed in storage and reduces the cost of transport. The leaf sheath is deficient in cellulose and may contain up to 10% silica, and are consequently discarded at harvest. Fiber length of the stalk ranges from about 0.35 to 3.35 mm with an average of 1.8 mm and the fiber width varies from 0.006–0.022 mm with a average of 0.014 mm. In blends of various proportions, it is used to make printing and writing paper, duplex and triplex paper, corrugating medium, linerboard and b grade wrapping paper.
>
> ***Wiedermann Alfred and Kocurek (1989); Chandra (1998)***

> Reed is a highly productive grass (Poaceae) with an above-ground net primary production ranging from less than 3 t ha-1 y -1 to as much as 30 t ha-1 y -1. Reed can be found all over the world except in Antarctica, but its core distribution area (mostly Phragmites australis Trin. ex Steud) is Europe, the Middle East and America.
>
> ***Allirand and Gosse (1995); Haslam (2010); Brix (1988); Ostendorp (1993); Thevs et al. (2007); Björk (1967); Huhta (2007); Chambers et al. (1999); Tewksbury et al. (2002); Derr (2008)***

> It is characteristic of wet sites, most often with water level ranging from slightly below the soil surface to one meter above ground level, and grows mostly at the shores of lakes and gulfs, along riverbanks and on nutrient-rich peatlands. It can grow in deeper water if sufficiently clear, and has been collected from depths up to about 4 m in the highly transparent oligotrophic waters of the Stechlinsee. Small stands can also be found at desert margins with water table from around four meter below to three meter above the ground surface. Reed grows mostly in fresh water, but also in brackish or (up to 16 %) salt water. Only the rhizomes are perennial and, in cooler climates, the above-ground part of the plant dies at the end of the growing season. At this time the nutrients are relocated from the stems and leaves back to the rhizomes and stored for the next growing season. Although reed can be grown from seed, vegetative propagation is much more common. It has a strong ability to spread from rhizomes, and parts of rhizomes deposited from moving water can initiate new reed stands. It is a pioneer plant that often occurs in mono-specific stands. As it can propagate very rapidly in new areas and grow to a height of several meter, it is seen as a threat to other aquatic vegetation in parts of North America.
>
> ***Kobbing et al. (2013/2014); www.mires-and-peat.net***

Reed biomass is a source of cellulose and hemicellulose and can be used for semichemical as well as chemical pulps. Depending on environmental factors, the cellulose content of reed ranges from 33%–59%. By and large, only the leaves have to be removed for semichemical pulp, and all above-ground parts of the plant can be utilized for papermaking. Reed is preferred for paper production because it contains high content of short fibers, though cellulose pulp produced from short-fiber reed should be mixed with a certain proportion of long softwood fibers for obtaining reasonable tear and paper density. Paper containing up to 30% reed is of good quality and suitable for almost all applications while paper with 80% reed can be utilized for producing wrapping paper (Haslam, 2010; Rodewald-Rudescu, 1958; Chivu, 1968a, 1968b; DeLaCruz, 1987; Al-Zubaidi, 2018; www.mires-and-peat.net).

Fig. 4.9 shows morphology of reed fibers under optical microscope (Al-Zubaidi, 2018).

> Reed paper mills were operated in Turkey, Sweden, Egypt Romania, Iraq, Italy, the former German Democratic Republic and the U.S.S.R. and are still existing in China and probably India. The best-known paper enterprise, producing several thousand tonnes per year, was in the Danube Delta. Reed pulp and paper are no longer produced in Europe, because of lack of reed supply and also due to economic and environmental reasons; but in China the quantity of reed used for paper production in 2004 was 2.5–2.7 million tonnes and is increasing. The dry (15 % moisture content) reed biomass (stems and leaves) is harvested in winter. The reed is chopped and pressed into bales after harvest to reduce its volume, facilitating storage of a year round supply for the pulp and paper mill, which runs continuously, and reducing transport costs. One tonne of paper pulp needs 5.3 m^3 of softwood, 4.1 m^3 of beech wood or 3.3–3.5 tonnes of reed. Four tonnes of reed per tonne of artificial fibre cellulose and three tonnes for normal cellulose are required. Investigation by the authors in Inner Mongolia

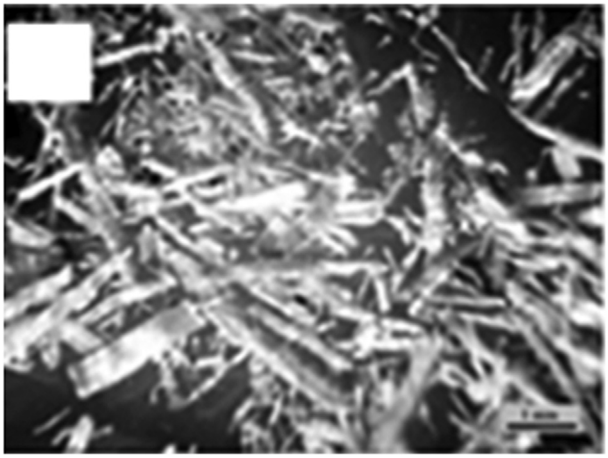


Figure 4.9

Morphology of reed fibers under optical microscope. *Source: Reproduced with permission Al-Zubaidi, A. B., 2018. Effect of natural fibers on mechanical properties of green cement mortar. In: Conference: Technologies and Materials for Renewable Energy, Environment and Sustainability: tmrees18. AIP Conference Proceedings, 1968(1):020003. http://doi.org/10.1063/1.5039162.*

> (China) showed that reed as raw material for paper production costs up to €90 t-1 ($\approx$750 CNY t-1) at the factory gate.
>
> ***Rodewald-Rudescu (1958, 1974); Wayman (1973); Zhu et al. (1998); Pöyry (2006); Chivu (1968b); Kobbing et al. (2013/2014); www.mires-and-peat.net***

*4.3.3.1 Sabai grass (*Eulaliopsis binata*)*

This is also an important raw material for producing paper. It was the only raw material before the introduction of bamboo as an important raw material, but its use has reduced significantly since then. The Sabai Grass is an exquisite gramineae. The plant is medium sized and can reach 2 m high. It assumes a greenish white colour in the spring, summer, autumn, and winter seasons. It retains its leaves in the winter and develop a round-shape shrub. Sabai grass is a very effective soil binder. It also provides raw material for paper industry and used for making ropes by the rural poor.

> Sabai grass grows wild in the lower Himalayas, central India and southern China. It is a tufted grass having stems 60–90 cm in height and long leaves which are present mostly at the base. Sabai grass has been a significant source of fiber for papermaking in India, and has also been used in Pakistan and Nepal. The species was a staple fibrous raw material before 1925 and is characterized by its durability, strength, and hardness. Quality of the pulp is similar to that of esparto and is therefore used for high-class book and printing paper. Until 1952, sabai grass represented about 22% of the total fibrous material pulped in India. Use in recent years has however declined due to difficulties in procurement, although some plantations have been established to produce the grass on a limited scale. Average fiber length is about 4.1 mm, with a range of 0.5 mm to 4.9 mm. Widths are about 0.01–0.016 mm. Fibers are relatively thick walled with narrow lumen, and the ends are pointed and never forked.
>
> ***Chandra (1998)***

Fig. 4.10 shows cross sectional image of sabai grass fiber and Fig. 4.11 shows the surface image of sabai grass fiber (Sahu et al., 2016a).

In India, Sabai grass makes up 7%–9% of the total cellulosic raw materials. Although sabai grass has long fibre and needs less chemicals in cooking, it grows in clumps intermixed with other vegetation. It is usually difficult to remove impurities from it. Furthermore, its supplies are much lesser in comparison to those of bamboo. In India, it mostly grows in the subHimalayan regions of Shiwaliks and Tarai area.

> For paper making, the grass is extracted every year in November and December, transported from forests on camels to yards where it is sun-dried and then sent to the paper mills. Grass cutting, transporting and sun-drying provide lean period employment to a large number of local people in the close vicinity of their villages. This job of converting grass into rope provides employment to women, landless and weaker sections of society.

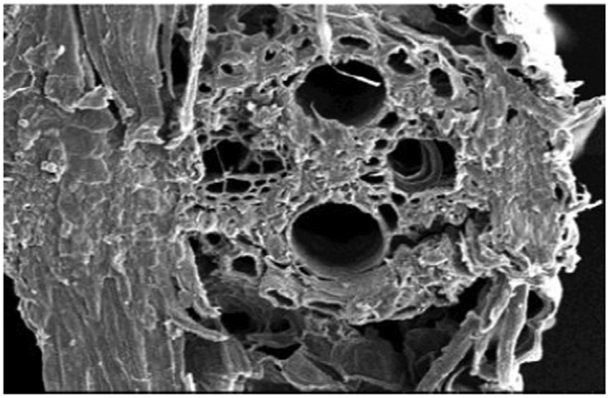


Figure 4.10

Cross-sectional image of Sabai grass fiber. *Source: Reproduced with permission Sahu, S., Khandual, A., Behera, L., 2016a. Sabai grass fibre: an insight into thermal stability, chemical constitution and morphology. Int. J. Adv. Chem. Sci. Appl. (IJACSA), 4 (4), 2016. ISSN (Online): 2347-761X.*

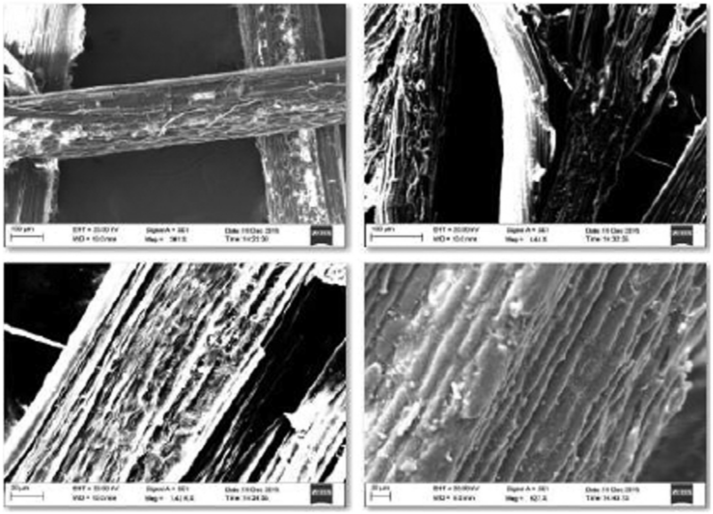


Figure 4.11

Surface image of Sabai grass fiber. *Source: Reproduced with permission Sahu, S., Khandualnd, A., Behera, L., 2016b. Sabai grass fibre: an insight into thermal stability, chemical constitution and morphology. Int. J. Adv. Chem. Sci. Appl. (IJACSA) 4 (4). ISSN (Print):2347-7601, ISSN (Online): 2347-761X.*

> Any increase in the availability of Sabai grass is, therefore, a sure means of additional employment to the poorer structure of the society.
>
> **www.tucson.ars.ag.gov**

Sabai grass has good flexibility and strength, higher content of leaf fiber (>55%), lower lignin content (<14%) and excellent average fiber length (20 mm). Therefore it is one of the best raw material among fiber grass plants for paper industry and rayon and woven materials (Sahu et al., 2016b). The fiber length of sabai grass in comparison to bamboo but fiber diameter is 2.5 times lower than bamboo. Sabai grass has high cellulose and pectose with lower lignin content.

> The fibers are derived from the vascular bundles of leaves. The pulp is used for the manufacture of all types of cultural and industrial paper. The fiber varies from 0.4- to 4.4 in length with an average of 1.6 mm and 5–15 ~ m in width (average 13.7 urn). The pulp consists of fibers, parenchyma, and vessel and epidermal cells. The fibers are narrow, long, straight and thick walls and pointed tapering ends and occasional transverse markings. The fibers are narrower than those of bamboo and bagasse. The parenchyma cells are small to medium sized narrow rectangular and numerous. The vessels are fairly long and narrow. The epidermal cells are numerous, rectangular in shape and conspicuous with serrated margins.
>
> ***Chandra (1998)***

4.3.4 *Papyrus* (Cyperus papyrus)

> Cyperus papyrus is a fast-growing perennial sedge native to central Africa and the Nile Valley, and has been introduced, often as an ornamental species, to other warm parts of the world. It can form dense and extensive wetland stands and grows either rooted in shallow water or in large, free-floating clumps. In its native environment it has been used for millennia as food for humans and livestock, as a source of herbal medicines and perhaps most importantly as the source material for the making of paper (papyrus), cordage, ropes, boats, matting, mattresses, cushions, roofing and flooring. More recently, it has been seen as a potential source of material for biofuel, as an effective natural biofilter for aquatic pollutants, and has been recognised for its contribution to ecosystem functions and services.
>
> ***www.platform.cabi.org; Duke (1983); Opio et al. (2014)***

The diameter of stem is 3–5 cm at its base and attains a height of 2–5 m. The stem is triangular, smooth-sided and leafless. It is composed of a cortex which surrounds a pith section. The pith portion itself is structured from fiber bundles entrenched in parenchyma. Vessels, sclerenchyma, and epidermal cells are also found to be present. The cortex consists a dense section of fiber bundles. Annual growth rate of Papyrus plants is 45 ton/ha, dry weight (McGovern et al, 1989).

> The pith section occupies 80–90% of papyrus stems volumetrically and 30–80% by dry weight. Inflorescence accounts for about 20% of the total plant, less roots. Fibers in the pith section amount to 10% of the total fiber weight. Thus, the proportion of fibers in the stem may vary from about 20–75%. Fibers themselves show a great range in length and diameter depending on species, origin and location in stem. Papyrus plants have an average fiber length of 1.8 mm and an average fiber width of 0.012 mm.
>
> ***Chandra (1998)***

4.4 Nonwood crops grown mainly for their fiber content

4.4.1 Bast fibers

Bast fiber is collected from the phloem or bast which surrounds the stem of certain flowering plants. It holds up the conductive cells of the phloem and imparts strength to the stem. Bast fibers are used for textiles, rope, and paper. Examples are, jute, abaca, flax, hemp, ramie, cantala, henequen, Sisal, pineapple, mitsumata, gampi, and kozo.

They are yearly renewable crops and take 90–100 days to grow. The fiber is outside of the plant and contains one-third of the weight. The core appears similar to balsa wood and has several uses, including oil absorbents and animal bedding. It is mostly used as firewood in India and Bangladesh.

Bast fibers consist of fiber bundles. These bundles are broken down by mechanical or chemical means for achieving the desired fineness. The degree of this breakdown, in turn, dictates their end use (www.bastfibersllc.com).

4.4.1.1 Jute

Jute is one of the most reasonably priced natural fibers and has a broad range of applications. It is second only to cotton in the amount produced. Jute has long fibers and very high cellulose content. Chemical and morphological properties are favorable for producing pulp (Akhtaruzzaman and Shafi, 1995). Jute is mainly grown in Thailand, Bangladesh, India, and China. The height of plant is 2.5–3.5 m. The outer bark contains approximately 40% of the stem by weight and is mostly used for producing low value products for instance—gunnysacks, rope, cordage, etc. The inner wood core accounts for the balance 60% of the stem (Sabharwal et al., 1995). Commercial jute contains fiber bundles having length of 1.8–3 m. Individual fibers have length of 2–5 mm. These are arranged in a parallel way with ends overlapping for producing continuous filaments having 10–30 fibers per cross-section. Like in case of wood tissues, individual fibers are joined together by lignin containing middle lamellae (Sarkanen and Resalati, 1988). Average fiber length and diameter of jute fibers is 2.5 and 0.02 mm, respectively (Ilvessalo-Pfaffli, 1995). Jute fibers are used for making printing and writing paper, and tag, wrapping and bag paper.

Jute fibers is a lingocellulosic fiber that is partially a textile fiber and partially wood. It contains mainly cellulose (main constituent of plant fiber) and lignin (main components of wood fiber).

Jute fiber are off-white to brown, and have a length of 3–12 feet long. The appropriate weather for growing jute is warm and wet climate offered by the monsoon climate during the monsoon season. Favorable temperatures for cultivation is 68°C–104°C and relative humidity is 70%–80%.

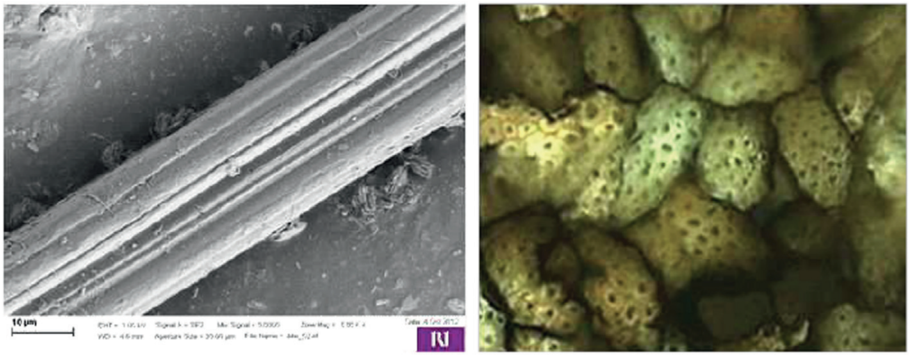
Jute plants are classified into two broad groups (www.dcpulppaper.org.gifs.report24).

- *Corchorus olitorius* (Tossa jute)
- *Corchorus capsularis* (White jute)

Tossa jute fiber is softer, silkier, and stronger in comparison to white jute. Presently West Bengal, India, and Bangladesh are the major producer of the tossa jute. Indians, particularly Bengalis, used ropes and twine made of white jute from very old time for home and other applications. India is the largest producer of jute and allied fibers in the world accounting for about two-third of the global production

The jute plant is an annual plant. It attains a height of 5–16 feet and generally do not have major branches. Diameter of the stem reaches up to 10–20 mm upon maturity. The stem portion has two discrete zones namely bark and core. The bark portion gets loosely attached to core when the plant is dry. The color of the dry bark is dark brown and the color of core is pale yellow or cream (www.makemarijuanalegal.org).

Bast fiber comprises about 36% of the weight in the whole jute, and the remaining 64% is core wood. Bulk density of the whole jute is quite low in comparison to the hardwood and softwood. Bulk density of jute bast fiber is very low in comparison to core wood. The bulkier nature of the raw jute fiber has drawbacks with regard to volumetric loading, throughput, etc. Impregnation of chips with liquor gets also affected because of the bulky nature, as the chips tend to float. Bast has higher ash content as it has extraneous silica. The holocellulose in the bark is relatively higher. Higher alpha *c*ellulose content in the bark shows that the pulp yield and the strength properties will be higher (Duan et al., 2017). Fig. 4.12 shows longitudinal view (5000 × magnification) and b) cross-section (180 × magnification) of jute fiber (Smole et al., 2013).



(A) (B)

Figure 4.12
(A) Longitudinal view (5000 × magnification) and (B) cross-section (180 × magnification) of jute fiber (Smole et al., 2013).

*4.4.1.2 Ramie (*Boehmeria nivea*)*

Ramie is, native to China and nearby countries. It is also known as China grass. It is perennial and grows to a height of 1.5–2.5 m. It is grown in a temperate weather in several countries including China, Japan, Russia, Egypt, Libya, and North and South America. Ramie is an oldest and valuable fiber crop and is recognized for its strongest and longest natural fiber in the world. The nature of Ramie fiber resembles with that of flax or hemp. Ramie (*Boehmeria nivea*) is a species of the Urticaceae family. It is being grown in North Eastern states of India since long time. Ramie plant grows in the form of stalks and has heart shaped leaves which sprout up from underground root system. The ramie stalk can be harvested up to six times in a year in favorable growth climate, though three to four crops of ramie annually are quite common. Ramie is a exceptional perennial producing highest green biomass per hectare/day even under less sun light. Ramie is an oldest and valuable textile fiber crop and is well known as one of the strongest and longest natural fiber in the world. Ramie fiber exhibits even superior strength when wet. It has little elasticity and is somewhat brittle and stiff. The fabric appears much stronger and tougher than cotton. Quality of ramie fiber is much better than the other natural fibers in several fibre quality parameters. Ramie fibers consist of pure cellulose, and are amazing for their length and width. They are quite strong and most long lasting of the vegetable fibers.

In 2014, more than 94% of the ramie produced in the world was harvested in China. The height of the plant is between 1.0 and 2.5 m, and its leaves are 7–15 cm long and 6–12 cm broad. The diameter of the stalks is in the range of 4.5–10 mm. Ramie is mainly grown for its fibers. The most favorable conditions for ramie production are in warm and humid climate having an average rainfall of 1 m per year (Robinson, 1940; Ciaramello et al., 1963). In China it has been used for producing paper for several centuries. Fig. 4.13 shows longitudinal view and cross-section (100 × magnification) of ramie fiber (Smole et al., 2013).

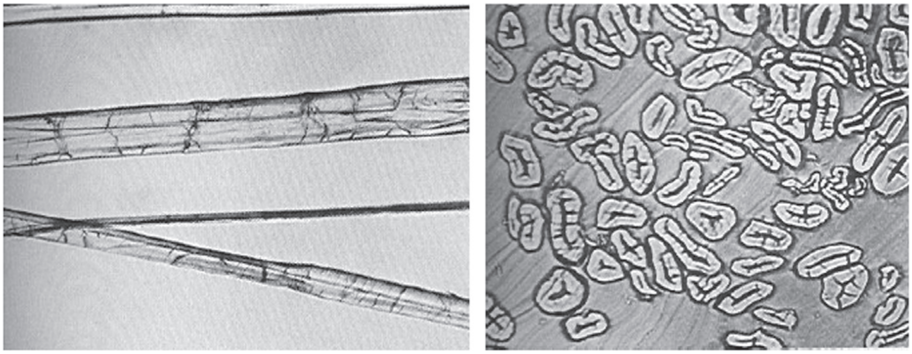
*4.4.1.3 Sunn hemp (*Crotalaria juncea*)*

Sunn hemp is grown mostly in India and Pakistan. The height of the plant is 2–3 m. Retting process is used for separating the fibers from the inner bark. The fibers are stronger in the wet form. Because of this property, the fibers are particularly desirable for producing fishing nets and ropes. Old fishing nets are one of the main source of crotalaria fibers for producing papers (Ilvessalo-Pfaffli, 1995).

The average fiber length and fiber width of sunn hemp is 8 and 0.03 mm, respectively.

Fig. 4.14 shows the SEM of Sunn hemp fiber (Kalia et al., 2011).

Sunn hemp fiber is used for producing cordage, fishing net, and paper. The fiber pulp sunn hemp is also utilized in producing currency note paper and cigarette paper (Korrapati and, Manasa, 2017). The genus, Crotolaria consists of over 200 species found in tropical and



(A)

(B)

Figure 4.13
(A) Longitudinal view and (B) cross-section (100 × magnification) of ramie fiber (Smole et al., 2013).

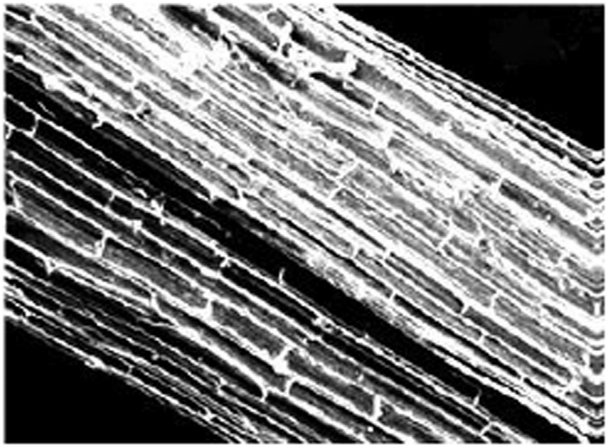


Figure 4.14
SEM of Sunn hemp fiber (Kalia et al., 2011). *SEM*, Scanning electron micrographs.

subtropical regions. From India, it was introduced to other countries and according to some researchers, this crop was grown originally in Myanmar. It is found there in its wild state. The crop can not tolerate frost and low temperatures. It can be also grown in rabi season when winter temperature is mild that is, in southern area. It is one of the green manure crops grown in areas having high relative humidity of 60%–85% and rainfall of 400–1000 mm throughout the growth and temperature ranging from 20°C–35°C (Tripathi et al., 2012). It is suited to almost all parts of India. Sunn hemp is able to fix atmospheric nitrogen, adds organic matter to the soil, suppresses weeds, and reduces erosion of soil (Ram and Singh, 2011). Good quality seeds are not available. This is one of the important reasons for reduced popularity of Sunn hemp (Chittapur and Kulkarni, 2003).

*4.4.1.4 Hemp (*Cannabis sativa*)*

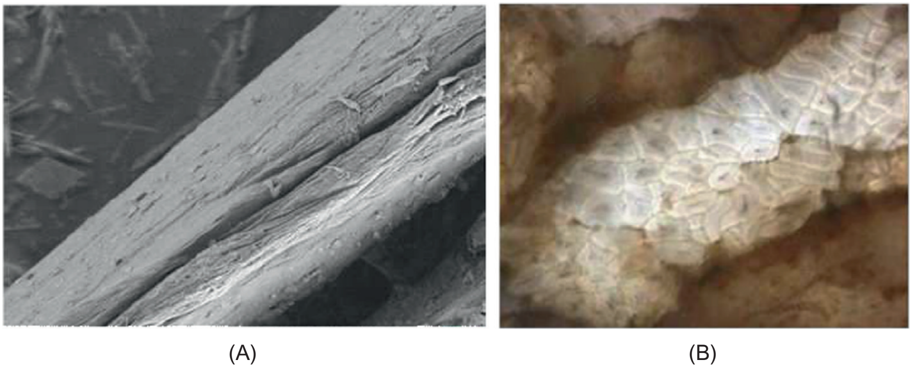
Hemp, or industrial hemp, is one of the fastest growing plants. It can be spun into usable fiber 10,000 years ago. It is a strain of the *Cannabis sativa* plant species which is grown specifically for the industrial uses of its derived products. Hemp is grown in several countries, including, China, Canada, Russia, the United States, and many European countries. In these countries hemp farming is regulated.

Fiber hemp is an annual plant. The height of the plant is 4–5 m and produces 12–14 tons of dry matter/yr. ha. About 10–12 tons dry matter/yr ha can be harvested as fiber mass. Of which, 35% are long bast fibers and remaining 65% are short core fibers (Zomers et al, 1995). Cellulose content of hemp fiber increases as the plant matures. In many countries, harvesting of hemp is performed manually (Jeyasingam, 1990).

The diameter ranges from 5 to 20 mm depending on the growth per hectare, location, and how seeds are sown. The female hemp plant produces seeds. In any field, the proportion of male to female plants are usually in the ratio of 50 to 50. The fiber in male plant is better as compared to the female plant. This is attributed to the fact that the lignification in male plants does not take place as rapidly as in female plants.

Plants take about 80–150 days to get matured for harvesting of fibers. It is important to harvest hemp at the appropriate time for improving the fiber quality. When harvesting is done early poor yield and weak fibers result whereas when harvesting is delayed, stems are difficult to separate during the retting process. Plants harvested late produce coarse and harsh fibers.

Hemp can have a fiber length from 15 to 55 mm and an average length of 20 mm for papermaking. The diameter is in the range of 0.016 and 0.22 mm, and the fiber is distinguished by having forked ends (Jeyasingam, 1994). Fig. 4.15 a shows longitudinal


(A)

(B)

Figure 4.15
(A) Longitudinal view (10,000 × magnification) of hemp fiber (Smole et al., 2013). (B) Cross-section (200 × magnification) of hemp fiber (Smole et al., 2013).

view (10,000 × magnification) of hemp fiber and Fig. 4.15b shows cross-section (200 × magnification) of hemp fiber (Smole et al., 2013).

Hemp is used for producing printing and writing paper, specialty papers such as cigarette paper, lightweight, condensor paper, and security and currency paper.

1 acre of hemp can produce as much paper as 2–4 acres of trees annually. Different types of paper products from tissue paper to cardboard can be produced from hemp.

The quality of hemp paper is better to tree-based paper. Hemp paper is quite durable and is able to last hundreds of years without getting degraded. It can be recycled many times as compared to paper produced from trees, and needs lesser chemicals in the production process in comparison to paper produced from trees.

Hemp is used for producing stronger and lighter fiberboard which is stronger and lighter in comparison to wood. Substitution of hemp fiberboard for timber would further reduce the requirement for cutting down our trees.

Hemp is used for producing strong, long lasting, and ecofriendly plastic substitutes. Many products produced from petroleum-based plastics can be produced from hemp-based composites.

Trees takes many years to grow until they can be harvested for wood or producing paper but hemp can be harvested in just a period of 4 months after it is planted. Hemp can grow on most land appropriate for farming, where forests and tree farms need larger areas of land available in few locations. Harvesting hemp rather than trees would also eradicate erosion because of logging, thus reducing loss of the top soil and water pollution caused by overflow of soil.

The protein present in hemp seeds is more healthy and more cost effective to produce as compared to soybean protein. Hemp seeds are not intoxicating. The protein of hemp seed can be used for producing practically any product produced from soybean: cheese, tofu, veggie burgers, butter, salad oils, ice cream, milk, etc. Hemp seed can also be ground to produce a nutritive flour that can be utilized for producing baked goods for instance bread, pasta, cookies, etc.

Hemp seed is also used for producing nontoxic diesel fuel, paint, varnish, detergent, ink and lubricants. Hemp seeds account for about half the weight of a mature hemp plant. Hence these seeds are a good source for such products.

Just like corn, ethanol which is a clean burning fuel can be produced from hemp. It shows great promise for becoming an important source of ethanol fuel as hemp produces more biomass as compared to other plant species (including corn) which can be grown in different weathers and places.

Factually millions of wild hemp plants are grown all through the United States. Wild hemp has no drug properties due to its low tetrahydrocannabinol content. United States marijuana laws stop farmers from growing the same hemp plant which propagates in nature by the millions.

> From 1776 to 1937, hemp was a main crop in United States. The textiles produced from hemp were widespread. Still, The American Textile Museum, The Smithsonian Institute, and most American history books do not mention hemp. The government's War on Drugs has produced an atmosphere of self censorship where talking of hemp in a positive manner is considered politically not correct.
>
> ***www.hempstersstitch.com***

United States Presidents George Washington and Thomas Jefferson grew hemp used products produced from hemp, and admired the hemp plant in one of their writings.

> No other natural resource offers the potential of hemp. Cannabis Hemp is capable of producing significant quantities of paper, textiles, building materials, food, medicine, paint, detergent, varnish, oil, ink, and fuel. Unlike other crops, hemp can grow in most climates and on most farmland throughout the world with moderate water and fertilizer requirements, no pesticides, and no herbicides. Cannabis Hemp (also known as Indian Hemp) has enormous potential to become a major natural resource that can benefit both the economy and the environment.
>
> ***www.makemarijuanalegal.org***

*4.4.1.5 Kenaf (*Hibiscus cannabinus*)*

The kenaf plant is an annual plant having a single, straight, and unbranched stem. It contains a outer fibrous bark and an inner woody core. The stalks grow to 5–6 m in length and 25–30 mm in diameter in a period of 5–6 months. After that it is harvested. Kenaf has been developed as a nonwood fiber crop as a promising raw material for producing paper (Tao et al.,1995; Mayers and Bagby, 1995).

> Kenaf is a valuable fiber and medicinal plant from the Malvaceae family. It is an alternative crop that may be a feasible source of cellulose which is economically viable and ecologically friendly. This plant is cultivated for its fiber although its leaves and seeds have also been used in traditional medicine in India and Africa for the treatment of various disease conditions. Kenaf fibers are commonly used for paper pulp and cordage, but it is also a promising lignocellulosic feedstock for bioenergy production. The kenaf seed oil can be used for cooking and in different industrial applications.
>
> ***Avila (2006); www.tandfonline.com***

> Raw kenaf fiber obtained from the outer bark is actually a bundle of fibers. The outer bark, or bast, is about 40% of the stem by weight and the inner woody core is about 60%. Kenaf has been used on a limited scale as a substitute for wood in the production of, pulp and paper in Thailand and China. It contains approximately 65.7% cellulose, 21.6% lignin and pectins. Kenaf pulped with kraft, soda, or neutral sulfite is superior to commercial hardwood pulps and except for tear, is comparable to softwood kraft pulps and superior to softwood sulfite pulps.
>
> ***Chandra (1998)***

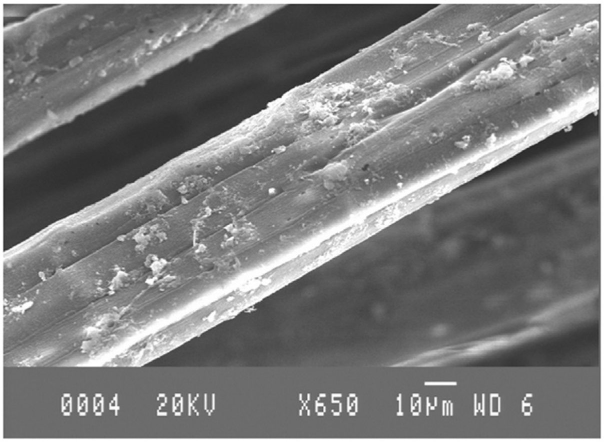


Figure 4.16
Scanning electron micrograph of kenaf bast fiber (Nirmal et al., 2014)

Bast Fibers are 3–4 mm long whereas those from the core are 0.6 mm long (Sabharwal et al, 1994; Kokta et al, 1993). Average diameters are 0.02 mm (bast) and 0.03 mm (core). Fig. 4.16 shows SEM of kenaf bast fiber (Nirmal et al., 2014).

> Kenaf is used to produce printing and writing paper, newsprint, multi-sack, linerboard, tissue paper, bleached paperboard, cigarette paper and other lightweight specialty papers.

Advantages of Kenaf are as follows:

- Kenaf pulping need less use of chemicals.
- Kenaf pulping consumes less energy then wood pulping (Kenaf lignin contnt is lower).
- Another advantage of Kenaf over wood is its higher rate of production in terms of tons of biomass for land/time units.
- Growing Kenaf in the tropics offers high flexibility to the industry management: while trees growing cycle is 10–25 years, Kenaf growing cycle is 4–6 months.

> Today there are several companies like Andritz, that possess the technology of Kenaf pulping. Many studies indicate that Kenaf pulp is equal or even better then wood pulp in some aspects. To enable existing pulping mill to receive Kenaf stalks rather than wood, some modifications should be done.
>
> ***www.fpl.fs.fed.us***

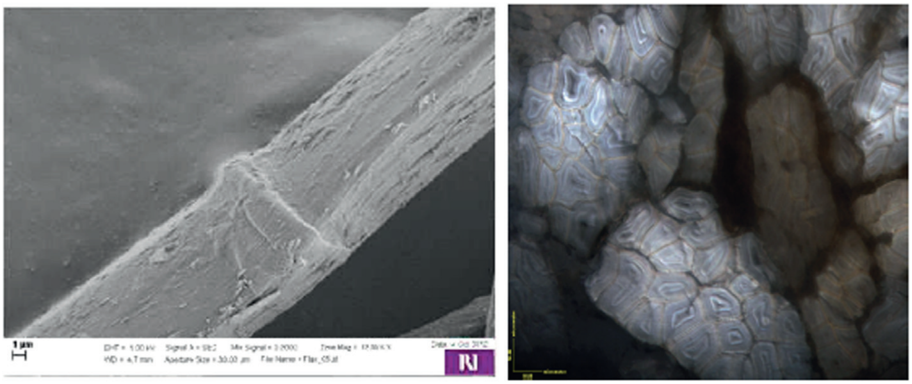
Kenaf is a fast growing nonwood crop that can be grown and harvested for fibers for making specialty papers and newsprints, cordage, animal feeds and bedding, insulator and industrial absorbents of good quality. This new crop can be grown in a comparatively different type of weather and soils (Taylor, 1995). It requires minimum fertilization and water in comparison to other traditional crops occupying large acreage. It grows very well in soil which is well drained under, sandy, and loamy (Johnson, 2001). It also thrives in areas with high humidity, loamy soils with plentiful of rainfall and long growing season (Burgess, 2004). It grows rapidly and reaches a height of 12–18 feet high in 4–5 months and can be grown in regions where cotton and tobacco prosper (Avila, 2006). Moreover, kenaf can be grown in rotation with corn and still yield viable results (Baldwin, 2000). In Indonesia, farmers can increase profits by following on rotation of corn followed by kenaf at existing corn yields and prices offering higher payment to farmers (Liu, 2002). Large amounts of herbicides are not needed as close planting density represses weeds growth. In addition, pesticides are not required as fibrous stems discourages insects from attacking the crop.

*4.4.1.6 Flax tow (*Linum usitatissimum*)*

Flax is an industrial plant of increasing interest. Since its domestication started from neolithic times more than 10,000 years ago (Quillien, 2014), this plant has been grown for its fibers, leading to its designation of "fiber crop" or "fiber plant."

> Flax is an annual plant that is grown in temperate climate for both its fibers and linseed oil. When planted densely for fiber production, the plant grows to a height of about 1 m. Bast fibers, known as linen, are separated from the inner bark by retting. Flax has an average fiber length of 30 mm and an average fiber diameter of 0.02 mm.
>
> ***Chandra (1998)***

Fig. 4.17 shows longitudinal view (10,000 × magnification) and cross-section (30 × magnification) of flax fiber (Smole et al., 2013).



(A) (B)

Figure 4.17
(A) Longitudinal view (10,000 × magnification) and (B) cross-section (30 × magnification) of flax fiber (Smole et al., 2013).

Raw material for flax pulp is obtained from three sources:

- Textile wastes (old rags and new cuttings). This is the purest form of raw material.
- Fiber waste remaining when bast fibers are removed from textile flax. Relatively clean raw material, known as textile flax tow.
- The entire plant after the removal of the seeds from seed flax. This raw material is of low quality, and is known as seed flax tow.

> In blends of various proportions, it is used to make specialty papers like book paper, lightweight printing and writing paper, condensor paper, currency and security paper, and cigarette paper.
>
> ***Chandra (1998)***

> Flax fibers have been used as textile raw material, composing cords and weaving yarn and later on more fashionable garments or high-quality fabric upholstery. Starting around the 1930s and supported by both mechanical performances and impressive length-to-diameter ratio of flax fibers (average diameter of 20 μm for a length of 25 mm) their applications have been extended to more technical uses, namely, as reinforcements for composite materials for the development of more sustainable materials.
>
> ***Goudenhooft et al., 2017, 2019; de Bruyne, 1939; van Dam and Gorshkova, 2003; Yan et al., 2014; www.frontiersin.org***

Nowadays, the plant fiber-based composites are becoming popular. These are used to replace glass fibers. The benefits of plant fibers in comparison with glass ones are their biological origin from photosynthesis and their sustainability, lower density, low risk producing process for human health, low abrasion of processing tools, etc. (Pickering et al., 2016). Flax fibers have a similar range of specific mechanical properties as compared to glass fibers. The average values of elastic modulus, strength at break and strain at break are 52.4 GPa, 976 MPa, 2.15% for a fiber density of 1.53, respectively (Lefeuvre et al., 2014a, 2014b).

> In the case of flax-based composite materials, the fibrous part or reinforcement consists of either technical flax fibers or short fibers, impregnated with a polymer matrix. The technical fibers are composed of fiber bundles (being more or less individualized) in a random aligned non-woven form unidirectional plies or as more complex fabrics. Short fibers of a few millimeters in length and well individualized can be used to process biocomposites too, through extrusion or injection routes.
>
> ***Merotte et al. (2016); Lefeuvre et al. (2015); Robitaille and Gauvin (1999); Bensadoun et al. (2017); Doumbia et al. (2015); www.frontiersin.org***

4.4.2 Leaf fibers

The leaves of certain plants are important for pulp and papermaking due to its high cellulose content, for instance banana leaves, Sisal, abaca, sugarcane leaves, and so on.

Actually some of these are superb fibers for producing paper. Two of the more commonly used plants are presented below.

*4.4.2.1 Abaca (Manila hemp) (*Musa textilis*)*

> Abacá binomial name is Musa textilis. It is a species of banana native to the Philippines, grown as a commercial crop in the Philippines, Ecuador, and Costa Rica. This plant is also known as Manila hemp and is of great economic importance, being harvested for its fiber, also called Manila hemp, extracted from the leaf-stems.
>
> ***www.hoisttechnologies.com***

> The abaca plant propagates itself through suckering, or growing of shoots from roots. When all the leaves have been formed from the stem, flower buds develop, at which time the plant is mature and is ready for harvest. Under normal conditions, the first harvest is completed from 18–24 months after planting. Subsequent harvests are completed at 3–4 month intervals. The harvesting process consists of two stages, namely topping, where the leaves are cut with the knife, and tumbling, where topped stalks are tumbled down with a cutting knife. The next step is tuxying, where the tuxy is extracted from the leaf sheath by hand or mechanical spindle stripping. The stripped fibers are then dried before grading. Quality of abaca pulp is affected by the type of cleaning which determines the grade of fibers.
>
> ***Chandra (1998)***

Abaca fiber is obtained from the leaves of the plant and is distinguished by its length, firmness, and durability (Moreno and Protacio, 2012; Peralta, 1996).

> In the paper industry, it is usually mixed with other fibres to increase the strength of the paper, or in the manufacture of thin papers or banknotes (the Yen is made with this pulp). It is especially used in the manufacture of strong, but porous paper such as that of teabags. Abaca allows to manufacture a very strong paper that is silky to the touch and translucent. If it is intensely refined, it can produce translucent paper with a parchment like quality. It is ideal for high volume work. The museum sells two types of abaca.
>
> ***www.mmp-capellades.net***

Most of abaca fibers are used for producing specialty papers (www.fao.org). This includes:

- Tea and coffee bags
- Sausage casing paper
- Currency notes (japan's yen banknotes contain up to 30% abaca),
- Cigarette filter papers
- Medical /food preparation/disposal papers
- High-quality writing paper
- Vacuum bags

> Excellent fiber grades are made into pulp for very porous and high strength specialty tissues, such as tea bag papers and meat casings. Fair to residual grades are made into pulp for specialty papers with high tear and tensile strengths such as vacuum bags and wrapping papers. Abaca plant has an average fiber length of 6.0 mm and it has an average fiber diameter of 0.024 mm. In blends of various proportions, it is used to make specialty papers like superfine, lightweight, bond, ledger, currency and security paper, tea bags, filters, linerboards, wrapping and bag paper.
>
> *Chandra (1998)*

Table 4.5 shows the uses of abaca (https://textilelearner.blogspot.com/2013/04/abaca-fiber-manila-hemp-usesapplication.html).

Fibers have uniform width, thin walled, and normally taper to a pointed end. The fibers appear stiffer and have smoother walls if compared to other bast fibers, with fine, occasionally diagonal striations. There are rectangular epidermal cells, which usually stain

Table 4.5: Uses of abaca fiber.

Pulp and paper	Cigarette paper, currency paper, chart file folders, envelopes, time cards, book binders and parchment paper Tea bags, filter paper, mimeograph stencil, base tissue, sausage skin, base paper Microglass air filters media, x-ray negative, optical lens wiper, vacuum filter, oil filter
Nonwovens	Medical gas masks and gowns, diapers, hospital linens, bed sheets
Handmade paper	Paper sheets, stationeries, all-purpose cards, lamp shades, balls, dividers, placemats, bags, photo frames and albums, flowers, table clock
Cordage products	Ropes, twines, marine cordage, binders, cord
Fibercrafts	Handbags, hammocks, placemats, rugs, carpets, purses and wallets, fishnets, door mats, table clock
Handwoven fabrics	Sinamay, pinukpok, tinalak, dagmay Sacks, hotpads, hemp, coasters Baskets Wallpaper
Furniture	
Fiberboards	Roofing tiles, floor tiles, hollow blocks, boards, reinforcing fiber concrete and asphalt
Fuels	Musafel
Miscellaneous applications	Wigs, grass skirts
Others	Wire insulator and cable, automobile, automobile components/composites

Source: Used with permission from Mazharul Islam Kiron. From Abaca Fiber (Manila Hemp) | Uses/Application of Abaca Fiber, <https://textilelearner.blogspot.com/2013/04/abaca-fiber-manila-hemp-usesapplication.html>.

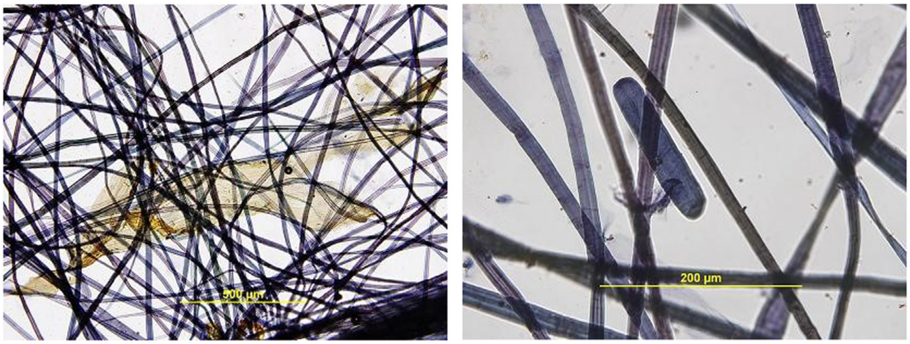


Figure 4.18
Manila Hemp/Abaca. *Source: Reproduced with permission <http://cultural-conservation.unimelb.edu.au/PapermakingFibres/manilahempabaca.html>.*

yellow (Fig. 4.18), with stomata with large subsidiary cells. Parenchyma cells are usually present and can be rectangular or 'pill' shaped, (Fig. 4.18). Spiral thickening is also sometimes present. http://cultural-conservation.unimelb.edu.au/PapermakingFibres/manilahempabaca.html

*4.4.2.2 Sisal (*Agave sisalana*)*

Sisal is a nonwood leaf plant native to Mexico. It flourishes in semiarid regions of Brazil, Tanzania, and Kenya. The width and length of Sisal leaves are around 10 cm, and 1–1.5 m, respectively and the weight is 500–700 g. Sisal grows all year long. The first harvest is usually made in 2–2.5 years after planting. Sisal produces 180–240 leaves during its productive period of 4–6 years.

Aztecs and Mayans were the first to use Sisal for making crude fabrics and paper. The native origin of the Sisal plant is uncertain, but thought to be a native of the Yucatan Peninsula. Plants were originally shipped from the Spanish colonial port of Sisal in Yucatan, which is where the name comes from.

In the 19th century, cultivation eventually spread to Brazil, and also countries in Africa, particularly Tanzania and Kenya. The first commercial plantings in Brazil were made in the late 1930s and the first exports were made in 1948. Brazil is the largest producer of Sisal in the world.

> Sisal leaves are harvested manually and are transversely cut to 50 mm length and hammer milled. Juice and pitch are removed through vertical screens, and chaffed Sisal fibers are transported by conveyers to the drying process. Sisal fiber chaff, after having been dried, is pressed into bales for pulping. Sisal leaves have an average fiber length of 3.0 mm and average fiber width of 0.02 mm.
>
> ***Chandra (1998)***

Fig. 4.19 shows SEM image of Sisal fiber (Sathishkumar et al., 2016).

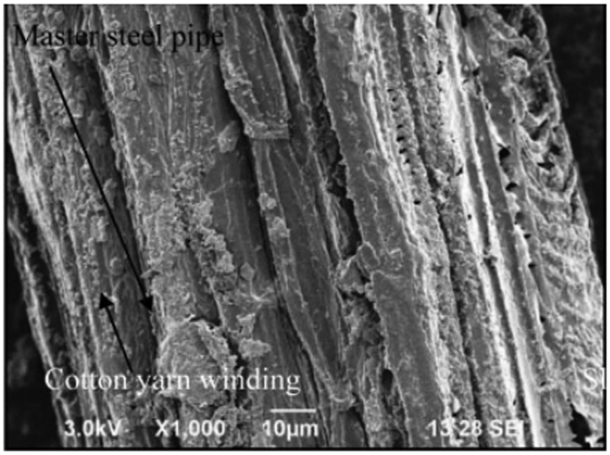


Figure 4.19

SEM image of Sisal fiber. *SEM*, Scanning electron micrographs. *Source: Reproduced with Permission Sathishkumar, T.P., Naveen, J., Navaneethakrishnan, P., Satheeshkumar, S., Rajini, N., 2016. Characterization of Sisal/cotton fibre woven mat reinforced polymer hybrid composites. J. Ind. Text. 47 (4). http://doi.org/10.1177/1528083716648764.*

Fiber extracted from the Sisal leaves and its hybrids can be utilized for producing pulp of superior quality. Sisal pulp has certain features which make this pulp suitable for several specialty papers. These features are listed below:

- High tear resistance
- High alpha cellulose content
- High porosity
- High bulk
- High absorbency
- High folding endurance

Furthermore, because Sisal pulp has better physical properties in comparison to softwood kraft pulp, opportunities exist for replacing softwood kraft with Sisal pulp in commodity papers in a cost effective manner. For instance, Sisal pulp can be utilized as a reinforcing fibre in high recycle content papers, or its use may allow reduction in basis weight while maintaining product quality. Sisal pulp is being used in the specialty paper segment. But, presently there is no market established in the commodity paper sector (www.hurterconsult.com).

Paper made from Sisal fibers show high tear strength and high opacity. It is used for making superfine, lightweight, bond and ledger paper, currency and security paper, tea bags, filters, publication paper, linerboard, wrapping, and bag paper, etc.

> Sisal is used by industry in three grades, according to www.Sisal.ws. The lower grade fiber is processed by the paper industry because of its high content of cellulose and

> hemicelluloses. The medium grade fiber is used in the cordage industry for making: ropes, baler and binders twine. Ropes and twines are widely employed for marine, agricultural, and general industrial use. The higher-grade fiber after treatment is converted into yarns and used by the carpet industry. Traditionally, Sisal has been the leading material for agricultural twine (binder and baler twine) but the importance of this is diminishing with competition from polypropylene and other techniques evolving. Apart from ropes, twines and general cordage, Sisal is used in low-cost and specialty paper, dartboards, buffing cloth, filters, geotextiles, mattresses, carpets, handicrafts, wire rope cores and macramé.
>
> *www.humanproteome.net*

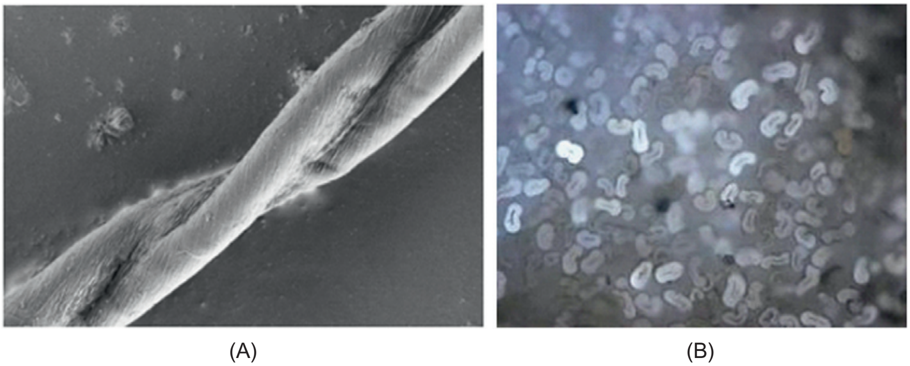
4.4.3 Seed hair fibers

Some plants have seeds covered with fibers. These fibers are found appropriate for producing paper. The discussion of four types of fibers used for papermaking are given below:

4.4.3.1 Cotton fibers

> Cotton fibers come from the seedpod of cotton plants. Regular cotton fibers are too long and too expensive for conventional papermaking. They are therefore only used in specialty papers. Most of the cotton fibers produced go to the textile industry. The average fiber length of cotton fibers is 25 mm and the average fiber diameter is 0.02 mm. In blends of various proportions, it is used to make high grade bond ledger book and writing paper.
>
> *Chandra (1998)*

Fig. 4.20 shows longitudinal view (5000 × magnification) and cross-section of cotton fiber (Smole et al., 2013).



(A) (B)

Figure 4.20
(A) Longitudinal view (5000 × magnification) and (B) cross-section of cotton fiber (Smole et al., 2013).

4.4.3.2 Cotton linters

> Cotton linters are short fibres (fuzz) located around cotton seeds. These fibres are separated from cotton seeds using a special machine, called linter machine or delinting machine. Cotton fibres collected after first pass using the delinting machine are called first cut linters and they are called second cut linters after second pass in the same machine. Third cut linters often called as hull fibres and mill runs are also available for pulp production. Cotton linters are delivered in bales; the weight of them depends on country origin. The bale weight is generally around 500 pounds. Main cotton species producing linters is Gossypium Hirsutum Latifolium. Other cotton species, such as Gossypium Barbadense, have naked seeds, so these species are not giving linters. Gossypium Hirsutum Latifolium represents roughly 87% of world cotton fibres production and Gossypium Barbadense around 8% of same production.
>
> ***www.textilesworldwide.blogspot.com***

Cottonseed oil mills purchase cotton seeds. These mills take out the cotton linters from the seeds. This is done by cutting them from the seeds using the circular saws which protrude through a grid. The linters can be taken out with one or more passes through the saws by controlling the depth the saw protrudes the grid and the residence time inside the cutting chamber. If they are taken out in just one operation, they produce a grade called mill run, which contains a mixture of long and short fibers. If more than one pass is used, then the long fibers are removed in the first pass and are termed as first cuts. The second pass removes the short fibers termed as the second cuts. These are used by the paper industry for producing cellulose derivatives as well as for rag content fine paper (Kilpinen, 1994). The fiber length of mill runs, first cuts and the second cuts are 3–5 mm, 3–7 mm, and 5–7 mm, respectively.

The average fiber diameter is 0.03 mm. In various combinations, it is used for making high grade bond ledger book and writing paper. Fig. 4.21 shows SEM image of cotton linters (Metzger et al., 2018).

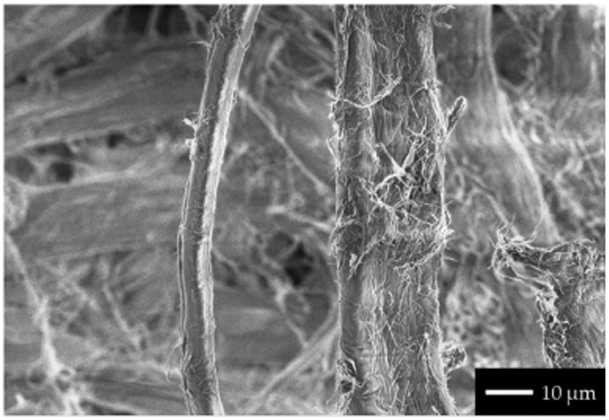


Figure 4.21
SEM images of cotton linters (Metzger et al., 2018). *SEM*, Scanning electron micrographs.

4.4.3.3 Cotton rags

Cotton rags are among the best fibers available for papermaking. These are the old cotton textiles that are not appropriate for their intended use. Because of the mechanical action that these fibers experience while in use as a cloth, they do not need extensive refining before making paper. The fiber lengths of the fiber are comparable to that of the cotton fibers. Important documents are often printed on cotton paper, as it is known to last several years without worsening.

> Cotton and linen fibres, derived from textile and garment mill cuttings; cotton linters (the short fibres recovered from the processing of cottonseed after the separation of the staple fibre); flax fibres; and clean, sorted rags are still used for those grades of paper in which maximum strength, durability, and permanence, as well as fine formation, colour, texture, and feel, are required. These properties are attributed to the greater fineness, length, and purity of rag fibre as compared with most wood pulp. Rag papers are used extensively for bank note and security certificates; life insurance policies and legal documents, for which permanence is of prime importance; technical papers, such as tracing paper, vellums, and reproduction papers; high-grade bond letterheads, which must be impressive in appearance and texture; lightweight specialties such as cigarette, carbon, and Bible papers; and high-grade stationery, in which beauty, softness, and fine texture are desired.
>
> ***www.britannica.com***

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CHAPTER 5

Problems associated with the use of nonwood fibers and how they are approached

Chapter outline

5.1 Storage and handling 84
5.2 Pulping 89
5.3 Bleaching 90
5.4 Papermaking 91
5.5 Chemical recovery 92
References 94
Further reading 97
Relevant websites 97

Use of nonwood plant fibers, is well liked but there are certain intrinsic disadvantages (Atchison, 1989a,b). Most of these problems are technical and need research in this area for becoming more viable with wood fibers. The main element for sustainable use of the nonwood fibers is to know their special character and how they have an effect on the technical aspects involved. Lower bulk density, short fiber, and the presence of high amount of fines are the most significant features (Rousu et al., 2002). Other drawbacks include transportation and storage issues; moderately high silica content; very fast degradation resulting in high losses (Bajpai, 2018). These disadvantages have prohibited the surfacing of nonwood fibers as a source of cost-competitive pulp for both writing and printing paper and cellulose products especially in those regions of the world where wood supplies are sufficient. Nevertheless, the use of nonwood fiber is common in wood limited countries, for instance, China and India, producing large amount of nonwood pulp.

Problems faced by the mills using nonwood fibers and some of the solutions that have been offered for making nonwoods more attractive as raw material for producing paper are discussed below. The problems are availability, storage and handling, pulping, bleaching, papermaking, and chemical recovery (Chandra, 1998).

Nonwood Plant Fibers for Pulp and Paper.
DOI: https://doi.org/10.1016/B978-0-12-821800-6.00005-3

5.1 Storage and handling

> Agricultural-residues are bulky and thus are not easy to handle. There is a need to develop efficient bailers to densify the material for efficient handling transport and storage. Bamboo has an unusual habit of flowering only once in its life. Flowering occurs in irregular cycles of 30–60 years. Nearly all the clums of one species start to flower at the same time, irrespective of their age, and the flowering spreads, covering large areas. After the flowering the plant dies, and there will be an interruption of supplies of 8–10 years. The phenomenon of flowering is not understood and more study needs to be done. Yield of most of these raw materials per hectare is low, about 1 ton/ha. in some of the cases. As a result, these raw materials need to be collected over a large area to meet the needs of a paper mill.
>
> Chandra (1998).

The comparison of some of these raw materials according to their yields and potential yields is presented in Table 5.1.

As most nonwood plants are annual, they have seasonal availability and a comparatively shorter harvesting time. Mills buy material during harvest and store it for the remaining operating year. During storage, the degradation of the raw materials takes place which result in reduced yield. A comparison between degradation suffered during storage of wood and some nonwoods are shown in Table 5.2. Data show, that efficient storage techniques should be developed for preventing or reducing this degradation.

Some attempts have dealt with storage problems of the nonwood fibers. Because of its unusual problems, extensive studies have been conducted on the storage and handling of bagasse. Although most of these studies are also applicable to other raw material.

Table 5.1: Dry matter yields for nonwood fiber crops.

Nonwood fiber crops	Annual yield (tons/ha.)	
	Average yield	Potential yield
Agricultural residues		
Straw	2	4
Annuals		
Flax	8	10
Hemp	10	15
Kenaf	10	40
Sorghum	9	30
Perennials		
Bamboo	7	20
Reeds	15	40
Elephant grass	17	60
Short rotation forestry	9	40

Source: Based on Judt, M., 1991. Desilication problem can be overcome. Pulp Pap. Int. 33 (6).

Table 5.2: Deterioration during storage of wood and some nonwoods.

	Fiber			
Storage method	**Hardwood Pile**	**Bagasse Piles or stacked bales**	**Straw Stacked bales**	**Kenaf Stacked bales**
Losses in fiber prep. (%)	5	ca 30	ca 30	ca 30
Power (kwh/ADMT)	480	ca 900	ca 900	ca 900
Steam (MT/ADMT)	4.5	ca 10	ca 9	ca 9

Source: Based on Perham, D. A.; 1990, Comparative economic and other factors effecting the viability of nonwood plant fiber bleached chemical pulp mills, TAPPI Nonwood Plant Fiber Pulping Progress Report No. 19, pp. 185–188.
Abbreviations: *ADMT*, air-dried metric ton

When bagasse is stored for a long time, biological action takes place which may rapidly result in yield loss and color degradation. The fiber properties are also degraded. Therefore special techniques of storage are required (Rainey and Covey, 2016).

Bagasse gets deteriorated during storage because of the actions of unwanted microorganisms (Al-Simaani et al., 1992). Substantial quantities of bagasse are rendered not suitable for pulping because of degradation by microorganisms. Leftover sugars, variety of tissues, and ecological conditions expedites the growth of microorganisms in bagasse piles. Damage done to bagasse is of the two types:

- Chemical degradation
- Discoloration

Chemical degradation is caused by biochemical reactions. This process influences yield and pulp properties (Rangan and Rangamannar, 1995).

The process for wet storage of bagasse was initially developed by E.A. Ritter and his colleagues in South Africa. It has proved to be a better method for storing bagasse (Atchison, 1989c). The preservation of the bagasse is excellent. The quality of the product is improved, and less chemicals are needed in pulping and bleaching processes (MacLeod, 1988; Hamilton, 1989). Wet (saturated) bulk storage is appropriate where the bagasse is to be used in a wet state, for example, for pulping. The bagasse is hydraulically transported and deposited in a pile that is kept saturated so as to minimize oxygen within the pile. This method has major application at present, but it has obvious disadvantages for bagasse that is to be used for combustion. In South Africa, it is applied at Felixton and Gledhow for depithed bagasse that is used in paper and cardboard (Purchase et al., 2013). There is some loss of material during storage and handling (Morgan et al., 1974). A disadvantage of this system is that the bagasse is laid down and retrieved as a dilute (3%–5%) slurry, meaning that considerable energy has to be spent in moving water. In another method—bulk storage without added water, the bagasse is piled without adjusting the moisture content. This method has been used for relatively small-scale projects, but is currently of interest for the increasing number of projects that require large-scale storage for cogeneration. There are, however, challenges associated with large-scale application of the method, and these justify a separate section within this paper. Another method is baled storage. It is one of the most common methods used in the industry of bagasse fiber boards and few pulp and paper mills in the world since the 1950s (Atchison, 1977; Lois, 1994). Bales are formed, either with or without binding material. The bale size and degree of compaction vary according to requirements. By selecting an appropriate bale size and by stacking bales with air spaces between them, it has been possible to control the heat build-up in the bales and to enable the heat and air circulation to dry the bagasse from 50% to about 20% moisture. This is the basis of the so-called 'Bagatex-20' method of bagasse storage (Anon, 1986). Compared to pile storage, it involves the additional expense of baling equipment and bale breaking equipment but it may reduce transport costs and allow long periods of stable storage. The moisture reduction leads to less loss of dry matter during prolonged storage and to higher net fuel value for combustion. Baling was commonly used when bagasse was stored for manufacture of boards because it was thought to give better quality boards than bagasse from wet bulk storage. However, there are examples of bales having to be discarded because deterioration during storage caused the bagasse to form boards of unacceptable quality. This, together with high labor requirement for handling of bales, caused some conversion from baling to wet bulk storage (Bernhardt, 1968).

Bagasse is a rich substrate for the growth of microorganisms when it is baled and stored as such obtained from the sugar cane mills (48%−52% humidity), (Lois, 1979). During the first few days of storage, the temperature increases quickly inside the bales, which along with other conditions initiates fiber degradation process. In addition, discoloration, high loss in fiber and other chemical and physical changes are observed (Lois, 1982; Schmidt and Walter, 1978). Another method for baled storage involves in drying the bagasse for reducing the humidity in the range of 20%−25% before baling. This technique substantially reduces the fermentation activity and, at the same time bigger bales, higher storage capacities can be produced and the fiber losses can be reduced (Lois, 1982). In spite of many studies about the behavior of baled bagasse (Lois and Suarez, 1983; Nakasone and Oda, 1976), there is no proof regarding enough trustworthy and truthful information upon the incidence of the various options of this technique on the quality of the stored material. Views differ regarding the figures of the loss during storage. During the recent past, many studies have been conducted by various researchers on the different techniques of storage.

In one study it was observed that due to microbiological action, weight loss in case of wet baled bagasse can go beyond 20%. In the case of the predried stored depithed bagasse, the weight loss was between 4.0% and 6.0% without substantial change in the morphological as well as chemical properties (Lois-Correa et al., 2010).

> The presence of pith in the bagasse has adverse effect in respect of lower pulp yield, high chemical consumption and quality related problems besides exhibiting runnability problems on the paper machine. Thus, there has always been interest in the efficient removal of this pith from the fibrous portion of bagasse so that the same can be used for pulp and papermaking in an efficient and better manner. Research work has been going on for producing efficiently depithed bagasse since the early 1900. These depithing processes have been mainly on methods which have used the dry/moist depithing or a combination of the moist and the wet depithing. In both processes, bagasse is mechanically abraded to break the clusters of pith away from the fibrous portion of bagasse.
>
> ***Rainey and Covey (2016); www.dcpulppaper.org***

> Dry depithing, moist depithing and wet depithing processes are used by paper industry for pith removal. However, in all these processes, bagasse is mechanically eroded for breaking the pith away from the remaining fibrous portion of bagasse. In wet depithing huge amount of water and energy is consumed. However, even by the best method (wet depithing), there is still substantial percentage of residual pith left in the bagasse (nearly about 18–20%).
>
> www.ijert.org

> Initial pith level in bagasse is around 36–38% which is reduced to 25% in dry depithing and to 18–20% by using wet depithing process. In the wet depithing, a suspension of 4–5% previously moist depithed bagasse is made in water, wherein after the pith is separated by utilizing the difference in the densities of the fiber and pith or this moist bagasse is treated in a hydrapulper or in a vertical wet aeration mill, wherein the pith passes through a screen and separated from fiber.
>
> ***Lois (2012); www.ijert.org***

There are several problems in wet depithing operations (Table 5.3). The pollution load generated in this effluent are shown in Table 5.4 (Dixit et al., 2014).

> A secondary wet depithing stage, just prior to charging to the digester, removes additional pith and any dust or dirt. Two stage depithing of bagasse has been the pattern for quite some years now. Two stage depithing, the process of separating the undesirable

Table 5.3: Problems in wet depithing.

A large amount of fresh water is consumed during the process (5000 tons of water in 500 tpd mill).
The high amount of water is discharged in to recipient stream as an effluent.
Problem of handling of wet pith.
Extra water accompanying the bagasse fiber. Nearly 2000 M3 effluent is generated in a 500 tpd paper mill in bagasse wet depithing. This water is laden with high effluent characteristics.

Table 5.4: Generation of pollutants in wet depithing.

Parameter	Value
COD (mg/L)	2200–2500
BOD (mg/L)	1200–1400
Suspended solids (ppm)	1000–1200
Color (PCU)	1200–1500

Source: Based on Dixit, A.K., Tarun, Sharma, A., Jain, R.K., 2014. ETWQQM -2014 Conference Proceedings. International Journal of Engineering Research & Technology (IJERT) 3 (3). ISSN: 2278-0181.

> pith content from the useful bagasse fiber, has also been successfully adopted for straw. In this case dry dusting is followed be wet cleaning. RAKTA a rice straw mill in Egypt was the first to install this process.
>
> ***MacLeod (1988); Hamilton (1989)***

In India Central Pulp and Paper Research Institute (CPPRI) has developed a method for dry depithing of bagasse. Bagasse after depithing contains only 5% pith and the results were better to those reached by most of the wet depithers being currently used in the paper mills. Thus the technology will provide a method for mitigating the use of fresh water and waste water pollution in pulp and paper industry.

> Studies in storage of straw have indicated that straw moisture content should be kept between 10–12%. At higher moisture content straw is subject to microbiological degradation and decay. Another problem is the danger of slow combustion developing in the stack creating a potential fire hazard.
>
> ***Jeyasingam (1988)***

> Wheat straw can be chemically treated with formic acid-based chemicals over a year without significant changes in the chemical composition. The chemical storage can be integrated with the suggested chemical or mechanical defibration process, soda pulping process or any other process utilizing nonwood fibers. In China, a clear demand for nonwood-based fibers exists due to a shortage of fiber and also because of the increasing demand for bioenergy. In Europe, the competitiveness of nonwood fiber utilization will only be established if combined with energy production.
>
> ***Leponiemi et al. (2010)***

A method for storage of green jute was developed in Bangladesh by Mohiuddin and Rashid (2001) bearing in mind the experience from United States, China, and El Salvador in kenaf storage. These researchers suggested that 12 inch diameter Jute bundles should be kept in vertical position with provision of air flow for a period of 10 days for bringing the moisture in the range of 15%–18%. If required, fungicide can be sprayed and bundles could be then arranged in horizontal two or three stories on bamboo/concreted frames or even criss-crossed.

5.2 Pulping

Pulping equipment generally used for producing wood pulp are not normally suitable for pulping of nonwoods. But chips from bamboo can be pulped. Nonetheless, pulping technology for nonwoods is well known. The soda, kraft and sulfite processes are used for producing a variety of semi-chemical and chemical pulps from different types of nonwood raw materials. Dissimilar to wood, the properties of pulps produced with the soda and kraft processes are similar. The selection of the process is based mainly on availability and the cost of make-up chemicals (www.hurterconsult.com).

It is easier to pulp nonwoods in comparison to woods. Nonwoods have a lower lignin content and so less chemicals are needed during cooking, where the raw material is treated with chemicals under high temperature and pressure for separating the lignin from the fibers. China is using sulfite method for pulping. Major development in the pulping of bagasse and straw was the introduction of rapid-cooking horizontal-tube continuous digester invented in the middle of 1950s. Earlier, rotating and tumbling batch digesters were being used. These digesters were able to cook a certain amount in 4–6 hours. In continuous digester bagasse and straw could be cooked in less than 10 minutes. In Table 5.5, comparison of cooking times is shown for different raw materials.

Table 5.5: Short-period continuous pulping of different raw materials.

Raw material	Pulping process	Chemical applied as Na_2O_2 (%)	Residence time (min)	Steam pressure (psi)	Pulp yield (%)	Perma-nganate number
Bagasse (cleaned)	Kraft	12.0	10	130	52	7.5
Wheat straw (uncleaned)	Soda	4.6	8	75	67	–
	Soda	10.0	8	80	50	–
Rice straw (uncleaned)	Soda	9.8	5.5	100	39	4.9
Reeds (uncleaned)	Soda	13.8	20	130	48	15.0
Reeds (cleaned)	Neutral-sulfite (chemical applied as Na_2SO_3)	19.1	25	150	53	12.3
	Neutral-sulfite (chemical applied as Na_2SO_3)	10.7	10	150	62	24.4
Esparto	Soda	12.4	20	120	52	6.0
Bamboo		18.2	30	130	45	10.0

Source: Based on Chandra (1998). Use of Nonwood Plant Fibers for Pulp and Paper Industry in Asia: Potential in China (Master's Thesis), State University.

> 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 while 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.
>
> ***Chandra (1998)***

High cost of energy and poorer quality of pulp, usually renders the mechanical pulping of jute less attractive despite the noticeable benefits of high yield and lesser generation of pollutants. Biological pretreatment of jute before refining reduces energy consumption during mechanical pulping (Sabharwal, 1995). Processing of kenaf is a problem as the fiber bundle are coarse and stiffer (Tao et al., 1995). Likewise, bamboo nodes are harder to cook as they are highly lignified. Extensive study with these fibers is needed before these can be utilized in an efficient manner. Most nonwood fibers have high silica content. Silica creates several problems. Washing gets difficult due to poorer drainage of pulp and higher viscosity of black liquor. Big washers about two times the normal size are needed for washing of 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. Another problem suffered by nonwood plant pulping has been low yield. Studies on anthraquinone pulping have been quite promising in this regard. Anthraquinone pulping improves yield by up to 5%.
>
> ***Yilmaz (1995a,b); Hart et al. (1994)***

Nonwood pulps such as cereal straws and bagasse show slower drainage in comparison to wood pulps. Thereby larger brown stock washer areas are required. However, flax, hemp and kenaf bast fiber pulps show faster drainage and need smaller washer areas. The same is applicable to bleach plant washers (www.hurterconsult.com)

5.3 Bleaching

Bleaching of nonwood fibers is not easy. It is relatively tougher as compared to bleaching of wood pulps. Studies show that pretreatment with enzyme can increase final brightness of pulp by 2% ISO (Prasad et al., 1996; Lin et al., 2013). With use of oxygen alone brightness ceiling of the straw pulps is not improved because of the formation of oxygen radicals produced from reaction of transition metals present in the pulp as well as oxygen (Bajpai, 2012).

Many studies have been conducted on totally chlorine free bleaching of wheat straw pulp using xylanase enzymes and ozone. Final brightness of bleached wheat straw pulp did not exceed 85% (Roncero et al., 2003; Singh et al., 2011). Different conventional and elemental chlorine free short sequence bleaching have been explored. Chlorine dioxide based bleaching sequence was found to be the best in bleaching of wheat straw pulp (Ghosh, 2006). Few studies were conducted to increase the brightness of wheat straw pulp by removing the formation of chromophoric compounds which hinder the brightness development. Bleach boosting chemicals and enzymes were studied (Bajpai, unpublished results). The incorporation of last peroxide stage in bleaching sequence, resulted in an increase of final pulp brightness by 2.5%–2.9% ISO (Bajpai, 2012). Hydrogen peroxide pretreatment of unbleached wheat straw pulp resulted in an increase in final bleached pulp brightness by 1.8%–2.1% ISO with significant reduction in chlorine chemicals and generation of polluting chemicals during bleaching. Addition of hydrogen peroxide in oxidative extraction stage of bleaching increased the final brightness of bleached pulp by 1.1% ISO and whiteness by 1.5% ISO with same amount of bleaching chemicals.

For some type of nonwoods such as bagasse and cereal straws, an important aspect of designing the bleach plant would be to avoid mechanical action on the pulp. These pulps are prone to mechanical action which will reduce the freeness of pulp. Use of high shear mixers should be avoided (Hurter, 1998).

5.4 Papermaking

The drainage is slower in case of nonwood fibers and create problems in the paper machine. Due to this, the paper machine cannot be run at high speed, thus reducing the production. Short fibered nonwoods such as wheat straw damage paper machine efficiencies. Table 5.6 shows this difference in the maximum speeds for different raw materials.

> Short fibers of most nonwood plants provide excellent formation and acceptable strength properties. However, these fibers also have low wet strength, and are therefore not easy to pick up at the couch. They therefore require a certain amount of wood pulp in the furnish to improve the runnability.
>
> ***Chandra (1998)***

Table 5.6: Typical paper machine speeds for different furnishes.

Furnish	Older machines (open draw) (m/min)	New machines (no draw press section) (m/min)
Bagasse	200–350	400–650
Rice straw	100–180	200–400
Other straws	150–250	300–500
Wood	250–500	500–800

Source: Based on Young, Raymond A.; 1997, Processing of Agro-Based Resources into Pulp and Paper, In Paper and Composites from Agro-Based Resources, Ed. R. M. Rowell, R. A. Young, and J. K. Rowell, Lewis Publishers, New York, pp. 137-245.

> Technically, to obtain the necessary quality profile and runnability of bagasse based newsprint, 15–20% of chemical pulp must be added to the furnish. Paper machines running on bagasse must also operate at lower speeds than those of wood-fiber machines. Typically, a paper machine using large percentage of bagasse in the furnish might run at 680–720 m/min., compared to 1,000–1,300 m/min. for a wide modern newsprint paper machine using wood pulp.
>
> ***Covey et al. (2006); Panwar et al. (2008)***

Bagasse stock is well hydrated with slow drainage characteristics (Jahan, 2006). It normally requires less rosin size and more alum than conventional wood fibers. Modifications in machine design are required to improve drainage. Due to low wet strength closed draws like suction pick up are necessary to transfer the web from the wire in the press part. The wire part should be longer with modern drainage elements such as multiple blade foils systems, more suction boxes. The felts should have high porosity.
Felts tend to clog due to higher amount of fines. The drying curve for bagasse furnish is greatly flattened compared to conventional fibers requiring more drying surface.

The design of paper machines differ for furnishes having a high amount of nonwood. For instance, more drainage elements in the wet end are needed for papers having a high content of cereal straw or bagasse. Press loading will be lesser for avoiding sheet crushing. Dryer section will need more sections to account for the greater shrinkage of the mainly nonwood sheet. Machine speeds for high nonwood content sheets are also generally lower as compared to wood pulp papers. But when the nonwood pulp in the sheet is in the range of 10%–30% with the balance being wood pulp and or recycled pulp, there should not be much effect on the design and operation of the paper machine. Actually there may be some improvement in quality. For instance, a furnish containing 20% cereal straw would help in improving the opacity as well as sheet density. Alternatively addition of 10% flax bast pulp as a substitute for softwood kraft pulp would permit for reduced basis weights or reduced use of long fiber in the furnish.

5.5 Chemical recovery

> For the pulping of the nonwood raw materials generally soda pulping process and Kraft pulping processes are used. Nonwood raw materials have very high silica content which varies from 1.5% to 20%. Most of the silica present in raw material passes into black liquor. Presence of silica in relatively high concentration causes several problems in chemical recovery plants. Evaporator, recovery furnace, and lime kiln operation are adversely affected by the presence of silica in black liquor. Nonwood plants, require more cooking liquor due to the open structure. Silica also reacts with alkali during

> pulping which further increases the alkali requirement and increases the inorganic chemical load in the recovery process. This results in lower organic/inorganic ratios, lower heating values, and more inorganic chemical to be reclaimed and reconverted.
>
> ***Bajpai (2008, 2017); Ibrahim (1988); Dixit et al. (2010, 2012); Grace (1987a,b)***

In most of the nonwood paper mills, chemical recovery system is not installed. These mills are smaller as compared to wood-based paper mills (Table 5.7). Most of these mills have a low profit margin of 6%–10%. Therefore these mills do not see any point in installing a chemical recovery systems. They are responsible for contaminating the environment with harmful substances. These mills are now under great pressure for cleaning up or closing down.

Pollution can be reduced significantly by using at source control measures instead of end of pipe treatment (Gupta, 1994). Table 5.8 shows the reduction in pollution load after these measures were adopted.

> This shows that with a little careful control of the waste generated in these paper mills, the overall pollution load can be greatly reduced. The main problems existing in Na-based sulfite pulping of bagasse are the technique and economy of pulping spent liquor treatment and chemical recovery. Spent liquor of ammonium sulfite pulping can be used as fertilizer material directly. The same advantage is offered by potassium-based sulfite pulping spent liquor. For small or medium scale pulp mills, whole potassium-based sulfite pulping liquor (with neutralization if required) may be used for agricultural purpose directly. The benefits of using of ammonium based liquor, are that the waste liquor instead of being a pollutant can be used as a fertilizer and has been shown to positively affect the crop yields.
>
> ***Chandra (1998); Huaiyu et al. (1995); Zhong (1995)***

Table 5.7: Size of nonwood pulp mills.

Tons/day	India (%)	China (%)	Thailand (%)	Indonesia (%)
Over 100	34	12	28	40
50–100	09	21	14	00
Less than 50	57	67	58	60

Source: Based on Sabharwal, H.S., 1995. Refiner mechanical and biomechanical pulping of jute. Holzforschung 49 (6), 537–544.

Table 5.8: Reduction in pollution load after implementation of waste minimization measures.

Parameter	Reduction (%)
Flow (m^3/ton)	30
COD (kg/ton)	34
BOD (kg/ton)	36
TSS (kg/ton)	39
TS (kg/ton)	41

Source: Based on Gupta, P.K., 1994. Environmental management of agro-based pulp and paper industry in India—a holistic approach. Water Sci. Technol. 30 (3), 209–215.

Large mills have chemical recovery but they also face problems. Black liquors from nonwood fiber pulping have very high viscosities about 10 times more as compared to kraft liquor from pine. They are difficult to handle at high solid contents. They also have high silica which create problems in evaporators, recovery boilers, causticizing equipment, and lime kilns. Other problems are formation of scale in the evaporator tubes, formation of deposits on the furnace walls of the recovery boilers, slower settling rates of recausticizing white liquor and unsuitability of lime sludge for reburning. These problems should be addressed.

The main problems are large amount of silica (1%−3% of dry solids), higher viscosity because of higher pentosan content and reduced heat value because of less lignin content and high content of carbohydrates resulting in reduced carbon content. Wood black liquor is foamy whereas bagasse black liquor is not. Because of difficulties in washing bagasse pulp, large amount of water is used which gives high sodium losses and reduced recovery efficiency. Also total solids in weak black liquor are lesser. High amount of silica goes to lime mud in the form of calcium silicate during recausticization. This reduces the efficiency of lime mud recovery and also reduces calcium oxide content of lime produced by reburning.

Desilication with lime has received a lot of attention as lime is inexpensive and calcium silicate is fairly insoluble. Several researchers have been involved in developing the process using carbonation (Kulkarni et al., 1991). The most exhaustive study was conducted in 1970 and 1980. Lurgi, Kraftanlagen Miinchen and some mills have been involved in developing suitable desilication technology. The technology developed by the CPPRI (India) along with United Nations Industrial Development Organization (UNIDO) and Swedish International Development Cooperation Agency (SIDA) has reached to an operating level (Judt, 1991). Lurgi, Dorr-Oliver have used boiler flue gas to precipitate the silica, and both processes have been operated at pilot scale at the RAKTA rice straw mill in Egypt. The Dorr-Oliver method uses lime for performing this task (MacLeod, 1988). The CPPRI/UNIDO process when compared with the Kraftanlagen and Lurgi process is quite simple. There is no requirement of high pressure flue gas. The carbonation is performed in three stages. This process is gentle, stepwise results in bigger silica gel particles. A high capacity axial flow pump having a low speed, low head preventing to high shear forces is used which can disintegrate gel particles. The belt filter is accessible, easier to clean, and reliable dissimilar to a separator centrifuge. One strategy developed in Austria is to use a submerged type of bubble reactor. In this reactor, flue gas is bubbled into the black liquor for adjusting the pH which results in silica precipitation. pH control is crucial but as pH at which lignin gets precipitated is very closer to that of the silica (Hurter, 1998).

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Relevant websites

http://www.dcpulppaper.org

http://www.ijert.org

http://www.hurterconsult.com

CHAPTER 6

Handling, storage, and preparation of nonwood raw materials for pulping

Chapter outline

References 104
Further reading 106
Relevant websites 106

The handling, storage, and preparation of nonwood raw materials for pulping differ in most cases from the well-established systems used for wood pulping processes (Azeez, 2018). The nonwood raw material preparation involves depithing (when bagasse is used as raw material), digesting, washing, screening, cleaning, etc.

> Small bamboos and reeds are handled and stored in bundles whereas the large bamboos are handled and stored in ranked piles as the woods are stored. The harvested grasses are usually baled for transportation unlike cereals, which are baled before being transported to the mill, and are stored in bale form in large piles. Sugarcane bagasse is obtained from the sugar mills after which sugarcane is being processed, and the residue (bagasse) is collected and baled for storage.
>
> *Liu et al. (2018), Rainey and Covey (2016)*

In those mills where the entire plant is processed for producing the bast fibers pulp, there is a need for removing the bast material from the woody stem and also remove the fibrous material from the leaves. In other cases, the separation or removal is made. So, it is not required. The whole stem of kenaf plant is chipped and pulped. It contains a mixture of long blast fibers as well as short fiber pulp from the woody core (Hurter, 1988; Chandra, 1998). Large bamboos are chipped in disk chippers or in large drum chippers or sometimes even crushed or merely chipped. Disk chippers are used in case of wood. For obtaining good results, the chippers used for bamboo can be joined with a force feed. The chips are screened and stored before pulping in bins. The dust produced during the chipping of bamboo is generally collected. It is utilized as fuel in the mill boilers (Hurter, 1988). In the majority of cases, cutters alike to those used for cereal straws are used for cutting reeds and bamboo. However, these cutters are heavier. A lot of leaf material is attached to the stalks. Therefore air separation stage is needed for removing the leaves from the reeds. This step is important in the reed screening system. The bamboo and reeds chips are generally stored in bins with traveling screws at the bottom.

Nonwood Plant Fibers for Pulp and Paper.
DOI: https://doi.org/10.1016/B978-0-12-821800-6.00006-5

> Special cutters are employed in the cutting of cereal straws, after which the cut hay is cleaned and screened by pneumatic and mechanical screening systems designed for this purposes. The straws are then hammer milled using hammer mills of special designs which are used to break the bales and cut the straw to the desired length. In most cases, the straw cutting and preparation may be operated only during digester filling. Rice straw contains a lot of impurities such as dirt and leaf materials. For this reason, it is subjected to a wet cleaning stage in addition to the standard dry cleaning process. The difference in the genetics of the biomass can result in variation and the quality of the pulp when the entire plants are used in the pulping process. Before cooking is done in the pulp mill, separation of dust leaves and dirt is done using air fractionation. The bleaching quality of the pulp is improved by the use of mechanical pretreatment which favours the decrease or removal of the silica and other unwanted particles from the raw material. In Sweden, a dry fractionation system was developed which is composed of a shredding, chopping, milling compartment in a disk mill and also used for the screening of reed canary grass.
>
> ***Ilvessalo-Pfaffli (1995), Saijonkari-Pahkala (2001), Azeez (2018)***

Biopulping is the treatment of lignocellulosic raw materials with oxidative lignin degrading fungi or enzymes prior to the pulping process (Akhtar et al., 1996; Martinez et al., 1994, 2000; Reid et al., 2010; Scott et al., 2002). This process reduces energy consumption and improves the pulp properties in case of mechanical pulping process. In the chemical pulping process, the chemical consumption is reduced and the quality of pulp is improved, and the environmental problems are also improved.

Treatment of kenaf (whole stalk) with *Ceriporiopsis subvermispora*, a white-rot fungus resulted in a saving of about 38% of electrical energy in comparison to control when pulping was done using refiner mechanical pulping (RMP) process or chemirefiner mechanical pulping process. Additionally the pulp properties were improved in terms of burst index, tear index, and tensile index. In case of RMP biomechanical pulps, the brightness reduced by 15%–20% but it could be increased upto 62% with use of 2.5% hydrogen peroxide in comparison to 1% hydrogen peroxide used in case of reference pulp (Ahmed et al., 1999).

In case of bast strands treated with fungi, the energy consumption in refining reduced significantly and the strength properties were better in case of biomechanical bast pulps (Sabharwal et al., 1994, 1995). The brightness was lower but the drainage and opacity were higher. Scanning electron microscopy (SEM) of bast strands treated with fungus after refining revealed that fibers were separated more readily from adjacent fibers as compared to reference treatments. Different enzymes were also used to treat nonwoods to save energy and reduce consumption of chemicals while maintaining acceptable properties of chemi-thermomechanical pulp (Giovannozzi-Sermanni et al., 1997). The savings in energy depended on the kind of raw material. The values ranged from 21% for rice straw and 40% for kenaf bast. Enzymatic treatment substantially improved tear index in spite of the cellulose source but the tensile index reduced in wheat straw as well as kenaf bast samples.

Burst index was better in case of biotreated samples, except kenaf. Pulp yields of the enzyme-treated samples were significantly higher as compared to those of the reference samples (without biotreatment). This was due to the reduced chemical requirement for enzyme-treated samples.

Mushrooms of *Pleurotus* sp. are able to degrade lignin preferentially from agricultural waste without much degrading cellulose. Nambisan and Koshy (2011) studied biopulping of paddy straw by *Pleurotus eous* using solid substrate fermentation method. "Spent mushroom substrate (SMS), the mushroom growing medium that results from cultivation process, is a good source of fiber and can be pulped easily. Ligninases present in SMS were found to reduce lignin content to nearly half the initial amount by 21st day of cultivation. Highest cellulose content (% dry weight) was observed on 21st day, whereas cellulase production started from 28th day of cultivation. SEM images showed that SMS fibers are still associated with noncellulosic materials when compared to chemically (20% w/v NaOH) extracted fibers" (researchpub.org).

> Biopulping of pineapple leaf fiber (PALF) by *C. subvermispora* showed good tensile properties at 0.3% of fungal treatment and desirable structural properties as characterized by Fourier transform infra-red spectroscopy. PALF paper achieved desirable tear index value and uniform morphological observations compared to the conventional chemical pulping method. This new approach of pulping PALF finds applications in paper and packaging products which requires biofriendly characteristic and cost effectiveness.
>
> ***Sikora et al. (2014); researchpub.org***

In another research, pretreatment of wheat straw was done with *C. subvermispora* and *Phlebia subserialis* before soda pulping with AQ. Pretreatments with fungi increased delignification and degradation of carbohydrates. Pretreatment with *P. subserialis* resulted in an increase in the brightness and reduction in the kappa number and pulp viscosity more than pretreatment with *C. subvermispora*. There was increase in bulk, brightness, and tear index of papers by the fungal pretreatments. However, the tensile index and burst index reduced at various refining levels (Fatehi et al., 2009).

Ates et al. (2008) observed a reduction in kappa number by 24% along with approximately 7% increase in the unbleached brightness of the wheat straw pulp pretreated with two white-rot fungi - *Ceriporiopsis subvesmispora* and *P. subserialis*. But there was slight drop in the strength properties of the unbleached and bleached chemical straw pulps after the fungal treatment. Fungal mycelium (*C. subvermispora*) showed a positive impact upon lignin degradation during organosolv pulping. The acetic acid charge was reduced by 21.5%. But reduction in cellulose was noted (Saad et al., 2008).

Bajpai et al. (2004b) pretreated wheat straw with white raw fungi for studying its effect on chemical pulping. When wheat straw was treated with *C. subvermispora*, the lignin content reduced by 16.5% and extractives content reduced by 44.3%. Pretreatment reduced the kappa number by 22%−27% at the similar alkali charge whereas for the similar kappa number, the alkali charge reduced by 30 kg/ton of raw material or the cooking time reduced by up to 30% (Tables 6.1 and 6.2). The biopulps showed an increase in brightness and whiteness in comparison to reference pulp (without fungal treatment). The chemical oxygen demand (COD) generation in the effluent was lesser for biopulping as compared to conventional pulping. Biopulping benefits obtained with other white-rot fungi, *P. subserialis*, and *Phlebia brevispora*, were lesser in comparison to benefits obtained with *C. subvermispora*.

> Treatment of depithed bagasse with different strains of *C. subvermispora* reduced the κ number by 10–15% and increased unbleached pulp brightness by 1.1–2.0 ISO points on chemical pulping at the same alkali charge. Bleaching of biopulps at the same chemical charge increased final brightness by 4.7–5.6 ISO points and whiteness by 10.2–11.4 ISO points. Fungal treatment did not result in any adverse effect on the strength properties of pulp.
>
> ***Bajpai et al. (2004a)***

Microbial retting is an old process dating to the beginning of civilization (Hoondal et al., 2002). This technique has been utilized for the processing of the bast fibers. But due to the extended duration time and generation of polluted water the traditional retting method is becoming less attractive. Other techniques include mechanical decortications, use of chemicals, heat, and enzymes (Tahir et al., 2011).

Table 6.1: Soda pulping of wheat straw with *C. subvermispora* Strains 1 and 2 at reduced alkali charges.

Parameters	Control	Strain 1	Strain 2	Strain 3
EA (%)	12	10	10	9.0
Kappa number	28.6	28.6	26.7	28.3
Yield (%)	45.9	48.1	45.9	46.7
Brightness (% ISO)	34.6	34.6	35.7	34.7
Residual alkali (g/L)	1.9	2.1	2.2	1.9

Source: Based on Bajpai, P., Mishra, S.P., Mishra, O.P., Kumar, S., Bajpai, P.K., Singh, S., 2004a. Biochemical pulping of wheat straw. TAPPI J. 3 (8), 3–6.

Table 6.2: Effect of cooking time on soda pulping of *C. subvermispora* treated wheat straw.

	Cooking time (min)	Kappa number	Yield (%)	Brightness (% ISO)
Control	60	28.1	45.9	34.1
	45	30.1	46.5	33.9
	30	31.5	47.1	33.1
	15	Ellipsis	–	–
C. subvermispora Strain 2	60	21.9	46.1	38.2
	45	22.5	47.2	37.6
	30	24.1	47.8	37.1
	15	26.1	48.1	36.2

Source: Based on Bajpai, P., Mishra, S.P., Mishra, O.P., Kumar, S., Bajpai, P.K., Singh, S., 2004a. Biochemical pulping of wheat straw. TAPPI J. 3 (8), 3–6.

The kappa number reduced by two points when wheat straw was pretreated with a crude enzyme containing mostly xylanase produced from *Aspergillus niger* strain An-76. There was lesser generation of rejects. The fines reduced, and brightness increased by 3% points (Zhao et al., 2002).

Crude xylanases and pectinases have been used in several studies. Pretreatment with enzymes from *Penicillium* A10 and *Aspergillus* L22 at a xylanase dose of 4 IU/g before pulping reduced kappa number of pulp by 6.29% and 12.07%, respectively, in comparison to the reference pulp (Zhao et al., 2006).

> Pulping of nonwoods raw material with the use of enzymes has better possibilities. High quality pulps of cotton and bast fibers of flax and hemp, is 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 shorten the beating time considerably. The technique has been tested in full scale.
>
> ***Bajpai (2018)***

The mechanical properties of the fibers improved when the jute, flax, and ramie were treated with cellulase enzymes. Flexibility was increased and tensile strength was better. Microbial pectinase enzymes (pectin-depolymerizing enzymes) liberate cellulosic fibers from fiber bundles (Hoondal et al., 2002).

> Pectinases have a leading role in removing interlamellar pectin which acts as a cementing substance between the fibers. It is essential to optimize the levels of the factors that the process depend on such as particle size of the substrate, initial moisture content of the medium, incubation temperature etc. A single pectate lyase enzyme successfully removes the pectate materials from the surface of hemp fibers.
>
> ***Jacob and Prema (2008); Ouajai and Shanks (2005)***

> Enzymatic pretreatment could be performed in the prebleaching sage or even during the papermaking process. Commercial xylanase preparation has beneficial effect on bleachability of nonwood ASAM, Organocell and Ethanol-Alkali organosolv pulps. Enzymatic pretreatment boosted the subsequent chemical bleaching of organosolv pulps with oxygen-based reagents. Increase in ISO brightness and decrease in lignin content along with reduced consumption of active bleaching chemicals was noted. Pretreatment of kenaf pulp with xylanase decreased the kappa number while improved the brightness.
>
> ***Shatalov and Pereira (2007); Latifah et al. (2007)***

Enzyme from *Pleurotus eryngii* was used to delignify wheat straw. Enzyme treatment did not have any unfavorable effect upon strength properties of the pulp (Martinez et al., 2000).

Prebleaching of whole jute kraft pulp with xylanases increased ISO brightness by 3%–4% without having any harmful effect on physical strength properties (Jain, 2004). During papermaking, pectinase can depolymerize pectins and then reduce the cationic demand of pectin solutions, and the filtrate generated from peroxide bleaching (Ricard and Reid, 2004).

The effect of xylanase pretreatment on bagasse kraft pulp was studied (Thakur et al., 2012). Pulp after treatment with enzyme was subjected to elemental chlorine free bleaching. Pulp kappa number was reduced by 14.0% in comparison to control and brightness increased by 2.17 units.

> Wheat straw pulp was mechanochemically processed in a PFI mill for improving the effect of laccase/xylanase system treatment before bleaching. The delignification of the prepared pulp could be enhanced with the mechanochemical processing (refining) and laccase mediator system treatment. The delignification was increased by 29.8% with refining 7000 revolutions and 5 IU/g enzyme dosage. The laccase mediator system treatment after the mechanochemical process could save 28.6% effective usage of chlorine in the subsequent hypochlorite bleaching process, compared with the traditional biobleaching. The crystallinity of cellulose was increased by the cotreatment with mechanochemistry and laccase mediator system treatment. This result was further supported by the observations from SEM. This cotreatment with mechanochemistry and biotreatment enhanced the delignification and bleachability of pulp.
>
> ***Lian et al. (2011); www.ncsu.edu*****.**

Pretreatment of wheat straw kraft pulp using laccases expressed in *P. cinnabarinus* or *A. niger* with 1-hydroxybenzotriazole as redox mediator resulted in about 75% delignification whereas with the recombinant laccase from *A. oryzae*, the delignification was not achieved.

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Relevant websites

http://www.ncsu.edu

http://www.intechopen.com

CHAPTER 7

Pulping properties/pulping

Chapter outline

7.1 Pulping properties of nonwoody raw materials 107
  7.1.1 Gramineous fiber materials 108
7.2 Pulping of nonwoody raw materials 111
  7.2.1 Alkaline pulping 114
  7.2.2 Sulfite pulping 120
  7.2.3 Organosolv pulping 123
  7.2.4 Chemimechanical pulping and other pulping methods 130
    7.2.4.1 CMP and CTMP processes 131
    7.2.4.2 Alkaline peroxide mechanical pulping process 132
    7.2.4.3 Steam explosion pulping 133
    7.2.4.4 Extrusion pulping (Bivis) 133
    7.2.4.5 Mild acid cooking method 134
    7.2.4.6 Biopulping 134
7.3 Washing, screening, and purification of nonwood pulp 135
References 138
Further reading 144
Relevant websites 145

7.1 Pulping properties of nonwoody raw materials

Pulping is a process of delignification. In this process, lignin is chemically dissolved by the use of chemicals and the fibers are separated in the raw material. This allows separation of fibers in the raw material. “Paper pulp” is in fact an aggregation of the cellulosic fibers which are released from the raw material (Bajpai, 2018a). The fibers are separated by treating with alkali, sulfite, or organic solvents to separate the fibers. This process partly removes the lignin and other noncellulosic components from the matrix. Fibers can also be separated in mechanical or chemimechanical pulping processes. The fibers are taken out from the aqueous suspension and are subjected to washing and bleaching. In the final process which is papermaking, a water suspension containing different fiber components and additives are pressed and dried on a fine screen which runs at high speed, and produces a thin paper sheet. In this process, fibers bond together and produce a layered network. The inter-fiber bonding determines the strength of the paper (Wood, 1981; Philip, 1992).

Nonwood Plant Fibers for Pulp and Paper.
DOI: https://doi.org/10.1016/B978-0-12-821800-6.00007-7

> The selection of different types of pulps depends on the quality desired in the final product. In fine papers the amount of short fibre (fibre length 0.6 to 1.9 mm) is 20 to 100%. Long fibres from softwoods (coniferous trees) or nonwood plants (flax, hemp, kenaf) are necessary to form a matrix of sufficient strength in the paper sheet. The shorter hardwood fibres (deciduous trees, grass fibres) contribute to the properties of pulp blends; especially opacity, printability and stiffness are improved. The role of the short fibre pulp in fine papers is to give good printability to the paper. On the other hand, the required strength for runnability is adjusted by adding long softwood fibres. In high quality papers such as writing and printing papers, chemical pulps are used. Mechanical and chemi-mechanical pulps are good raw materials for newspapers.
>
> ***Atchison (1987b); Paavilainen (1996a,b)***

In nonwoods, the high concentration of minerals and particularly silica is present, which causes problems in pulping (Azeez, 2018). Silica gets dissolved into the pulping liquor in alkaline pulping, and when the black liquor is evaporated in the recovery boiler, the concentration of SiO_2 increases causing problems in the process (Hultholm et al., 1995). Several desilication methods have been developed which show that removing of SiO_2 is possible (Judt, 1991; Kulkarni et al., 1991), but these methods are not often used in small mills, where most of the commercial nonwood pulp is produced (Sadawarte, 1995).

7.1.1 Gramineous fiber materials

The delignification process can be divided into following three stages (Liu et al., 2018):

- Main stage of lignin removal
- Supplementary stage of lignin removal
- Stage of residual lignin removal

The delignification process is different with gramineous straw materials in comparison with wood fiber. This is presented in Table 7.1.

Lignin of gramineous straw materials gets easily solubilized as compared to those of softwood materials in pulping process with alkali. The reasons are shown in Table 7.2.

The causes for the difference between grass and wood can be attributed to the biological composition of grass, and also the type of cell constituting grass. Fiber cells account for 40%−60% of total cell mass. It is the main cell of gramineous fiber. The fiber length is 1.0−2.0 mm with the exception for bamboo and the diameter is usually 10−20 μm. Tables 4.2 and 4.3 show the fiber properties of common grass fiber materials. Parenchyma is another type of major cell in the raw material; the shape and size are found to vary. The cell wall is thinner and the cell cavity is bigger. The water absorption is 15 times more in comparison to the fiber cells. This results in an increase in the liquid ratio in the pulping process. Furthermore, the length of the parenchyma cell is smaller. This affects the paper

Table 7.1: Delignification stages of straw and softwood.

Items	Straw		Softwood
	Sodium hydroxide method	AQ–sodium hydroxide method	
The first stage of lignin removal	The main stage of lignin removal		The initial stage of lignin removal
Temperature (°C)	<100	< 100	<140
The removal rate of lignin (%)	60	61–62	20–25
The dissolution rate of hemicellulose (%)	45	45	–
The second stage of lignin removal	The supplementary stage of lignin removal		The main stage of lignin removal
Temperature (°C)	100–160	100–160	140–170 and the earlier stage of heat preservation
The removal rate of lignin (%)	25–28	28	60–70
The dissolution rate of hemicellulose (%)	9	9	–
The third stage of lignin removal	The stage of residual lignin removal		The stage of residual lignin removal
Temperature (°C)	Heat preservation at 160°C	Heat preservation at 160°C	The later stage of heat preservation (170°C)
The removal rate of lignin (%)	5–10	5–10	10–15
The dissolution rate of hemicellulose (%)	2–3	1–2	–

Source: Based on Li, Z.Z., 2011. Overview of recent development of nonwood fibers pulping in China. China Pulp Pap. 30(11), 55–63.

Table 7.2: Reasons for faster solubilization of lignin in gramineous straw materials.

Fibrous structure of gramineous straw materials is loose, lignin content is low and hemicellulose content is high. The rapid cooking process is closely related to the structure of lignin. Containing high percentage of phenolic hydroxyl and acid groups which can be easily ionized in alkaline medium, the gramineous straw lignin is lyophilic and readily soluble. The lignin is easily removed; it has low molecular weight and high dispersity. The hemicellulose in gramineous straw material gets easily degraded and dissolved during cooking process with temperature increasing to 100°C, which is accompanied by the reduction of lignin-carbohydrate complex content. The dissolution of hemicellulose can also open the channel for the penetration of the cooking liquor and the digestion of lignin, thereby promoting the removal of lignin from the cell wall.

Source: Based on Liu et al (2018). Liu, Z., Wang, H., Hui, L. (2018). Pulping and papermaking of nonwood fibers, pulp and paper processing, Salim Newaz Kazi, IntechOpen. Available from: https://doi.org/10.5772/intechopen.79017. <https://www.intechopen.com/books/pulp-and-paper-processing/pulping-and-papermaking-of-nonwood-fibers>.

strength and stability (Huamin, 1988). Hence, if higher content of parenchyma cells are present, the pulping value would be lower. The vessels transport nutrients and water by the plant, containing several vessel elements. In the pulping process, the vessels are the major path for penetration of the pulping liquor. The liquid chemicals first pass into the vessel from one side of the material, and then it enters the other cell through the pits. The vessel elements of bamboo are generally larger unlike the ordinary straw. The long cell improves the binding strength between cells. The silicon cell of short cell is the major source of silica. In the alkaline pulping process, silica cells get dissolved by alkali. This results in an increase in the sodium silicate content in the waste liquor. Also, the viscosity of black liquor increases, and consequently, the danger of "Silicon Interference" in alkali recovery process increases. When acid pulping process is used, epidermal cell are seen in the pulp, which can cause paper disease. Sclereid which is a sclerenchyma cell has two types of cell walls: primary wall and secondary wall. The secondary wall is quite thick and highly lignified (15%–35%) and imparts a great firmness and hardness to the cell and the tissue. Two major types of sclerenchyma cells are found: sclereids and fibers. Sclereid belongs to nonfibrous cells, and is present mostly in the cortex and pith, particularly in bamboo fiber.

7.1.1.1 Bast fiber materials

Bast fiber is also called phloem fiber and is an excellent fiber material. It is a powerful mechanical tissue. It is a type of plant fiber and can be collected from the phloem or bast which surrounds the stem of certain dicotyledonous plants. The strands of bast fibers are generally liberated from the cellular and woody tissues of the stem by using chemical, mechanical, or biological methods. Bast materials have thin and long fibers, such as hemp, flax, jute, kenaf, and so on Hurter (1988). The comparative performances are shown in Tables 4.2 and 4.3. The kenaf bast fiber has long length, large length to width ratio. These fiber properties are advantageous for pulping. The chemical and energy consumption are lower. But, the characteristic of large wall thickness to lumen ratio (1.73) may inflict adverse impact on pulping and beating. The average length of fax fiber is 20 mm. It is substantially long. The length of the longest fiber is 47 mm. The outer wall of flax fiber is smoother, the cell cavity is smaller, both ends are gradually pointed, the tube wall has very few pits, and the transverse knot is noticeable. Tables 4.2 and 4.3 show that flax fiber has higher cellulose and reduced lignin content which would result in reduced chemical requirement, milder pulping process, higher pulp yield, and better strength properties (Yu, 1996). Hemp fiber resembles flax fiber, but the length is shorter. The characteristics of hemp fiber are the transverse knots, thick fibrous cell wall, and smoother surface. The degree of lignification is higher in comparison to flax fiber. It is a very good raw material for pulping (Tables 4.2 and 4.3).

Jute fiber is smooth and has a shiny surface. The cell wall has uneven thickness. Its pulping properties are poorer to hemp and flax as it is highly lignified.

7.1.1.2 Seed hull fiber materials

In all types of natural fibers, cotton fiber has very high cellulose, excellent flexibility, good elasticity and strength, and very good resistance to dilute acid and alkali. This type of material is a very good fiber for pulp and papermaking. Its relative properties are presented in Tables 4.2 and 4.3.

7.1.1.3 Leaf fiber materials

Leaf fiber materials has high content of holocellulose and less lignin. Chemical pulping process involves mild pulping, reduced requirement of chemicals and high pulp yield. The properties of leaf fiber materials are presented in Tables 4.2 and 4.3.

7.2 Pulping of nonwoody raw materials

> Pulping of nonwoods is generally easier in comparison 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.
>
> ***Akgül et al. (2018)***

> 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 as well as board grades. The soda anthraquinone method is replacing the soda method and the results of the soda/ anthraquinone 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 wood.
>
> ***Bajpai (2018a)***

These days, the delignification technology in alkaline pulping of woody materials has been used in nonwood fiber pulping. Generally alkaline pulping needs addition of some pulping chemicals, such as sodium hydroxide, sodium carbonate, and so on.

Nonwoods are capable of being renewed annually. In general, the growing cycle in nonwood plants are short with reasonable irrigation needs, and a high yield of cellulose in comparison to wood (Alila et al., 2014). Pulping of nonwood plants is beneficial in comparison to wood fiber as nonwood materials can be pulped with simple chemical systems (caustic soda). The alkali dose required for these materials is generally lesser than what is required for woody raw materials in which the similar degree of delignification is achieved thereby reducing the energy required in this process. The methods used for producing pulp are categorised as mechanical, thermal, semichemical, or totally chemical methods. Sabharwal et al. (1994) reported that globally 74.1% of the pulp was produced using the chemical pulping methods whereas 21.4% of pulp was obtained by mechanical pulping method and the remaining pulp was produced by using other methods.

> Chemical methods are mostly utilised when pulping nonwood fibres and they include Kraft, sulphite, soda and organosolv pulping processes. The major aim to be achieved when using chemical pulping is the degradation of lignin and hemicelluloses into small water-soluble molecules which can be washed away from the cellulose fibres without depolymerising the cellulose fibres. Specific end-products are produced from a given nonwood fibrous raw material based on the choice of process such as; technique used, size of mill, the chemicals available, and their relative cost. The pulping process applied in pulping of nonwood fibres determines the quality and properties of the total yield of pulp to be obtained. This is a significant factor in considering the type of paper to be produced. Some of these pulping techniques have been in use since the ancient times and are ultimately due for improvement to overcome their drawbacks.
>
> ***www.intechopen.com***

Fig. 7.1 shows the process flow diagram for pulp and paper production.

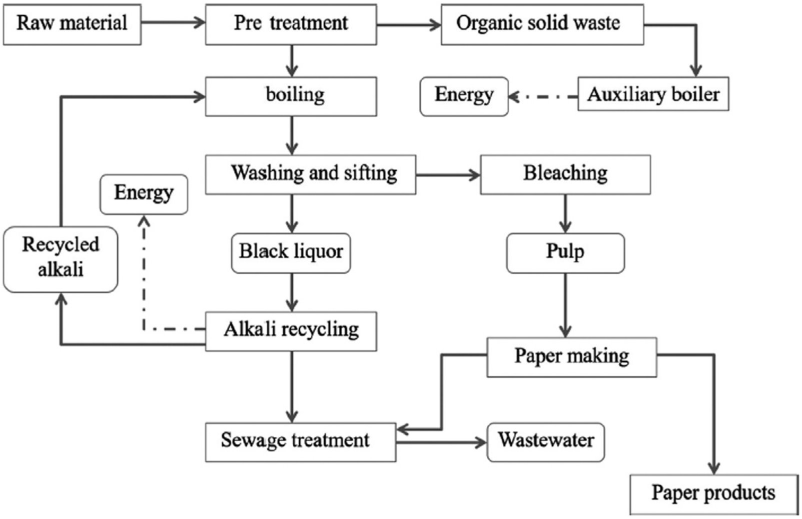

Figure 7.1

Process flow diagram for pulp and paper production. *Source: Based on Azeez, M.A., 2018. Pulping of Nonwoody Biomass, Pulp and Paper Processing, Salim Newaz Kazi, IntechOpen, doi: 10.5772/intechopen, 79749, Available from: https://www.intechopen.com/books/pulp-and-paper-processing/pulping-of-nonwoody-biomass; From Wang, Y., Yang, X., Sun, M., Ma, L., Li, X., Shi, L., 2016. Estimating carbon emissions from the pulp and paper industry: a case study. Appl. Energy 184, 779–789.*

About 40 different processes are found appropriate for pulping of nonwoody plants. However, only a few processes are being used commercially (Ranua, 1977). The most widely used processes include alkaline processes such as sulfate (Kraft) method, soda method, and also sulfite method (Table 7.3). The most commonly used commercial process

Table 7.3: Pulping methods for nonwoody plants.

- Alkaline pulping
  - Caustic soda pulping
  - Kraft pulping
  - NACO (Alkaline pulping process using sodium carbonate, oxygen and sodium hydroxide as the cooking chemicals in a digester called Turbo pulper) pulping
  - SAICA (Spanish paper company Sociedad Anónima Industrias Celulosa Aragonesa, an alkaline semichemical pulping process using sodium hydroxide as the cooking chemical) pulping
- Sulfite pulping
  - Neutral sulfite pulping
  - Alkaline sulfite pulping
- Organosolv pulping
  - Methanol pulping
  - Ethanol pulping
    - ASAE (Alkaline sulphite-anthraquinone-ethanol pulping process) pulping
    - ALCELL (Alcohol cellulose, a pulping process using ethanol as the sole pulping chemical) pulping
    - IDE pulping
    - Punec pulping
  - Organic acids pulping
    - Milox pulping
    - Acetosolv pulping
    - Acetocell pulping
    - Formacell pulping
    - CIMV (Compagnie Industrielle de la Matière Végétale (Industrial Company for Vegetal Material), an organosolv pulping process using acetic acid and formic acid as the cooking chemicals) pulping
- Chemi-mechanical pulping
  - CMP and CTMP
  - APMP
  - Steam explosion pulping
- Biological pulping

Source: Based on Saijonkari-Pahkala K., 2001. Nonwood plants as raw material for pulp and paper. Agric. Food Sci. Finl. 10, Suppl. 1, p. 101, Dissertation, Helsinki University; Paavilainen, L., 1996a. Reed canary grass as raw material for paper making pulp, Pap. Puu 78(10), 580–583; Paavilainen, L., 1996b. Reed canary grass. A new Nordic material for high-quality fine papers. Know-How Wire. Jaakko Pöyry Mag. 2, 8–11; Atack, D., Heitner, C., Karnis, A., 1980. Ultra-high yield pulping of eastern black spruce. Part 2. Sven. Papperstidning 83, 5, 133–141; Janson, J., Jousimaa, T., Hupa, M., Backman, R., 1996. Phosphate-based pulping of agrofibre including papermaking and spent liquor recovery. Nordic Pulp Pap. Res. J. 1, 4–14; Seisto, A., Sundquist, J., 1996. Agrokuitujen keitto ja valkaisu Milox-menetelmällä. In: Laamanen, J. & Sundquist, J. (eds.) Agrokuidun tuotanto ja käyttö Suomessa. Tutkimuksen loppuraportti, III osa. Vaihtoehtoiset kuidutusmenetelmät. Maatalouden tutkimuskeskus. Maatalouden tutkimuskeskuksen julkaisuja. Sarja A 5, pp. 61–88; Backman M., Lönnberg, B., Ebeling, K., Henricson, K., Laxén, T., 1994. Impregnation–depolymerization–extraction pulping. Pap. Timber 76, 644–648; Winner, S.R., Goyal, G.C., Pye, E.K., Lora, J.H., 1991. Pulping of agriculture residues by the Alcell process. In: Proceedings of TAPPI Pulping Conference 1991, Orlando, FL, USA, pp. 435–439.

APMP, Alkaline peroxide mechanical pulping; *IDE*, impregnation, depolymerisation, and, extraction; *CMP*, chemimechanical pulp; *CTMP*, chemithermomechanical pulp; *APMP*, alkaline peroxide mechanical pulp.

in pulping nonwoody raw materials in countries producing nonwood pulp is still the soda process (Sadawarte, 1995). There are also many new processes which show good potential for producing high quality pulp from nonwoody raw materials (McDougall et al., 1993).

7.2.1 Alkaline pulping

> In alkaline pulping, the aqueous solution of alkaline chemical agent is used to treat fiber materials to dissolve most of the lignin and separate the fibers from the material into pulp. According to the diversity of cooking agents, the alkaline pulping process of non-wood can be divided into oxygen alkali method, sulfate method, caustic soda method, lime method, and so on. After the preparation of raw material, the digester would be used to hold the qualified material, which is followed by feeding cooking liquor (made from white liquor, black liquor, and water at a given concentration) into digester. After that, in order to make the cooking reaction uniform, the digester can be idled firstly, which precedes the indirect heating or direct steam heating to the required temperature for cooking (general 150–170°C). Then this temperature should stay for a period to remove the lignin and separate the fibers. When the cooking end point is reached, the pulp in digester should be blown or pumped into the blow tank.
>
> ***www.intechopen.com***

The pulping conditions and resulting pulp properties for alkaline pulping processes are presented in Table 7.4. The average kappa number of unbleached alkaline pulps is in the range of 10–20 and unbleached pulp yields are 45%–50%, except for the semichemical SAICA process, which shows pulp yield of more than 60% (www.vtt.fi).

7.2.1.1 Soda pulping

Soda pulping was invented in England by Burgess and Watts in 1851. This process uses sodium hydroxide as the pulping chemical. This process did not find much enthusiasm in England. In 1854, Burgess introduced this process to the United States. The first mill was started in 1866. Several of the early soda mills started using the kraft process after its discovery.

The soda pulping method is the most widely used method in the pulping of nonwoods (Lönnberg et al., 1996; Sharma et al., 2015; Iskalieva et al., 2012; Paavilainen, 1996b). In the soda method, the pulping chemical is mostly sodium hydroxide. Sometimes, sodium carbonate is also used. The dosage is dependent on the fiber properties. This method leaves more insoluble carbohydrates in pulp and provides a superior pulp yield in comparison to Kraft process. But, the strength properties and lignin content are comparable with pulps produced using the Kraft method (Ranua, 1977). The pulping temperature also depends on the pulping time and alkali charge. Typical sodium hydroxide charge is around 16% and pulping temperature is 140°C–170°C (Mohta et al., 1998; Tutus and Eroglu, 2003; Feng and Alen, 2001; Finell and Nilsson, 2004; Okayama and Li, 1996; Jeyasingam, 1987). In

Table 7.4: Properties of pulp produced with different alkaline pulping methods.

Process	**Kraft**	**Soda**	**Soda–AQ**	**Soda**	**Soda–AQ**	**Soda–oxygen**	**NACO**	**NACO**	**SAICA**
Raw material	**Reed canary grass**	**Bagasse**	**Bagasse**	**Wheat straw**	**Wheat straw**	**Wheat straw**	**Bagasse**	**Wheat straw**	**Wheat straw**
Effective alkali charge (%) (as NaOH)	14.0	12.0	12.0	16.0	16.0	16.0	16.0	16.0	6.5–8.5
Sulfidity (%)	35								
AQ (%)			0.1		0.1				
Temperature (°C)	160	165	165	140	140	140	135	130	94–97
Time (min)	10	60	60	60	60	60	75	60	150–210
Oxygen pressure bar						8	6	6	
Kappa number	9.3	21.5	13.3	20.9	18.6	18.4	14.4	14.0	
Yield (%)	54.0	53.6	50.5				48.4	42.1	67.1
Screened yield (%)		50.1	49.3	45.0	50.0	46.2			
SR number	21						40	40	
Tensile index (N.m/g)	49.1						62	69	
Burst index (kPa.m_2/g)				5.0	5.4	3.5	4.0	4.2	
Tear index (mN.m_2/g)				3.9	3.7	6.0	4.0	3.5	
Brightness % ISO	45.8	25.6	37.2	49.0	53.1	57.8	48.0	42.0	

Source: Based on Leponiemi, A., 2008. Nonwood pulping possibilities—a challenge for the chemical pulping industry. APPITA J. 61, 3, 234–243; Paavilainen, L., Tulppala, J., Finell, M., Rehnberg, O., 1999. Reed canary grass pulp produced on mill scale. In: Proc. TAPPI pulping Conf., Orlando, Florida, vol. 1, pp. 335–341; Mohta, D., Upadhyaya, J.S., Kapoor, S.K., Ray, A.K., Roy, D.N., 1998. Oxygen delignification of soda and soda-AQ bagasse pulps. Tappi J. 81(6), 184–187; Tutus, A., Eroglu, H., 2003. A practical solution to the silica problem in straw pulping, Appita J. 56(2), 111–115; Recchia, L., Bilancini, L., Brizzi, M., 1996. Production of chemical nonwood pulps with NACO process. In: 4th European workshop on lignocellulosics and pulp, Stresa, Italy, pp. 103–123; Lora, J.H., Escudero, E., 2000. Soda pulping of agricultural fibres for boardmaking applications, Pap. Technol. 41(4), 37–42.
AQ, Anthraquinone.

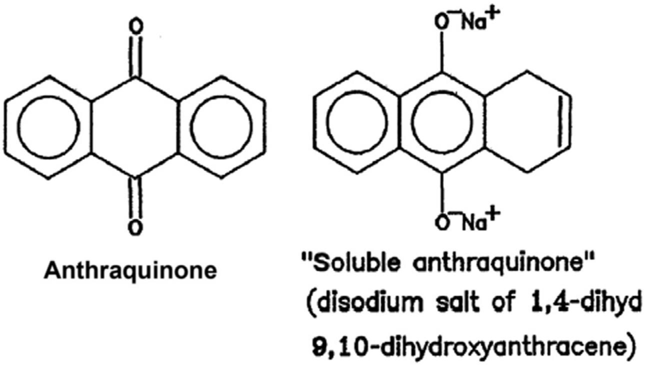

Figure 7.2

Structures of anthraquinone and soluble Anthraquinone. *Source: Reproduced with permission from Bajpai, P., 2018a. Handbook of Pulp and Paper. Vol. 1: Raw Material and Pulp Making. Elsevier, Amsterdam, 2018.*

actual fact, the soda method was the basis for the development of the straw pulping industry in Europe (Ranua, 1977; Winner et al., 1991) (Fig. 7.2).

Soda pulping process is being replaced by soda anthraquinone pulping process. The results of this process are comparable with those achieved with kraft pulping of straw. Anthraquinone improves the pulping effect of caustic soda. Because of the fact that anthraquinone enhances the pulping rate and protects the carbohydrates, in the similar conditions of pulping, the use of anthraquinone results in reduced kappa number and increased yield as compared without the use of anthraquinone. Addition of anthraquinone to the pulping liquor, speeds up the lignin removal, reduces the kappa number, and alkali consumption. The pulp yield, whiteness, and viscosity are also improved. It works by reducing the lignin and oxidizing the reducing end group of cellulose from an aldehyde to a carboxylic acid (Fig. 7.3). The carbohydrates get stabilized against the alkaline peeling reaction, resulting in an increase in pulp yield. For the reason that anthraquinone goes through a cyclic process, it is generally used at a dose level of approximately 0.1% on raw material. The pulp yield is increased by 1%–3%. Anthraquinone was first used in the year 1977. Modified anthraquinone such as soluble anthraquinone-1,4-dihydro-9,10-dihydroxyanthracene, have been found to be even more effective (Fig. 7.2). In North America, anthraquinone is not used widely but in Japan and other countries it is used widely. In these countries, fiber supply is fairly limited and costly.

> The advantage of soda cooking compared to kraft cooking is the absence of sulphur. This avoids the generation of malodorous cooking gases and simplifies the recovery boiler construction. The soda process can be improved by adding anthraquinone or oxygen or both during cooking. Anthraquinone accelerates the cooking and protects the

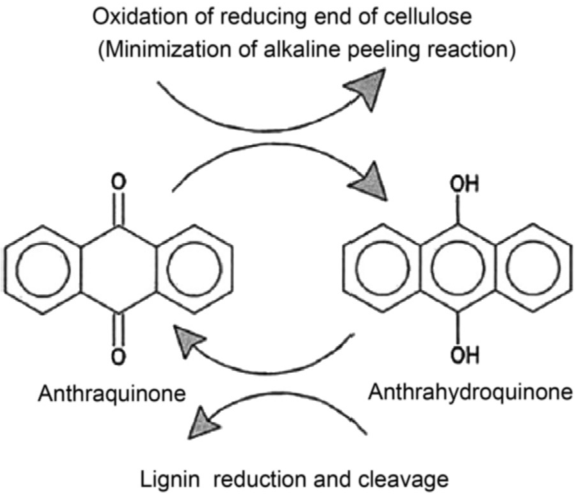

Figure 7.3
Cyclic action of anthraquinone. *Source: Reproduced with permission from Bajpai, P., 2018a. Handbook of Pulp and Paper. Vol. 1: Raw Material and Pulp Making. Elsevier, Amsterdam, 2018.*

> carbohydrates, so that lower kappa numbers are obtained with the same cooking conditions compared to non-anthraquinone soda cooking. At the same time the pulp yield remains high.
>
> ***Leponiemi (2008); Jeyasingam (1987); Mohta et al. (1998)***

Addition of anthraquinone in soda cooking of kenaf increased delignification, decreased alkali requirement, kappa number and pulp rejects, improved pulp brightness, yield and viscosity, and produced pulps with better properties as compared to those obtained from reference soda pulping (Khristova et al., 2002).

In soda cooking, the use of oxygen increases the delignification rate (Tutus and Eroglu, 2003). The pulp yield and physical properties are improved when anthraquinone is added to the cooking liquor (Leponiemi, 2008; Saeed et al., 2017; Zhan, 2011).

An important feature of soda–oxygen pulping is that the major portion of the dissolved silica precipitates on the fibers instead of remaining in the pulping liquor. It is possible to precipitate up to 96.5% of the silica in the raw materials on fibers as kaolin by the addition of 3% aluminium oxide to soda–oxygen pulping (Tutus and Eroglu, 2003). Precipitation of silica depends on the pH of the pulping liquor. In soda and soda–oxygen pulping, reducing the pH from 11.3 to 10.2, increased reprecipitation of silica significantly from approximately 10% to 90% (Okayama and Li, 1996).

In England, the soda process was used to produce much of its straw pulp at one time. In 1945, in United Kingdom, virtually 350,000 tons of straw was pulped for producing paper

(FAO, 1952). Esparto uses lesser alkali and produced a higher yield in comparison to the cereal straws. Usually esparto straw is pulped with 12% sodium hydroxide (on straw) for 5 h at 160°C. Yield of 36%–40% was achieved in hypochlorite bleaching.

In France, Huguenot developed process for pulping straw (Anon, 1948). This method involves cooking chopped straw with sodium hydroxide at 90°C–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 found to be appropriate for waste paper.

In Shandong, China, the continuous cooking system for pulping of wheat straw was installed at Quanlin Paper Group. The annual capacity was 100,000 metric tons of wheat straw pulp (Li et al., 2009).

7.2.1.2 Kraft process

The Kraft process is the major process used for manufacturing chemical pulp from wood (Bajpai, 2018a). However, it is not very common in nonwood pulping (Leponiemi, 2008). "The kraft process dominates the industry because of advantages in chemical recovery and pulp strength. It represents 91% of chemical pulping and 75% of all pulp produced. It evolved from an earlier soda process (using only sodium hydroxide as the active chemical) and adds sodium sulfide to the cooking chemical formulation. In Finland about 90% of all the chemical paper pulp is made using the Kraft process and globally it is 80%. The raw material is treated with a highly alkaline solution of sodium hydroxide, which is known to cleave lignin, but also eliminates a part of the hemicellulose. The undesirable breakdown of hemicellulose is largely avoided by adding sodium sulfide in the solution, and in this way a very high concentration of sodium hydroxide can be avoided in the pulping liquor. The Kraft process produces papers with increased fiber strength and density and low electrical conductivity" (Paavilainen, 1996a,b; Ervasti, 1996; McDougall et al., 1993).

Most of the nonwood pulp mills in the world are producing below 5000 tons per year and only 11 mills are producing 100,000 tons or more nonwood pulp. There are several issues with the local availability of nonwoods which reduce the optimum size of the pulp mills making the kraft method, less lucrative for nonwood pulp mills. Kraft process is only competitive at higher throughput. The strength properties of nonwood kraft pulps are not particularly better to those of soda pulps and it brings odour issues too (Paavilainen, 1998; Jeyasingam, 1987).

The major components of kraft pulping liquor are sodium hydroxide and sodium sulfide. During the pulping process, except for the strong base sodium hydroxide, the S2 − and HS − also play a significant vital role in pulping, which would be produced by the ionization of sodium sulfide and the hydrolysis of S2 −, respectively. Increasing the pulp yield is very important for the pulp and paper industries. Use of modified kraft pulping, such as with addition of sodium borohydride, is one way to increase pulp yield (Courchene, 1998; Tutus and Eroglu, 2003, 2004; Tutus and Usta, 2004; Hafizoğlu and Deniz, 2007; Istek and Gonteki, 2009).

7.2.1.3 NACO pulping

The NACO process is a variation of soda oxygen pulping. Straw pulp has been produced in commercial scale using this process. NACO process uses oxygen and alkali (sodium carbonate and some sodium hydroxide) for pulping of nonwoody raw materials and upgradation of secondary fibers on a comparatively smaller scale (Anon, 1984). A continuous, pressurized reactor (Turbo-Pulper) was developed as part of the process (Recchia et al., 1996; Fiala and Nardi, 1985; Paul, 2001).

> At present, some pulp and papermaking mills have used NACO to produce straw pulp. The main principle of the NACO method is to remove the lignin in the sodium carbonate solution, with sodium hydroxide as a supplementary chemical to reduce the Kappa number. The NACO process involves the pretreatment of raw materials, delignification, pulp bleaching, combustion of waste liquid, and recovery of chemicals. First, the mechanical pretreatment of raw materials is carried out under the condition of 1–2% of sodium hydroxide dosage and temperature 50°C. The primary purpose of pretreatment is to remove heavy impurities in the material to reduce the silicon content and remove wax.
>
> ***Azeez (2018)***

NACO process uses oxygen delignification for reducing kappa number in a sodium carbonate solution, with some sodium hydroxide as an activating and make-up chemical (Leponiemi, 2008; Recchia et al., 1996; Fiala and Nardi, 1985). Oxygen delignification takes place in a special type of reactor—pressurized turbopulper. The reactor contains a perforated plate and rotor arrangement in the base which extracts cooked fiber out from the reactor. Generally two turbopulpers are used in series operating at 6–7 bar pressure, with a pulp consistency of 8% (Paul, 2001).

> The NACO process (US patent 4,612,088 issued in 1986) 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%.
>
> ***Bajpai (2018a)***

7.2.1.4 SAICA pulping

SAICA is a semichemical pulping method, using sodium hydroxide as a chemical agent (Lora and Escudero, 2000; Leponiemi, 2008). Chopped and cleaned wheat straw is first chopped by hammer milling and then dried by pneumatic dry cleaning. The chopped and dried wheat straw is steeped with black liquor in the hopper. Impregnated straw is introduced to a continuous digester (indirectly heated), which operates at atmospheric pressure at 94°C–97°C. Preimpregnation with spent pulping liquor helps the straw to absorb the fresh pulping liquor and increases its specific weight. This improves feeding conditions. It also allows the use of any active chemicals which remain in the spent liquor (Lora and Escudero, 2000). Pulping is performed at atmospheric pressure at a temperature of 94°C−97°C for 2−4 h. The digester is kept in a slightly inclined position. Two counter-rotating screws transport the straw upwards as liquor moves downwards. Sodium hydroxide is introduced at the intermediate point of the digester, whereas water is introduced near the discharge zone, providing washing. The black liquor is extracted from the bottom of the digester continuously and partly washed straw is removed from the top. Some black liquor is recycled for preimpregnating the raw straw. The semichemical pulp obtained is subjected to washing and refined and is generally used in manufacturing corrugating paper (Lora and Escudero, 2000).

7.2.2 Sulfite pulping

In sulfite pulping, aqueous solution of sulfur dioxide in the presence of alkali is used (e.g., calcium, magnesium, sodium, and ammonium) (Atack et al., 1980; Costantino et al., 1983). Sulfonates are produced and are hydrated. The swelling of fibers assists in removing further lignin. In harmful side reactions, the strongly ionized sulfonic acids increase the acidity of the cooking medium. This results in condensation reactions between phenolic moieties in lignin, produces insoluble resin-like polymers, and degrades the hemicellulose and amorphous regions of cellulose. This has an impact on both lignin removal and the fiber quality (McDougall et al., 1993). Sulfite pulp is used for producing sanitary and tissue papers, which must be soft, absorbent, and quite strong (McDougall et al., 1993).

> The products obtained in this process are lighter and easier to whiten, however, they have much lower strength compared to the more frequently used sulfate pulping. The sulfite process also requires careful selection of raw material. The sulfite process compared to kraft pulping is more efficient, produces less unpleasant gases and also allows to obtain a very light pulp, which is easily leached. Unfortunately, the fiber quality is lower, energy consumption is higher and recoverability of the chemical raw materials is lower
>
> ***www.products.pcc.eu***

7.2.2.1 Neutral sulfite process

In this process, the active chemical is sodium sulfite. It is produced by dissolving sulfur dioxide in sodium carbonate. The residual of sodium carbonate in the pulping liquor buffers the pH in the range of 7−8. The dose of sodium sulfite is 10%−15% for bleachable grades of wheat straw pulp, the pulping temperature is 165°C, yield is 8%−10% higher and the pulp can be easily bleached than comparable soda pulps (Ali et al., 1991). These studies did not explain where the silica from the raw material is located after pulping. Anthraquinone can be also used as an additive in the neutral sulfite process. This process reduces the amount of organics in the spent liquor and produces a strong pulp at a higher yield. But, recirculation of the spent liquor reduces delignification and has a negative impact on pulp yield and quality (Bose et al., 1999). A high yield pulp, with reduced kappa number, can be obtained in the pulping of rice straw by using the neutral sulfite semi-chemical (NSSC) process. The pulp shows good opacity and strength. However, tear factor is lower. The kappa number of the rejects and the accept pulp is similar, hence the rejects can be re-refined and added back to the pulp. In the NSSC process, the yield is about 65% at kappa number of 11. When the sodium carbonate or sodium hydroxide buffer is added, the yield is reduced to 62% and kappa number drops to 7.5. Shorter pulping times of 30 min result in 80% yield and kappa numbers of about 20 (Nassar, 2004). Some mills in China are using the NSSC process with rice straw for the production of containerboard (Savcor Indufor, 2006).

Neutral sulfite (NSSC) method has been extensively used in Europe (Stephenson, 1951). Sodium sulfite (10%) and sodium hydroxide (5%) are mixed and added to straw. The pulping is done at 160°C for 6 h. A pulp yield of about 55% is obtained. Use of hypochlorite (5% on pulp) in bleaching reduces the pulp yield to 42%.

NSSC process for cooking of wheat straw was suggested by Aronovsky et al. (1948). In this case, 8% sodium sulfite and 2%−3% sodium carbonate (on dry basis) were used. The liquor to straw ratio was 7:1 and the pulping time and temperature were 2 h and 170°C, respectively. The pulp yield was 52%−55%. It could be bleached to 70% with total chlorine dose of 5%−7%. Bleaching beyond 70%, required a three-stage bleaching sequence. The freeness was in the range of 400−500 ml. Neutral sulfite process was not suitable at atmospheric pressure, but atmospheric pulping for 1 h with 12% kraft chemicals in a hydrapulper at temperature of 90°C−98°C was very effective. In other study (1947), Aronovsky suggested 2% lime and 2% sodium sulfite for getting an extremely free pulp, although it would appear that calcium sulfite might precipitate. Acid sulfite method for pulping of straw produce weak and brittle pulps because of the comparatively labile carbohydrates of straw. The process is not suitable for materials having high silica content.

7.2.2.2 Alkaline−sulfite process

In alkaline−sulfite pulping process, the pulping liquor contains sodium hydroxide and sodium sulfite. The cooking is done at a pH of 10−13.5. In the alkaline−sulfite process, the malodorous gases are absent unlike the kraft process. The use of anthraquinone in alkaline−sulfite pulping results in superior yield and viscosity at a given kappa number (McDonough et al., 1985). Much research on alkaline−sulfite−anthraquinone pulping of straw materials has been conducted in China. The selectivity of delignification as well as pulp yield increases with the increase of sulfite concentrations under the similar cooking conditions. For wheat straw pulping, the optimum sulfite concentration in the pulping liquor is 0.3−0.5 (Wang et al., 1996). With kenaf bark, yield, viscosity, brightness, and the strength properties of alkaline−sulfite−anthraquinone pulps were found to be better than those of soda and soda–AQ pulps (Khristova et al., 2002). Alkaline–sulfite method based on potassium was also developed for agricultural fibrous raw material (Wong and Chiu, 2001). The process emerged from studies of biomass potassium management involving the pulping of agricultural residues. The chemical recovery systems used in sodium-based wood pulp mills are complex for use in pulp mills using agricultural residues. Alternatives for managing the biomass potassium are to provide constant discharge of effluent in the form of utilizable fertilizer by using ammonium-based or potassium-based pulping process (Wong, 1994). Ammonium-based pulps however, have low brightness which would need more rigourous bleaching. Potassium-based process shows equal pulping rates and the quality of pulps produced are similar to those produced in sodium pulping in straw pulping studies (Wong, 1989).

Table 7.5 presents properties of pulp produced with different sulfite pulping methods.

Table 7.5: Properties of pulp produced with different sulfite pulping methods.

Process	**Neutral sulfite**	**Neutral sulfite**	**Neutral sulfite**	**Neutral sulfite**	**Neutral sulfite**	**Neutral sulfite**	**Alkaline sulfite**
Raw material	**Wheat straw**	**Wheat straw**	**Wheat straw**	**Wheat straw**	**Wheat straw**	**Wheat straw**	**Bagasse**
Na_2SO_3 charge (%)	8.0	8.0	12.0	12.0	15.0	15.0	18.0
Na_2CO_3 charge % ISO	1.7	1.7	2.6	2.6	3.2	3.2	
NaOH charge (%)							3.0
Temperature (°C)	165	165	165	165	165	165	160
Time (min)	30	90	30	90	30	90	60
Kappa no.	18.6	18.8	17.2	14.5	15.9	12.8	9.7
Yield (%)	71.3	64.7	62.4	61.4	61.8	55.0	63.9
SR number	48.0	39.0	26.0	24.0	33.0	20.0	
Tensile index (N.m/g)	25.9	38.2	38.3	51.2	58.6	52.0	
Burst index (kPa.m_2/g)	1.2	1.9	1.8	2.2	2.6	2.3	
Tear index (mN.m_2/g)	2.2	3.4	3.9	4.3	5.6	4.3	
Brightness % ISO	26.4	28.8	34.6	39.7	37.3	42.	52.6

Source: Based on Leponiemi, A., 2008. Nonwood pulping possibilities—a challenge for the chemical pulping industry. APPITA J. 61, 3, 234–243; Ali, S.H., Asghar, S.M., Shabbir, A.U., 1991. Neutral sulfite pulping of wheat straw. In: Proc. TAPPI Pulping Conf., Orlando, Florida, Book 1, pp. 51–60; Chen, G., Tao, J., Yu, J., Chen, J., 2002. Characteristics of high yield chemical pulping of bagasse. In: 2nd International Symposium on Emerging Technologies of Pulping & Papermaking, Guangzhou, China, pp. 229–235.

Table 7.6: Solvents used in Organosolv pulping.

Alcohols solvents:
methanol, ethanol, *n*-butanol, amyl alcohol, ethylene glycol, propylene glycol, and so on
Organic acids solvent:
formic acid, acetic acid, and formic acid + acetic acid, and so on.
Ester organic solvent:
ethyl acetate
Compound organic solvent:
methanol + acetic acid, ethyl acetate + ethanol + acetic acid, and so on.
Phenol organic solvents:
phenol, cresol, and mixed cresol
Active organic solvents:
dimethyl sulfoxide, dioxane, diethanol amine, and so on.

7.2.3 Organosolv pulping

Organosolv pulping methods are based on pulping with organic solvent such as alcohols or organic acids. "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" (Bajpai, 2018a). Table 7.6 shows the various solvents used in Organosolv pulping.

> Solvents are used alone or in combination with other chemicals. Methanol and ethanol are common alcohols used, as are formic acid and acetic acid. Other more exotic solvents include various phenols, amines, glycols, nitrobenzene, dioxane, dimethylsulfoxide, sulfolane, and liquid carbon dioxide. Organosolv methods based on alcohols or organic acids have been tested at pilot-scale but none of these processes is in full mill scale production yet. If organic solvents are used in an alkaline process, the process requires both alkali recovery and solvent recovery systems, which complicates the recovery system.
>
> ***Leponiemi (2008); Sunquist (2000)***

In the Organosolv process the lignocellulosic biomass are broken to obtain cellulosic fibers for producing:

- Pulp and paper
- High-quality hemicelluloses
- Lignin degradation products produced from black liquors, thus eliminating emissions and effluents

Various advantages of Organosolv processes are shown in Table 7.7.

Table 7.7: Advantages of Organosolv process.

Use either low boiling solvents (e.g., methanol, ethanol, and acetone), which can be easily recovered by distillation, or high boiling solvents (e.g., ethylene glycol and ethanolamine), which can be used at a low pressure. Thus, it is possible to use the equipment used in the classic processes, for example, the soda and kraft processes, hence saving capital costs.
Pulps with properties such as high yield low residual lignin content high brightness and strength can be produced.
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.

> 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.
>
> ***Bajpai (2018a)***

7.2.3.1 Methanol pulping

Methanol is currently been used in several pulping processes. The use of methanol promotes the dissolution of lignin and protects carbohydrates, among which alkaline–sulfite–anthraquinone–methanol (ASAM) process is considered to be a superior method (Muurinen, 2000). "Methanol has been used in kraft, sulfite and soda pulping processes. Demonstration plants using the ASAM and the soda pulping method with methanol (Organocell) have been built. The ASAM method is also considered as a modified sulfite cooking method in many quarters. However, the use of methanol may be hazardous however, since methanol is a highly flammable and toxic chemical" (Leponiemi, 2008).

In the ASAM process, the pulping chemicals are sodium hydroxide, sodium carbonate, and sodium sulfite. The pulping temperature and time are 175°C and 60–150 min, respectively. The maximum pressure goes beyond 10 bars. The hemicelluloses, yield, and optical properties of the pulp can be controlled by changing the ratio of sulfite to sodium bases (Patt et al., 1999). Another process, the FreeFiber process, has been developed by Metso (Enqvist et al., 2006). "The process includes sodium carbonate impregnation before cooking in gaseous methanol. After the impregnation the excess liquor is removed and concentrated for reuse and the raw material is brought in contact with a gaseous methanol in the heat-up stage. Condensation of the heated methanol releases energy, thus heating the chips to the reaction temperature. The temperature is maintained by adding methanol as required. After the reaction period the pulp is washed and cooled. The process does not present obvious economic advantages at the moment but the pulp properties are claimed to be attractive" (Savcor Indufor, 2007).

The main advantages of ASAM pulping are presented below: "not entirely depended upon one particular raw material (hardwood, softwood and nonwood materials are all equally usable), sustaining high productivity and causing rather less environmental pollution that's why it is considered as environmentally friendly" (Patt et al., 1994, 1998).

By the addition of methanol and anthraquinone to the alkaline–sulfite liquor, several benefits such as higher pulp yield, lower lignin content, higher brightness and better strength properties can be obtained (Patt and Kordsachia, 1986). The pulp produced can be easily bleached. The yield after bleaching is 5% higher as compared to the kraft pulp yield. Approximately 70%–80% of the inorganic chemical charge is sodium sulfite, and the pulp yield is 14%–18% more in comparison to kraft pulping (Patt et al., 1987).

> The leftover lignin content is lower, as there is no lignin condensation. The pulp can be bleached without using any chlorine. As a result of this, the strength properties are higher in comparison with those of the kraft pulps. Furthermore, the methanol content of the cooking liquor can be reduced from 35% to 20%, without having any adverse effect on the pulp quality. When the pressure of the digester is released more than 95% of methanol could be recovered.
>
> ***herkules.oulu.fi***

Addition of methanol or ethanol was found to extend delignification to levels below kraft or sulfite pulps. ASAM pulping process has twin benefits of paper properties and higher pulp brightness. Additionally ASAM pulping results in pulp with higher yield, lower Kappa number and higher paper strength properties. In addition, the bad smell from methyl mercaptans that is produced during kraft pulping is completely absent in ASAM pulping (Patt and Kordsachiam, 1986).

> The Organocell process uses only methanol, sodium hydroxide and catalytic amounts of anthraquinone as cooking chemicals. Originally the Organocell process was a two-stage process in which the first stage was a mildly acidic stage and the second stage was an alkaline stage. In the first stage cooking was performed with aqueous methanol at 190–195°C. The second stage was carried out in aqueous methanol-sodium hydroxide solution at temperatures up to 180°C. The process has been tested at 5 tpd demonstration plant level. Fluctuations in temperature at such high temperatures cause significant variation in the blow line kappa number. However, it has been shown that the first stage can be eliminated from the process. The cooking temperature of such a one-stage Organocell process can be lowered to 170°C, where the methanol content of the cooking liquor is 30% by volume. The one-stage process is therefore easier to control and the elimination of the first stage results in stronger fibres than those from the two stage process.
>
> ***Leponiemi (2008, 2011); Schroeter and Dahlmann (1991)***

7.2.3.2 Ethanol pulping

The ethanol Organosolv process was initially developed to produce clean pulping. This process 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 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 to 195°C for 1 h. The typical liquid to biomass solid ratio is 4 to 7 and a liquor pH of about 2 to 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" (Bajpai, 2018a).

The ALCELL process uses an aqueous solution of ethanol as the only delignifying agent. The process has been studied in a pilot scale plant producing 15 tonnes of unbleached pulp per day. Cooking was done at 195°C. The cooking medium contained a 50% (w/w) ethanol/water mixture. Nitrogen was used for maintaining a slight overpressure in the pulping vessel. There is no requirement of addition of acid or alkali to the pulping liquor and therefore the pH is about 4 because of deacetylation of raw materials (Pye and Lora, 1991). Distillation process is used for recovering ethanol. The main by-products from the wheat straw ALCELL process are lignin and furfural, acetic acid, and hemicelluloses. The main part of the silica remains in the pulp. About 13%−15% of the raw material silica goes into the pulping liquor, about 5% leaves the alcohol recovery system with the lignin and the remaining 8% is removed with the xylose rich stillage (Winner et al., 1997).

ASAE process is a modification of the ASAM process. Because of the higher boiling point of ethanol, pulping under lower pressure is possible. But, the amount of ethanol needed is more than the amount of methanol required in ASAM pulping. Wheat straw ASAE pulps contain lesser lignin, show superior strength properties, and good beatability. In ASAE pulping, high yield is obtained and energy consumption is reduced in papermaking as compared to kraft pulping (Usta et al., 1999).

> ASAE was improved on the basis of alkaline sulfite AQ-methanol pulping. However, the amount of ethanol required for alkaline sulfite AQ-ethanol cooking is much greater than that of methanol needed for alkaline sulfite AQ-methanol cooking. Nevertheless, the pulp produced by ASAE is characterized by low lignin content, favorable physical properties, high yield, and good beatability, which manifests that this method can save a large amount of energy, compared with the sulfate process.
>
> *Azeez (2018)*

The so-called IDE-process is an alkaline solvent pulping process including three consecutive steps. These are:

- Impregnation (I)

  In this step, the raw material is treated with strong aqueous sodium carbonate solution.
- Depolymerisation (D)

  In this step, the bulk delignification takes place where the raw material is pulped with aqueous ethanol solution.

- Extraction (E)

  In the step, the degraded lignin is extracted from the pulp with fresh ethanol—water solution.

As no sulfur and sodium hydroxide are used, the recovery is less difficult as compared to the conventional alkaline pulping processes. IDE-process can handle different types of raw materials. If the final pulp is bleached at a different location, in a kraft pulp mill close by, the IDE-pulp mill would be almost effluent free. The IDE-pulp mill can be profitable at a small-scale and be located near the fiber supply (Hultholm et al., 1995).

> The Punec process is a pulping method that uses ethanol, anthraquinone and caustic soda as cooking chemicals. The raw material is firstly treated with aqueous alcohol after which delignification is performed in a high pressure digester. The lignin and hemicellulose are dissolved into the cooking liquor and flashed into a flash tank after which lignin is separated from the flash liquor by acidification. The hemicellulose rich liquid is then distilled to recover the remaining alcohol. Finally the aqueous fraction of hemicelluloses is treated anaerobically to produce biogas, or converted into animal feed, or fertilizer. The process has been tested in a 4 tpd demonstration plant but no information on the exact process conditions or the pulp quality is available. The process is claimed to be pollution free making the process worthy of more investigation
>
> ***Khanolkar (1998); Leponiemi (2008)***

Table 7.8 shows the properties of pulp produced with different alcohol pulping methods.

7.2.3.3 Organic acid pulping

Typically formic acid and acetic acid are used in acidic pulping methods. Formic acid can be also used for enhancing acetic acid pulping. When formic acid is used in pulping, the temperature and pressure are lower in comparison to that used in acetic acid or alcohol pulping (Rousu et al., 2002). Formic acid and acetic and react with lignocellulosic raw materials during delignification and form corresponding esters (Saake et al., 1995). Formic acid and acetic acid are also produced during the acidic processing of lignocellulosic raw materials. This is the benefit of using formic and acetic acid (Rousu et al., 2002). But, organic acids, paticularly formic acid, cause corrosion in process equipment. The Milox process is an Organosolv process. This process uses peroxyformic acid or peroxyacetic acid for cooking. These chemicals are produced in situ using hydrogen peroxide and formic acid or acetic acid. The consumption of hydrogen peroxide can be reduced by conducting the process in multiple stages. In the Milox process performed in three stages, acetic acid or formic acid is treated with the pulp in an intermediate stage with no peroxide. The two-stage peroxyacetic acid process produces higher delignification in comparison to the three-stage process and vice-versa with peroxyformic acid (Poppius-Levlin., 1991). The Milox process is a sulfur free process (Bajpai, 2012). Bleaching can be performed without using any chlorine chemicals. Recovery of cooking chemicals from the Milox process causes

Table 7.8: Properties of pulp produced with different alcohol pulping methods.

Process	ASAM	Free fiber	ASAE	ASAE	ASAE	ALCELL	ALCELL	ALCELL	IDE
Raw material	**Bagasse**	**Wheat straw**	**Wheat straw**	**Wheat straw**	**Wheat straw**	**Reed**	**Straw**	**Kenaf**	**Reed**
Na_2SO_3 charge (%)	16–18		12.0	14	16				
Alkali ratio	0.7								
NaOH charge (%)		Na_2CO_3	3	3.5	4				Na_2CO_3
AQ (%)		–	0.1	0.1	0.1				0.022
Methanol/ Ethanol (%)	15–20 *	methanol gas phase	50	50	50	~ 50	~ 51	60	50%
Cooking temperature (°C)			170	170	170	195		200	
Kappa number	3–6	10.8	17.4	16.4	16.4	22–24	27–32	~ 30	~ 21
Screened yield (%)	61–63		55.5	56.1	54.4	48–53	51–53	~ 60	38–46
SR number		42	25	25	25				
Tensile index (N.m/g)		86							50
Burst index (kPa.m_2/g)		4.3	2.43	3.24	2.99			4.4	
Tear index (mN.m_2/g)		4.4	5.9	7.3	6.1			9.9	7.8
Brightness % ISO	49–62								

Source: Based on Leponiemi, A., 2008. Nonwood pulping possibilities—a challenge for the chemical pulping industry. APPITA J. 61, 3, 234–243; Shukry, N., El-Kalyoubi, S.F., Hassan, E.B.M., 2000. Preparation of high quality bagasse pulp by using the ASAM process. In: 4th International Nonwood Fibre Pulping and Papermaking Conf., Jinan, China, pp. 217–225; Savcor Indufor, 2007. Pulp quality comparison, Technical report—Module 6, 13 p. Available from: <http://www.ktm.fi/files/17224/Module_6_Final.pdf>; Usta, M., Eroglu, H., Karaoglu, C., 1999. ASAE pulping of wheat straw (Triticum aestivum L.), Cellul. Chem. Technol., 33(1–2), 91–102; Winner, S.R., Minogue, L.A., Lora, J.H., 1997. ALCELL pulping of annual fibers. In: 9th International Symposium On Wood And Pulping Chemistry, Poster Presentations, pp. 120-1–120-4; Westin, C., Lonnberg, B., Hultholm, T., 2000. IDE-pulping of common reed. In: 4th International Nonwood Fibre Pulping and Papermaking Conf., Jinan, China, pp. 96–104.
ASAM, alkaline–sulfite–anthraquinone–methanol; *AQ*, anthraquinone; *IDE*, impregnation, depolymerisation, and extraction.

many problems. Some acetic acid and formic acid are produced. The separation of the acetic acid, formic acid, water mixture is obtained by extractive distillation. Butyric acid has been recommended as a solvent for the distillation. The Milox process can become more economical if a mixture of acetic acid and formic acid can be used as solvent (Muurinen et al., 1993).

The Chempolis pulping process is based on cooking with formic acid. The process is a one-stage approach, cooking temperature is 110–125°C and cooking time is 20–40 min. In addition to formic acid, acetic acid can also be used in the process, a small amount of

> which is formed during the process. After cooking, the pulp is washed and pressed in several stages (between 2 and 6) with formic acid. The last washing stage is at high pulp consistency with performic acid. The acid is then removed from the pulp by washing with water. Lignin, hemicelluloses and fatty acids are washed from the pulp in an acid washing stage. Finally the unbleached pulp is bleached with alkaline peroxide (charge 3−6.5% hydrogen peroxide). Formic acid and acetic acid percentages have ranged from 80/15 to 40/40 respectively (the balance being water). Reported bleached pulp yield is 39%. Spent cooking liquor can be evaporated to 90% dry solids without viscosity problems because silica does not dissolve in the cooking liquor. After evaporation the spent liquor can be incinerated. Evaporation is accompanied by the formation of formic acid, acetic acid and furfural. The formation of formic acid is claimed to reduce the demand for makeup formic acid. As with formic acid, acetic acid and furfural are volatile compounds so they can be separated from evaporation condensates by distillation.
>
> ***Rousu and Rousu (2000); Rousu et al. (2003); Savcor Indufor (2007); Anttila et al. (2006)***

In the Acetosolv method, the hydrochloric acid is used as a catalyst. It is one of the acetic acid pulping methods. The process is not pressurised. Cooking is conducted at a temperature of 110°C. Dissolved lignin and furfural are obtained from the waste liquors (Nimz, 1989).

From the Acetosolv concept, the Acetocell process has been developed. The pulping is conducted with acetic acid at high temperature without using any catalyst. The delignification results in reduced kappa numbers at high pulp yield (Neumann and Balser, 1993).

> The Formacell process was developed from the Acetocell process. It is an organosolv pulping approach in which a mixture of formic and acetic acid is used as the cooking chemical, acetic acid is 75% and formic acid 10%, the rest being water. The cooking temperature is 160- 180°C, after which cooked pulp is washed with acid and bleached with ozone. Dissolving and paper grade pulps can be produced by the Formacell process.
>
> ***Saake et al. (1995); Leponiemi (2011)***

Further development of the Formacell approach is the CIMV process. A small scale agro-fiber mill, producing 50,000 tons of paper and 50,000 tons of by-products per year, has been built (2008−09) in the Champagne-Ardenne area in France. "The CIMV process uses cereal straw or sugar cane bagasse to produce bleached paper pulp, xylose syrup, and sulphur free lignin. Organic acids are recycled from waste liquor via evaporation. Water is used to treat the remaining syrup to precipitate lignins, which are easily separated. References to this process do not describe the process in detail but it is probably based on the use of acetic acid, formic acid and water as cooking chemicals (formic acid 20−30%, acetic acid 50−60% and 20% water). The process is atmospheric and cooking temperature is close to 100°C" (Leponiemi, 2011; Delmas et al., 2006; Kham et al., 2005a; Lam et al., 2004; Kham et al., 2005b; Lam et al., 1999, 2005; Mire et al., 2005). Bleaching needs

Table 7.9: Properties of pulp produced with different organic acids.

Process	**Chempolis**	**CIMV**	**CIMV**	**CIMV**	**CIMV**
Raw material	**Wheat straw**	**Wheat straw**	**Bagasse**	**Rice straw**	**Rice straw**
Formic acid (%)		60	30	30	20
Acetic acid (%)		20	55	50	60
Water (%)		20	15	10	20
Temperature (°C)		107	107	107	107
Time (min)		120	180	120	180
Kappa number	6.1	6.1 50.4	28.2	34.6	45.8
Yield (%)		43	49.4	47.5	52.9
SR number	42	49	45		45
Tensile index (N.m/g)	53				
Burst index (kPa.m$_2$/g)	2.4	2.14	3.21		2.52
Tear index (mN.m$_2$/g)	2.35	3.27	4.23		4.38
Brightness % ISO		36.5			

Source: Based on Leponiemi, A., 2008. Nonwood pulping possibilities—A challenge for the chemical pulping industry. APPITA J. 61, 3, 234–243; Savcor Indufor, 2007. Pulp quality comparison, Technical report—Module 6, 13 p. Available from: <http://www.ktm.fi/files/17224/Module_6_Final.pdf>; Kham, L., Le Bigot, Y., Benjelloun-Mlayah, B., Delmas, M., 2005a. Bleaching of solvent delignified wheat straw pulp, APPITA J. 58(2), 135–137; Lam, H.Q., Le Bigot, Y., Delmas, M., Avignon, G. 2004. Production of paper grade pulp from bagasse by a novel pulping process, APPITA J. 57(1), 26–29; Delmas, M., Lam, H.Q., le Bigot, Y., Avignon, G., 2003. A new nonwood pulping process for high silicon content raw materials. Appl. Rice Straw Appita J. 56(2), 102–106.

4% peroxide and 12% sodium hydroxide using a PPP peroxide bleaching sequence. Bleached pulp yield is about 32% (Kham et al., 2005a).

Table 7.9 shows properties of pulp produced with different organic acids.

7.2.4 Chemimechanical pulping and other pulping methods

The use of chemimechanical process in pulping of nonwoods has attracted a significant interest. Chemical treatment before mechanical pulping of wood improves the pulp quality and reduces energy consumption. The benefits of Chemimechanical pulping process are high pulp yield. Also, there is no requirement for chemical recovery systems.

> Unlike CMP (Chemi-mechanical pulp) obtained by grinding at atmospheric pressure, CTMP (chemi-thermomechanical) pulp is grinded under pressure, so the chemical dosage required in the chemical pretreatment stage is relatively low. For CMP and CTMP, the cooking temperature is 100–160°C, and the cooking time is 10–30 min. The reason why fibers are softened and the energy consumption is decreased is chemical pretreatment by sodium sulphite and sodium hydroxide. Therefore, the amount of sodium sulphite and the maximum temperature of pretreatment would affect sulfonation degree and swelling of lignin; the dosage of sodium hydroxide and the pretreatment time may influence the brightness and yield of pulp. For unbleached reed pulps, if the amount of sodium

Table 7.10: Properties of pulp produced with different chemi-mechanical pulping methods.

Process	**Extrusion pulping**	**Steam explosion**	**APMP**	**APMP**	**APMP**	**APMP**
Raw material	**Wheat straw**	**Bagasse**	**Wheat straw**	**Kenaf**	**Kenaf**	**Bagasse**
Na_2SO_3 charge % as NaOH		8				
NaOH charge (%)	3	1	3	3	3	10
H_2O_2 charge (%)			3	3	2	3
Temperature (°C)	140	190–210		90	80	
Time (min)	120	1–4		50	40	
Yield (%)		60	84			
SR number	35			56	61	20
Tensile index (N.m/g)		56				
Burst index (kPa.m_2/g)	2.41	3.00				2.38
Tear index (mN.m_2/g)	3.2	5.7		4.2	3.7	3.0
Brightness % ISO			50.01	53.2	54.0	72.1

Source: Based on Leponiemi, A., 2008. Nonwood pulping possibilities—A challenge for the chemical pulping industry. APPITA J. 61, 3, 234–243; de Choudens, C., Angelie, R., 1996. The Bivis process and the annual plants (wheat straw and fibre sorghum) for the manufacture of pulps for packaging paper. In: 4th European Workshop on Lignocellulosics and Pulp, Stresa, Italy, pp.124–132; Richard, J.A., D'Agostino, D., 1997. Continuous steam explosion pulping: process optimization for nonwoody fibers. In: Proc. TAPPI Pulping Conf., San Francisco, CA, Book 1, pp. 161–167; Pan, G.X., Leary, G.J., 1998. Alkaline peroxide mechanical pulping as a novel method to make high-yield and high-brightness pulp from wheat straw: progress and barrier. In: 84th Annual Meeting Technical Section, Montreal, Canada, Preprints B, pp. B219–B224; Shiyong, L., Yan, W., Yanbo, Z., 2006. Studies on optimization kenaf APMP pulping. In: 5th International Nonwood Fiber Pulping and Papermaking Conf., Guangzhou, China, pp. 200–203. Kamyar et al., 2001 Kamyar, S., Ahmad J.-L., Abdolrahman, H., 2001. Application of APMP pulping on bagasse. In: Proc. 55th Appita annual Conf., Hobart, Australia, pp. 219222.
APMP, Alkaline peroxide mechanical pulping.

> hydroxide is increased from 1–4%, the degree of sulfonation will rise, but the whiteness and yield of the pulp will reduce
>
> *Azeez (2018)*

Pretreatment chemicals which have been used are sulfite, sodium hydroxide, or alkaline peroxide. Modifications of the mechanical defibration for nonwood pulps have also been developed. For example, extrusion pulping and steam explosion pulping (SEP). Biopulping process which is biological treatment before chemical treatment can reduce energy requirement in refining, chemical requirement during pulping and adverse impact on the environment (Bajpai, 2018b; Ge et al., 2004). In the chemimechanical process, pulp yield is higher and there is no requirement of chemical recovery. The effluent treatment can be done in biological treatment systems. Table 7.10 shows properties of pulp produced with different chemimechanical pulping methods

7.2.4.1 CMP and CTMP processes

"CMP can be produced by refining at atmospheric pressure, however the chemical treatment stage is more severe than in the CTMP process which uses pressurized refining and where relatively low chemical doses are applied. CMP and CTMP pulping are carried out at temperatures ranging between 100–160°C for 10–30 min. The chemical treatment is responsible for fibre softening and decreases the subsequent refining energy requirements. The chemicals used in pre-treatment are sodium sulphite and sodium hydroxide. The sodium sulphite charged and the maximum temperature of pre-treatment influence the degree of sulphonation, and subsequent lignin swelling. The sodium hydroxide charge and pre-treatment time have an effect on brightness and pulp yield. Increasing the sodium hydroxide charge from 1% to 4% can increase the degree of sulphonation but at the same time the brightness and the yield (of unbleached giant reed pulp) decreases. High pretreatment temperature decreases pulp yield, with the optimum temperature being 140°C" (Lindholm and Kurdin, 1999; Ruzinsky and Kokta, 2000; Yulong et al., 2006).

Taizen Co., Ltd. has developed technology for pulping of nonwoods. This technology allows production of chemimechanical pulp of higher quality with reduced impact on environment at lower cost. This technology has been patented and examined on several types of nonwood fibers, including rice straw, wheat straw, kenaf, bagasse, oil palm fiber, bamboo, pineapple fiber, etc. This system works well for pulping of different nonwoods. Taizen's method involves chemimechanical pulping. The fundamental concept of this process is concurrent separation of fibers and treatment with alkali for weakening the bond between fibers. Nonwoods have lesser lignin as compared to wood. Because of this defibration becomes easier during treatment with alkali. Most of the lignin and hemicellloses remain unharmed within the fiber wall. This results in a higher pulp yield in comparison with conventional chemical pulping. The ecological implications of this process is low as dissolved organic materials are negligible and chemical usage is much.

7.2.4.2 Alkaline peroxide mechanical pulping process

> "The APMP method is based on the incorporation of peroxide bleaching in the chemical impregnation and refining stages in which bleaching action is used not only to eliminate alkali darkening but to brighten the pulp as well. The chemicals used in APMP are sodium hydroxide and hydrogen peroxide. Inhibitors such as diethylenetriaminepentaacetic acid (DTPA), magnesium or silicate must be used to reduce the degradation of peroxide. A typical APMP process consists of two impregnation steps, a first stage performed with a chelating agent, residual caustic and peroxide and after that the raw material is steamed. The second stage is impregnation with alkali, peroxide and more chelation agents to remove metal contaminants. The process is performed at high consistency 20–45%. The temperature range reported during impregnation is from 85°C to 95°C. Chemical charges depend on the nonwood raw material used. Kenaf APMP requires 4.0% sodium hydroxide and 3.1% hydrogen peroxide. The charges are much higher for straw and bagasse.
>
> *Xu (1998, 1999, 2001); Bohn (1989); Kamyar et al. (2001)*

7.2.4.3 Steam explosion pulping

This process consists of the following steps:

- impregnation of raw material with chemicals
- Cooking with saturated steam for shorter duration
- Quick release of pressure
- Atmospheric refining
- Bleaching if needed

The solution used for impregnation contains 8% sodium sulfite with, optionally, 1% sodium hydroxide, magnesium chloride, sodium bicarbonate, or magnesium carbonate. High brightness pulps can be produced at around 90% yield (Kokta et al., 1992).

Cooking is conducted for 5 min at temperature of 180°C–210°C (Kokta and Ahmed, 1998). The presence of swelling agents (sodium hydroxide, sodium bicarbonate, and magnesium carbonate) in the impregnation solution results in a reduction in the requirement of refining energy (Ruzinsky and Kokta, 2000). The SEP method is found suitable for pulping of nonwoods. The pulp properties are comparable or superior than the properties of chemi-mechanical pulp (CMP) and chemi-thermomechanical pulp (CTMP) (D'Agostino et al., 1996). But, the yield obtained is lesser than that of CMP and CTMP pulps (Ruzinsky and Kokta, 2000).

7.2.4.4 Extrusion pulping (Bivis)

Extrusion pulping is conducted mechanically or chemimechanically. The shear forces are used for processing the fibers (Westenbroek, 2004, 2000). This process is based on the use of internal corotating intermeshing screws in the process vessel. The raw material is introduced into the barrel by transport screws. The key screw element used in this process is the reversed screw element (RSE). The RSE is a threaded element having opposite pitch to that of the transport screws. This results in accumulation and compression of fibers in the space between the transport screws and the RSE (Westenbroek and van Roekel, 1996). Aside view of the pulping extruder is shown in Fig. 7.4 (Westenbroek, 2000).

> The high compression and shear forces generated cause defibration, fibrillation and the shortening of fibres. Excess filtrate is pressed out through barrel filters and placed upstream from the RSE. The pressure drop created in passing the RSE heats the pulp and provides rapid impregnation of liquids which can be supplied through an injection port down-stream from the RSE. This combination of transport screw, RSE, filter and injection port can be repeated along the barrel. The chemical charge in the extrusion pulping of wheat straw is 3%, temperature 140°C and pressure is 6–7 bar. Pulp is further reacted in a retention chest for 120 min at 100°C
>
> ***Westenbroek and van Roekel (1996); de Choudens and Angelie (1996)***

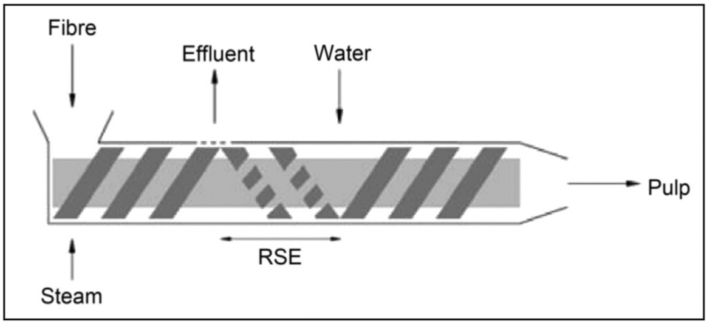

Figure 7.4
Side view diagram of the pulping extruder (Westenbroek, 2000). *Source: Reproduced with permission from Westenbroek, APH (2000). Extrusion pulping of natural fibers, determination, implementation and verification of constitutive equations required for modelling. Wageningen, 150 p. Ph.D. Thesis. Wageningen University and Research Centre.*

The energy consumption in case of this pulping is lower as compared to the CMP process (Petit-Conil et al., 2001). Nonwood pulps are being produced by extrusion pulping at commercial scale. The Bivis process needs lesser addition of chemicals, water, power, space and manpower in comparison to alternative systems. High yields are also obtained (Roberts, 2000).

7.2.4.5 Mild acid cooking method

For further simplifying the nonwood pulping process, a process involving cooking under mildly acidic conditions has been suggested. "The idea of the process is to utilize the unique structure of annual plants in terms of their low lignin content. Processing is via a low temperature, un-pressurized, mildly acidic stage where the raw material is essentially cleaned/cooked using a liquor containing a mixture of formic and acetic acids, and chelating agents. The actual defibration then takes place in subsequent peroxide bleaching stages. Although capable of small scale operation without recovery, the effluents from the mild acid cook and bleaching stages can be easily treated for instance in traditional biological effluent treatment systems. The process is simple and does not require special process equipment. In the case of wheat straw, a pulp with an ISO brightness of over 80% and a yield of over 50% is achievable. Silica is partly extracted into the bleaching effluents" (Johansson et al., 2000).

7.2.4.6 Biopulping

Biopulping is an environment-friendly process as it reduces electrical energy consumption and the requirement of chemicals thus reducing pollution (Bajpai, 2018b). Biopulping also shows economic benefits as compared to the other pulping methods.

This process uses white rot fungus for converting lignocellulosic raw material to paper pulp. Hence can be an alternative to the conventional method of pulping. This method provides a solution to the problems faced in chemical and mechanical paper production. It uses natural fungi having the ability to degrade lignocellulosics and therefore softens the raw material. As the raw material gets softened when it goes to the final steps to be made into paper, the remaining steps of the process need lesser energy and the need of chemicals is reduced which helps in reducing the environmental impact caused by conventional pulping. Biopulping reduces electrical energy consumption by about 25%–30%, it also saves money. White rot fungi are found to be the best candidates for biopulping process. They are choosen for faster delignification and can show selective delignification (leaving fibers untouched). White rot fungus are mostly used in biopulping. “Treating the raw material with steam and creating a ventilation system provides a good environment for fungi to thrive in. Overall, biopulping uses the knowledge gained from a natural process to produce high quality paper while reducing the energy needed and the pollutants that escape out into the air during the process” (www.biopulping.com).

Biological pulping includes biochemical (Biokraft and biosulfite) pulping and biomechanical pulping. This process selectively decomposes lignin by the use of microorganisms or biological enzymes (Bajpai, 2018b).

> Biomechanical pulping of nonwood fibers—straw, kenaf, and jute has been successful. The energy consumption in refining was substantially lower and the strength properties higher for the fungal-treated bast strands. The opacity and drainage properties were also superior for biomechanical bast pulps but the brightness level was lower. Scanning electron microscopy of fungus-treated bast strands after refining showed that fibers appeared to separate more readily from adjacent fibers than in non-inoculated treatments. Italian researchers studied treatment of nonwoody raw materials with a mixture of various types of enzymes for saving energy and reducing chemical consumption while maintaining good properties of CTM pulp. The level of energy savings was found to depend on the type of raw material, ranging from 21% for rice straw up to 40% for kenaf bast. Enzyme treatment significantly improved tear index regardless of the cellulose source, whereas the tensile index decreased in wheat straw and kenaf bast samples. Burst index was slightly improved in all the biotreated samples, except kenaf. Pulp yields of the biotreated samples were, without exception, significantly higher than those of the corresponding control samples. This was apparently due to the lower chemical charge needed for biotreated samples
>
> ***Giovannozzi-Sermanni et al. (1997); Martinez et al. (1994); Sabharwal et al. (1994, 1995); Bajpai (2018a,b)***

Biopulping of rice and wheat straw have been also studied, and some success has been also achieved in biochemical pulping of sugarcane bagasse (Schiesser et al., 1989a,b; Johnsrud et al., 1987).

7.3 Washing, screening, and purification of nonwood pulp

“The purpose of pulp washing is to obtain pulp that is free of unwanted solubles. In the most basic case, this can be done by replacement of the contaminated liquor accompanying

Table 7.11: Benefits from pulp washing.

Minimizing the chemical loss from the cooking liquor cycle
Maximizing recovery of organic substances for further processing or incineration.
Reducing the environmental impact of fibreline operations.
Limiting the carry-over between process stages.
Maximizing the re-use of chemicals and the energy conservation within a single bleaching stage.
Obtaining a clean final pulp product.

the pulp fibers by clean water. In a modern pulp mill, washing operations include also 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" (Azeez, 2018; Krotscheck, 2006). Various benefits result from pulp washing (Table 7.11).

Preferably pulp washing may be conducted with the least amount of water for saving fresh water and to take away load from downstream areas which process the wash water. Pulp washing is actually a compromise between the pulp cleanliness and the amount of wash water to be used. Pulp washing in the mills are seen in brownstock washing and the bleaching sections and, also in digesting and dewatering machines (Smook, 1992; Krotscheck, 2006).

After the pulp is produced, it is processed for removing the impurities, like the undigested raw material, and recycles any remaining pulping liquor through the pulp washing process (Smook, 1992). Pulps are processed in a many ways, depending on the methods which produce them. Some pulp processing steps which remove impurities include screening, defibering etc. Pulp can also be thickened by removing some amount of water. Pulp can also be blended for guaranteeing product homogenety. If pulp is to be stored for longer duration, drying is required for preventing the growth of fungi or bacteria. Residual spent pulping liquor from chemical pulping is washed using pulp washers. These washers are called brown stock washers for Kraft pulp and red stock washers for sulfite pulp. Efficient washing is crucial for maximizing return of pulping liquor to chemical recovery and for reducing carryover of pulping liquor into the bleach plant, as surplus pulping liquor increases bleach chemical consumption (Bajpai, 2008). Particularly, the dissolved organic compounds such as hemicelluloses and lignins contained in the liquor will bind to bleaching chemicals and hence increase the requirement of bleach chemicals. Furthermore, these organic compounds function as precursors to organochlorine compounds (e.g., dioxins and furans), increasing the chances of their generation.

> The most common washing technology is rotary vacuum washing, carried out sequentially in two, three, or four washing units. Other washing technologies include diffusion washers, rotary pressure washers, horizontal belt filters, wash presses, and dilution/extraction washers. Pulp screening removes remaining oversized particles and uncooked

> raw material. In *open* screen rooms, wastewater from the screening process goes to wastewater treatment prior to discharge. In *closed loop* screen rooms, wastewater from the process is reused in other pulping operations and ultimately enters the mill's chemical recovery system. Centrifugal cleaning (also known as liquid cyclone, hydro-cyclone, or centri-cleaning) is used after screening to remove relatively dense contaminants such as sand and dirt. Rejects from the screening process are either repulped or disposed of as solid waste
>
> ***Gullichsen (2000)***

The purpose of brown stock washing, is to use very little wash water as possible for removing the maximum amount of liquor dissolved solids from the pulp. Actually these dissolved solids which are left in the pulp after washing interfere with bleaching and papermaking operations and increase the costs. The loss of liquor solids because of solids left in the pulp means that lesser heat would be recovered in the recovery furnace. Makeup chemicals also need to be added to the liquor in order to account for lost chemicals (Gullichsen, 2000).

Very high washing efficiencies can be achieved if unlimited amount of wash water is used. So, a compromise between high washing efficiency and a low amount of added wash water is to be made. The water added to the liquor during washing should be removed in the evaporators before burning the liquor in the recovery furnace. This is an expensive process and usually a bottleneck in pulp mill operations. By reducing the usage of wash water, the cost of steam for evaporation will be reduced.

> In dilution/extraction washing, the pulp slurry is diluted and mixed with weak wash liquor or fresh water. Then the liquor is extracted by thickening the pulp, either by filtering or pressing. This procedure must be repeated many times in order to sufficiently wash the pulp. In displacement washing, the liquor in the pulp is displaced with weaker wash liquor or clean water. Ideally, no mixing takes place at the interface of the two liquors. In practice, however, it is impossible to avoid a certain degree of mixing. Some of the original liquor will remain with the pulp and some of the wash liquor will channel through the pulp mass. The efficiency of displacement washing then depends on this degree of mixing and also on the rate of desorption and diffusion of dissolved solids and chemicals from the pulp fibres
>
> ***Azeez (2018)***

The pulp washing equipment are based on one or both of these basic principles.

Displacement washing is used in a digester washing zone. A rotary vacuum washer uses both dilution/extraction and displacement washing, whereas a series of wash presses uses dilution\extraction. In most of the pulp washing systems, there is more than one washing stage. High washing efficiency can be obtained if fresh water was used in each stage. But, this strategy needs huge amount of water and so not used. Countercurrent washing is mostly used. "The final stage pulp is washed with the cleanest available water or fresh water before leaving the system. The drained water from this stage is then sent backwards through each of the earlier stages in a direction opposite to the flow of pulp" (Bajpai, 2018a; Smook, 1992).

> A new type of pulp washer series, i.e., serialized ZXV-type pulp washers, has been innovated by Wenrui Machinery Co. Ltd., Shandong, China. The new pulp washers, with the maximum filtration area of each drum being up to 120 m2, and with a conical chamber structure designed and plane distributing valves being applied to improve water flow turnover and keep higher vacuum degree in sucking chambers, resulted in a good pulp cleanness and high extraction rate of black liquor; on the other hand, dispersing press, agitating device applied to improve washing efficiency. The proposed acceptable washing-screening process is the sequence with press extraction—replacement washing—closure screening; it has been proven by many commercial operations that the new concept of the combined countercurrent washing sequence improves black liquor extraction rate significantly, resulting a remarkable water-saving effect. For instance, the black liquor extraction rate reaches up to 94.6%. The water consumption can be reduced to 40m3/t pulp or less in Xinya Paper Group, contrasting to normal water consumption of more than 100 m3/t pulp by traditional process.
>
> ***Fang and Shen (2018); Lin (2005)***

Pulp is screened for removing oversized and unwanted particles from good fibers so that the screened pulp becomes more appropriate for the paper or paperboard product in which it is to be used (Bajpai, 2018a; Ljokkoi, 2000; Krotscheck, 2006). The largest oversized particles in pulp are termed as knots. Knots are uncooked wood particles. These are removed before washing and fine screening. In case of low-yield pulps, these are broken down in refiners and/or fiberizers. Special coarse screens called knitters are used for removing knots in case of low-yield pulps.

The major objective of fine screening is to remove shives. Shives are small fiber bundles which have not been separated by chemical pulping or mechanical action. Debris is the name for shives, and any other material that would have any type of adverse impact on the papermaking process or on the properties of the paper produced.

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Relevant websites

http://www.products.pcc.eu

herkules.oulu.fi

http://www.biopulping.com

http://www.intechopen.com

http://www.vtt.fi

CHAPTER 8

Bleaching

Chapter outline

8.1 General background 147
8.2 Bleaching of nonwood pulps 155
References 162
Relevant websites 166

8.1 General background

In the raw pulp, the lignin and other discoloration are present. Because of this, it is essential to use bleaching or brightening process. Bleaching of pulp is conducted for achieving several objectives. The prime purpose is to improve the brightness of the pulp so that it becomes suitable for use in paper products for instance printing and tissue papers (Bajpai, 2012, 2015, 2018). In case of chemical pulps, a significant advantage is that the pulp becomes cleaner. Bleaching also avoids the problem of yellowing of paper in light, as the residual lignin in the unbleached pulp is removed. During the bleaching process, resins and other extractives which are present in the unbleached chemical pulps get also removed. The absorbency is improved, which is a very important property for toweling and other tissue products.

> Bleached pulps create papers that are whiter, brighter, softer, and more absorbent than unbleached pulps. Bleached pulps are used for products where high purity is required and yellowing is not desired (example printing and writing papers). Unbleached pulp is typically used to produce boxboard, linerboard, and grocery bags. Any type of pulp may be bleached, but the type(s) of fiber and pulping processes used, as well as the desired qualities and end use of the final product, greatly affect the type and degree of pulp bleaching possible. The lignin content of a pulp is the major determinant of its bleaching potential. Pulps with high lignin content (example, mechanical or semi-chemical) are difficult to bleach fully and require heavy chemical inputs. Excessive bleaching of mechanical and semi-chemical pulps results in loss of pulp yield due to fiber destruction. Chemical pulps can be bleached to a greater extent due to their low (10 percent) lignin content. Whereas delignification can be carried out within closed water systems, bleach plants tend to discharge effluent to external treatment. Effluents from the bleach plant cannot easily be recirculated into the chemicals recovery mainly because they would

Nonwood Plant Fibers for Pulp and Paper.
DOI: https://doi.org/10.1016/B978-0-12-821800-6.00008-9

> increase the build-up of chlorides and other unwanted inorganic elements in the chemical recovery system, which can cause corrosion, scaling, and other problems.
>
> ***Bajpai (2016)***

The papermaking properties of chemical pulps get changed after bleaching (Voelker, 1979). Fiber flexibility and strength properties are improved when the residual lignin is removed from the pulp. On the contrary, a reduced amount of hemicellulose results in a reduced swelling ability of the fibers as well as a reduced bonding ability of the fiber surfaces. Fiber damage results, if stern bleaching conditions are used. This results in reduced strength properties of the paper. Bleaching actually dissolves and removes the lignin from wood for producing the pulp of required brightness (Reeve, 1989; Farr et al., 1992; Fredette, 1996; McDonough, 1992; Reeve, 1996a; Smook, 1992).

> Bleaching is carried out in a multistage process that alternate delignification and dissolved material extracting stages. Additional oxygen- or hydrogen peroxide-based delignification may be added to reinforce the extracting operation. Since its introduction at the turn of the century, chemical Kraft bleaching has been refined into a stepwise progression of chemical reaction, evolving from a single-stage hypochlorite (H) treatment to a multi-stage process, involving chlorine (CI2), chlorine dioxide (CIO2), hydrogen peroxide and ozone (O3). Bleaching operations have continuously evolved since the conventional CEHDED sequence and now involve different combinations with or without chlorine containing chemicals.
>
> ***Bajpai (2012); Rapson and Strumila (1979); Reeve (1996a)***

The common compounds used in bleaching are listed in Table 8.1.

The introduction of Chlorine and Chlorine dioxide increased noticeably the efficacy of the bleaching process (Rapson and Strumila, 1979; Reeve, 1996a; Fredette, 1996; Sixta, 2006). Chlorine was introduced in the 1930s and chlorine dioxide was introduced in the beginning of 1940s. Chlorine is much more reactive and selective as compared to hypochlorite. Chlorine has lesser tendency of attacking the cellulose and other carbohydrate constituents

Table 8.1: Chemicals used in bleaching processes.

Symbol	Chemical
C	Chlorine
D	Chlorine dioxide
H	Hypochlorite
0	Oxygen
P	Hydrogen peroxide
Z	Ozone
E	Sodium hydroxide
X	Enzymes
Q	Chelating agents
A	Acid

of wood, producing pulp of superior strength properties. Chlorine does not brighten the pulp like hypochlorite; it significantly degrades the lignin. Much, of the lignin gets washed out and removed with the spent liquor in the succeeding alkaline extraction stages. The brownish kraft pulp which is produced ultimately needs additional bleaching stages for increasing brightness. This led to the development of the multistage bleaching process. Chlorine dioxide brought the efficacy of kraft process one step closer (Rapson and Strumila, 1979; Reeve, 1996a).

> Between the 1970s and 1990s, a series of incremental and radical innovations increased again the efficiency of the process, while reducing its environmental impacts. Development of oxygen delignification, modified and extended cooking, improved operation controls, e.g. improved pulp and chemical mixing, multiple split chlorine additions, and pH adjustments increased the economics of the process and led to significant reduction of wastewater. In addition, higher Chlorine dioxide substitution, brought down significantly the generation and release of harmful chlorinated organic compounds.
>
> ***Bajpai (2012); Reeve (1996b); McDonough (1995); Malinen and Fuhrmann (1995)***

Tables 8.2 and 8.3 present the function, advantages, and disadvantages of different bleaching agents.

> Up until recently, it was believed that a 90° brightness could not be achieved without the use of chlorine and chlorine containing chemicals as bleaching agents. The implementation of modified cooking and oxygen-based delignification impacted on the entire process by lowering the kappa number of the pulp prior to bleaching, thereby reducing further the amount of bleaching chemicals needed. Under tightening regulations and market demands for chlorine-free products, the industry eventually accelerated the implementation of elemental- and totally-chlorine free (ECF and TCF) bleaching processes, by substituting hypochlorite, Chlorine and Chlorine dioxide, with oxygen-based chemicals although the timing and scale of these trends have varied between regions.
>
> ***Bajpai (2012); McDonough (1995)***

Table 8.2: Functions of different bleaching agents.

Bleaching agent	Function
Chlorine gas	Oxidizes and chlorinates lignin.
Oxygen gas used with sodium hydroxide solution	Oxidizes and solubilizes lignin.
Calcium hypochlorite or sodium hypochlorite	Oxidizes, brightens, and solubilizes lignin.
Chlorine dioxide	Oxidizes, brightens, and solubilizes lignin.
Sodium peroxide 2%—5% solution	Oxidizes, brightens lignin.
Ozone gas	Oxidizes, brightens, and solubilizes lignin.
Sodium hydroxide 5%—10% solution	Hydrolyzes and solubilizes lignin.

Source: Based on 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, p. A19; Reeve, D.W., 1996a. Introduction to the principles and practice of pulp bleaching. In: Dence, C.W., Reeve, D.W. (Eds.), Pulp Bleaching: Principles and Practice. Tappi Press, Atlanta, Section 1, Chapter 1, p. 1.

Table 8.3: Advantages and disadvantages of different bleaching agents.

Bleaching agent	Advantages	Disadvantages
Chlorine gas	Effective, economical.	Can cause loss of pulp strength.
Oxygen gas used with sodium hydroxide solution	Low chemical cost, provide chloride-free effluent for recovery.	Large amount required expensive equipment, can cause loss of pulp strength.
Calcium hypochlorite or sodium hypochlorite	Easy to make and use.	Can cause loss of pulp strength if used improperly, expensive.
Chlorine dioxide	Achieves high brightness without pulp degradation, good particle bleaching.	Expensive, must be made on-site
Sodium peroxide 2%—5% solution	Easy to use, high yield and low capital cost.	Expensive, poor particle bleaching
Ozone gas	Effective, provides chlorine-free effluent for recovery	Expensive, poor particle bleaching
Sodium hydroxide 5%—10% solution	Effective and economical.	Darkens pulp.

Source: Based on 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, p. A19; Reeve, D.W., 1996a. Introduction to the principles and practice of pulp bleaching. In: Dence, C.W., Reeve, D.W. (Eds.), Pulp Bleaching: Principles and Practice. Tappi Press, Atlanta, Section 1, Chapter 1, p. 1.

Bleaching is performed in a multistage sequence using alternate stages of delignification and extraction. The dissolved material is removed in the extraction stages. In this stage oxygen or hydrogen peroxide is added for reinforcing the extracting operation.

> Since its introduction at the turn of the century, chemical Kraft bleaching has been refined into a stepwise progression of chemical reaction, evolving from a single-stage hypochlorite (H) treatment to a multistage process, involving chlorine, chlorine dioxide, hydrogen peroxide and ozone. Bleaching operations have continuously evolved since the conventional CEHDED sequence and now involve different combinations with or without chlorine containing chemicals.
>
> ***Bajpai, 2012; Rapson and Strumila, 1979; Reeve, 1996a, 1996b, 1989***

The main bleaching chemicals can be divided into three groups based on their reactivity (Gierer, 1990; Lachenal and Nguyen-Thi, 1993). This concept is presented in Table 8.4.

Each chlorine chemical has an equivalent amount of oxygen-based chemical. Ozone and chlorine are positioned in the same group as they react with aromatic rings of etherified as well as nonetherified phenolic structures in lignin and also with the double bonds. The selectivity of ozone is lesser as compared to chlorine. It affects the pulp carbohydrates. These chemicals are very effective at degrading lignin. Therefore these chemicals are most suitable for use in the early stage of bleaching. Chlorine dioxide and oxygen both react mainly with free phenolic groups so these are grouped together. These are not so effective

Table 8.4: Classification of bleaching chemicals.

Category		
1	2	3
Reaction with any phenolic group + double bond	Reaction with free phenolic group + double bond	Reaction with carbonyl groups
Cl_2 O_3	ClO_2 O_2	NaOCl H_2O_2

Source: Based on Lachenal, D., Nguyen-Thi, N.B., 1993. Rationalization of chlorine-free bleaching. In: Proceedings 7th International Symposium on Wood and Pulping Chem. Beijing, P.R. China, vol. 1, p. 166.

like chlorine and ozone in degrading lignin. Chlorine dioxide is used mostly in the initial stages of bleaching for replacing chlorine although it is somewhat less effective.

> This classification is somewhat simple in this respect and, furthermore, does not take into account that chlorine dioxide is reduced to hypochlorous acid and that oxygen is reduced to hydrogen peroxide during the bleaching reactions. Chlorine dioxide is also used as a brightening agent in the latter part of a sequence. Sodium hypochlorite and hydrogen peroxide react almost exclusively with carbonyl groups under normal conditions. This results in the brightening of pulp without appreciable delignification.
>
> ***Bajpai (2012)***

Lachenal and Nguyen-Thi (1993) have discussed the selection of an appropriate bleaching sequence based on this classification. A good bleaching sequence must contain at least one chemical from each category. CEHD, a chlorine-based sequence is an example of this principle. An example of a TCF sequence is OZEP (Singh, 1979).

> Concerns over chlorinated compounds such as dioxins, furans, and chloroform have resulted in a shift away from the use of chlorinated compounds in the bleaching process. Bleaching chemicals are added to the pulp in stages in the bleaching towers. Spent bleaching chemicals are removed between each stage in the washers. Washer effluent is collected in the seal tanks and either re-used in other stages as wash water or sent to wastewater treatment.
>
> ***Bajpai (2012)***

Bleaching of mechanical pulps is based upon lignin preserving methods and bleaching of chemical pulps is based upon removal of lignin. Therefore these methods are basically different. During the bleaching of mechanical pulp, chromophoric groups present in the lignin polymers are changed into a colorless form. Hence, the bleaching of mechanical pulp increases mainly the brightness of the pulp. There is not much loss of yield as well as dry solids. The effect is not lasting, and the paper turns yellow with time. Brightness gain is not stable. Therefore bleached mechanical pulp is more appropriate for newsprint and magazine papers as compared to books or archive papers. The lignin preserving bleaching is performed in one or two stages, depends on the final brightness of the pulp.

The bleaching stages can be distinguished according to the type of bleaching agent used. In reductive bleaching, sodium dithionite is used. It does not dissolve organic material from the pulp, and thus results in only a negligible loss in yield. Residues of dithionite in the pulp may cause corrosion of metals downstream in the process. In most mills, metal chelating agents, for instance, ethylenediaminetetraacetic acid (EDTA), diethylene triamine pentaacetic acid (DTPA) are used for preventing degradation of the dithionite. Hydrogen peroxide is used in oxidative bleaching. Peroxide bleaching reduces the yield by about 2%, mainly because of the alkalinity during the bleaching which results in some dissolution of organic substances in the raw material. The pollution load is also increased. In addition, peroxide bleaching improves the strength properties as well as water uptake capacity of the pulp. The bleaching process results in reduced brightness in the presence of heavy metal ions. So, chelating agents (e.g., EDTA, DTPA) are usually added before bleaching. These chelating agents form complexes with heavy metals (e.g., iron, manganese, copper, and chromium), which prevents the pulp from discoloration and the peroxide from decomposing. EDTA and DTPA contain nitrogen, which goes in to the wastewater. Use of a washing stage between pulping and bleaching is found to be effective in reducing the difficult metals and thereby reduce the quantity of chelating agent needed and improve the efficacy of the added peroxide. The bleached pulp is acidified with sulfuric acid or sulfur dioxide to a pH of 5–6.

Pulps produced from nonwood plants have high amount of calcium, potassium, manganese, copper, iron (which makes up the ash content). These pulps when bleached without using chlorine chemicals, the transition elements present in the pulp produce radicals which react in an unselective manner with the pulp resulting in a loss of pulp yield and strength properties. These pulps can be bleached with oxalic acid. Calcium oxalate is produced when calcium reacts with oxalic acid. Calcium oxalate is deposited easily.

For avoiding environmental problems, bleaching is carried out without chlorine chemicals. This is not possible in alkaline pulping process because of the presence of inorganic compounds. Separation of silicon from the liquor was suggested by Rousu et al. (2002), for solving this problem.

The fibers are delignified in the chlorination and oxidation stages of bleaching. Additional lignin from the pulp is solubilized in these stages. Bleaching agents such as chlorine gas, chlorine dioxide, sodium hypochlorite, hydrogen peroxide, and oxygen are used and applied in different stages within the bleaching sequence. Strong alkali (sodium hydroxide) is generally applied between bleaching sequence for extracting the dissolved lignin from the surface of the fibers. The bleaching agents used depends upon the following factors:

- Relative cost of bleaching chemicals
- Type and condition of the pulp

- Desired brightness of the paper to be produced
- Environmental guidelines and regulations

Chlorine is used as a bleaching agent for pulps obtained from bagasse. Bagasse needs less bleaching chemicals for achieving a bright white sheet paper (Poopak and Reza, 2012). With the aim of reducing the bleaching chemicals and the discharge of detrimental organochlorine compounds, oxygen delignification process is being used for nonwoods. This method reduces the kappa number by 40%–50%.

Chemicals used for bleaching cover oxidizing bleaching agent, reductive bleaching, agent, sodium hydroxide, chelating agents, and enzymes. These chemicals can be used alone or in various combinations. The CEH three-stage bleaching process is mostly used in conventional nonwood pulping. But, this process generates pollutants which are quite difficult to degrade. Since the 1980s, it has been found that most of the organochlorine compounds are highly toxic as well as mutagenic, and some compounds were also found to be carcinogenic. As a result, the emission of adsorbable organic halides (AOX) in bleaching wastewater is becoming more and more stringent.

> Each country has specific regulations on AOX emission limits in bleaching effluents: Switzerland = 0.1–0.2 kg tp^{-1}, Finland = 0.2–0.4 kg tp^{-1}, Canada = 0.25 kg tp^{-1}, America = 0.272 kg tp^{-1} and China = 0.72 kg $tp^{-1.}$
>
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Currently the major clean bleaching processes are ECF and TCF (Nelson, 1998).

The key chemical in ECF bleaching is chlorine dioxide. This bleaching agent has strong oxidation capacity (Mckague and Reeve, 1995). Chlorine dioxide bleached pulp possess high brightness and very good strength properties. Nevertheless, chlorine dioxide is produced when it is needed. The production cost is high. The main problem faced in chlorine dioxide bleaching is its preparation. As shown in Fig. 8.1,

> Chlorine dioxide, a kind of free radical, can easily attack phenol-type lignin to make it become free radical, followed by a series of free radical reactions, which are the main reactions in chlorine dioxide bleaching process. Besides, this reaction can also increase the water solubility and alkali solubility of residual lignin. Another important step is the oxidation demethylation reaction. In reaction, the o-quinone derivatives are formed, and the double bonds of quinone ring are attacked by chlorine dioxide or chlorite. In addition, chlorine dioxide can also react with non-phenolic structures and form the corresponding chlorides and oxidation products, but the reaction rate is very slow.
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In TCF bleaching mostly oxygen, hydrogen peroxide and ozone are used. This type of bleaching agent does not produce toxic and detrimental substances after bleaching (Gellerstedt, 2009; Pyrke, 1996; Roncero et al., 2003a,b).

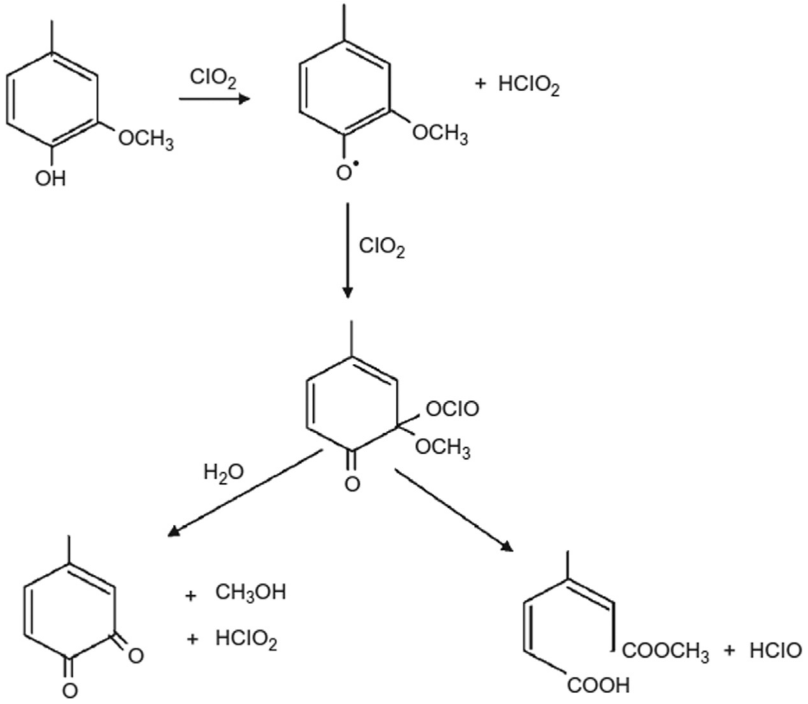

Figure 8.1

Reaction between phenolic lignin units and chlorine dioxide. *Source: Reproduced with permission from Nelson, P.J., 1998. Elemental chlorine free (ECF) and totally chlorine free (TCF) bleaching of pulps. In: Young, R.A., Akhtar, M. (Eds.), Environmentally Friendly Technologies for the Pulp and Paper Industry. John Wiley & Sons, Inc., New York, USA, p. 215, John Wiley & Sons.*

Molecular oxygen is a superb oxidant. It tends to react with organic substances and causes a chain reaction of free radicals. As a delignification agent, molecular oxygen, is able to react strongly with organic compounds through two unpaired electrons.

> Lignin oxidation is carried out through a series of electron transfer, and at the same time, oxygen is gradually reduced and generates a variety of free radicals and ions, which varies with the pH values. These free radical and ionic groups play an important role in lignin degradation. Hydrogen peroxide is a weak oxidizing agent. It can react with lignin through. There are complex series of reactions of lignin and hydrogen peroxide, including reactions with side chain carbonyl groups and double bonds, to oxidize lignin and change the structure of chromophoric group to be of colorless. To a certain extent, the various free radicals generated in bleaching process can also react with lignin. Hydrogen peroxide is a nonvolatile water solution, in which hydrogen peroxide anion is the main reactant. Therefore, in hydrogen peroxide bleaching process, sufficient ion concentration should be ensured to reduce the decomposition of hydrogen peroxide and improve the bleaching effect.
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Ozone is not a selective oxidant. When it is used for removing lignin, the carbohydrates get subjected to substantial degradation. The reaction behavior of ozone with lignin is similar to elemental chlorine. Under acidic conditions, ozone is an oxidizing electrophilic reagent. It is able to oxidize the conjugated double bond and free phenolic as well as etherified phenolic hydroxyl groups. After that, the lignin molecule diminishes and dissolves in water or alkali for achieving bleaching.

8.2 Bleaching of nonwood pulps

Different conventional, ECF and TCF bleaching sequences have been studied for bleaching of nonwood pulps (Azeez, 2018).

Multistage conventional bleaching sequence CEH was used for bleaching of nonwood pulps—bagasse and wheat straw. Final pulp brightness gain of more than 75% was obtained with nonwood pulps pulped to 8−12 kappa number. Furthermore, studies showed that more than 85% brightness could be obtained for different types of nonwood pulps by changing the chemical doses and stages in a bleaching sequence (Misra, 1974).

Rao and Maheshwari (1986) studied the bleaching of wheat straw pulp (kappa number 9.2−30.0) which was produced using soda method with different bleaching sequences: HH, CHH, and CEH. Maximum brightness of 78% was achieved with a HH bleaching sequence. The response of soda pulps in terms of brightness development was found to be more in a HH sequence in comparison to CHH and CEH sequences. Conversely strength properties were better in the CEH sequence in comparison to HH and CHH sequences.

Lele et al. (1998) used singlet oxygen treatment for CEH bleaching of wheat straw pulp. Reduction in the requirement of bleach chemicals by about 30%−50% was obtained when the pulp was treated with singlet oxygen and hydrochloric acid before the hypo stage. The pulp properties were found to be comparable.

Use of ammonium salts and surfactants was studied as bleaching aids to bleach wheat straw pulp (Deng et al., 2002). Both surfactants and ammonium salts increased the whiteness of pulp and also reduced the requirement of chlorine chemicals. This resulted in reduction in the pollution load in the effluent.

ECF bleaching is a better option for bleaching as compared to traditional chlorine bleaching processes. DQP bleaching sequence was studied as an alternative bleach sequence to bleach wheat straw and other nonwood pulps. Final pulp brightness of more than 80% ISO was obtained. The pulp viscosity, brightness stability, and strength properties of bleached pulp were superior showing that DQP sequence was selective. Furthermore, chemical oxygen demand (COD), biological oxygen demand (BOD), suspended solids, and AOX values were much lower by using a DQP sequence in comparison to conventional CEH sequence (Zhan et al., 2005).

Oxygen delignification and ECF bleaching of wheat straw soda pulp was studied (Ghosh, 2006). The bleaching sequence used was OD50EpD50. The final pulp properties were higher than 84% ISO and the strength properties were excellent. The COD and AOX loads were also reduced.

In case of another ECF bleaching sequence OD1EopD2, pulp of about 87% ISO brightness was obtained and the strength properties were comparable. The bigger benefit of using such ECF bleaching sequences has been the reduced generation of pollutants in the effluent (Kar et al., 2006).

Diverse chemical agents have been examined for enhancing the bleaching efficacy by activation of the bleaching chemicals. Vanadium pentoxide was found to be one of the activating agents for enhancing the bleachability of chlorine dioxide stage for wheat straw pulp produced using the soda-anthraquinone process (Li et al., 2007).

Use of enzymes in bleaching is also attracting a lot of attention during the last few years (Liu et al., 2018). Pretreatment of pulp with enzyme is one of the promising options for reducing the use of chlorine chemicals and other bleaching chemicals during the bleaching process. Enzyme bleaching has been in commercial operation in several countries for several years. Usually these enzymes are obtained from fungal sources like *Trichoderma reesei*. The enzyme bleaching studies first used mixture of natural enzymes which attacked a broad range of materials in the pulp. Most of these studies used xylanases which hydrolyzed xylan. Response to enzyme is found to vary with type of raw material and the pulping processes which impacts the final pulp properties (Bajpai, 2018; Chauhan et al., 2006). The enzymatic treatment efficiency is affected by source and purity of enzymes. Also the sequence of enzyme application in a bleaching sequence can affect the selectivity and efficiency of the treatment. Several researchers have explored enzymes in bleaching of nonwood pulps (Ziaie-Shirkolaee et al., 2008; Chauhan et al., 2006; Jiménez et al., 1996, 1997; Chen et al., 1999, 2003; Hong et al., 2001; Feng et al., 2002; Han et al., 2002; Herpoël et al., 2002; Shobhit, et al., 2002; Tuncer and Ball, 2002; Record, et al., 2003; Feng et al., 2003; Wang et al., 2004; Mao et al., 2003a, 2003b; You et al., 2003; Mao et al., 2007; Roncero et al., 2003a, 2003b; Zhao et al., 2003; Ge et al., 2005; Li et al., 2005a, 2005b, 2006; Mao et al., 2005; Jiang et al., 2006; Kapur et al., 2006; Ninawe and Kuhad, 2006; Zhao, et al., 2006; Ates et al., 2008; Mathur et al., 2005; Sharma, 2008; Singh et al., 2008).

Jiménez et al. (1996) bleached enzyme treated wheat straw pulp with two bleaching sequences DE(p)D and P. Enzyme treatment was done with Cartazyme HS. The bleach chemical consumption was reduced from >3% to 5% and the pulp brightness increased by 3.7%. However, pulp yield and strength properties reduced.

Chen et al. (1997) used xylanase enzyme in bleaching of wheat straw pulp. Xylanase was used in different bleaching sequences for increasing the bleachability of pulp. Final pulp brightness of more than 80% ISO brightness was achieved with 50 IU xylanase/g pulp in XCH, CXH, and CH/X bleaching sequences. The use of alkaline extraction stage before H treatment in multistage bleaching sequences—XCEH, CEHX, and CEH/X increased the brightness to more than 85%. The fiber strength properties were also improved.

Hong et al. (2001) studied use of xylanase to improve the bleachability of wheat straw chemimechanical pulp. Xylanase was obtained from *Trichoderma ressei* Rut C-30. The corncob meal was used as carbon source for producing xylanase. Pretreatment with xylanase increased the bleachability and also reduced peroxide consumption by about 50%. Brightness increased to more than 60% ISO when second peroxide stage was used (XP3P3 - X represents xylanase stage and P3 represents 3.0% hydrogen peroxide on o.d basis in each stage).

Feng et al. (2002) isolated alkali and acid-stable xylanase enzymes from soil containing *Aspergillus niger*. Pretreatment of wheat straw pulp with this xylanase reduced hypochlorite consumption by 20%−30%. This resulted in reduced pollution load in the effluent.

> The bleaching techniques had experienced a long-term development in China's wheat straw pulping practices. Early, the single-stage low consistency bleaching with hypochlorite was commonly applied in many nonwood pulping lines, and a three-stage bleaching sequence of CEH (chlorination—alkali extraction—hypochlorite) was not applied until the 1980s of the twentieth century. All of the above bleaching sequences contain elemental chlorine chemicals with generation of AOX and other organic toxicities in these bleaching effluents. Due to poor bleaching selectivity upon residue lignin, there were a large amount of carbohydrates degraded while bleaching, resulting a large water consumption and high chemical dosage, to produce bleached pulps with low brightness and weak physical strength as well as poor drainability of water. Following more and more strict regulations to effluent discharge, elemental chlorine chemicals were forbidden to be used for pulp bleaching, and the bleaching techniques were developed toward more environmentally friendly processes, such as ECF and TCF bleaching sequences. The first mid consistency and shortened TCF bleaching sequence in the world, namely, OQPo (oxygen delignification—chelating metal ions—peroxide bleaching assisted with oxygen) sequence, was successfully commercially operated with the capacity of 150 t/d by Xianhe Co., Henan, China in 2008. With this bleaching sequence, bleached wheat straw pulps with brightness of more than 80% ISO, pulp viscosity of 653 ml/g and breaking length of more than 7000 m were obtained. Lesser amount of bleaching effluent was generated (about 30 m3/t pulps). Effluent generation decreased by more than 60% of a traditional CEH bleaching process for wheat straw pulps.
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> ***Fang and Shen (2018); Zan et al. (2011); Li et al. (2009)***

Table 8.5 shows physical strength properties of bleached wheat straw pulps by an OQPo sequence and Table 8.6 shows the properties of wheat straw pulps from different stages.

Table 8.5: Physical strength properties of bleached wheat straw pulps by an OQPo sequence.

Grammage (g/m^2)	58.3
Beating degree (oSR)	44.3
Tensile (N.m/g)	71.23
Breaking length (km)	7.16
Tear (mN. m^2/g)	4.83
Burst (kPa m^2/g)	4.68
Fold endurance times (1.5 kgf tension)	24

Source: Li, J., Li, K., Wu, H.M., Li, W.W., Zeng, J., Xu, J., et al., 2009. Commercial operation of wheat straw pulping bleaching by a OQPo sequence. China Pulp Pap. 28 (10), 79–81.

> A bleached wheat straw pulp production line by TCF sequence with an annual capacity of 200 t/d was installed in Baiyuan Paper Co., Henan, China. Also, enzymes have been considered by many researchers to assist bleaching operation for reducing the use of chlorine chemicals and improving the bleached pulp quality.
>
> *Fang and Shen (2018)*

Ahmad et al. (2014) developed a pulping process for wheat straw to be used as supplementary pulp for producing fine paper. Production of bleachable chemimechanical pulp from wheat straw at varying sodium hydroxide level and treatment time was studied. The yield after chemical treatment ranged from 64.6% to 72.7% and the total yield after defiberization varied between 53.4% and 62%. The pulp produced using 10% sodium hydroxide, 40 minutes pulping time, and 95°C pulping temperature was chosen for ECF bleaching studies. Use of 3% (oven dry weight of the unbleached pulp) chlorine dioxide in D0EPD1 bleaching (2% in D0 stage and 1% in D1 stage) increased the brightness to 62.2% ISO. The kappa number dropped from 40.1 to 13.4 for bleached pulp.

The bleachability of wheat straw pulp obtained through alkaline peroxide mechanical pulping (APMP) process was investigated by Pan and Leary (2000). The bleaching trials involved the application of oxidative and reductive bleaching chemicals. Reductive bleaching chemicals were not found to be effective in bleaching wheat straw mechanical pulp. Peroxide and peracetic acid could be used to bleach the pulp to reasonable brightness levels. Ozone enhanced pulp bleachability, but there was significant losses in yield, especially when it was followed by peroxide bleaching.

Table 8.6: Properties of wheat straw pulps from different stages.

Wheat straw pulps	Brightness (% ISO)	Viscosity (mL/g)
Screened brown pulp	34.7	965
Pulp after oxygen stage	48.0	850
Pulp after Po stage	81.6	653

Source: Li, J., Li, K., Wu, H.M., Li, W.W., Zeng, J., Xu, J., et al., 2009. Commercial operation of wheat straw pulping bleaching by a OQPo sequence. China Pulp Pap. 28 (10), 79–81.

Zhao et al. (2004) examined APMP of wheat straw with enzyme. Instead of enzyme treatment on wheat straw, an alternative method was used, in which coarse pulps from refiner defibrated wheat straw were treated with a crude xylanases, then impregnated with alkaline hydrogen peroxide and further refined.

> The optimum conditions of enzyme treatment were xylanase dosage of 10-15 IU/g of oven-dried wheat straw, 90 min, 50-60 degrees C, pulp consistency of 5-10%, and initial pH of 5.0, and those for chemical impregnation were 6% sodium hydroxide, 70-80 degrees C, 60-90 min, and 4 to 5% hydrogen peroxide. Enzyme treatment improved pulpability of wheat straw by the APMP process, and final pulp quality such as brightness, breaking length, and burst index of pulp. Pulp from the APMP process with enzyme treatment could be bleached to a brightness of 70.5% ISO by two-stage hydrogen peroxide bleaching sequence with only 4% hydrogen peroxide, and breaking length of the bleach pulp reached 4470 m.
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In Table 8.7, the results of ECF bleaching of wheat straw, bamboo, reed and bagasse pulps are presented. The brightness of the four bleached pulps are equal to or even higher in comparison to the conventional three-stage bleaching process showing the suitability of ECF bleaching technology for bleaching of nonwood pulps.

Extensive research has been conducted on TCF bleaching of nonwood pulps (Pekarovicova et al., 1994; Chen et al., 1999; Han et al., 2002; Roncero et al., 2003a, 2003b; Wang et al., 2003a, 2003b; Xu et al., 2004; Cao et al., 2005a, 2005b; Jahan Latibari et al., 2006; Tong et al., 2006; Hedjazi et al., 2007, 2009; Niu et al., 2007; Fang and Shen, 2018; Quia et al., 2000).

> When TCF was used for bleaching wheat straw pulp, it was found that the brightness of bleached pulp was as high as 83.5% ISO, and the physical properties of the paper were admirable. This kind of bleached pulp could be used instead of high-quality pulp for the production of writing paper and printing paper. For reed pulp, the same effect was achieved with TCF, and the brightness was even higher, with a maximum 87.6% ISO.
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Liu et al. (2009) explored TCF sequence OpQP, for wheat straw soda-anthraquinone pulp. It was found that hydrogen peroxide reinforced oxygen delignification increased the delignification selectivity by improving bleachability and brightness stability of pulp. However, the strength properties were slightly reduced (prr.hec.gov.pk).

Yaqoob et al. (2011) reviewed TCF bleaching sequences used in bleaching of wheat straw pulp. Pekarovicova et al. (1994), produced organocell organosolv straw pulp and used six different bleaching sequences to bleach it (Table 8.8). They introduced an enzyme stage that was included as intermediate to increase the effectiveness of final bleaching stage.

Table 8.7: ECF bleaching of nonwood pulps.

Bleaching process	Brightness (ISO%)	Viscosity (mL/g)
Wheat straw		
HD/H	78.6	
ODQ(PO)	85.47	813
CEH	538	538
Bagasse		
ODQ(PO)	86.38	807
CEH	86.5	543
DEpDD	85.98	
Bamboo		
D0(EOP)D1	87	
DEpDD	85.11	
Reed		
ODQ(PO)	84.31	821
CEH	83.2	583

C- chlorination (Cl2); E-alkali extraction (NaOH); H-hypochlorite bleaching; D-chlorine dioxide bleaching; P-hydrogen peroxide bleaching (H2O2 + NaOH); O-oxygen bleaching (O2 + NaOH); Q-chelating treatment (EDTA, DTPA, STPP).

Source: Based on Liu, Z., Wang, H., Hui, L., 2018. Pulping and Papermaking of Non-Wood Fibers, Pulp and Paper Processing. Salim Newaz Kazi, IntechOpen. <https://www.intechopen.com/books/pulp-and-paper-processing/pulping-and-papermaking-of-non-wood-fibers>.

They found ligninase and chelation treatment both to be effective in increasing the bleaching with peroxide.

Chen et al. (1999) studied TCF bleaching (OMnP) of soda-AQ pulp. Potassium permanganate was used in intermediate bleaching stage between oxygen and peroxide. It was found that chelation prior to peroxide treatment helps in increasing brightness to 80% ISO.

Using four different TCF bleaching sequences ZpP, ZpY, ZpEPY, ZpEYP, Wang et al. (2003b) reported that wheat straw pulp could be bleached up to a whiteness of 80%–83%.

Cao et al. (2005b) cooked wheat straw to low lignin content for TCF bleaching. It was found that use of AQ(PN)P and QZEYP bleaching sequences can achieve brightness of more than 80% ISO. Viscosity of bleached pulp and brightness stability were better in comparison to pulp obtained with CEH sequence.

Tong et al. (2006) used AZEYP sequence to bleach wheat straw kraft pulp and achieved a brightness of 86.9% ISO. This sequence combination of oxidative reductive-oxidative bleaching steps was found to be selective in terms of lignin solubilization without cellulose degradation.

Table 8.8: TCF bleaching sequences used for wheat straw pulp.

Pekarovicova et al. (1994)	Organocell organosolv straw pulp	O-L-P O-X-P O-P EOP-X-P EOP-L-P EOP-P
Chen et al. (1997)	Soda-AQ wheat straw pulp	OMnP OMnQP
Han et al. (2002)	Wheat straw pulp pretreated with laccase mediator system	OEPP QPP QPaP
Roncero et al. (2003a, 2003b)	Wheat straw pulp	XOAZRP
Wang et al. (2003a)	Low kappa number kraft wheat straw pulp	ZpP ZpY ZpEPY ZpEYP
Xu et al. (2004)	Auto-catalyzed ethanol wheat straw pulp	OOpZP ZOOpP
Cao et al. (2005b)	Low kappa number kraft wheat straw pulp	AQ(PN)P QZEYP
Jahan Latibari et al. (2006)	Soda-AQ wheat straw pulp	OQ(OP) or OQ(OP)P
Tong et al. (2006)	Wheat straw kraft pulp	AZEYP
Hedjazi et al. (2007)	Wheat straw	O/Q/OP
Niu et al. (2007)	Soda-AQ wheat straw pulp	(OpQPo)
Hedjazi et al. (2009)	AS/AQ wheat straw pulp	OQ(OP) or OQ (OP)P

TCF, Total chlorine free.
Source: Reproduced with permission Yaqoob, N., Cheema, K.J., Mateen, B., 2011. Review on total chlorine free bleaching sequences of wheat straw pulp. Asian J. Chem. 23, 8, 3317–3319.

Hedjazi et al. (2007) achieved more than 80% ISO brightness in O/Q/OP sequence with wheat straw pulp cooked by soda process. Hydrogen peroxide treatment in alkaline medium was optimized with different chemical agents. The addition of only 2.0% sodium silicate was found to be quite effective for reducing the peroxide bleach consumption and to achieve brightness of 80% ISO.

Niu et al. (2007) used OpQPo sequence for soda-AQ wheat straw pulp. Oxygen treatment coupled with optimized peroxide dosage boost the delignification process in oxygenation stage of pulp. Further chelation and peroxide treatment yielded total chlorine free bleached pulp brightness of 80.2% ISO.

In another study, Hedjazi et al. (2009) used OQ(OP) or OQ(OP)P sequences to bleach AS/AQ pulp. Brightness and tear strength were higher in comparison to Soda-AQ pulp.

Nowadays there is increasingly strict requirement of environmental protection. Therefore the contradiction between cleaner production level of pulp and papermaking and environmental needs is becoming important, particularly straw pulping.

> Straw pulp production has become the main source of pollution in the paper industry. It is well known that chemical components of the straw and the wood are different, so the pulping characteristics of these two kinds of raw materials are different. For straw materials, the pulp has poor filtration property, and the black liquor has high ash content and high sugar content, which is also the reason for the high viscosity of black liquor, so it is difficult for extraction, evaporation and combustion of black liquor. Viscosity, an important physical property of black liquor, has a great impact on the extraction of black liquor, flow, evaporation and combustion. There is a great difference in the viscosity of different black liquor. Generally, rice straw > wheat straw > bagasse > bamboo > wood.
>
> *Liu et al. (2018)*

Usually the remaining lignin content of straw pulp produced using the chemical process is lower as compared to wood pulp. The molecular weight of this lignin is small. So, the bleachability of straw pulp is better as compared to wood pulp. Using conventional hypo bleaching, upto 70% brightness can be achieved but the bleaching effluents contains toxic organochlorine compounds. Hence, the elimination of hypochlorite bleaching of straw pulp and the development of chlorine free bleaching are very important for bleaching of straw pulp.

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CHAPTER 9

Chemical recovery

Chapter outline

9.1 The chemistry of silica 170
  9.1.1 Mineral composition, especially silica 170
9.2 Desilication of black liquor 171
  9.2.1 Partial desilication by raw material cleaning 171
  9.2.2 Spontaneous partial desilication of black liquor by storing (ageing) 172
  9.2.3 Desilication of black liquor by lime addition 173
  9.2.4 Desilication by black liquor by carbonation 173
9.3 Desilication of green liquor 177
9.4 Soda recovery 178
9.5 Alternative recovery processes 181
  9.5.1 Direct alkali recovery system 181
References 184
Further reading 186
Relevant websites 186

Chemical recovery is a vital section of the chemical pulping process. In this section, chemicals are recovered from the spent pulping liquor for using again. There are several environmental and economic advantages in using the chemical recovery (Table 9.1).

> Implementation of chemical recovery in nonwood pulp mills is an issue of survival as pollution limits are getting more stringent and also due to the economical situation. Prices of raw materials are increasing by 60 to 100% but prices of paper are not increased in line with prices of raw materials.
>
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Table 9.1: Environmental and economic benefits of chemical recovery process.

Economic benefits
Savings on chemical purchase costs due to regeneration rates of process chemicals approaching 98%
Energy generation from pulp residue burned in a recovery furnace
Environmental benefits
Recycle of process chemicals
Lack of resultant discharges to the environment

Nonwood Plant Fibers for Pulp and Paper.
DOI: https://doi.org/10.1016/B978-0-12-821800-6.00009-0

Table 9.2: Presence of lignin and silica in main nonwoody raw materials in percentage.

	Silica	Lignin
Wood	Traces	18–29
Bamboo	0.6–3.5	22–30
Bagasse	1.1–2.5	18.5–25
Reed	2.0–3.0	21
Wheat straw	3.0–7.5	16–18.5
Rice straw	8.0–12.0	12–14

"Nonwood pulping plants are normally small, typically producing less than 100,000 t/year of pulp, and so lack the economies of scale that make environmental investments economical at the larger facilities. Because of this, many nonwood mills have limited or no recovery of chemicals and have substantially higher emissions of waste per ton of product than modern Kraft mills" (Bajpai, 2016). Nonwoody plant materials generally have high amount of silica as compared to wood (Table 9.2).

Nonwoods are generally pulped with soda pulping and Kraft pulping methods. Nonwoods have high silica which ranges from 1.5% to 20%. A large amount of the silica presents in the raw material goes into black liquor (Bajpai, 2008, 2016). The occurrence of silica in nonwood fibers creates many problems in the pulping process and limits the use of these raw materials (Bist et al., 1981; Dixit et al., 2010, 2012; Liu et al., 2018) (Table 9.3).

In the soda as well as kraft process, most of the silica reacts with the hydroxide and produces ions which are water soluble. The silica content in the spent pulping liquor is found to range from 10 Kg SiO_3 per ton of total dissolved solids with bagasse and 150 Kg SiO_3 per ton of total dissolved solids with rice straw. Evaporators, recovery furnace, and lime kiln operations are also affected by the presence of silica in the spent liquor (Ibrahim, 1988).

Mostly silica increases the scale formation in the liquor evaporators and decreases the effectiveness of the causticizing process and also the conversion of lime mud to calcium oxide in the lime kiln. To offset these effects, nonwood pulping facilities usually discharge high amount of lime mud and buy high quantity of lime or limestone as make up chemicals.

Table 9.3: Problems associated with the presence of silicate ions in black liquor.

Scaling of the multiple-effect evaporator heat transfer surfaces
High black liquor viscosity, which makes it difficult to concentrate the liquor
Poor settling of lime mud and lower conversion of carbonate to sodium hydroxide in the causticizing system To maintain a tolerable silica content in the black liquor, mills purge silica from the process by:
Sending some or all of the black liquor to the sewer
Landfilling lime mud

Some nonwoody fiber materials have unusual and important properties for specialty products. For example, cotton linters, flax, hemp, and abaca fibers are long and valuable for products such as document papers having water marks, banknote paper, security papers, and tea bags. These specialty papers are not produced much and, hence, not of much concern in terms of possible environmental impact.

> In the soda pulping process, the active pulping chemical is sodium hydroxide whereas in the Kraft pulping process, the active chemicals are sodium sulfide and sodium hydroxide. Cellulose and hemicelluloses are separated during the pulping process, and lignin with some other chemicals like silica and extractives get solubilized in the cooking liquor which is separated from the pulp and is termed as black liquor. These cooking chemicals are recovered from the black liquor in recovery process for reutilization in the system for making pulping process economical and environment friendly. In the recovery process black liquor is first concentrated in evaporators and burned under reductive conditions in a recovery boiler then the sodium and sulfur which are present in the black liquor are converted to sodium carbonate and sodium sulfide. An aqueous solution of these chemicals is called green liquor. This is further causticized with calcium oxide to regenerate the pulping chemicals. The calcium carbonate produced during causticizing may be recovered as calcium oxide after reburning it in kiln.
>
> ***Bajpai (2008, 2016)***

Because nonwood plants have open structure, they need more pulping liquor. Silica is also able to react with alkali during pulping which further increases the alkali dose and increases the inorganic chemical load in the recovery process. This results in reduced ratio of organics and inorganics, reduced heating value, and more inorganic chemicals to be recovered and reconverted (Grace, 1987a,b).

When the liquors having high content of silica are combusted, silicate glass of high viscosity are formed. This results in the formation of “honeycombs” on the wall of the boiler, plugging of convective boiler passages, problems in smelt drainage, and impaired combustion. Hence regular shutdowns for cleaning are needed. In few cases where problems are particularly harsh, generation of steam from liquor burning is not tried. Direct contact evaporators provide only heat recovery. In these evaporators hot gases are used for the concentration of liquor.

> Silicates in green liquor will react with lime and precipitate as calcium silicate. This interferes with lime mud settling so that mud washing and filtration are more difficult and soda losses are increased. Silica forms glassy silicates in the kiln leading to sticky rings and low efficiency. These problems are usually so severe that lime reburning is not attempted when pulping siliceous fiber sources. Disposal of the lime mud then becomes a problem as residual sodium in the mud acts to prevent its use as a soil conditioner, even in lime deficient regions.
>
> ***Grace (1987a,b); Grace and Timmer (1995)***

Many techniques are available to remove silica from chemical recovery systems. Weak black liquor is the best point for removing silica, although desilication of green liquor can also be conducted. This eliminates interference with the organic compounds in the black liquor, but it does not avoid problems in the evaporation or combustion stage.

Several precipitating agents have been used. These include lime, ferric oxide, and alumina. Method used for desilication by using acidification is carbonation.

9.1 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 H_2SiO_3 and is the basis of silica gel desiccant and opal. The soluble ion under alkaline conditions is $SiO_3{}^{2}$- or $[SiO_2(OH)_2]_2-$.
>
> ***Biermann (1996)***

Dean (1985) reported 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" (Biermann, 1996).

9.1.1 Mineral composition, especially silica

The mineral (and elemental) composition of cereal stalks was studied by Delga (1947). Soluble ash was in the range of 1.54%–4.7%; potassium in the range of 0.77%–3.44%, and silicon ranged of 0.35%–0.73%. The highest level of sodium—0.85%, was found in oat straw, while the highest calcium content—0.26% was found in the rye grain straw. Sulfur and phosphorus contents were found to be lower. The composition of oat straws grown in two different soils were not found to be different. Egyptian wheat straw contained 8.34% ash and 3.44% silica (Fahmy and Fadl,1958). The leaf (sheath) has high ash content—14.9% ash and silica is 6.90% whereas the stem has 5.90% ash and 2.24% silica. Wet or dry sorting of the prehydrolyzed raw material was found to remove the silica–rich epidermis with a 4% loss of material. Ethanol–benzene extraction allowed silica to be removed with a second extraction stage.

In bamboo, silica is in the range of 2.5%–3.5%. It is more concentrated in the nodes, where it may occur as virtually pure silica, as compared to the internode region. Bagasse contains about 1.5% silica. In the straw leaves, the silica content is more as compared to the stems. This shows that if straw is preprocessed for removing leaves and nodes, then several benefits can be obtained.

9.2 Desilication of black liquor

> Various processes have been proposed to exclude silica from the cooking and chemical recovery process and thus to make pulping of nonwood fibrous raw materials especially straw more effective. Black liquor is the initial medium/input material of the chemical recovery system. Desilication of black liquor will eliminate or at least substantially depress all difficulties in the recovery system caused by silica. In some cases silica content in black liquor can be reduced by modifying cooking conditions. Except of raw material cleaning and in one case green liquor desilication in the NACO process, no mill with desilication was identified. Basically there are two possibilities to eliminate silica dissolved in alkaline solution i.e. in black liquor and green liquor.
>
> 1. Reduction of solubility and precipitation of silica by decreasing RAA and pH especially by carbonation with carbon dioxide.
> 2. Reaction of sodium silicate with metallic ions (calcium, aluminum) resulting in insoluble silicates.
>
> Neither of these reactions is quantitative
>
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Panda (1988) and Bleier (1988) have reviewed the desilication methods.

9.2.1 Partial desilication by raw material cleaning

Cleaning of raw material must be done for removing silica in the recovery system. Dedusting of straw is an easy method of silica reduction, but is not found to be very effective.

In bagasse depithing is done for reducing silica in bagasse. This is a standard process in bagasse pulping. At the same time, the dust containing silica is removed from the surface.

In bamboo, chips are washed for removing silica. Panda (1988) reported about 50% silica removal. The equipment is similar as used in washing of wood chips. This method is used in many mills using bamboo.

> Wheat straw pretreatment is used in the Italian Foggia straw pulp mill. Straw bales are fed without chopping into a continuous NACO-pulper. Crude contaminants (metals, stones, plastic material) are continuously discharged from the pulper. The pretreated straw is pumped to a fluidification device to separate small contaminants and sand. 1–2% alkali on straw is added and the defibrated material is washed and pressed to 25–30% dry content. The yield range is 80–90%, reduction of silica about 50%. NaCl is also reduced, if content in straw is higher due to soil contamination. An additional benefit is, that the fibrous raw material is free from waxes and easy to impregnate with chemicals. The NACO cleaning process is included in a new Chinese mill project. The Central Pulp and Paper Research Institute (CPPRI), India tested straw cleaning in pilot scale using a disc mill comprising of a stationary and a rotating disc with exchangeable grinding elements and a universal separator. By excluding fractions containing high silica about 50% of silica could be removed. No information is available about application on mill scale.
>
> ***open.unido.org; Nardi (1993, 1995); Dhingra and Pant (1993)***

9.2.2 Spontaneous partial desilication of black liquor by storing (ageing)

Storing at high temperature is used for removing silica from black liquor. In this case silica along with some lignin gets precipitated (Zhang, 1991). The changes are presented in Table 9.4.

Extensive research has been conducted in China. A 200 m^3 tank was used with a cone (Li Ming Fang, 1988). After treatment for 8 h at 80°C, the SiO_2 concentration in alkaline sulfate black liquor reduced from 4–4.65 to 0.63–0.93 g/L in the clean liquor. The sludge volume was 8% of original containing 20.3 g/L SiO_2.

The sludge composition in another case was—Ash, 38.34%; SiO_2, 16.42%; Lignin, 12.78%; Incineration losses 61.66%; high heat value, 4.4 MJ/kg solid. The desilication efficiency was about 80%. The sludge which was approximately 10% of original solid content contained substantial quantity of lignin and other organics (collectively about 60%). About 10% of organic substance is lost and cannot be burnt in a recovery boiler. This type of volantry desilication may be practical for small pulp mill. However, pollution will be still higher and removal of sludge would be perhaps problematic. This aspect needs to be studied in detail.

Table 9.4: Effect of storage on desilication of black liquor.

Time of storage (h)	pH at 23°C	RAA NaOH (g/L)	SiO_2 (%w/w)	TS (%w/w)
0	11.81	4.52	3.43	15.5
24	10.53	1.2	0.347	15.63

Evaluation of technologies on recovery of black liquor chemicals For small and medium size pulp mills using nonwood fibrous raw materials www.unido.org.

9.2.3 Desilication of black liquor by lime addition

> Desilication with lime has received significant attention because lime is cheap and calcium silicate is quite insoluble, but no industrially viable process has been developed. Lime dosages have to be about six times the stoichiometric amount required to form calcium silicate and the filtration properties of the resulting lime mud are unfavorable. Many of these difficulties are reduced with green liquor desilication, but this does not alleviate evaporator or recovery furnace problems. However, concentrating the black liquor, which is already a part of the recovery process, reduces the lime consumption to twice the stoichiometric quantity. Aluminum silicate is also insoluble and can be produced in black liquor by addition of bauxite, which mostly consist of aluminum hydroxide. This induces silica precipitation, therefore silica can be removed by filtering the precipitate from the black liquor.
>
> ***Jayme (1958); Grace (1987a,b); Roberts (1982)***

Gruen (1955) studied desilication of lime at high temperature using large quantity of lime (about 6 times of stochiometric amount). Jayme (1958) used a modified process. In this case semi-concentrated black liquor containing 30% solids were used and the amount of lime was reduced to about two times the stochiometric amount. This method was also studied by West Coast Paper Mills in India (Kalyan Sundram and Ganesh, 1972). The desilication efficiency of the lime process was found to be high (85%–90%). However, the quantity of sludge generated is huge and some lignin may also get coprecipitated. Calcium also reacts with organic acids of the black liquor. This results in heavy scaling in the evaporators. The process was not used on a commercial scale.

9.2.4 Desilication by black liquor by carbonation

> In black liquor, the main component (about 50%) is alkali lignin containing phenolic and carboxylic groups. These are in form of sodium phenolates and carboxylates i.e. in alkaline medium are hydrophilic and are keeping lignin in solution. Besides this black liquor contains hemicelluloses, sacharinic acids and inorganic components (sodium hydroxide, sodium salts and silica). Silica is in the form of sodium silicate. Both lignin and silica can be precipitated when lowering pH with acids. Carbonation with carbon dioxide was found by several authors as the only practical way to precipitate silica. Selective precipitation of silica is a very sensitive process as coprecipitation of lignin should be avoided. The phenolic groups of lignin in black liquor have an acidity in the range $pK = 9.4$ to 10.8, whilst silicic acid value is between this i.e. pK 9.8. Nevertheless silica can be preferentially precipitated as silica forms by polymerization large molecules bound by covalent siloxane linkage (–Si–O–Si–). The high salt concentration of black liquor favors silica gel formation. The main problem is to attain by carbonation a pH which is very close to silica precipitation without over-carbonating i.e. lowering pH too much as this would cause lignin precipitation. Silica gels are difficult to filter and early attempts failed on filtration.
>
> ***open.unido.org; Panda (1988); Bleier (1988)***

Slow carbonation with flue gas was found to improve filtration of silica gel (Franzreb, 1958). Kuna and Kuna (1963) used precipitated silica for nucleation. But silica gets dissolved rapidly in alkaline black liquor and no concrete effect was obtained. Several researchers were involved in development of desilication by carbonation in 1980s. The most exhaustive work was conducted in 1970s and 1980s. Several companies, for example, Lurgi, Kraftanlagen Miinchen, and few mills have been involved in developing a suitable desilication technology by black liquor carbonization. But, only the technology developed by CPPRI, India along with UNIDO and SIDA has reached to an industrial level. These results were published in detail in the Proceedings of the International Seminar and Workshop on Desilication (UNIDO/CPPRI, 1991).

> Carbon dioxide is found to be effective for silica precipitation by partial acidification because of the requirement to realkalize the liquor to regain lignin stability. Using the proper conditions it is possible to precipitate silica without precipitating lignin. The critical pH limit must be established for each liquor. As the pH drops sodium bicarbonate is produced and silica precipitates according to the following reaction:
>
> $$Na_2SiO_3 + H_2O + 2CO_2 = 2NaHCO_3 + SiO_2$$
>
> Carbonation is usually carried out at higher temperatures, in spite of the fact that silica solubility increases with increasing temperature. It is very important to obtain the silica in a flocculated, easily filterable form, but this is not a straightforward case. Efficiency of silica removal by acidification method depends on the following two factors:

1. pH
2. Temperature

> According to Kulkarni et al. (1984), it is possible to precipitate silica at higher pH range whereas at high temperature, lower pH ranges are required.
>
> ***Bajpai 2016***

Table 9.5 shows that silica removal efficiency is high at high temperature and reduced pH.

CPPRI in India has conducted comprehensive study on use of nonwoods as raw materials for producing pulp and paper. They also tried to solve the problems observed with these raw materials during processing to pulp and paper. “Two major agroresidue raw material used in India are wheat straw and bagasse. Silica content in bagasse black liquor is in the range of 0.4%–0.5% whereas in wheat straw it is 4.0–5.0%w/w. Because of the presence of this very high amount of silica, processing of wheat straw black liquor in chemical recovery is very difficult. To solve this problem CPPRI conducted detailed studies on desilication of wheat straw black liquor. Black liquor was collected from an integrated wheat straw-based mill. Silica content in the original black liquor was in the range of 3.5–5.0 g/L. The black liquor was

Table 9.5: Desilication of black liquor at different temperatures[a].

Temperature (°C)	pH	Silica as SiO_2 (g/L)	Silica removed (%)
21	10.90	2.60	50.0
	10.65	1.10	78.8
	10.40	0.50	90.4
	10.30	0.50	90.4
52	10.10	4.10	21.2
	9.90	3.00	42.3
	9.75	2.65	49.0
	9.65	1.45	72.1
64	9.80	4.60	11.5
	9.60	0.90	82.7
	9.50	0.55	89.4
75	9.60	3.30	36.5
	9.40	0.55	89.4
	9.30	0.10	98.1

Source: Based on Kulkarni et al. (1984).
[a](Initial pH of black liquor, 11.9; Silica, 5.2 g/L).

subjected to carbonation under controlled conditions using recovery boiler flue gas as source of carbon dioxide. Controlled pH reduction led to selective precipitation of silica without coprecipitation of lignin. Residual silica content in the black liquor after desilication was 0.4 g/L and about 90% desilication was obtained. The results show improved black liquor properties after desilication. Viscosity was reduced to about 60% whereas swelling volume ratio increased by 1.5 times. The black liquor was colloidally stable up to 65% total solid concentration and no precipitation was noticed. Improved black liquor properties of wheat straw black liquor after desilication makes it suitable for processing in conventional chemical recovery system" (Bajpai, 2016; Kulkarni et al., 2005).

CPPRI and Enmas have performed few pilot and commercial-scale study for removing silica from black liquor. Silica removal up to 85%—98% was achieved (Table 9.6) (Nair et al., 1999).

Table 9.6: Desilication of black liquor of various raw materials.

Particulars	Straw/sarkanda based mill	Bamboo/reed based mill	Bamboo-based mill	Rice straw-based mill
Initial Silica in BL (g/L)	3.7	3.7	3.7	12.3
Final Silica in BL (g/L)	0.17	0.6	0.5	0.28
Desilication (%)	95	85	87	98
Status	Semi pilot	Commercial	Commercial	Semi pilot

Source: Based on Nair et al. (1999).
BL, Black liquor.

Siloxy has commercialized another similar process where silica and lignin are not separated (Myreen, 2001). “When the alkalinity, i.e., pH, of black liquor is reduced, the silicate ion and a part of the organic material in the liquor agglomerates to a colloidal form. When the pH is sufficiently low, it solidifies as amorphous silica and organic matter. The solidified matter can be separated from the liquor by filtration or centrifugation. Low-purity carbon dioxide has been used in laboratory and pilot-scale trials to reduce liquor pH for silica precipitation. A commercial system has never been built, in part because of excessive foaming caused by the large amount of inert gas passing through the reactor. The Siloxy desilication process, which uses high purity carbon dioxide, can eliminate the problems associated with the use of low-purity carbon dioxide. The siloxy desilication process was tested successfully in Finland and in the People’s Republic of China in cooperation with the China National Environmental Protection Corporation and the Shandong Huajin Group at their straw pulp mill at Sishui, Shandong Province” (www.siloxy.com). A difficult pH control is avoided when a excess of high purity carbon dioxide is used for neutralizing silica in black liquor. The pH decreases rapidly to 8.0−8.5, which removes the intermediate colloidal state of the silica. A solid silica precipitate is produced which can be separated in an efficient manner. About 95% of the dissolved silica in the black liquor of rice straw was removed as filter cake. The use of high purity carbon dioxide of high purity can also avoid foaming and reduce the size of the desilication reactor as the carbon dioxide partial pressure inside the gas bubble will be higher by approximately five times as compared to other carbon dioxide gas streams used earlier. This siloxy process uses carbon dioxide gas which is produced by using carbon dioxide capture technology. Any carbon dioxide which is not used by desilication process is either discharged to atmosphere, used within the mill, or potentially sold as merchant carbon dioxide (www.siloxy.com).

Mishra (1982) studied black liquor desilication by carbonation. Partial carbonation and lime treatment at 90°C was used.

Acid treatment was used to study desilication of weak black liquor by Froundjian (1971). This technique was also studied by West Coast Paper Mills in India (Kulyan Sundram and Ganesh, 1972).

“Kraftanlagen in Heidelberg and Munich (Germany) studied a black liquor desilication process. Another desilication process was developed by the China Paper Industry Research Institute. This was evaluated in a 15 m^3/h weak black liquor pilot plant. The weak black liquor containing silica (628 g/L) was reacted with flue gas in a Venturi nozzle and the pH was reduced to 10.3. CPPRI technology has reached to an operating level” (Kopfmann and Hudeczek, 1988; UNIDO/CPPRI, 1991; Kulkarni et al., 1993; Francis and Nair, 1991). The major issue with this process is coprecipitation of lignin. The separation of the precipitate from the liquor becomes difficult and the calorific value of black liquor reduces.

CONOX has developed novel plug flow reactor and obtained 90% desilication (Bertel, 2000). Desilication studies were also conducted in Jet Loop Reactors. The efficiency of these reactors has been established in the chemical processes (Blenke, 1985; Vogelpohl and Wachsmann, 1987).

> A high mass transfer efficient, compact Jet Loop Reactors or sometimes called as Highly Compact Reactor (HCR) are used for desilication to obtain exact pH control. An attempt was made to remove silica from Kraft black liquor obtained from straw-based pulping material by carbonation technique. Batch and continuous experiments were carried out in bubble column reactor and energy efficient and high mass transfer Jet Loop Reactors. The results showed that the technique can be applied to mills having no chemical recovery facility where precipitation of both lignin as well as silica is possible. Selective precipitation of silica can be carried out for high capacity mills and silica so precipitated can have good byproduct value.
>
> ***Bajpai (2016); Mandavgane et al. (2006, 2007)***

9.3 Desilication of green liquor

In the chemical recovery section of a pulp mill, the smelt from the furnace is green liquor dissolved in water, and this green colored solution is called green liquor. The green liquor obtained from pulp mills using nonwood raw materials contains a higher amount of silica, which interferes in causticisation as well as in lime recovery. "The lime sludge obtained from the causticisation of silica-rich green liquor is not suitable for recalcination and is generally discarded because the higher silica present in the lime mud prevents the conversion of calcium carbonate to calcium oxide. This may be due to the formation of trisodium silicate. It also induces uneven burning of the lime and increases furnace oil consumption" (Bajpai, 2016).

For a proper recovery operation, the silica present in the green liquor should be removed before causticisation. These methods are based on acidification using flue gas, or treatment with lime (Veeramani, 1977).

When green liquor is carbonated with flue gas, silica is precipitated by reacting silicate with carbonic acid. Laboratory scale results indicate that carbonation at a temperature of 80°C, pH 9.5 can remove up to 85% of silica (Idrees and Veerami, 1977). This method is not used greatly on a large scale.

Desilication of green liquor with sulfuric acid can also remove up to 90% of the silica, but the full scale applications show some limitations (Ikram and Ali, 2006).

> A green liquor from which 97% of the silica had been removed was compared with an untreated green liquor in the operations of clarification, washing and the filtration of lime mud. Removing the silica resulted in an increase in the solids content of the lime mud.
>
> ***Wang et al. (2003)***

Table 9.7: Advantages of desilication of green liquor with lime.

Low cost
Reduced lime requirements
Less lime sludge generation
Reduced loss of organics
Loss of sulphate ions is reduced as side-reactions are suppressed

Table 9.8: Effect of two-stage causticization of green liquor.

Particulars	1	2	3
Initial Silica in green liquor (g/L)	3.6	3.6	3.7
Lime used (g/L)	16.3	19.6	20.5
Final Silica in green liquor (g/L)	1.3	2.0	1.8
Desilication (%)	63.9	44.4	51.4

Source: Based on Kashikar et al. (2007).

Several mills have started to desilicate green liquor with lime. The advantages of lime addition are presented in Table 9.7:

Causticization method using two stages for the desilication of Kraft green liquor can be used by the mills as the amount of desilicated sludge to be handled is smaller and the settling rate is rapid (Rao et al., 1988). In this process, lime is added in the first stage for removing the bulk of the silica and part for causticizing, whereas in the second stage it is used for causticizing efficiency up to 80%. When lime is mixed in the green liquor, it preferentially reacts with sodium silicate and produces calcium silicate. After that lime reacts with sodium carbonate and produces calcium carbonate. This benefit is now being used for precipitating the silicates in first stage. About 60%–65% of the lime mud produced with green liquor can be burnt in the kiln by using two-stage causticization process (Kashikar et al., 2007) (Table 9.8). In the Italian Foggia mill, green liquor desilication was used (Nardi, 1995).

9.4 Soda recovery

The chemistry of soda recovery is clear cut. During combustion of the black liquor, sodium compounds are converted to sodium carbonate. Causticization of the carbonate solution with lime produces sodium hydroxide. The main elements of soda recovery are like Kraft recovery. The liquor is washed from the pulp and is concentrated by evaporation and burnt. If caustic is wanted then causticization and calcining of the green liquor follows (Grace, 1987a,b). Generally washers and evaporators are similar to those used in case of Kraft process but some differences are also seen. In case of high-yield wood pulps or when agricultural residues are used, press washers or other special equipment may be needed to effectively remove the liquor from the pulp. More scale formation is observed in case of soda liquor. It is a major issue with agricultural residues. This forces the use of such types of evaporators which are more resistant to scaling or reduce the level to which the liquors could be concentrated. Combustion of liquors produced from soda pulping may take on different forms in comparison to that used for Kraft. As sulfide is not needed, there is no requirement for maintaining a local reducing environment in the combustion stage.

Soda liquor combustion can be conducted in equipment like fluidized beds which are not appropriate for Kraft liquor. Most of the variations in soda process are connected with the combustion step. Causticizing and calcining steps, are similar to Kraft. Presence of large amount of silica makes reburning of lime impossible. In this case, causticization is followed by mud disposal.

Soda liquor is combusted in smelter furnaces in which the combustion temperature is above the melting point of the sodium carbonate. The smelt gets collected on the hearth and gets drained off through spouts. The smelter has water cooled walls similar to a Kraft recovery boiler or can be of simpler construction with refractory brick walls.

> Soda liquor burns quite differently than Kraft liquor and the smelt can be more viscous and difficult to drain. To successfully operate, some modifications in firing techniques and additives to improve smelt drainage characteristics may be necessary. Bed burning of soda liquor is very slow, and there is normally only a minimal char bed. Combustion of liquor in waterwalled furnaces requires feed liquor solids levels above about 55%. The walls tend to cool the flame, and stable combustion can only be supported if the internal evaporative load is reduced. Thus the waterwalled smelter furnace is normally used only with an effective set of evaporators in a configuration where steam and power generation is maximized. Simpler types of refractory lined smelters, such as a Broby furnace, can also be used. These give less overall energy recovery but have lower installation costs and are more suitable for small mills. The refractory lined smelter has been used where evaporation is difficult. Firing solids contents can be lower, since heat is not absorbed by the walls to the same extent. Simple smelters are often used in conjunction with a direct contact evaporator (odors are not a problem with soda liquors). The direct contact evaporator makes some use of the heat content of the combustion gases and is not as prone to scaling and fouling problems. This approach is particularly attractive for liquor containing large amounts of silica, since it avoids boiler surface that could slag and also provides for concentration of liquor very prone to fouling. Soda liquors have been successfully burned in fluidized beds. The combustion is carried out below the melting temperature and the sodium carbonate product forms the bed material.
>
> *Bajpai (2016)*

Corrugating medium mills have most of the experience with this approach.

These mills converted from neutral sulfite semichemical (NSSC) pulp to sulfur-free semichemical pulp. Incineration of NSSC liquors in fluidized bed was extensively used. The sulfur-free liquor was found to be more difficult to burn autogenously due to the inclination of producing more volatile gas which burned in the freeboard zone above the bed, but these issues have been resolved. The major plus point for incineration in fluidized bed is that the liquors should be concentrated to about 35%–40% solids before feeding into the fluidized bed. The water evaporation helps in maintaining combustion temperatures below the slagging temperature. This approach is promising for liquors which are difficult to evaporate. Fluidized bed incinerators are sensitive to impurities. The combustion temperature has to be no less than 700°C for burning up the carbon. Higher temperatures provide better operation. The temperature cannot approach the melting temperature, or slagging and defluidization of the bed may take place. Substances that produce low-melting eutectics, like chloride or potassium, may cause defluidization. Fluidized beds show lower tolerance to chlorides. Most of the original fluidized beds are operated as so-called bubbling beds. These are prone to defluidization. The developing tendency in fluidized bed combustion of coal for power generation is to utilize entrained beds. In these beds, the gas velocity is high and the solid phase is conducted with the gas, separated by high temperature cyclones, and returned to the combustion chamber. The Ahlstrom Pyroflow system is an example of this type of unit. Entrained bed reactors could extend the use of fluidized bed incinerators to liquors prone to slag. There are many advantages of fluidized bed reactor system including (Table 9.9):

> Shreyans Paper mill in India installed 75 tons per day (TPD) black liquor solids fluidised bed reactor (FBR) in 1995 after studying various alternate options available. FBR technology based on modified copeland process as developed by M/s Enders Process Equipment Corp., USA became a major breakthrough for technological development after successful commissioning and operation of FBR at Shreyans for last 20 years and total black liquor generated in the mill is being burnt and converted into soda ash pellets and disposed off to various manufacturers using soda ash as raw material for sodium silicate manufacturing. Removal of black liquor from effluents makes it possible to meet environmental standards in outgoing effluent.
>
> ***Sharma et al. (1998)***

Table 9.9: Advantages of fluidized bed reactor.

Low capital investment
Safe operation as there is no smelt
Applicability to all cellulosic raw materials except raw materials having high chloride and potassium contents, although the chloride content in almost all cellulosic raw material can be brought down through wet cleaning
It is not essential to install a recausticizer plant
It is very easy to run the plant with little manpower

Saroha et al. (2003) performed experiments for evaluating the possibility of recovering soda from nonwood spent pulping liquors. Lignin-bound sodium into free sodium was converted and subsequently causticized for producing sodium hydroxide. Soda recovery was 79% after direct causticization. Recovery was improved by converting lignin-bound sodium into free sodium with an oxidizing agent. Potassium permanganate proved best to be the optimum oxidizing agent. It produced 93% of the total sodium recovered in the form of sodium hydroxide.

"Sodium hydroxide from bagasse or soda anthraquinone hardwood spent liquor can be directly recovered using calcium oxide. The sodium bound in the lignin molecule is exchanged for calcium, the sodium hydroxide goes into solution and the calcium lignite precipitates. The degree of removal of the organic material depends on the amount of calcium oxide and coagulant added. Yields of up to 98% have been obtained. The method leads to a closed loop for sodium. The recovery efficiency depends on pulp washing efficiency. The concentration of the sodium hydroxide filtrate depends on the water input into the cycle" (Seppa and Venter, 1988). Above processes are not commercialized yet. Ellis (1982) has reported soda recovery from nonwood cooking liquor by means of wet air oxidation.

9.5 Alternative recovery processes

9.5.1 Direct alkali recovery system

Direct alkali recovery system (DARS) is one of the first alternative recovery processes. In this process, an in situ causticizing agent is added to spent pulping liquor before combustion (Tadashi et al., 1976; Covey and Ostergren, 1985; Kulkarni et al., 1987, 2007; Rao and Kumar, 1987; Venkoba Rao, 1987). "In the basic process, patented by the Toyo Pulp Company in 1976, iron oxide combines with sodium carbonate to form sodium ferrite, which expels carbon dioxide to the flue gases (Reaction 9.1). When the sodium ferrite is dissolved in water, the salt decomposes to form sodium hydroxide plus insoluble iron oxide (Reaction 9.2), which can be removed from the caustic liquor and recycled to the fired black liquor thus:

$$\mathrm{Na_2CO_3 + Fe_2O_3 = Na_2Fe_2O_4 + CO_2} \tag{9.1}$$

$$\mathrm{Na_2Fe_2O_4 + H_2O = 2NaOH + Fe_2O_3.} \tag{9.2}$$

Coarse particles (1–3 mm in diameter) are maintained to allow more efficient de-watering of the ferric oxide after leaching. The fluid bed is a 'bubbling bed' type combustor to minimize particle size reduction, which would occur with a circulating bed" (Tadashi et al., 1976; Grace, 1987a,b).

The apparent benefit of this process is that the lime-based causticizing process is eliminated. In this process, fossil fuel is needed to drive the lime mud calcination reaction. The DARS process is applicable to non sulphur pulping as iron reacts with the reduced sulphur to produce unwanted compounds which cannot be recovered in utilizable forms for reusing in pulping. The commercialization of the DARS process merged this concept with a Copland like fluidised bed combustor and related solids handling equipment. Toyo licensed this concept and effectively showed by what is now Australian Paper in the beginning of 1980s using pilot plant which included a batch digester, spent liquor evaporator, and a fluidised bed combustor having a diameter of 76 cm.

In 1986, a full DARS plant was put up by Associated Pulp & Paper Mills for replacing rotary incinerators at its Burnie, Tasmania mill using the soda pulping process. The fluidised bed combustion zone operated at approximately 1000°C. As no sulfur was produced in the process, it was not essential to drive in a reducing mode. From the combustor, the sodium ferrite bed solids were taken away and leached with water in a counter-current contactor. The equilibrium concentration of sodium hydroxide from sodium ferrite hydrolysis was able to reach levels about two to three times as high as with traditional causticisation based on lime. The solids were removed from the caustic liquor and were mixed with make up iron oxide, and returned to the fluidised bed. "An expected challenge to operating this process was managing the fine dust generated from attrition of the porous leached bed solids. Accordingly a bag house filter was used to remove the dust from the flue gas, and this material was agglomerated by mixing it with a small amount of black liquor prior to recycling it to the fluidised bed combustor. Difficulties were faced during the first five years of operation, especially in maintaining fluidization and managing the large quantities of sodium ferrite dust. The system was able to operate for an extended period only after three major equipment rebuilds. By 1995, the Burnie mill had been acquired by Australian Paper, and the DARS plant was processing about 150 ton of dry solids per day and supporting two-third of the mill production. By the late 1990s, the process was running well enough that a second DARS plant and expansion of the mill was under evaluation, but a decision was reached that, even with a capacity increase, the pulp mill was too small to be economically viable and so the entire operation was shut down. Several companies have evaluated DARS for use in nonwood pulping operations, and at least two additional pilot plants have been built, but a second commercial unit has not yet been commissioned" (open.unido.org).

The DARS process appears promising for providing a simple recovery technology appropriate for small mills. The economic analysis shows that it offers a significant reduction in both the capital expenditure and operating costs in comparison with conventional recovery systems (Table 9.10).

One disadvantage of this process is that it can not be applied to kraft recovery as the iron oxide is reduced under the conditions needed for producing sulfide (Rao and Kumar, 1987).

Table 9.10: Cost comparison of the cost of conventional and ferrite recovery processes.

	Conventional recovery system			Ferrite recovery system		
Pulp mill capacity (TPD)	30	40	50	30	40	50
Capital investment (€ million)	0.24	0.28	0.33	0.16	0.19	0.22
Cost of sodium hydroxide production (€/tonne)	112.2	106.0	102.0	80.2	75.6	72.6
Reduction in capital investments (%)	–	–	–	32.6	31.5	30.7
Reduction in operating costs (%)	–	–	–	28.5	28.7	28.8
Depreciation (€/year)	16.833	19.667	23.333	11.333	13.333	15.500
Savings (€/year)	8.833	28.167	48.500	43.166	70.833	99.500
Payback period (years)	9.4	5.9	4.5	3.0	2.3	1.9

Source: Based on data from Rao, N.J., Kumar, R., 1987. Ferrite recovery process—a promising alternate for small paper mills. IPPTA 24 (3), 30–37.
TPD, Tonnes per day.

Silica is an unwanted element in the spent liquors generated from the pulping of agricultural residues. Exhaustive studies on the effect of the presence of silica impurity in the recovery loop have shown that during the ferrite autocausticisation process only a minor proportion of silica passes into white liquor (Table 9.11). This is a benefit of the process, and unlike traditional recovery it may not be essential to have a supplementary stage of desilication of spent liquor before the recovery process (Kulkarni et al., 1987).

Leaching is a key step of the ferrite process, and the conditions should be maintained for allowing maximum causticity and soda recovery. It is necessary to make certain that the sodium ferrite is completely hydrolyzed and that maximum extraction of sodium hydroxide in the form of concentrated solution is achieved. The most efficient leaching configuration will be pure counter-current contacting. A minimum of four stages of extraction would be required for sodium recovery of more than 90% (Kulkarni et al., 1987). A substantial quantity of natural hematite ore as a source of iron oxide for autocausticising has been used in the ferrite process. There is a likelihood of the presence of some soluble iron compounds in the ore, which are afterwards carried into the white liquor regenerated during the ferrite process. Studies on the solubility of iron reveal that when high purity hematite ore is used, the solubility of iron is small and does not have any adverse effect.

The DARS process offers the following advantages and constraints:

Table 9.11: Solubility of silica in regenerated alkali.

Mps	Concentration of regenerated alkali as sodium hydroxide (g/L)	Causticity (%)	Silica in white liquor (ppm)	Silica passed to white liquor (%)
1	36	83.7	Nil	Nil
2	132	93.9	433	0.83
3	218	92.1	1634	1.47

Source: Based on data from Kulkarni, A.G., Mathur, R.M., Naithani, S., Pant R., 1987. Present status of "DARS" technology and perspectives of its application to small pulp mills. IPPTA 24 (3), 71–79.

9.5.1.1 Advantages

Operational flexibility—it is compact and simple in operation and requires less space than conventional systems:

Fuel economy—it minimizes the quantity of high cost fuel needed

Does not require a high degree of process automation

Unlike the smelt in conventional recovery processes, the combustion product is solid, so the process is safe

The capital cost is low.

9.5.1.2 The constraints

From the activity of regenerated iron oxide, ore should not be recycled more than six times. The reduced activity of silica-rich ore can be attributed to brittleness.

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Relevant websites

http://open.unido.org

http://www.siloxy.com

CHAPTER 10

Beating/refining and papermaking

Chapter outline

10.1 Beating/refining characteristics of nonwood pulp 187
10.2 The papermaking performance of nonwood pulp 196
  10.2.1 The strength properties of wet paper 196
  10.2.2 The adhesion properties of wet paper 197
  10.2.3 Drainage properties of nonwood pulps 197
References 198
Relevant websites 201

10.1 Beating/refining characteristics of nonwood pulp

Papermakers are pushed to use nonwood fibers for several reasons though not much information is available on treating these fibers. The papermaking process, machine runnability, and quality of paper are extensively affected when the fibers are subjected to mechanical treatment. This process is known as beating or refining of pulp. Paper machines with higher production rates tend to show higher production time due to breaking of paper. Savings in energy and the preferred paper properties can be obtained by selecting proper process conditions in the refining process.

> Pulp produced in a mill without mechanical treatment is unsuitable for most paper grades. Paper made from unbeaten virgin pulp has a low strength, is bulky and has a rough surface. In good quality paper, the fibers must be matted into a uniform sheet and must develop strong bonds at the points of contact. Beating and refining are the processes by which the undesirable characteristics are changed.
>
> ***Bajpai (2018b)***

Mechanical treatment is one of the most important steps in the preparation of papermaking fibers (Ruhr, 2003, 2004; Lumiainen, 2000; Clark, 1985; Young, 1981; Baker, 1991, 2000a,b, 2005; Ebeling and Hietanen, 1986; Hietanen and Ebeling, 1983, 1990a,b; Ebeling, 1980, 1983; Smook, 1992; Frair, 1982; Noe, 1984; Batchelor et al., 1996, 1999; Liu et al., 2018). “The term beating is applied to the batch treatment of stock in a Hollander beater or one of its modifications. The term refining is used when the pulps are passed continuously through one or more refiners, whether in series or in parallel” (Bajpai, 2018b).

Nonwood Plant Fibers for Pulp and Paper.
DOI: https://doi.org/10.1016/B978-0-12-821800-6.00010-7

The beating or refining of pulp before papermaking is one of the most important operations in the papermaking process. It is an important factor in papermaking process control and quality of final paper. One of the main objectives of refining is to attain a higher sheet strength through developing fiber to fiber bonds. It is commonly applied to increase quality of pulp by modifying the structural properties of the fiber, including hydration, fiber swelling, internal/external fibrillations, fines formation, fiber shortening, etc. (Shao et al., 2017; Oksanen et al., 1997; Fasdim and Duran, 2003; Lecourt et al., 2010; Gharehkhani et al., 2015). Normally those changes happening to fibers are characterized by the beating degree value, °SR (Mutjé et al., 2005; González et al., 2013). On the contrary, treatment of the pulp is found to change the electrokinetic properties of the fibers treated (Nishi et al., 2007), and change fiber swelling and inter-fiber bonding strength (Nishi et al., 2004). All of these characterizations tend to play vital roles, not only in the dewatering rate of the stock, but also in the quality of the end products.

The statement that "paper is made in the refiners" is true in that incorrect refining cannot be corrected elsewhere. Very often poor runnability on a machine and poor product performance can be related to incorrect refining practices. With optimized refining, high quality products can be produced using less costly fiber while reducing the usage of chemical and energy. The importance of proper refining is greater than ever because of the increased use of recycled fibers, faster paper machine speeds. Beating has an important effect on the operation of paper machines and the strength properties of paper.

> Refining develops different fiber properties in different ways for specific grades of paper. Usually it aims to develop the bonding ability of the fibers without reducing their individual strength by damaging them too much, while minimizing the development of drainage resistance. So the refining process is based on the properties required in the final paper. Different types of fiber react differently because of differences in their morphological properties The refining process must take into account the type of fibers.
>
> ***Bajpai (2018b); Baker (1991, 2000a); Kibblewhite and Bawden (1991)***

Most of the strength properties of paper are found to increase with pulp refining, as they depend on fiber to fiber bonding. But, the tear properties, which depend greatly on the strength of the individual fibers, reduce with refining. After a certain point, the factor which limit the strength is not the fiber to fiber bonding, but the strength of the individual fibers. Refining beyond this point results in a reduction in other strength properties beside tear properties.

When pulp is refined, the flexibility of fiber increases. This results in denser paper; bulk, opacity, and porosity reduce during the process (Lumiainen, 2000; Stevens, 1992, 1999; Young, 1981). "Mechanical and hydraulic forces are used to change the fiber properties. Shear stresses are imposed by the rolling, twisting, and tensional actions occurring between the bars and in the grooves and channels of the refiner. Normal stresses (either tensional or

Table 10.1: Response of fibers during beating and refining.

Fibers develop new surfaces externally through fibrillation and internally through fiber wall delamination
Fibers deform, resulting in changes in their geometric shape and the fibrillar alignment along their length. Overall, the fibers flatten or collapse. Fiber curl changes and kinks are induced or straightened. On the small scale, dislocations, crimps, and microcompressions are induced or diminished
Fibers break, resulting in changes in length distribution, and a decrease in mean-fiber length. A small amount of fiber wall material also dissolves. All these changes occur simultaneously and are primarily irreversible

Source: Based on Seth, R.S., 1999. Beating and refining response of some reinforcement pulps. Tappi J. 82 (3), 147, Tappi Press, USA, March 1999.

compressive) are imposed by the bending, crushing, and pulling/pushing actions on the fiber clumps caught between the bar-to-bar surfaces" (Bajpai, 2018b).

When the fibers are beaten and refined, fibers randomly and repeatedly experience compressive, tensile shear, and bending forces. They react in three ways (Table 10.1).

The factors affecting refining fall into three catagories: fiber variables, equipment, and process variables (Smook, 1992; Stevens, 1992; Valmet, 2001) (Table 10.2).

Different types of pulps respond in different ways to a given level of refining (Kibblewhite and Bawden, 1991; Smook, 1992; Lumiainen, 2000; Biermann, 1996; Clark, 1985). In general, kraft pulps are more difficult to refine as compared to sulfite pulps. These pulps require more energy. Soda pulps are very easy to refine. Unbleached pulps are more difficult to refine in comparison to bleached pulps. The pulps having a higher lignin content do not response much to beating as lignin is not able to absorb water, so the fibers do not swell as much. High yield mechanical pulps and chemimechanical pulps are not refined in the paper mill as their high fiber stiffness cause extensive cutting. Sometimes mechanical pulps are lightly postrefined as this enhances the drainage, but they are not refined for developing the fiber properties.

Moberg and Daniel (2003) described note-worthy differences in beating results between high yield and low yield commercial never dried kraft pulps. High yield pulps were found to consume more refining energy and were more sensitive to refining conditions. Also these pulps showed higher levels of external fibrillation in comparison to low yield chemical pulps. Both types of pulp, responded less to fillings than was anticipated after earlier results on commercial, dried, and fully bleached pulps.

Hiltunen and Paulapuro (1999) reported that highly ionically charged fibers resulting from totally chlorine-free (TCF) or elemental chlorine-free (ECF) bleaching experience less harm and have fewer fiber cell wall dislocations than fibers carrying lower ionic charges during processing. There was not much difference in the fracture energy versus tensile strength between high and low charged fibers. However, larger fiber swelling was observed in highly charged fibers at similar tensile strengths. Lumiainen (1998) reported that ECF and

Table 10.2: Factors affecting refining.

- Fiber variables
  - Type of fiber
  - Type of pulping
  - Degree of pulping
  - Bleaching
  - Drying history
  - Fiber length distribution
  - Fiber coarseness
  - Early wood/late-wood ratio
  - Chemical composition
- Process variables
  - Consistency
  - pH
  - Temperature
  - Pressure
  - Additives
  - Pretreatments
  - Production rate
  - Applied energy
- Equipment characteristics
  - Bar size and shape
  - Area of bars and grooves
  - Depth of grooves
  - Presence or absence of dams
  - Construction materials
  - Wear patterns
  - Bar angles
  - Speed of rotation (peripheral speed)

TCF pulps are more sensitive to refinement than traditional pulps bleached with chlorine. Usually pulps having large percentages of hemicelluloses are easier to refine and respond well to mechanical energy. The great affinity of hemicellulose for water promotes swelling and fibrillation. In contrast, dissolving type pulps, which are high in α-cellulose, refine slowly and produce weaker sheets. Dried chemical pulps, including secondary fibers, do not absorb water as readily and are more difficult to refine in comparison to never dried pulps. Over-drying or uneven drying of pulps may contribute to paper products with a lower strength, because of uneven strength development if sufficient time is not allowed for re-wetting. The refinability of mixed-furnish pulps depends mainly on the chemical pulp content. The higher the proportion of chemical fibers, the greater the potential for the development of pulp properties through refining. Refining chemical pulps increase inter-fiber bonding and produces fines. The net result is increased strength, but decreasing opacity. Refining mechanical pulps increase inter-fiber bonding and produces more fines relative to bonding.

Table 10.3: Major effects of refining.

Fiber cutting or shortening
Formation of fiber debris or fines
External fibrillation, the partial removal of the fiber wall leaving it still attached to the fibers
Internal changes in the wall structure described as delamination, internal fibrillation, or swelling
Curling of fibers
Strengthening of fibers at low consistency
Changes in fiber shape and number of micro-compression
Dissolution of colloidal material
Redistribution of hemicellulose and development of a more gelatinous surface
Lumen reduction
Axial compression

Source: Based on Page, D.H. (1989). 'The Beating of Chemical Pulps — The Action and the Effect', Fundamentals of Papermaking, 9th Fundamental Research Symposium, Cambridge, Mechanical Engineering Publications Ltd., UK, Volume 1, p 1, 17-22 September 1989. Hietanen, S., Ebeling, K., 1983. Heterogeneity in refining action; effects on fiber and paper structure. In: Proceedings of the Tappi International Paper Physics Conference, Harwich port, Ma, Atlanta, p. 27, September 1983; Hietanen, S., Ebeling, K., 1990a. Fundamental aspects of the refining process. In: Paperi ja Puu—Paper and Timber, Finnish Pap. Timber J. Publ. Co., 72(2), 158; Ebeling, K., 1983. The effect of refining on wood pulp fibers. In: Handbook of the Finnish Paper Engineers Assoc, Arjas, A. (Ed.), Part III, Turku, second ed: 67, 1983; Ebeling, K., Hietanen, S., 1986. Control of heterogeneity of the refining action. In: Advances in Refining Technologies, Pira International, Leatherhead, UK, 1, 4, 1986.

Table 10.4: Factors influencing the response of pulp fibers to refining.

Quality of fiber coarseness, cross-section dimensions, and length
Differences between hardwood and softwood fibers and the proportion of each in any pulp
The refiner type
Conditions of refining
Refining tackle
Stock concentration
Specific edge load
Overall energy input

Table 10.3 shows the major effects of refining and Table 10.4 shows factors influencing the response of pulp fibers to refining.

> Beating can make fiber transformative, swelling, and fibrotic and so on, so that the binding forces between the fibers are improved, and paper strength is improved.
>
> ***Ljungqvist et al. (2005)***

To properly understand the beating characteristics of fiber, it is important to understand the structure of the fiber cell wall: "The cell walls of plant fiber are divided into middle lamella (M), primary wall (P) and secondary wall (S), and secondary wall is separated into, outer layer (S1), middle layer (S2) and inner layer (S3). Thereinto, the existence of the primary wall can impede the contacts between the secondary wall and the outside, besides the swelling and the fibrillation may also be influenced. Therefore, the primary wall needs to be broken in the beating process. In addition, although the S1 layer is the transition layer of the S2 and P layers, it may limit the swelling and fibrillation of the S2 layer, so S1 layer also need to be removed during the beating process. For the S2 layer, the main object of beating, it is the main body of the fiber cell wall. Beating which can cause displacement and deformation of S2 makes it possible to increase the interspace between the fine fibers, and permeate the water molecules easily. With respect to S3, it is usually not considered in the beating process.

In addition, for some nonwood fiber raw materials, since there are numerous parenchyma cells in the fibers, the function of beating is also slightly different to them. Generally, in the structure of straw fibers, the parenchyma cell with thin wall content is high and both ends of the catheter are flat, so both of them are easy to become debris in the beating process and exist in the pulp, which makes the pulp filter difficult. Sclereids, one kind of non-fibrous cell with thick wall, are easily washed away by washing. Epidermal cells are generally difficult to break in the beating process" (Liu et al., 2018).

In comparison with woody raw materials, it is not easy to beat and attain the external fibrillation for gramineous fiber materials. In case of wheat straw, in the early stage of beating, the fiber starts fluffing and the thin secondary wall gets broken and falls, so the beating degree increases quickly. When the secondary wall is completely separated, with the beating continuing, the morphology of the fiber does not get changed much. By improving the beating degree, the fiber is cut off slowly. The fiber will have clearly longitudinal devillicate till the beating degree is 80°SR–90°SR, but at this time, degree of detaching is great. This shows that wheat straw fiber is not easy to fibrillate. The major reasons are presented below:

> The gramineous fiber materials feature with small cell cavity and thick S1 layer which is difficult to break during beating process. Furthermore, the close connection of S1 and S2 would limit the swelling of S2 layer. In addition, the secondary wall of some grasses is made up of multilayer structure, and the arrangements of micro fibers in different layer are often diverse. As to bamboo, the arrangements of micro fibers are mostly horizontal, which may restrict the devillicate of longitudinal micro fibers.
>
> ***Liu et al. (2018)***

In the case of nonwood materials there is not much information as how to treat them for optimum performance (Baker, 1998). The optimized level of refining for bamboo pulp occurs at an specific edge load (SEL) of 2.5 Ws/m as at this SEL there is an increase in strength development and development of drainage is not as fast (Baker, 2000a). The optimized level of refining for manilla hemp pulp also occurs at an SEL of 2.5 Ws/m as the increase in strength development is greater for burst index (Baker, 2000a). However, the development of drainage is much faster at 2.5 Ws/m compared to 1.0 Ws/m, which has the slowest development in drainage. The optimized level of refining for straw pulp is at an SEL of 0.5 Ws/m as the increase in strength development is greater for tensile index and breaking length (Baker, 2000a). Also tear index does not drop so fast. However, due to the very high drainage, it is probably sensible to use this pulp as part of a mixed furnish. For hemp and bamboo, the need is for more cutting than for softwoods and hardwoods. However, standard refiner filling can be used.

Refining of bamboo long fiber fraction pulp has been reported (Bhardwaj, 2019). "The wet web tensile index, wet web elongation and water retention value of bamboo long fiber fraction pulp increased with refining. In general, the freeness and bulk decreased, whereas the tensile and burst strength increased with increasing net specific energy. Bamboo long fiber fraction pulp responds better to lower intensity refining (1000 Ws/km specific edge load), in terms of pulp strength, decreasing net energy requirements. Significant gains in tensile index at a given freeness level can be gained by refining at lower intensity. There is a huge difference (110 kWh/t) in the specific energy required to reach a given wet web strength at the two SELs, about 210 kWh/t for 1500 Ws/km, compared with around 110 kWh/t for 1000 Ws/km. A linear correlation was observed between the water retention value and the tensile strength of paper. Refining at 1500 Ws/km has a positive impact on the evolution of bursting strength of paper, as it depends on fiber strength, and on bonding strength. Lower intensity refining at higher net specific energy consumption leads to more internal fibrillation and higher bursting strength" (www.cellulosechemtechnol.ro).

Energy conservation is becoming very important in the pulp and paper industry. Any type of treatment which substantially reduces the energy requirement will have an advantageous effect on the overall energy input. In the last decade, interest in the use of enzymes for modifying fiber properties to improve the beatability/refinability of pulps has increased (Bolaski et al., 1959; Comtat et al., 1984; Diehm, 1942; Mora et al., 1986; Noe et al., 1986; Yerkes, 1968; Bhardwaj et al., 1996; Keskar et al., 1989; Pastor et al., 2002; Garcia et al., 2002; Torres et al., 1999; Ishizaki, 1992; Scartazzini et al., 1995; Wong et al., 1999; Bajpai, 1999, 2005a,b, 2006, 2009, 2015, 2018a,b). The use of cellulose and hemicellulose-hydrolyzing enzymes before beating and refining appears helpful in saving energy (Noe, 1984; Noe et al., 1986; Bhardwaj et al., 1996; Bajpai and Bajpai, 2001; Bajpai et al., 2004; Bajpai, 2005a,b).

Use of enzymes for modifying pulp is not a new idea. In 1942, a patent was filed claiming that hemicellulase enzymes from *Bacillus* and *Aspergillus* species could help in refining (Diehm, 1942). In Bolaski et al. (1959), obtained a patent on the use of cellulases from *Aspergillus niger* for separating and fibrillating pulps, mostly in case of cotton linters and other nonwood pulps. Cellulases from a white rot fungi used at a dose level of 0.1%−1% by weight, reduced the beating time (Yerkes, 1968). The enzyme also improved drainage by the removal of fines. In other applications cellulases were used for removing fines from pits and felts in the paper machines.

French researchers used xylanases from mutants of *Sporotrichum pulverulentum* and *Sporotrichium diorphosphorum* for fibrillating pulps while repressing the cellulase activity

(Comtat et al., 1984; Mora et al., 1986; Noe et al., 1986; Barnoud et al., 1986). Treatment with enzyme resulted in an increase in the °SR of the pulp. Comparison of the enzyme pulps with reference pulps (no enzyme treatment) showed that the time needed for obtaining the same degree of freeness reduced by about 60%. The drainage reduced and the water retention increased by approximately 40% after enzymatic treatment, and more than two times after refining. There was also an increase in tensile strength and the zero-span breaking length of the enzyme pulp.

Comtat et al. (1984) reported similar results using xylanase enzyme produced by cloning the DNA for the enzyme into a bacterium. Water retention was increased. Mora et al. (1986) found that the mean pore radius of aspen decreased by a factor of 10 following xylanase treatment. Most likely this could be because of the opening of small cracks in the walls of the pores. Electron microscopy revealed improved fibrillation in case of enzyme pulps.

Noe et al. (1986) studied the characteristics of xylanase-treated pulps. There was an increase in °SR value, the breaking length, the apparent density and the water retention. However, the viscosity reduced by more than 30%. The wet zero-span breaking length also reduced substantially. Enzyme-treated pulps showed improved beatability and enhanced bonding as a result of increased fiber flexibility, but that the intrinsic fiber strength reduced because of the loss of xylan.

Bhardwaj et al. (1996) studied the efficacy of several xylanases, to save energy in beating and refining. Bleachzyme F and Hemicellulase "Amano" 90 were used for treating unbleached kraft bamboo pulp. Treatment with Bleachzyme F reduced the beating time by approximately 18% and treatment with Hemicellulase "Amano" 90 reduced the beating time by 15%. There was no adverse impact on the strength properties of the pulp.

Bajpai et al. (2004) and Bajpai (2005a) performed several bench-scale and plant-scale studies with a neutral cellulase/hemicellulase enzyme. They used FibreZyme LBR which

Table 10.5: PFI-refining of enzyme-treated and control (no enzyme treatment) LF-3 pulps.

		°SR Cy 5%, Temp. 50°C, pH 6.8, Enzyme 0.03%		
No. of PFI revolutions	**Control**	**1.0 hr**	**1.5 hr**	**2.0 hr**
0	15.0	17.5	18.0	19.0
3200				30.5
3300			30.5	
3500		30.0		
4100	30.0			

was obtained from a *Chrysosporium* strain (US Patent Nos. 5,811,381 and 6,015,707) to reduce the energy requirement in the refining/beating of LF-3 bamboo pulp. Significant reduction in energy requirement was observed (Table 10.5).

The amount and intensity of refining depend on the types of fibers, pulping methods, and the desired qualities of paper being produced. A few studies were conducted for optimizing the refining conditions of wheat straw pulps (Mackean and Jacobs, 1997a,b; Guo et al., 2009). They found that the unexpected reduction in freeness of the wheat straw pulp may be because of an increase in primary fines with refining (lignocellulose.sbu.ac.ir).

Vichnevsky and Chute (2001) performed separation of the main structural types of wheat straw Alkaline Peroxide Mechanical Pulp) fibers and studied their effect on the physical properties of the straw mechanical pulp. They recommended that the removal of fines should be considered depending on the desired product.

Guo et al. (2009) and Ljusgren et al. (2006) observed that the fines from wheat straw pulps do not add to strength. So the strength properties of straw pulp could benefit from removal of fines.

Heijensson-Hulten et al. (2012) reported that the removal of fines from wheat straw pulps by fractionation improves the bleachability and the drainage properties. Simultaneously the fines can be modified and used as a strength enhancer (lignocellulose.sbu.ac.ir).

The effect of fiber fractionation and separate refining of long fiber fraction on refinability and strength properties of wheat straw pulp was studied by Fadavi et al. (2012). Wheat straw pulp cooked by Soda-AQ process was fractionated, using a modified Bauer Mc-Nett fiber classifier having only a 50 mesh screen, into a long fiber fraction and a short fiber fraction at two different mass split ratios of LFR80 (80:20) and LFR60 (60:40). The refined long fiber fractions were remixed with the related unrefined short fiber fraction, and their properties were determined in comparison with the reference sample. The tensile, and burst indices and air resistance, were improved by the fractionation treatments, particularly in the case of LFR80, because of higher refining energy used, which resulted in high fiber to fiber bonding. By fractionating wheat straw pulp and separately refining longer fiber fraction, it is possible to increase PFI revolutions or refining energy for developing inter-fiber bonding strength without reducing the tear index.

> With thin and long fibers, bast fiber raw materials generally are excellently advanced raw material of pulp and papermaking. This section will take flax and Kenaf as examples. Due to the constraint of the primary wall and S1 layer, the flax long fibers have difficulty to beat. However, once the primary wall and S1 layer are removed, the beating degree will rise rapidly and the fiber diameter will gradually become thin, accompanied by longitudinal devillicate. The S1 layer of kenaf fiber is thin, and the structure

> is not obvious. The S2 layer is the main portion of the cell wall, and the internal structure of S2 layer is loose, which may result in dislocation of micro fibers, so the inner of fibers is prone to be fibrillated. Therefore, the beating degree in preliminary stage rise rapidly and the consumption of beating energy is low. However, due to the large winding angle of micro fiber of S2 layer, longitudinal devillicate is difficult to generate. Only in the case of more power consumption, the micro fiber can produce more dislocation.
>
> *Liu et al. (2018)*

The dynamic drainage, zeta potential, cationic demand, fiber morphology, ash content, and silica content of rice straw soda-anthraquinone (soda/AQ) pulps were measured to study the effects of a mechanical treatment on the drainage performance. The physical properties of handsheets prepared from each beaten sample were also analyzed. It was indicated that pulp fibers played an important role in increasing the beating degree in comparison with non-fibrous cells during refining. The dynamic drainage curve could be divided into three different stages in terms of the drainage rate, and the difference between the pulps screened-out non-fibrous cells, and unremoved nonfibrous cells decreased with refining. Because of the absence of a large quantity of nonfibrous cells, as the beating proceeded, the straw pulp presented an ever-increasing tendency in terms of kink index and curl index. Also, cationic demands of pulps increased linearly and the zeta potential of the fibers decreased gradually with beating. Rice straw was found to be favorable for papermaking, helping to compensate for an acute shortage of wood in China.

10.2 The papermaking performance of nonwood pulp

The papermaking performance of pulp mostly includes three aspects, the strength of wet paper, the adhesive properties of wet paper, and the water filtering performance of the pulp (Hii et al., 2012; Shi, 1989). For pulping, nonwood fiber has several benefits which are wide source, lower price, easier pulping, and smoother surface of paper. But, the nonwood fiber pulps have reduced paper strength, poor drainage, and papermaking performance (Bajpai 2018b).

10.2.1 The strength properties of wet paper

> It is accustomed to indicate the wet paper strength only with the tensile strength of the wet paper, which is feasible to some certain degree, but does not apply to nonwood pulps. The tensile strength of some nonwood fiber pulps is often higher than that of wood chemical (mechanical) pulps, but nonwood fiber pulps often are broken into actual papermaking process. The reason, affecting the wet strength, is not only related to the wet tensile strength, but also the elongation of the wet paper. Therefore, to measure the wet paper strength of nonwood fiber paper, every aspect should be considered comprehensively. For example, although the kenaf chemical pulp has higher tensile strength of

Table 10.6: The wet strength properties of nonwood pulps.

Nonwood pulp	Tensile index (N · m/g)	Elongation (%)
Sulfite reed pulp	0.683	17.51
Kraft reed pulp	0.676	17.50
Bamboo kraft pulp	0.601	9.663
Bagasse CMP	0.695	6.09
Bagasse chemical pulp	0.636	9.67
Kenaf xylem CMP	0.648	5.07
Kenaf stalk CMP	0.521	10.31

Source: Based on Liu Z., Wang, H., Hui, L., 2018. Pulping and Papermaking of Non-Wood Fibers, Pulp and Paper Processing, Salim Newaz Kazi, IntechOpen, doi: 10.5772/intechopen.79017. Available from: https://www.intechopen.com/books/pulp-and-paper-processing/pulping-and-papermaking-of-non-wood-fibers.
CMP, chemimechanical pulp.

> wet paper, the elongation of wet paper is low and its comprehensive strength is low, so it is prone to break in production.
>
> *Liu et al., 2018*

The wet strength of some nonwood fiber pulps is shown in Table 10.6.

The basic of wet tensile strength is the length of fibers. The tensile strength of wet paper is found to increase with the increase of fiber length. The elongation of wet paper is dependent on the synergistic action of all fiber components. Beating increases the elongation of wet paper, which results from the increase of fiber crimp index. For the same degree of pulping, proper beating makes the fiber to swell and fibrillate, increases the contact area between fibers and promotes the function of van der Waals force, so as to achieve larger wet paper strength (www.intech.com).

10.2.2 The adhesion properties of wet paper

Nonwood pulps possess higher adhesion force. This may be ascribed to higher hemicelluloses content, shorter average fiber length, more detailed groups and higher content of parenchyma cell, among which, the pentosans have the greatest effect on the adhesive force. In comparison with wood pulp and cotton pulp, the adhesion of wheat straw pulp is much higher, largely due to higher hemicelluloses content in wheat straw pulp, particularly pentosans rather than the difference in shape of fiber (Liu et al., 2018).

10.2.3 Drainage properties of nonwood pulps

The drainage property of pulp is a major factor in the production of paper, which affects the production of paper machine. There are several factors which affect the filtration property. These are fiber fines content, beating/refining degree and water retention value.

For example, straw pulp shows poor drainage properties, which results from the high content of fines and parenchyma cell in the straw fibers. In addition, after squeezing, the dryness of pulp is lesser in comparison with wood pulp as the water filtration of the straw pulp gets adversely affected during the beating process. Furthermore, the water filtration of straw pulp gets affected by water retention.

> As for bagasse pulp, the fibers have the features of short fiber length and the difficulty of fibrillation. Since parenchyma cell, with a high content, can only be swelled and smashed in beating process, the connections of parenchyma cell and fiber are weak. These properties can usually bring about the difficulty of filtering water at wet end, low wet strength and strong adhesive force in the production process
>
> ***Liu et al., 2018***

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Relevant websites

http://www.cellulosechemtechnol.ro

http://lignocellulose.sbu.ac.ir

http://www.intechopen.com

CHAPTER 11

Use of nonwood plant fibers in specific paper and paperboard grades

Chapter outline

References 209
Further reading 210
Relevant websites 210

Nonwood plant fibers offer broad range of physical and chemical properties. These fibers offer essentially never ending opportunities for producing paper. Blends of regular and specialty nonwood pulps would allow the production of essentially any type of paper for meeting the quality requirements needed in the worldwide market. Addition of different combinations including pulp from wood, nonwood fiber, and recycled fiber from wastepaper increases the possibilities for developing paper with specific sheet properties designed for meeting specific requirement of customer. It is possible to produce any type of paper from several nonwood plant fibers and in combination with wood fibers (Table 11.1).

> Some grades of paper have been produced from 100% nonwood pulps. Abaca or manila hemp is the best papermaking fiber available. Abaca is an excellent raw material for manufacture of specialty paper. Its long fiber length and high strength make it a superior material for the production of thin lightweight papers of high porosity and excellent tear burst and tensile strengths. It has special properties for making strong products like tea bags, large sausage casings, currency paper, cigarette and filter paper, and specialty products that require high wet strength combined with high porosity. 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, liner board, bleached boards and coating base stocks.
>
> *Chandra (1998)*; *scholar.lib.vt.edu*; *Peralta (1996)*

> Newsprint is produced on a industrial scale using a kenaf peroxide chemithermomechanical pulp (CTMP). 25% kenaf CTMP has been used as reinforcing pulp in recycled newsprint. 30%–50% kenaf CTMP is blended with a loblolly pine kraft pulp for producing linerboard with adequate strength properties. Kenaf possesses several natural advantages over wood pulp. This 14-foot high plant's rapid growth permits two harvests per year in

Nonwood Plant Fibers for Pulp and Paper.
DOI: https://doi.org/10.1016/B978-0-12-821800-6.00011-9

Table 11.1: Paper produced from nonwood pulps.

Printing and writing papers
Linerboard
Corrugating medium
Newsprint
Tissue
Specialty papers

Source: Based on Hurter, R.W., 2001. Nonwood Plant Fiber Uses in Papermaking, Extracted From "Agricultural Residues", TAPPI 2001. Nonwood Fibers Short Course Notes.

> some areas. Comparatively soft and fibrous, kenaf requires less energy to pulp than wood. Owing to the absence of lignin, kenaf is naturally bright. It requires neither chemical delignification nor peroxide bleaching, and kenaf newsprint does not yellow with age and exposure to light as with that made from wood.
>
> ***Bajpai (2018); Rosenberg (1996)***

> Sisal can be made into very strong products such as liner board, wrapping and bag paper. Flax and true hemp are used to make cigarette paper around the world. 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 like bible, cigarette, currency, insulating and condenser tissue paper. Esparto, with a little addition of softwood pulp for strength, makes good writing, postage stamp, and check papers. It is specially preferred for those application that need a clear watermark with an accurate register. In China, sabai grass is used for carbon body paper.
>
> ***Chandra (1998); MacLeod (1988); Atchison (1988, 1993, 1996); Mayers and Bagby (1995); Pekarovicova et al. (1994); Zomers et al. (1995); Ilvessalo-Pfaffli (1995); Paavilainen (1997)***

In general, common nonwood pulps or hardwood substitutes are manufactured in the integrated pulp and paper mills, and softwood sulfite or kraft pulp is blended for providing the strength properties to the paper. But, specialty nonwood pulp can be utilized instead of softwood sulfite or kraft pulp hence producing a 100% nonwood paper. In few cases, wastepaper pulp can be added to the furnish. The percentage of nonwood in the furnish usually varies from 20% to 90% and can even contain 100% depending on the type of paper and the desired quality. The possible combinations are too many and can be changed to meet market demand. In addition, it is possible to blend small quantities (~20%–30%) of common nonwood pulps to largely wood pulp-based papers without having any impact on paper properties or runnability of paper machine. This provides wood-based mills which are hardwood deficient but located within a region with available nonwood fiber raw materials such as cereal straw or corn stalks with the choice of including a nonwood pulping line for supplementing the requirement of fiber.

Generally the specialty nonwoods possess physical properties better to softwoods and can be used in smaller amounts in the furnish when used as a substitute for softwood. Specialty papers like tea bags currency, dialectric paper, cigarette papers, etc. may be produced from 100% nonwood specialty pulps.

> According to Hurter (2001), specialty nonwood pulps may be used in various combinations with wood pulps for producing lightweight and ultralightweight writing and printing papers. Combinations of common and specialty nonwood pulps will actually allow producing almost any grade of paper for meeting the quality requirements needed in the international market. Addition of possible combinations which include wood pulp, nonwood pulp and recycled wastepaper pulp increases the possibilities to develop paper with specific properties designed for meeting specific requirements of buyers.

Tables 11.2–11.15 show paper and paperboard produced from Bagasse, Straw (cereal and rice), Kenaf (whole stalk), Kenaf (bast fiber), Reeds, Sisal, Jute (bast fiber), Bamboo, Abaca, Cotton, Ekara, Knagra & Nal grass mixed, Esparto, Flax (bast fiber) and true Hemp (bast fiber) (Hurter, 2001).

Table 11.2: Paper produced from Bagasse.

Type of paper/paperboard	Bagasse[a] (%)	Balance of furnish
Bristol board	60%–100%	Woodpulp
Corrugating medium	60%–90%	Wastepaper
Duplex & triplex board	50%–80%	Woodpulp
Glassine & greaseproof	40%–90%	Sulfite pulp
Linerboard	50%–80%	Kraft pulp
Multiwall sac (requires Clupak)	30%–80%	Kraft pulp
Newsprint substitute	70%–90% (chemimechanical)	Kraft pulp
Newsprint substitute	70%–80% (mechanical)	Kraft pulp
Newsprint substitute	50%–65% (chemimechanical)	20% woodpulp, balance bleached bagasse
Printing & writing–mechanical	30%–60% (chemimechanical)	20%–30% woodpulp, balance groundwood
Printing & writing–woodfree	20%–100%	Woodpulp
Tissue	60%–90%	Woodpulp
Wrapping & bag papers	50%–85%	Kraft pulp

Hurter, R.W., 2001. Nonwood Plant Fiber Uses in Papermaking. <www.hurterconsult.com/resources>.

[a] Chemical pulp unless otherwise stated.

Notes: Balance of furnish—"kraft" or "sulfite" means kraft or sulfite chemical pulp made from softwoods, and bleached, semi-bleached, or unbleached depending on the type of paper or paperboard. The term "woodpulp" is used when either softwood kraft or softwood sulfite chemical pulp or a mixture of the two may be used. In some cases, where the nonwood fiber content of the furnish is low or the nonwood fiber is very strong, part of the furnish may be hardwood kraft together with softwood kraft and/or softwood sulfite.

Table 11.3: Paper produced from Straw (cereal and rice).

Type of paper/paperboard	Straw* (%)	Balance of furnish
Corrugating medium	60%–90%	Wastepaper
Duplex & triplex board	40%–80%	Woodpulp
Glassine & greaseproof	40%–90%	Sulfite pulp
Printing & writing—woodfree	20%–90%	Woodpulp
Printing & writing—mechanical	30%–50%	15%–30% wood pulp, balance groundwood
Strawboard	80%–100%	Wastepaper
Wrapping paper—"B" grade	50%–60%	Wastepaper and/or woodpulp

Hurter, R.W., 2001. Nonwood Plant Fiber Uses in Papermaking. <www.hurterconsult.com/resources>.
**Notes*: See Table 11.2.

Table 11.4: Paper produced from *Phragmites communis* Reeds.

Type of paper/paperboard	Reeds* (%)	Balance of furnish
Corrugating medium	60%–90%	Wastepaper
Duplex & triplex board	30%–80%	Wood pulp
Linerboard	50%–70%	Kraft pulp
Printing & writing—mechanical	20%–50%	20%–40% wood pulp, balance mechanical pulp
Printing & writing—woodfree	20%–90%	Woodpulp
Wrapping—"B" grade	50%–60%	Kraft pulp

Hurter, R.W., 2001. Nonwood Plant Fiber Uses in Papermaking. <www.hurterconsult.com/resources>.
**Notes*: See Table 11.2.

Table 11.5: Paper produced from Bamboo.

Type of paper/paperboard	Bamboo* (%)	Balance of furnish
Bristol board	50%–100%	Woodpulp and/or bagasse pulp
Duplex and triplex board	30%–80%	Woodpulp and/or straw or bagasse pulp
Linerboard	60%–100%	Kraft pulp
Multiwall sack	80%–100%	Kraft pulp
Newsprint substitute	50%–70%	Groundwood pulp
Printing & writing—mechanical	40%–60%	Groundwood pulp
Printing & writing—woodfree	70%–100%	Woodpulp and/or straw or bagasse pulp
Wrapping and bag papers	80%–100%	Kraft pulp

Hurter, R.W., 2001. Nonwood Plant Fiber Uses in Papermaking. <www.hurterconsult.com/resources>.
**Notes*: See Table 11.2.

Table 11.6: Paper produced from Kenaf (whole stalk).

Type of paper/paperboard	Kenaf (whole stalk)* (%)	Balance of furnish
Bleached paperboard	40%–50%	Woodpulp
Corrugating medium	50%–100%	Wastepaper
Linerboard	40%–50%	Kraft pulp and wastepaper pulp
Multiwall sack	20%–40%	Kraft pulp
Newsprint	80%–90% (chemimechanical)	Woodpulp
Printing & writing—mechanical	20%–50% (chemimechanical)	Woodpulp
Printing & writing—woodfree	20%–80%	Woodpulp
Tissue	50%–60%	Woodpulp

Hurter, R.W., 2001. Nonwood Plant Fiber Uses in Papermaking. <www.hurterconsult.com/resources>.
**Notes*: See Table 11.2.

Table 11.7: Paper produced from Kenaf (bast fiber).

Type of paper/paperboard	Kenaf (bast fiber)* (%)	Balance of furnish
Bleached paperboard	50%–100%	Woodpulp, bagasse or straw pulp
Cigarette paper	50%–100%	Woodpulp, flax, hemp or abaca pulp
Lightweight specialty papers	50%–100%	Woodpulp, flax, hemp or abaca pulp
Linerboard	50%–100%	Kraft, bagasse, straw or wastepaper pulp
Multiwall sack	50%–100%	Kraft, bagasse or straw pulp
Newsprint	20%–30%	Woodpulp bagasse or kenaf core mechanical pulp
Printing & writing—mechanical	20%–50%	20%–40% woodpulp, balance mechanical pulp
Printing & writing—woodfree	20%–100%	Woodpulp, bagasse, straw, reeds or bamboo pulp
Tissue	60%–90%	Woodpul p bagasse or straw pulp

Hurter, R.W., 2001. Nonwood Plant Fiber Uses in Papermaking. <www.hurterconsult.com/resources>.
**Notes*: See Table 11.2.

Table 11.8: Paper produced from Esparto.

Type of paper/paperboard	Esparto* (%)	Balance of furnish
Blotting paper	50%–80%	Woodpulp
Cigarette burning tube	20%–30%	Flax pulp or woodpulp
Cigarette filter tip paper	50%–70%	Flaw pulp or kraft pulp
Lightweight papers	50%–70%	Woodpulp
Printing & writing—woodfree	30%–100%	Woodpulp

Hurter, R.W., 2001. Nonwood Plant Fiber Uses in Papermaking. <www.hurterconsult.com/resources>.
**Notes*: See Table 11.2.

Table 11.9: Paper produced from Flax (bast fiber).

Type of paper/paperboard	Flax (bast fiber)* (%)	Balance of furnish
Cigarette burning tube	20%–100%	Woodpulp
Currency	50%–80%	Cotton pulp or woodpulp
Lightweight printing & writing	20%–80%	Cotton pulp or woodpulp
Ultra lightweight paper (bible)	50%–100%	Cotton pulp or woodpulp
Writing & book	20%–60%	Cotton pulp or woodpulp
Security paper	50%–80%	Cotton pulp or woodpulp

Hurter, R.W., 2001. Nonwood Plant Fiber Uses in Papermaking. <www.hurterconsult.com/resources>.
Notes: See Table 11.2.

Table 11.10: Paper produced from true Hemp (bast fiber).

Type of paper/paperboard	Hemp (bast fiber)* (%)	Balance of furnish
Cigarette paper	50%–100%	Woodpulp, bagasse, straw, kenaf bast or jute bast pulp
Condenser paper	20%–60%	Woodpulp, flax or cotton pulp
Currency	50%–80%	Flax, cotton or woodpulp
Lightweight printing & writing	20%–80%	Woodpulp, flax or cotton pulp
Security paper	50%–80%	Flax, cotton or woodpulp

Hurter, R.W., 2001. Nonwood Plant Fiber Uses in Papermaking. <www.hurterconsult.com/resources>.
Notes: See Table 11.2.

Table 11.11: Paper produced from Jute (bast fiber).

Type of paper/paperboard	Jute (bast fiber)* (%)	Balance of furnish
Cigarette paper	30%–50%	Hemp pulp
Printing & writing—woodfree	20%–80%	Woodpulp
Tag paper	40%–80%	Woodpulp or bamboo pulp
Wrapping & bag paper	40%–80%	Woodpulp or bamboo pulp

Hurter, R.W., 2001. Nonwood Plant Fiber Uses in Papermaking. <www.hurterconsult.com/resources>.
Notes: See Table 11.2.

Table 11.12: Paper produced from Sisal.

Type of paper/paperboard	Sisal* (%)	Balance of furnish
Currency	20%–50%	Cotton pulp
Filter paper	10%–80%	Cotton pulp or woodpulp
High-grade book & writing	20%–100%	Abaca, cotton or woodpulp
High-grade bond & ledger	20%–100%	Abaca, cotton or woodpulp
Lightweight bond & ledger	10%–80%	Abaca, cotton or woodpulp
Nonwovens	10%–50%	Synthetic fiber
Printing & writing—wood free	20%–100%	Woodpulp
Publication grades	15%–20%	10%–15% woodpulp, balance groundwood
Sausage skins	90%–100%	Abaca or flax pulp
Security paper	20%–100%	Cotton pulp or woodpulp
Tea bags	50%–80%	Abaca or flax pulp

Hurter, R.W., 2001. Nonwood Plant Fiber Uses in Papermaking. <www.hurterconsult.com/resources>.
Notes: See Table 11.2.

Table 11.13: Paper produced from Abaca.

Type of paper/paperboard	Abaca* (%)	Balance of furnish
Currency	20%–50%	Cotton pulp
Filter paper	10%–80%	Cotton pulp or woodpulp
High-grade book & writing	10%–100%	Cotton pulp or woodpulp
High-grade bond & ledger	10%–100%	Cotton pulp or woodpulp
Linerboard	10%–30%	Bagasse or straw pulp
Nonwovens	10%–50%	Synthetic fiber
Sausage skins	90%–100%	Flax or sisal pulp
Security paper	20%–100%	Cotton pulp or woodpulp
Tea bags	90%–100%	Flax pulp
Wrapping & bag	10%–30%	Bagasse or straw pulp

Hurter, R.W., 2001. Nonwood Plant Fiber Uses in Papermaking. <www.hurterconsult.com/resources>.
**Notes*: See Table 11.2.

Table 11.14: Paper produced from Cotton.

Type of paper/paperboard	Cotton* (%)	Balance of furnish
Currency & security paper	50%–100%	Flax pulp
High-grade book & writing	20%–100%	Woodpulp
High-grade bond & ledger	20%–100%	Woodpulp

Hurter, R.W., 2001. Nonwood Plant Fiber Uses in Papermaking. <www.hurterconsult.com/resources>.
**Notes*: See Table 11.2.

Table 11.15: Paper produced from Ekara, Knagra & Nal grass mixed.

Type of paper/paperboard	Ekara, Knagra & Nal grass* (%)	Balance of furnish
Printing & writing—woodfree	50%–70%	Woodpulp
Wrapping	40%–60%	Woodpulp

Hurter, R.W., 2001. Nonwood Plant Fiber Uses in Papermaking. <www.hurterconsult.com/resources>.
**Notes*: See Table 11.2.

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Relevant websites

http://scholar.lib.vt.edu

CHAPTER 12

Advantages and disadvantages of using nonwood fiber for papermaking

Chapter outline

References 214
Further reading 215
Relevant websites 215

High market demands and also the environmental problems due to the large usage of wood in pulp and paper industry have increased the interest to explore nonwood plants as substitution fiber which is also environment friendly (González-García et al., 2010; Jiménez et al., 2002; Mohd Aripin, 2014; Atchison, 1989a,b,c; Chen et al., 2019; Hammett et al., 2001; Hurter, 1997, 1998, 2001, 2013; Kneer, 2019; Liu et al., 2018; Saijonkari-Pahkala, 2001; Alireza, 2006). Hence, the utilization of nonwood fiber is a superior option for producing pulp and paper for reducing deforestation of rain forests or primitive forests in the world. “From supply of raw material to the properties of finished paper, majority of nonwood resources has proven to be economically inferior to wood. But during the last few years, technological breakthrough in almost all the fields of papermaking have made nonwood fibers more competitive with wood as a raw material for papermaking” (Bajpai, 2018). “Although till recently, use of nonwood fibers for pulp and paper making was concentrated in countries with limited wood supply, it is now showing an increasing trend even in countries with adequate wood supply due to environmental considerations. With time this trend can be expected to grow further and it can be safely said that the future of nonwood plant fibers as pulping and papermaking raw material looks bright” (Chandra, 1998).

Some nonwood fibers used for papermaking have high annual yields per hectare (scholar.lib.vt.edu). The average annual yield per hectare of kenaf is around two times higher in comparison to that of fast growing softwoods (Table 1.6). The lignin content in nonwoods is lower in comparison to woods. In general, it is easier to delignify nonwoods, because they possess lower activation energies (Table 12.1).

Pulping of nonwoody materials is easier compared to woody fiber in many ways.

Nonwood Plant Fibers for Pulp and Paper.
DOI: https://doi.org/10.1016/B978-0-12-821800-6.00012-0

Table 12.1: Advantages of using nonwood fiber.

It is the fast annual growing fiber resource.
Chipping is not required.
Debarking is not required.
Most of the nonwood fibrous raw materials contain very little lignin as compared to 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.
Nonwood pulp can be produced at low temperatures.
Due to 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 requires less energy than wood fibers.
From the agricultural point of view, the nonwood fiber materials pulping can bring additional economic benefits from the food crops.

Source: *Rousu, P., Rousu, P., Anttila, J., 2002. Sustainable pulp production from agricultural waste. Resour. Conserv. Recycl. 35 (1), 85–103; Rodríguez, A., Moral, A., Serrano, L., 2008. Rice straw pulp obtained by using various methods. Bioresour. Technol. 99 (8), 2881–2886; Kissinger, S., Gerard, G., Victoria, M., Nicole, R., Ford, J., Kelly, S., et al., 2007. Wood and non-wood pulp production comparative ecological footprinting on the Canadian prairies. Ecol. Econ. 62, 552–558.*

However, there are many disadvantages too which are listed below:

- The availability of a constant, year-round supply of fiber is a primary concern for paper mills. Given that most nonwoods are annual plants, a large storage capacity must be developed to ensure a constant supply. This is further complicated by the fact that most nonwood fiber sources are high in volume and low in density when compared with wood (woodethic.blogspot.com).
- Straw is prone to attack by molds and rot and undergoes natural combustion. Therefore the storage conditions and moisture level is very important. Chemical consumption in pulping is more in case of straw. The strength properties of straw pulp are relatively lower.
- Agricultural residues are difficult to handle in comparison to wood chips and are bulkier. Cost of transportation and storage is high due to its bulky nature. The density is lower and the volume is high which necessitates local processing.
- Agricultural residues are a by-product of food and feed production and not harvested under best conditions for fiber production. Therefore the pulp yield is lower.
- Collection, transportation, and storage of agricultural residues require special attention.
- A larger storage capacity is needed to support continuous production of pulp.
- The ash content of nonwood plants is in the range of 1% and 20% which is quite high. The ash is generally less than 1% in case of hardwoods and softwoods. The fiber length of nonwoods is generally shorter. This puts a limit on the range of papers that can be produced.

- Straw from cereal is also highly dependent on agricultural subsidies. This makes a long-term availability unreliable, particularly in the Nordic countries.
- The drainage properties of pulp are lower because of the presence of large amount of fines and the shorter fiber length. Slow drainage needs either a reduction in processing speed or a lengthening of the drying section, which substantially increases the energy and processing costs.
- More pulping liquid and more volumes in process equipment is needed because of the low density of the crops.
- Higher pollution levels associated with low technology production methods.
- Pollution generated from nonwood pulp mills can be up to 20 times in comparison to wood mills.
- Nonwoody fibers contain higher amount of silica. During pulping the silica is dissolved and goes in the black liquor and results in several problems in the chemical recovery system including higher black liquor viscosity at high solids concentration.
- Formation of hard deposits in the recovery boiler and hard scales in the evaporator reduces the effectiveness of some equipment and in fact can plug it.
- In the recausticizing system, colloidal gels are formed. This lowers the settling rate.
- In the lime kilns, glassy material are formed and slacking rate is reduced. Due to this chemical recovery becomes difficult and less proficient and more costly in comparison to recovery of black liquor from woods.
- Due to the high water retention capacity of nonwoody fibers especially straw, each separation step needs about three times more separation capacity as for hardwood processing. This significantly increases the capital investment.

In the case of specialty paper production, nonwood plants are used for the production of specialty papers of high quality (Gominho et al., 2001; Wan Rosli et al., 2004). Nonwoody plants have shown several advantages (Table 12.1). Furthermore, an additional advantage for these fibers is it can give additional revenue generation to the farmers for food crop-waste such as straw, bagasse, and grasses (Salmela et al., 2008).

These days, several other countries are exploring nonwoody plants fiber resources as alternative fibers in pulp and paper industry. This is due to the exhaustion and increasing prices of wood resources and readily available nonwood fiber resources in these countries (Atchison, 1992).

> The United States is also looking for nonwood fibers to be the resources of pulp and paper-based as alternative fiber in this industry to replace the virgin fiber. At the same time, Europe has a shortage of short fiber hardwood pulp and is thus an importer of this kind of pulp. They found out that some of the nonwood fibers have the properties to replace these fibers. Hence, the use of nonwood fiber for pulp and paper-making is thus also expected to grow in Europe. Indeed, China and India are the leading countries that

use nonwood fibers in pulp and paper production rather than other countries in the world. The total of nonwood plants (8%–10%) pulping capacity worldwide is increasing faster than the wood pulping capacity. In China, the consumption of nonwood resources in pulp and paper-based industries is higher than wood sources from the year 1995 to 2005. The development of these industries will need a continuous and sustainable forestry around the world. This is also due to the fact that nonwood plants sources have displayed different kinds of advantages in pulp and paper-based production compared to the wood resources.

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The future

Chapter outline

References 221
Relevant websites 221

In the developed countries, about 90% of the pulp and paper is produced from wood. "However, environmental concerns and short supply are increasing the pressure to use alternative sources for raw material in both the developed and developing countries. The use of agriculture-based fibers is particularly relevant in countries where demand for pulp and paper is increasing but the wood resources are limited" (eprints.uthm.edu.my).

The worldwide capacity for production of agriculture-based fiber pulps has increased substantially (Atchison, 1994). Straw, bagasse, and bamboo are the primary agricultural fibers used in pulp and paper, but other similar fibers are used in a variety of specialty papers. In several countries, the pulp production is based totally on nonwood fibers; more than 25 countries depend on agro-fibers for more than 50% of their pulp production. China and India are the leading countries producing pulp and paper from nonwood fibers. China has more than 73% of the agro-based pulp capacity. China and India collectively account for about 80% of the total nonwood pulping capacity (Bajpai et al., 2004; Jiménez et al., 2006; Madakadze et al., 2010).

"In recent years, the three major problems that would continue to puzzle the development of the paper industry are as follows:

- The shortage of resources.
- Contamination of environment.
- The level of technical equipment.

The most dominating factor is the shortage of raw material resources, which is largely due to the contradiction between the structure of the raw material and the structure of the fiber resources. Thereby, nonwood fibers possess a rich variety of excellent properties in physical and optical aspects, which could be used to improve their products. However, throughout the world, nonwood fiber accounts for only a small fraction of the raw material of paper and paperboard. However, in some developing countries, about 60% of the cellulose fiber comes from nonwood materials, such as bagasse, corn straw, bamboo, reed, grass, jute, flax, sisal, and so on. Particularly in China and India, 70% of the raw materials used in the pulp

Nonwood Plant Fibers for Pulp and Paper.
DOI: https://doi.org/10.1016/B978-0-12-821800-6.00013-2

industry come from nonwood plants including cereal straw and bagasse and these two countries own 80% of the total nonwood pulp production" Liu et al. (2018); Laftah and Wan, (2016); El-Sakhawy et al. (1996); Judt, Manfred, (1994); Alireza (2006); Jahan et al. (2009).

As the demand of paper is increasing, the existing woody raw materials may not be sufficient for meeting this increasing demand for paper. Hence, it is important to consider nonwood pulp for meeting the possible deficit of wood fiber for papermaking. Besides, this has also led to the developing of alternative pulping technologies that are environmentally friendly (Liu et al., 2018).

> As for raw materials of paper manufacturing, rice straw and wheat straw are easily available and relatively cheap to use. However, the environmental concerns over small mills that use straw offset this advantage. As the government enforces environmental regulations, the amount of rice straw and wheat straw used in pulping might be reduced considerably.
>
> ***Liu et al. (2018)***

Bamboo and other potential nonwood materials are expected to become more popular in pulp and paper industry. Hence, it is important to develop cleaner production technology, reduce the cost of pulping, improving the quality of product, and realizing industrial upgradation.

The cost of imported pulps and waste is increasing, and the woody raw materials are getting limited for the developing countries. Therefore the technology of nonwood pulping would develop at a faster rate. This, along with the speedy increase in requirement for paper products, represents a main potential market to pulp and paper industry suppliers. It is expected that the present surge in new mills would continue for several decades. Furthermore the population is rapidly increasing in most of these countries. This is putting extra pressure on the available land resources which reduce the growth of forest plantations. Consequently alternative raw materials are playing an important role in the pulp and paper industry in the developing nations.

> Around the world, there is a case for use of nonwood fibers for papermaking.There is a shortage of short fibers in the European Union due to lack of hardwood trees. They are at present discovering the advantages of using nonwood fibers to fill this need. In the United States, pressure from environmental groups and rising cost of wood, may force the use of nonwood plants for papermaking.
>
> ***Chandra (1998)***

Pulping of agricultural by-products from harvesting and processing of agricultural crops residues is of growing interest because of economic and environmental factors (Chaudhuri, 1993). Some of these factors are shown in Table 13.1.

Recent interest toward increased implementation of sustainable forest management is also motivating paper industry to look for alternative fiber sources. Over the years, research in the

Table 13.1: Interest in the use of agricultural residues for papermaking.

For fine papermakers, short fibered pulp gives better formation and opacity. These can be provided by nonwood fibers, especially straw pulp, which consumes less refining energy than wood fiber.
Governments of the United States and the EC countries are trying to curtail surplus grain production by encouraging the farmers to grow nonfood crops on agricultural land.
Environmental regulations prohibit burning of stubble in the fields, and this has increased the availability of straw for nonagricultural use in North America and western Europe.
Environmental pressure groups are trying to limit clear felling of old growth forests to protect animal life, and to protect sensitive forests and favor bio-diversity in plantations.

field of nonwood pulping has yielded many results. Consequently use of nonwood raw materials in paper industry has not been as difficult as in the past. But, several issues are still continuing to plague the nonwood paper industry. “On the supply side, new harvesters and balers are being developed. The harvesters will allow better harvesting of straw and other agricultural residues making harvesting more economical while the new balers will provide more compact bales thus reducing the transport costs. Development is also being made in design specialized harvesting equipment for other raw material as well. New and improved chemical treatment methods are being applied to prevent nonwood fibers from deteriorating over their long storage periods while at the same time reducing their pulping costs. Individual raw materials have also seen large scale research in various pulping and papermaking fields to improve their economic viability as raw material. Significant progress has been made to develop bagasse pulping, which has turned out to be the most promising nonwood raw materials for papermaking. Developments in depithing, storage, pulping, and bleaching of bagasse have resulted in lower production costs. These developments have also found implementation in the use of other nonwood plants. Bagasse fibers also have good papermaking properties. Use of bagasse has a further advantage of having lower collection costs since it is obtained from sugar mills, which take care of collection. Therefore in countries where the replacement fuel cost for bagasse in sugar mills is low, use of bagasse as papermaking raw material is an attractive prospect. There have also been studies on establishing joint sugar-paper mill complexes, further lowering the production costs” (Chandra, 1998).

Besides China, bamboo is also an important raw material for paper making in several countries. With time, most of the technological issues associated with its use have been solved. Because it grows, and can be harvested throughout the year, there is no need for the mills to maintain a large inventory. This makes it one of the better raw materials among nonwoods. Its fiber properties are also superb for papermaking.

Straw is another major nonwood raw material. Although, its use as a raw material for producing paper had some problems, now the solutions are available. In the area of bailing and storage new developments have been made. Efficient equipment for desilication have been developed (Judt, Manfred, 1991). As straw has high silica content, particularly rice straw, this has reduced the problems which are faced during pulping of straw. Added to that, the widespread availability of straw should make it an important raw material for producing paper in countries with low collection costs.

Kenaf has been another important raw material that has been a center of attraction, particularly in the United States. Studies on some other raw materials have also shown interesting results. Pollution which is one of the main problems associated with nonwood fiber pulping, has also been tackled. Most nonwood pulp mills are small and are not operating at large profit margins. Hence, the mills do not find it economical to install a chemical recovery system. Consequently these mills are among the major polluters. Pollution control at source has been identified. Use of ammonium sulfite pulping liquor has been suggested.

In China, use of nonwood raw materials in producing paper is continuing to grow. Although in recent years, the stress has been on the growth of paper mills based on wood, the growth of paper mills using nonwood has not slowed. Actually it is expected to grow faster in comparison to wood-based paper mills for some time to come. Chinese government is taking steps for closing polluting mills. This led to more developments in the pollution control methods. Several government agencies have sponsored research in the area of nonwood fiber papermaking. In countries where presently nonwood fibers are not a major source of fibrous raw material, increasing the amount of nonwood fibers used in papermaking, the experiences in China will be very important reference.

> China is the largest producer of nonwood pulp paper. Therefore, these experiences with practical aspects of nonwood papermaking will be helpful since they will provide us with the data required to set up profitable nonwood fiberbased paper mills. Since China is conducting a major expansion in its papermaking capacities, there is a potential for investment in the Chinese paper industry. Although, the Chinese government does not allow foreign ownership in the paper industry, there is a big, and growing, market for the equipment suppliers. At present most paper mills in China have old equipment. This results in costly paper with paper quality being poor. They will therefore be needing newer and more efficient machinery for papermaking. With increasing global business presence, China will have to adhere to more strict environmental standards. This will result in a need for pollution control technology and equipment. These are just two of the potential markets for equipment suppliers.
>
> ***Cao (1996); Chandra (1998)***

Fueled by several environmental and other factors, the use of nonwood plant fibers for pulping and papermaking would grow in those countries where its use till now has been largely overlooked. Reduction in burning of straw needs that straw will be used for alternate use. Paper production is one use where extensive research has been conducted around the world. In addition, curtailing grain production for maintaining grain prices would need the farmers for growing alternate crops and here also papermaking raw material is a real choice.

> With these considerations it can be safely said that use of nonwood plant fibers for pulp and paper industry will continue to grow at a fast rate and also grow as a percentage of total papermaking raw material for some time to come.
>
> *Chandra (1998)*

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Index

Note: Page numbers followed by "*f*" and "*t*" refer to figures and tables, respectively.

A

Abaca (*Musa textilis*), 7, 22, 67–69, 69*f*, 203–205
  uses of abaca fiber, 68*t*
Acetic acid, 127–129
Acetocell process, 129
Acetosolv method, 129
Acid pulping process, 108–110
Acid treatment, 176
Adhesion properties of wet paper, 197
Adsorbable organic halides (AOX), 153
Agave sisalana. *See* Sisal (*Agave sisalana*)
Agricultural residues, 6–7
  of nonwood raw materials, 36–46
    cereal straw, 45–46
    corn stalks, 40–41
    cotton stalks, 41–42
    rice straw, 43–44
    sugarcane bagasse, 37–40
    wheat straw, 44–45
  for papermaking, 219*t*
Agriculture-based fibers, 217
Alcell process, 125–126
Alkaline peeling, 116–117
Alkaline peroxide mechanical pulping process (APMP process), 132, 158
Alkaline pulping, 111, 114–120. *See also* Sulfite pulping
  Kraft process, 118–119
  NACO pulping, 119
  SAICA pulping, 119–120
  soda pulping, 114–118
Alkaline–sulfite pulping process, 121–122
Alkaline–sulfite–anthraquinone–methanol process (ASAM process), 124
Alpha-cellulose content, 15–16
Alternative recovery processes, 181–184
  DARS, 181–184
Ammonium-based pulps, 121–122
Angiospermae, 12, 29–30
  dicots, 12
  monocots, 12
Anthraquinone, 116–117
  cyclic action, 117*f*
  structures, 116*f*
ASAE process, 126
Ash, 4
Aspergillus, 193
  A. niger, 104, 157, 193
    strain An-76, 103
  A. oryzae, 104
  Aspergillus L22, 103
Availability of nonwood fibers, 83–84
AZEYP sequence, 160
Aztecs, 69

B

Bacillus, 193
Bagasse, 16, 22–23, 37–38, 85–86, 99, 203–205, 217
  pulping, 218–219
  pulps, 39
  SEM images, 38–39, 38*f*
Baled bagasse, 86
Bamboo (*Dendrocalamus strictus*), 6, 14, 46–50, 99, 205, 217, 219
  fibers of, 14*f*
  pulp, 48
  SEM, 47*f*
  in Vietnam, 22
Banana stem fiber, 5–6
Barley (*Hordeum* spp.), 14
Bast fibers, 7, 57–66, 110. *See also* Leaf fibers
  flax tow, 65–66
  hemp, 61–63
  jute, 57–58
  kenaf, 63–65
  materials, 110
  ramie, 59
  Sunn hemp, 59–60
Beating characteristics of nonwood pulp, 187–196
  response of fibers during, 189*t*
Beating degree, 158*t*, 188, 192, 195–196
Biochemical pulping, 135
Biological pulping, 135
Biomechanical pulping, 135
Biopulping, 100, 131, 134–135
  of pineapple leaf fiber, 101
Black liquor. *See also* Green liquor
  desilication of, 171–177
    by carbonation, 173–177
    by lime addition, 173
    partial desilication by raw material cleaning, 171–172
    spontaneous partial desilication of black liquor by storing, 172
  viscosity, 213
Bleached pulps, 147–148

Bleaching, 90–91, 147–155
  advantages and disadvantages, 150*t*
  chemicals used in, 148*t*, 151*t*
  functions of different bleaching agents, 149*t*
  of nonwood pulps, 155–162
Bleachzyme F, 194
Boehmeria nivea. *See* Ramie (*Boehmeria nivea*)
Branching veins, 12
Breaking length, 45, 157, 158*t*, 159, 192–194
Brown stock washing, 137
Butyric acid, 127–129

C

Calcining, 178–179
Calcium oxalate, 152
Cannabis, 13*f*
Cannabis Hemp, 63
Cannabis sativa. *See* Hemp (*Cannabis sativa*)
Canola straw, 5
Carbon dioxide, 174, 176
Carbonation, black liquor desilication by, 173–177
Cationic demand, 103–104, 196
Causticization method, 178
Causticizing, 94, 168–169, 168*t*, 178–179, 181–182
CEH three-stage bleaching process, 153
CEHD, 151
Cellulases, 193
Cellulose, 4, 7, 36–37
Cell wall, 48–49, 108–110, 189–192, 195–196
Central Pulp and Paper Research Institute (CPPRI), 88, 171–172, 174–175
Centri-cleaning, 136–137
Centrifugal cleaning, 136–137
Cereal stalks, mineral composition of, 170–171
Cereal straw, 29–30, 45–46
  chemical composition of, 11*t*
Ceriporiopsis subvermispora, 100–102
  effect of cooking time on soda pulping of, 102*t*
  soda pulping of wheat straw with, 102*t*
Chelating agent, 134, 148*t*, 152–153
Chemi-thermomechanical pulp (CTMP), 133, 203–204
Chemical methods, 111–112
Chemical pulps, 147–148
Chemical recovery, 3, 167
  alternative recovery processes, 181–184
  chemistry of silica, 170–171
  desilication
    of black liquor, 171–177
    of green liquor, 177–178
  environmental and economic benefits, 167*t*
  lignin and silica in nonwoody raw materials, 168*t*
  of nonwood fibers, 92–94
  soda recovery, 178–181
Chemimechanical pulping methods (CMP methods), 130–135
  alkaline peroxide mechanical pulping process, 132
  biopulping, 134–135
  CMP and CTMP processes, 131–132
  extrusion pulping, 133–134
  mild acid cooking method, 134
  steam explosion pulping, 133
Chempolis pulping process, 127–129
China, 21–22
  nonwood fibers production in, 29*t*
  using nonwood raw materials, 25
  paper production in, 19–20
  pulp and paper industry, 48–49
China grass. *See* Ramie (*Boehmeria nivea*)
Chippers, 99–100
Chlorinated organic compound, 148–149
Chlorination—alkali extraction—hypochlorite (CEH), 157
Chlorine (CI_2), 148, 153
Chlorine dioxide (CIO_2), 148, 150–151, 153
Chlorine dioxide substitution, 148–149
Chrysosporium strain, 194–195
CIMV process, 129–130
Coniferous trees, 29–30, 107–108
CONOX, 177
Conventional bleaching, 155
Combustion, 85–86, 88, 119, 162, 169–170, 178–181, 184
Corchorus capsularis. *See* Jute (*Corchorus capsularis*)
Corn, 40–41
Corn stalks (*Zea mays*), 40–41
  SEM images, 38–39, 38*f*
Corrugating medium mill, 179
Cotton, 14, 205
  fibers, 7, 71
    cotton seed hairs, 14*f*
  linters, 22–23, 72, 203–204
    images, 72*f*
  rags, 73
Cotton stalks (*Goossypium*), 41–42
  SEM images, 42*f*
Crotalaria juncea. *See* Sunn hemp (*Crotalaria juncea*)
Crotolaria, 59–60
Crude xylanases, 103
Cyperus papyrus. *See* Papyrus (*Cyperus papyrus*)

D

Deciduous trees, 29–30, 107–108
Dedusting of straw, 171
Defluidization, 180–181
Delignification
  process, 108
  stages of straw and softwood, 109*t*
Dendrocalamus strictus. *See* Bamboo (*Dendrocalamus strictus*)
Depithing, 16
Depolymerisation, 126
Desilication
  of black liquor, 171–177
  of green liquor, 177–178

Dicots, 12, 13*f*
Dicotyledonae, 29–30
Dicotyledoneae, 12
Dicotyledons, 12
Diethylenetriaminepentaacetic acid (DTPA), 132, 152
Diffusion washers, 136–137
Dilution/extraction washers, 136–138
Direct alkali recovery system (DARS), 181–184
  advantages, 184
  constraints, 184
Disk chippers, 99–100
Dispersing press, 137–138
Displacement washing, 137–138
Dorr-Oliver method, 94
DQP bleaching sequence, 155
Drainage properties of nonwood pulps, 197–198
Dry depithing, 87
Dumping, 5–6
Dynamic drainage, 196

E

ECF bleaching. *See* Elemental-chlorine free bleaching process (ECF bleaching process)
Ekara, 205
Electrical energy, 100, 134–135
Elemental-chlorine free bleaching process (ECF bleaching process), 149–150, 153, 155–156, 158–159, 160*t*, 189–190
Elephant grass, 6–7
Energy conservation, 193
Environment-friendly fiber, 5–6
Enzymatic bleaching, 156
Enzymatic pretreatment, 103
Enzyme bleaching, 156
Epidermal cells, 192
Epidermis, 12–14
Esparto (*Stipa tenacissima*), 14, 50–51, 203–204
  SEM of, 50*f*
Esparto grass. *See* Esparto (*Stipa tenacissima*)
Ethanol, 62
  pulping, 125–127
Ethylenediaminetetraacetic acid (EDTA), 152
Eulaliopsis binata. *See* Sabai grass (*Eulaliopsis binata*)
Evaporation, 127–130, 137, 162, 170, 178–181
Extended cooking, 148–149
External fibrillation, 188–189, 191*t*, 192
Extraction, 90–91, 125–127, 136–138, 148–150, 162, 183
Extractives, 4
Extrusion pulping, 131, 133–134

F

Festuca arundinacea Schr. *See* Tall fescue (*Festuca arundinacea* Schr.)
Fiber(s), 14
  of bamboo, linen, cotton seed hairs, 14*f*
  cell wall, 191–192
  hemp, 61
  length, 23
  properties
    of nonwood fibers, 10*t*, 34*t*
    of some woody raw materials, 10*t*
  for pulp and paper, 3–4
Fiber morphology, 196
FibreZyme LBR, 194–195
Fibrillation, 133–134, 189–192, 189*t*, 198
First cut linters, 71
Flax (*Linum usitatissimum*), 12, 14, 65–66, 203–204
Flexibility, 50–51, 55–56, 64, 103, 111, 148, 188–189, 194
Florida Vincent Corporation, 39
Fluidized bed reactor system, 180–181, 180*t*
Fold endurance, 158*t*
Forest resources, 3
Formacell process, 129
Formic acid, 127–129
Fractionation, 99–100, 195–196
FreeFiber process, 124
Free radical, 153–155

G

Giant reed, 5
Global demand for paper, 2
Goossypium. *See* Cotton stalks (*Goossypium*)
Gramineae, 29–30
Gramineous fiber materials, 108–111
  bast fiber materials, 110
  leaf fiber materials, 111
  seed hull fiber materials, 111
Green liquor. *See also* Black liquor
  advantages, 178*t*
  desilication of, 177–178
  two-stage causticization effect, 178*t*
Gymnospermae, 12, 29–30

H

Hardwoods, 12
  chemical composition of, 4, 4*t*
Heat preservation, 109*t*
Heat transfer, 168*t*
Heavy market demands, 5–6
Hemicellulase "Amano" 90, 194
Hemicellulose, 4, 36–37
Hemp (*Cannabis sativa*), 12, 14, 61–63, 205
  seed, 62
Hibiscus cannabinus. *See* Kenaf (*Hibiscus cannabinus*)
Highly Compact Reactor (HCR), 177
Hordeum spp. *See* Barley (*Hordeum* spp.)
Horizontal belt filters, 136–137
Horizontal tube digesters, 3
Hull fibres, 71
Hydro-cyclone, 136–137
Hydrogen peroxide, 148, 154–155
1-Hydroxybenzotriazole, 104

I

Impregnation, 58, 124, 126, 133–134, 159, 212*t*
Impregnation, depolymerisation, extraction process (IDE-process), 126–127

India
  forest-based resources in, 21–22
  wheat production, 44–45
Indian Hemp. *See* Cannabis Hemp
Industrial hemp. *See* Hemp (*Cannabis sativa*)
Inflorescence, 15–16
Inter-fiber bonding, 107–108, 188–190, 195–196
Internal fibrillation, 191*t*, 193

J

Jute (*Corchorus capsularis*), 7, 57–58, 205
  fiber, 110

K

Kamyr-type digesters, 3
Kappa number, 103
Kenaf (*Hibiscus cannabinus*), 2–3, 5–7, 12, 14, 22, 63–65, 90, 203–205, 220
  SEM, 64*f*
Knitters, 138
Knot, 110, 138
Kraft process, 114–116, 118–119

L

Landfilling, 168*t*
Leaching, 183
Leaf fibers, 7, 66–71. *See also* Bast fibers; Nonwood fiber(s)
  abaca, 67–69
  materials, 111
  sisal, 69–71
Leguminosae, 29–30
Lignin, 4, 36–37
  of gramineous straw materials, 108, 109*t*
  oxidation, 154–155
Lignin removal, 108, 116–117, 120
Ligninases, 101
Lignocellulosic biomass, 123
Lime addition, black liquor desilication by, 173
Lime mud, 94, 168–170, 168*t*, 177–178, 182
Linen, 65
  fibers of, 14*f*
Linters, 7
Linum usitatissimum. *See* Flax (*Linum usitatissimum*)
Liquid cyclone, 136–137
Logging, 2
Long fiber, 27
Lumen, 51, 54, 110, 191*t*
Lygeum spartum, 50

M

Malvaceae, 29–30
Manila hemp. *See* Abaca (*Musa textilis*)
Mayans, 69
Methanol pulping, 124–125
Microbial
  pectinase enzymes, 103
  retting, 102
Middle lamella, 57, 191–192
Mild acid cooking method, 134
Mill run, 72
Milox process, 127–129
Moist depithing, 87
Molecular oxygen, 154–155
Monocots, 12, 13*f*
Monocotyledonae, 29–30
Monocotyledons, 12
Multiple-effect evaporator, 168*t*
Multiple split chlorine additions, 148–149
Multistage bleaching, 148–149, 156–157
Musa textilis. *See* Abaca (*Musa textilis*)

N

NACO pulping, 119
NAEM, 123
Napier grass, 6
Natural growing plants
  bamboo, 46–50
  esparto, 50–51
  papyrus, 56
  reeds, 51–56
Neutral sulfite process, 120–121
Neutral sulfite semi-chemical process (NSSC process), 120–121, 180–181
Newsprint, 203–204
Nonwood fiber(s), 3, 6–7, 19–20, 23, 83, 217. *See also* Leaf fibers
  advantages, 212*t*
  availability, 28*t*
  bleaching, 90–91
  chemical composition, 35*t*
  chemical properties, 11*t*
  chemical recovery, 92–94
  fiber properties, 10*t*
  identification, 15
  papermaking, 91–92
  for papermaking, 211
  production in China, 29*t*
  pulping, 89–90
  reasons for use, 20*t*
  sources, 7–8
  storage and handling, 84–88
  users in papermaking, 8*t*
Nonwood pulp(ing), 19–20, 25–27, 83, 92
  beating/refining characteristics of, 187–196
  bleaching of, 155–162
  drainage properties, 197–198
  imports/exports, 28*t*
  for paper, 5
  papermaking performance of, 196–198
  papers produced from, 204*t*
  percentage of types, 5*t*
  plants, 168
  production, 27*t*
    distribution, 26*t*
    production/consumption, 28*t*
  specialty nonwood pulp, 8–9
  world production for papermaking, 26
  washing, screening, and purification of, 135–138
Nonwood raw materials, 5, 26
  agricultural residues, 36–46
    cereal straw, 45–46
    corn stalks, 40–41
    cotton stalks, 41–42
    rice straw, 43–44
    sugarcane bagasse, 37–40
    wheat straw, 44–45
  categories, 33–35, 36*t*

  estimated annual collectable yields, 34*t*
  natural growing plants
    bamboo, 46–50
    esparto, 50–51
    papyrus, 56
    reeds, 51–56
  nonwood crops growth for fiber content
    bast fibers, 57–66
    leaf fibers, 66–71
    seed hair fibers, 71–73
  preparation, 99
  presence of lignin and silica in, 168*t*
  pulping, 111–135
    properties, 107–111
  renewed interest in, 25
Nonwoods, 19–21, 111–112
  crops growth for fiber content
    bast fibers, 57–66
    leaf fibers, 66–71
    seed hair fibers, 71–73
  fiber properties, 34*t*
  plants, 5–6
    fibers, 83, 203–204
    paper producing from
      nonwood pulps, 204*t*
Nonwoody annual plants, 203–204
Normal stresses, 188–189
Northern Bleached Softwood Kraft (NBSK), 11

O

Oil palm fibers, 5–6
Old corrugated container (OCC), 119
Opacity, 38–39, 70–71, 92, 100–101, 107–108, 120–121, 135, 188–190
OpQP TCF sequence, 159
OpQPo sequence, 161
Organic acid pulping, 127–130
Organocell process, 125
Organosolv pulping, 123–130
  ethanol pulping, 125–127
  methanol pulping, 124–125
  organic acid pulping, 127–130
Oryza spp. *See* Rice (*Oryza* spp.)
Oxygen delignification, 119, 156
Ozone (O_3), 148, 155

P

Panicum virgatum L. *See* Switchgrass (*Panicum virgatum* L.)
Paper pulp, 107–108
Papermakers, 187
Papermaking, 91–92
  performance of nonwood pulp, 196–198
    adhesion properties of wet paper, 197
    drainage properties of nonwood pulps, 197–198
    strength properties of wet paper, 196–197
  raw materials
    annual yields of, 8–9
    average pulp yields of, 9*t*
Papyrus (*Cyperus papyrus*), 6, 56
Parenchyma cell, 55–56, 68–69, 108–110, 192, 197–198
Partial desilication by raw material cleaning, 171–172
Pectinases, 103
Penicillium A10, 103
Peroxide bleaching, 20–21, 90, 103–104, 152, 158
PFI revolutions, 194*t*, 195–196
Phlebia brevispora, 101–102
Phlebia subserialis, 101–102
Phloem, 12
Phloem fiber. *See* Bast fibers
Phragmites communis Trinius. *See* Reeds (*Phragmites communis* Trinius)
Pile, 99
Pineapple leaf fiber (PALF), 101
Plant species, 29–30
Pleurotus sp., 101
  P. eous, 101
  P. eryngii, 103
Pollution, 213, 220
Potassium permanganate, 160
Potassium-based process, 121–122
Pressurized reactor, 119
Primary wall, 108–110, 191–192, 195–196
Printability, 38–39, 46, 107–108
Printing paper, 203–204
Pulp(s), 203–204
  mills, 21
  and paper industry, 1, 25, 88
    comparison of nonwood and wood resources, 6*t*
    world paper and paperboard production and consumption, 2*f*
  washing, 136
Pulping, 89–90, 99, 107–108. *See also* Biopulping
  of nonwoody raw materials, 111–135, 113*t*
    alkaline pulping, 114–120
    chemimechanical pulping and pulping methods, 130–135
    Organosolv pulping, 123–130
    sulfite pulping, 120–122
  properties of nonwoody raw materials, 107–111
    gramineous fiber materials, 108–111
  straw, 118
Punec process, 127

R

Rags, 7
Ramie (*Boehmeria nivea*), 7, 59
Reeds (*Phragmites communis* Trinius), 6, 51–56, 99, 205
  biomass, 52–53
  paper mills, 53–54
  Sabai grass, 54–56
Refiner mechanical pulping (RMP), 100
Refining characteristics of nonwood pulp, 187–196
  effects, 191*t*
  factors affecting, 190*t*
  factors influencing response of pulp fibers to, 191*t*
  response of fibers during, 189*t*
Refining energy, 131, 189, 195–196, 212*t*
Retting process, 59
Reversed screw element (RSE), 133–134
Rice (*Oryza* spp.), 14, 43–44
Rotary pressure washer, 136–137
Rotary vacuum washing, 136–137
Runnability, 8–9, 23, 86–87, 91–92, 107–108, 204–205
Rye straw, 45–46, 46*f*

S

Sabai grass (*Eulaliopsis binata*), 6, 54–56
  cross-sectional image, 55*f*
  surface image, 55*f*
Saccharum officinarum. *See* Sugarcane (*Saccharum officinarum*)
SAICA pulping, 119–120
Scanning electron microscopy (SEM), 100–101
Sclereids, 108–110, 192
Sclerenchyma cells, 108–110
Second cut linters, 71
Secondary wall, 108–110, 191–192
Seed hair fibers, 7, 71–73
  cotton fibers, 71
  cotton linters, 72
  cotton rags, 73
Seed hull fiber materials, 111
Serialized ZXV-type pulp washers, 137–138
Shear stresses, 188–189
Shives, 138
Short fibers, 26–27
Shreyans Paper mill, 180–181
Silica, 38, 168–170, 213
  chemistry, 170–171
Silicates, 169–170
Silicic anhydride. *See* Silica
Silicon, 170
Silicon dioxide (SiO_2). *See* Silica
Silicon Interference, 108–110
Siloxy desilication process, 176
Sisal (*Agave sisalana*), 22–23, 69–71, 203–205
  SEM image, 70*f*
Smelt, 177, 179, 180*t*, 184
Soda
  liquor combustion, 179
  pulping process, 3, 114–118
  recovery, 178–181
  soda–oxygen pulping, 117
Sodium borohydride, 118–119
Sodium carbonate, 120–121
Sodium ferrite, 181
Sodium hydroxide, 118–119
Sodium sulfide, 118–119
Sodium sulfite, 120–121
Softwood, chemical composition of, 4, 4*t*
Soluble anthraquinone-1,4-dihydro-9,10-dihydroxyanthracene, 116–117
Solvents, 123
“Spanish” grade, 50–51
Specialty nonwoods, 8–9, 205
Specialty papers, 8–9
Specialty pulps, 205
Specific edge load (SEL), 192–193
Spermatophyta, 29–30
Spontaneous partial desilication of black liquor by storing, 172
Sporotrichum diorphosphorum, 193–194
Sporotrichum pulverulentum, 193–194
Spruce, 21–22
Steam explosion pulping (SEP), 131
Stiffness, 107–108, 189
Stipa tenacissima. *See* Esparto (*Stipa tenacissima*)
Straw, 22–23, 203–205, 217, 219–220
  morphology considerations, 15–16
  pulp, 119, 198
Strength properties of wet paper, 196–197
Sugarcane (*Saccharum officinarum*), 14, 37–40
Sulfite pulping, 120–122. *See also* Alkaline pulping
  alkaline–sulfite pulping process, 121–122
  neutral sulfite process, 120–121
Sulfonates, 120
Sunn hemp (*Crotalaria juncea*), 59–60
  SEM, 60*f*
Surfactant, 155
Swelling, 120, 130–131, 133, 148, 174–175, 191–192
Switchgrass (*Panicum virgatum* L.), 29–30

T

Taizen Co., Ltd., 132
Tall fescue (*Festuca arundinacea* Schr.), 29–30
TCF bleaching, 49–50, 149–150, 153, 155, 157, 159–160, 161*t*
Tear index, 38–39, 42–43, 100–101, 115*t*, 122*t*, 128*t*, 130*t*, 131*t*, 195–196
Tobacco stalks, 5
Tossa jute fiber, 58
Totally-chlorine free bleaching process (TCF bleaching process), 149–150, 159–160, 161*t*, 189–190
Transportation, 212
Trichoderma reesei, 156
  T. ressei Rut C-30, 157
“Tripoli” grade, 50–51
Triticum aestivum. *See* Wheat straw (*Triticum aestivum*)
Triticum dicoccum, 44–45
Triticum durum, 44–45
Triticum spp. *See* Wheat (*Triticum* spp.)
“True hemp”, 2–3, 203–204
Tunisian alfa, 5
Turbo-Pulper, 119

U

Unbleached pulp, 147–148

V

Vanadium pentoxide, 156
Vietnam, bamboo in, 22
Vine stems, 5
Voith Paper, 39

W

Wash presses, 136–138
Washing, screening, and purification of nonwood pulp, 135–138
Wet depithing, 87
  generation of pollutants in, 88*t*
  problems in, 87*t*

Wet paper
  adhesion properties, 197
  strength properties of, 196–197
Wet strength, 197, 197*t*
Wheat (*Triticum* spp.), 14
  stem cross section, 15*f*
Wheat straw (*Triticum aestivum*), 3, 5, 44–45, 88, 203–204
  pulps, 104, 195
  SEM images, 45*f*
Wood, 4
  environmental impact of wood fiber paper production, 20–21
Woody nonwoods, 21
Writing paper, 203–204

X

Xylanase, 156–157
Xylanase-treated pulps, 194
Xylem, 12

Y

Yucatan, 69

Z

Zea mays. *See* Corn stalks (*Zea mays*)
Zeta potential, 196

Nonwood Plant Fibers for Pulp and Paper

Pratima Bajpai

Nonwood Plant Fibers for Pulp and Paper examines the background in the use of nonwood plant fibers for pulp and paper; worldwide pulping capacity of nonwood fibers; categories of nonwood raw materials; problems associated with the utilization of nonwood fibers and how they are approached; pulping, bleaching, chemical recovery, and papermaking of nonwood raw materials; use of nonwood plant fibers in specific paper and paperboard grades; advantages and drawbacks of using nonwood fiber for papermaking and future prospects. This book provides 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 and paper making from nonwood.

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- Comprehensive coverage of all aspects of pulping and papermaking of nonwood fibers
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- Focuses on biotechnological methods, a distinguishing feature of this book and its main attraction
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About the Author

Dr. Pratima Bajpai is a renowned author of numerous books, research, patents, and products for the pulp and paper industry. She earned her Doctorate degree from National Sugar Institute in Kanpur, India. She currently serves as technical consultant on pulp and paper and has over 30 years of experience in research at the National Sugar Institute, University of Saskatchewan, the University of Western Ontario, in Canada, in addition to the Thapar Centre for Research and Industrial Development, in India. She also worked as a visiting professor at the University of Waterloo, Canada and a visiting researcher at Kyushu University, Fukuoka, Japan. She has more than 150 publications in international journals and conferences. She has written several advanced level books in the area of pulp and paper published by leading global publishers—Smithers PIRA, Smithers Rapra; Springer, United States, Europe, and Singapore; Miller Freeman, United States; John Wiley and Elsevier Science. She has also contributed to a number of chapters in books and encyclopedias, obtained 11 patents and has written numerous technical reports. She has collaborated in the implementation of numerous processes in pulp and paper mills both in India and globally and is the reviewer for many international journals.

ISBN 978-0-12-821800-6

9 780128 218006

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