Refiner Mechanical Pulping of Kenaf

by

Dinesh Chand Mohta

Faculty of Forestry

A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy at the Faculty of Forestry, University of Toronto

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I dedicate this thesis to my beloved parents for their affection, moral support, motivation, and numerous sacrifices to see their son to fulfill his ambition of graduating from a North American University.

I want to tell you that I should have not completed all this without your blessings.
I love you Mom and Dad.

* * *

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* * *

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Abstract

Kenaf (Hibiscus cannabinus), consisting of two fibrous components, long fiber bark and short fiber core, is being promoted because of its high fiber quality. The objective of this research is to analyze the fundamental aspects of kenaf refiner mechanical pulping (RMP) to provide scientific information on the behaviour of non-woods for newsprint production particularly in countries experiencing wood shortfall.

The data obtained from the refining of bark containing 22% core (bark22) at various consistencies and raw material soaking temperature indicate that the temperature had no effect on pulp properties except on the fibrization energy. Kenaf RMP properties indicate that the tear and burst indices are better than the kenaf thermomechanical pulp (TMP) as reported earlier. Bark22 RMP has shown better strength properties than black spruce RMP, while bark RMP is superior to black spruce TMP. Core refined separately provides a soft, bulky and poorly bonded sheet; thus core refining needs to be modified to enhance its papermaking properties. Strength and surface properties can be further improved if the percentage of unrefined core fibers and bundles are reduced considerably by modifying refiner plate pattern. Kenaf and bark22 pulps have shown high bleaching efficiency and can be bleached to the newsprint brightness level (around 65%) with small dosages of H₂O₂ and NaOH. The unique finding of this study is that the core fibers are protected when refined in the presence of bark fibers. It has also been observed that the fiber length is independent of refiner plate gaps.

Microscopic study indicates that the thick cell-walled bark fibers responded positively to bar actions to develop adequate papermaking properties. A relationship between fiber coarseness, and sheet density and stiffness provides a better understanding of wet fiber flexibility. It has been
demonstrated that the lignin removal pattern and fiber surface analysis by X-ray photoelectron spectrophotometer explains fiber development during refining in a better way.

This study clearly shows that newsprint with adequate strength and optical properties can be produced from kenaf RMP, while bark RMP can be used for value-added applications e.g. lightweight-coated grade, because of its having strong papermaking properties.
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I take this opportunity to thank my Co-supervisor Dr. P. Whiting for his valuable and constructive feedback on technical matters of the experimental work throughout the four years. His vast knowledge in the field of pulp and paper helped me immensely in the writing of this thesis. In addition to all this, I really enjoyed his friendly nature.

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# Glossary of Terms

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Explanation</th>
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<tr>
<td>ANOVA</td>
<td>analysis of variance</td>
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<tr>
<td>bark22</td>
<td>bark with 22% core</td>
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<tr>
<td>C-C/C-H</td>
<td>carbon-to- carbon/carbon-to-hydrogen bond</td>
</tr>
<tr>
<td>CPPA</td>
<td>Canadian Pulp and Paper Association</td>
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<td>CSF</td>
<td>Canadian standard freeness</td>
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<tr>
<td>CTMP</td>
<td>Chemithermomechanical pulp</td>
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<tr>
<td>CY.</td>
<td>Consistency</td>
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<tr>
<td>°C</td>
<td>degree Celsius</td>
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<tr>
<td>eV</td>
<td>Electron volt</td>
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<tr>
<td>FQA</td>
<td>fiber quality analyzer</td>
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<tr>
<td>G</td>
<td>gram</td>
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<tr>
<td>H₂O₂</td>
<td>hydrogen peroxide</td>
</tr>
<tr>
<td>Kenaf</td>
<td>whole kenaf (65% core and 35% bark)</td>
</tr>
<tr>
<td>KPa</td>
<td>kilo Pascal</td>
</tr>
<tr>
<td>kWh/t</td>
<td>kilowatt hour per metric ton</td>
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<tr>
<td>m</td>
<td>Meter</td>
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<tr>
<td>LWC</td>
<td>lightweight-coated</td>
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<tr>
<td>Mg</td>
<td>milligram</td>
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<tr>
<td>Mha</td>
<td>Million hectare</td>
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<tr>
<td>Ml</td>
<td>Milliliter</td>
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<td>mm</td>
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mN  milli-Newton
N   Newton
NaOH sodium hydroxide
O/C oxygen-carbon ratio
RBA relative bonded area
RMP refiner mechanical pulp
Rpm revolutions per minute
R² coefficient of relation
S seconds
 t t-statistic
TEA tensile energy absorption
TMP thermomechanical pulp
XPS X-ray photoelectron spectrophotometer
+48 Fraction fibers retained on the 48-mesh screen
- 48 Fraction fibers/fines passed through the 48-mesh screen
Pulp and Paper Terminology

This list of terminology has been taken from the "Handbook of Pulp and Paper Terminology—A guide to industrial and Technological Usage by G.A. Smook, Angus Wilde Publications, Vancouver, Canada (1990)". The list is intended to help non-pulp and paper readers to understand the content of the thesis clearly. It may not be possible to define all the jargons here in this thesis. However, if the reader needs more knowledge, he should read 'Handbook for Pulp and Paper Technologists' by the same writer besides the above mentioned book.

**Average Fiber Length**
Fundamental property or characteristic of papermaking pulps indicative of their suitability for different applications. The weight average fiber length is the relevant measurement of this property, as distinct from the numerical average fiber length.

**Bagasse**
Sugarcane residue after extraction of sugar, consisting of both fibrous and non-fibrous (pith) cells.

**Bast or Bark Fiber**
Fiber obtained from the inner bark (phloem) of woody plants.

**Cellulose**
\((C_6H_{10}O_5)\) material that forms the solid framework or cell walls of all plants; the most abundant organic compound in nature. It is a straight-chain (linear) polysaccharide composed of repeating glucose units, the number of which can vary over a wide range.

**Cell Wall**
Membrane that encloses the cell contents. In a mature cell, the cell wall is compound e.i. it consists of several layers.

**Collapsed Fiber**
Ribbon-like element formed when the cell wall collapses into the lumen.

**Conformability**
Ability of pulp fibers to be formed, matted and compressed into a uniform sheet.

**Consistency**
Mass or weight percentage of bone dry fiber in a stock.

**Defibration/Defiberization**
Separation of wood (or any other plant material) into fibers or fiber bundles by mechanical means, sometimes assisted by prior chemical action.

**Degree of Swelling**
Amount of water entering the cell wall, and hence a measure of water absorptivity and/or accessibility by aqueous reagents. It is also taken as an indication of fiber conformability.
External Fibrillation
Changes in the external structure of the fiber due to beating or refining, seen as the unraveling of microfibrils, which make the fiber surface look ‘hairy’.

Fiber Coarseness
Weight of fiber wall material per unit length of fibers, usually measured in mg per 100 m.

Fibril
Thread-like component of cell walls visible under an optical microscope. Fibrils are composed of more elementary morphological units called microfibrils, which are only visible under electron microscope.

Fibrillation
Refining action, which disrupts lateral bonds between adjacent microfibrillar layers of pulp fibers. “External fibrillation” refers to the loosening of fibrils and raising or partial detachment of microfibrils of the surface of fibers. “Internal fibrillation” refers to the less visible disruption of bonds within the fiber.

Fines
Very short fibers, fiber fragments, ray cells or debris from mechanical treatment. Typically all material that passes through the final 200-mesh screen is collectively referred as fines.

In this thesis, fines refer to -48 fraction of the Bauer-McNett classification.

Freeness
Measurement of pulp drainability, usually by means of the Canadian Standard Freeness (CSF) test. The CSF is defined as the number of ml of water collected from the side orifice of the standard tester when a dilute stack drains through a perforated plated under carefully controlled conditions.

Glass Transition
Change in an amorphous polymer from a hard, brittle condition to a visco-elastic or viscous condition. During mechanical pulping, if fibers are separated above the glass transition temperature for lignin, the fibers are easily separated at low energy consumption; but the fibers are then coated with soft lignin which reverts on cooling to the hard glassy state, a serious impediment to further fibrillation and development of the fibers.

Hemicellulose
Short-chain polysaccharides having a DP of 15 or less, mainly polymers of sugars other than glucose; any of the non-cellulosic cell-wall polysaccharides. Principal Hemicelluloses are xylans in hardwood and glucomannon in softwoods.

Internal Fibrillation
Loosening of the internal structure of the fiber due to beating or refining, which enables the fiber to swell and makes the fiber soft and flexible.

Intrinsic Fiber Strength
Usually refers to the tensile strength of individual pulp fibers.
**Kink Index**
Number of kinks along a fiber multiplied by the severity of the angle of kinking selected from four ranges.

**Latency**
Refers to the "unraveled" appearance of fresh refiner pulp. It is necessary to disintegrate the fibers in hot water to remove this latency. The term evolved from the fact that freeness decreases as latency is removed.

**Lignin**
Natural binding constituent of the cells of wood and plant stalks, a complex three-dimensional polymer of phenylpropane or propylbenzene structure.

**Long-fibered Fraction**
Term used for the quantitative characterization of mechanical pulps, usually referring to the percentage of fibers retained on the 16 and 28-mesh screens of the Bauer McNett fiber classifier. Sometimes, this designation also includes the fibers retained on the 48-mesh screen rejects, especially when the screen is operated as a fiber fractionation device.

In this thesis, fibers retained on 16, 28 and 48-mesh screen are referred as long-fibered fraction.

**Maceration**
Process of separating small pieces of wood into constituent cell elements for morphological study.

**Matrix**
Refers to intercellular substance. The wood matrix is made up of lignin, cellulose, hemicellulose and extractives.

**Mechanical Pulp**
Any pulp obtained from wood (or other plant material) principally by mechanical means, including stone groundwood, refiner mechanical pulp, thermomechanical pulp and chemimechanical pulps above 85% yield.

**Microfibril**
It is a threadlike component of the cell wall structure composed of cellulose polymer chains and associated polysaccharides united through crystalline regions (crystallites) and amorphous regions.

**Middle Lamella**
General term for the lignin-rich cementing layer between cell walls in plants, usually referring to the intercellular layer, but sometimes including the primary walls of adjacent cells and even the outer layers of the secondary wall. Compound middle lamella is sometimes applied to the compound layer or "intercellular matrix" between the secondary walls of contiguous cells.

**Morphology**
Refers to the study of form and structure of different raw materials.
Morphological Properties
Pulp properties or characteristics that are dependent on the form and structure of the fibers. Basic morphological properties include average fiber length, cell wall thickness, cross sectional area, fibril angle, fiber coarseness, and specific surface.

Non-wood Fibers
Usually referred to papermaking fibers from fibrous plants other than trees.

Parenchyma
Short, thin-walled cells having simple pits and functioning primarily in the metabolism and storage of plant food materials. They live longer than most cells, sometimes for many years. Two types of parenchyma cells are recognized: those in vertical strands known as axial parenchyma, and those in rays, called ray parenchyma.

Primary Wall
Outermost, very thin, highly lignified layer of the cell wall.

Post Color Value/Number
Change in the ratio of absorption coefficient to scattering coefficient for a sheet of paper upon aging under standard conditions. The Post Color number is related to the change in brightness before and after aging.

Refiner Mechanical Pulping (RMP)
Any mechanical pulping process in which chips or other wood subdivisions are refined into pulp at atmospheric pressure with no pretreatment.

Residual Chemical
Active bleaching chemical remaining in contact with pulp.

Shive Content
Percentage of o.d. pulp retained on a standard slotted fractionating plate, usually with slit width 0.15-mm.

Secondary Wall
Portion of the cell wall that contains most of the fiber substance, formed in three distinct layers characterized by different fibril alignments.

Softwood
Wood produced by coniferous trees, i.e. nonporous wood. The term has no reference to the actual hardness of the wood.

Swelling
Sorption of water by fiber to cause an increase in volume.

Specific Energy
Energy consumed per unit weight of pulp production, usually in units of kWh or mega joules per tonne of pulp.
Chapter 1

General Introduction

Forests play a vital role in the social, economical, and environmental development of any country. However, forests are declining at an alarming rate of 13.0 million hectare per year in developing countries (1). Rising population, better literacy, improving communication, and industrialization in developing countries are expected to increase the demand for paper and paperboards by 4.3% per annum as compared to 1.2% in developed countries (1). Moreover, the cost of delivered wood is increasing because of higher demand, more costly means of harvesting, and rising stumpage fees (2). New legislative regulations enacted in response to the demand of environmentalists in various countries are restricting the cutting of trees, which is expected to affect the supply of wood to the pulp and paper industry (3).

In preparation for an expected shortfall in the wood supply particularly in developing countries, the pulp and paper industry is exploring various alternative fiber sources. Foresters are vigorously striving to increase the supplies of wood raw material available for pulping through reforestation of cutover and understocked timberlands, improved efficiency of tree harvesting techniques, and greater utilization of wood manufacturing residue. Massive plantations of fast growing wood species (e.g. eucalyptus, poplar, radiata pine etc.) in various developing countries are expected to meet the growing demand (4).

Because of reduced forest area, increasing pulpwood costs, and an increasing demand for pulp and paper products, it might be expected that the focus would shift to more waste paper recycling, high yield pulping processes or the use of cellulosic non-wood raw materials. The use of waste paper is expected to gain momentum only in countries where softwood is the main source of papermaking. However, process problems, product quality, and cost effectiveness will still be great challenges in the recycling of waste paper.

On the other hand, non-wood fibers are available in good supply all over the world, but
are currently under-utilized. It is estimated that the substitution of 5-10% of wood pulp by non-wood pulp would have an important impact on the conservation of forests and the environment (5). Although there are problems such as raw material availability throughout the year, transportation, and storage associated with the use of non-woods, they may be solved over time with intensive research into these areas.

Recently, the focus of pulp and paper manufacturers has shifted to increasing the productivity of the process through technological advancement. Efforts are being made to increase the yield of pulping processes without affecting the quality of the end product. More attention is being given to increasing the use of mechanical pulp in papermaking. As per a recent FAO survey, mechanical pulp (refiner, and thermo-mechanical, chemi-mechanical pulp) is expected to increase by 9.0 per cent by the year 2000 with 1995 as the base year (6).

In general, non-woods have been used to manufacture mostly chemical or to some extent, chemi-mechanical pulps (1, 7, 8). Not much progress has been made in the production of mechanical pulps from the non-woods because of their morphological and anatomical characteristics particularly those from agricultural residues such as bagasse, wheat and rice straw. However, mechanical pulp from annual plants such as kenaf and hemp may be produced with properties comparable to those from softwood. This is because the average length and strength of fibers from these non-woods are better than hardwoods and are comparable to those of softwood tracheids (9).

In this project, out of the variety of non-woods available (e.g. bagasse, hemp, cornstalk, wheat straw, kenaf), kenaf was chosen as the raw material to work with because it is widely grown in tropical and subtropical regions and its high fiber quality. It is regarded as the most promising and suitable raw material for both developing and developed countries. Given the supply of wood, particularly in developing countries, it was decided to study kenaf for the production of mechanical pulp for newsprint. An extensive literature review revealed that few efforts have been made in the mechanical pulping of kenaf. The U.S. Department of Agriculture carried out preliminary research in the production of thermo-mechanical pulp and chemi-thermo-
mechanical pulp, but the pulp quality was inconsistent (10, 11). Hence, it was decided that the process of refiner mechanical pulping is optimized for whole kenaf and two of its fiber components: bark and core.

This thesis, based on the optimization studies for kenaf refining, has been structured in nine chapters. After this introductory chapter, Chapter 2 deals with the general health of forests all over the world, the availability of raw material to the pulp and paper industry, the use of non-woods including kenaf for pulp and paper manufacture, and the process of mechanical pulping including developments carried out to improve the quality of mechanical pulps. Chapter 3 provides details of the various objectives to be achieved over the time of this project. Chapter 4 describes the materials and methodology in achieving various objectives. In Chapters 5-7, detailed results of various experiments are examined and discussed with the support of currently published knowledge. Chapter 8 summarizes the findings of this project, while Chapter 9 discusses some shortcomings of the project and suggests future work, which could be useful in improving the process efficiency and the quality of the end product.

The whole project was targeted to optimize and understand the refining of kenaf and its components for newsprint production. It is expected that the use of kenaf will reduce the pulp and paper industries' dependence on forests for the fiber requirement. It is expected that the findings of this project will be useful for the pulp and paper industry as a whole and that the use of kenaf and mechanical pulping will be a step forward in enhancing the long-term sustainability of forests and the pulp and paper industry.

The background and use of various non-woods including kenaf for papermaking, a paper based on Chapter 2, has been published in the Forestry Chronicle (April 1999). Three papers from chapter 5, 6 and 8 have been presented at the 1999 Tappi Pulping conference, Orlando; 1999 CPPA conference, Montreal; and the 1999 ISWPC, Japan respectively. The paper, presented at the CPPA conference, has been published in the Pulp and Paper Canada magazine (August 2000). The papers presented at the ISWPC Conference and Tappi Pulping Conference are being reviewed by the Tappi journal.
Chapter 2

Background and Literature Review

2.1 Introduction

Declining forests and subsequent wood fiber supply constraints, combined with related environmental issues, have long restricted the growth of the pulp and paper industry. In the past, the industry faced concerns about the gaseous emissions of compounds of sulfur (12). More recently, the use of chlorine and its derivatives for bleaching pulp has been the subject of debate (13). Increasing public awareness and movements such as Greenpeace have encouraged the industry not only to buy new equipment for the treatment of effluent and stack emissions but also to invest in technological upgrading to make pulp and paper manufacturing processes more eco-friendly. Various environmental groups have especially targeted the industry over the use of clear-cutting logging practices (3). In the given scenario, increasing use of alternative raw materials for pulp and paper manufacture particularly in developing countries could be a remedial solution to the escalating demand for fibrous raw material.

2.2 State of the world’s forests

Forests have played a significant role in bringing about social, economical, and environmental development. In the recent past, however, excessive use of forests for industrial and social development has caused a sharp decline in the world’s forested area. Population growth and the associated demand for food and housing will put at risk up to 157 million hectares of forests by the year 2030 (14). Although in a global perspective the forest area is declining, the decline is more threatening in developing countries particularly in Africa and Latin America (Fig.1). Degradation of forests in developing countries is mainly attributed to poor management, as well as an increasing population, over harvesting of fuelwood, and grazing practices.
Overall, demand on the world’s forest resources has exceeded gains in supply, ultimately leading to loss of forested area. A strict monitoring of the balance between forest growth and removals from forests in view of the demand for wood for various uses is needed. This will help achieve greater sustainability, productivity, and survival of the forest. Long-term forestry policies and practices, reduced losses during the harvesting of wood, increased recycling of waste paper, higher yield of pulps, and more use of alternative cellulosic raw materials for various forest based products could be some of the possible solutions to achieving greater sustainable development of forests.

2.3 Status of availability of raw material to pulp and paper industry

Taking 1995 as the base year, world's pulping capacity is projected to increase by 9.2% by the year 2000 (6). The demand for pulp is expected to rise by 4.3% per annum in developing
countries as compared to that of 1.2% per annum in developed countries. On an average, paper consumption in developed countries is 150 kg/person compared to just 12 kg/person in developing countries (15). The per capita consumption of paper and paperboard is bound to rise as economic development continues in the developing countries.

The global consumption of wood has doubled since 1961 (16). It is expected that by year 2010, an additional 50-100 million hectares of forests will be needed to maintain the projected demand for wood in developing countries alone (16). On the basis of projected global pulp and paper requirements, the pulp and paper industry will need an additional 157 million metric tons of fiber, or a forest area of 11 million hectares per year, by 2010. Of the additional global fiber requirement, the virgin fiber fraction is estimated at 87 million metric tons (17).

It is evident that the supply of wood for the pulp and paper industry will be restricted in the future (2, 17, 18). Moreover, the cost of wood has increased over time because of the higher cost involved in growing it (19). Stumpage fees have multiplied in the last few years in almost every country (20). The question arises of how the increasing global demand for paper and paperboard at 2.0-3.0% can be met (1). A few possible solutions to this could be: (i) the establishment of plantations of rapid growing species to increase the productivity of existing land including improved forestry practices; (ii) technological innovations to improve the efficiency of wood use, including increasing pulp yield; (iii) enhancing the use of mechanical pulp; (iv) more recycling of wastepaper and paper boards; (v) increased use of cellulosic non-woods for paper-making; or (vi) reduced human consumption of nature's limited resources.

Recycling of wastepaper has considerably reduced the wood demand of paper mills in the last two decades (18). However, operating problems, product quality concerns, and reduced profitability has slowed growth in this sector. Moreover, the recycling of wastepaper will have smaller effects on wood harvests in Asia, South America, Africa, and Oceania. This is because paper and paperboard production in these regions is mainly from eucalyptus and non-wood fibers while the proven technology for recycling of such fibers is not yet available. However, in the
given scenario, the focus for pulp and papermaking has shifted to an increased use of non-woods and high yield pulping.

### 2.4 Pulp and paper industry and use of non-woods

Some non-woods were used before the means of using wood for papermaking were available (2, 21, 22). Non-woods are abundantly available all over the world and are the major source of fiber for papermaking in some developing countries, particularly China and India (6). Approximately 2.5 billion metric tons of non-wood raw material is available each year worldwide; however, most of this raw material is currently untapped for pulp and papermaking (2). Presently, the fraction of non-wood fiber in the manufacture of pulp and paper is 13%, a figure not reflecting the huge quantities of non-woods available around the world (6).

It is certain that wood is one of the best raw materials for papermaking. However, there is scope for 10-15% of wood pulp being replaced by non-wood pulp without affecting much of the strength, optical, and surface properties of paper. Recent developments in economical and efficient collection and transportation of non-woods have added a new dimension to the manufacture of pulp and paper from this source.

The annual yields of some non-woods are much higher than softwood and are comparable to the fast-growing hardwoods (23). The yield of kenaf per hectare per annum is three to five times higher than that of pine (24, 25) while the production cost is half the cost of pinewood (24). Agricultural residues, mainly involving collection and transportation costs, could be a useful source of papermaking even in developed countries where its incineration as a means of disposal is causing a threat to the environment.

Table 1 lists the physical and chemical properties of some non-woods in comparison to those of wood. The dimensions of non-wood fibers are between those of hardwoods and softwoods. The holocellulose content of most of the non-woods listed in Table 1 is comparable to that of the different woods, while lignin content is much lower than woods. Hence, it is expected that delignification of non-woods will be easy and consume less chemicals. Strength properties of
various pulps listed in Table 2 show that the pulp properties of non-woods are lower than those of softwood pulps, although they are comparable to those of hardwoods. A proper blend of non-wood plant fibers can produce most grades of paper and paperboards.

Higher bulk and silica content in some non-woods e.g. bamboo and straws fibers may create problems in processing. Non-wood pulps tend to be slow draining, which is a key reason that the runnability of non-wood pulps may affect papermaking productivity (21). Desilication technology has reduced the silica problem (36). The availability of non-woods on a seasonal basis requires a huge raw material inventory that is economically hard to justify. Cubing of the non-wood raw material has, to some extent, reduced the transportation and storage cost.

Non-woods such as bagasse, wheat and rice straws, bamboo, and kenaf are being used in the manufacture of pulp and paper all over the world (40). However, kenaf (*Hibiscus cannabinus*), a native to Africa and India, is being explored as a useful raw material for papermaking in developing and developed countries (25). Kenaf is mainly grown in USA, China, Australia, Japan, India, and Thailand (17).

### 2.5 Kenaf and its use in papermaking

Kenaf is a dicotyledonous annual plant, which grows to a height of 5-6 m on a 5-7 month growth cycle in suitable tropical and sub-tropical climates. Kenaf yield is 16-20 metric ton per hectare on an air-dry basis (17), which is much higher than that of wood. Moreover, it takes only 5-7 months to grow while eucalyptus, a fast growing tree species, takes approximately 7 years to grow to harvest size (41). Even in United States, the kenaf fiber cost at US $60 per metric ton is comparable to softwood fiber (42). Improvements in the growing, harvesting and mechanical separation of bark and core fibers have made kenaf available at a reasonable price (43).

Kenaf has found its main use in cordage. The bark fraction is used in making yarns (24). Lately, whole kenaf (core and bark fractions together) is being used for commercial papermaking
in Thailand and China (44). A kenaf newsprint plant with a capacity of 70,000 metric ton per annum in Texas is planned to become operational shortly (45).

The kenaf stem consists of two fiber components, different morphologically and chemically; however, both are suitable for producing paper and paperboards (9, 17, 46). The bark fibers are about 2.5-4.0 mm in length and slender, and constitute 35-40% by weight of the kenaf stem; the shorter core fibers, about 0.5-0.7 mm in length, constitute 60-65% by weight. The bark fiber has high quality papermaking properties that are similar to softwood fibers while the core fiber has strength properties similar to hardwood fiber (9). However, both the components of kenaf are different to that of wood fiber in chemical (26, 45), morphological, physical, and anatomical characteristics.

The separation of the two fiber fractions will provide more flexibility in using bark as a long fiber source for the countries where softwood or any other long fiber is not available. Bark and core fractions can be separated into a bark fiber of 94-95% purity by weight (47).

Early efforts initiated by United States Department of Agriculture (USDA) in the use of kenaf for papermaking (48) were concentrated on producing different chemical pulps (46-48). Later, attempts were made to produce thermo-mechanical pulp (TMP) (10, 11), and chemithermo-mechanical pulp (CTMP) (53) from whole kenaf. A range of chemical, semi-chemical, and mechanical pulps were separately produced from different components of kenaf by Australian researchers (53). Japanese workers also reported pulping results from whole kenaf grown in Japan; however, details are not available (53). Recently, anthraquinone pulping (9), oxygen delignification (54), delignification kinetics (27), and papermaking properties in relation to kenaf growing (55) were studied for whole kenaf and for bark and core fractions. Newsprint characteristics made from 100% kenaf chemi-thermomechanical pulp in a joint pilot trial by Voist-Alpine, Austria and C.E. Bauer, USA were comparable to the quality of newsprint made from softwood TMP (56). Commercial kenaf newsprint was produced at the Canadian International Paper (CIP) mill at Trois Rivieres, QC, Canada with the furnish of 82% kenaf
Table 1: Comparison of physical and chemical properties of non-wood fibers with that of wood raw materials.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Kenaf (26, 27)</th>
<th>Straw (28, 29)</th>
<th>Bagasse (27, 30)</th>
<th>Eucalyptus (31)</th>
<th>Bamboo (32)</th>
<th>Birch (33)</th>
<th>Spruce (34, 35)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fiber length, mm</td>
<td>1.3</td>
<td>1.3</td>
<td>1.7</td>
<td>1.0</td>
<td>2.3</td>
<td>1.9</td>
<td>3.6</td>
</tr>
<tr>
<td>Fiber diameter, μm</td>
<td>27.0</td>
<td>12.9</td>
<td>20.0</td>
<td>18.0</td>
<td>14.4</td>
<td>25.0</td>
<td>35.0</td>
</tr>
<tr>
<td>L/D ratio</td>
<td>49.0</td>
<td>102.0</td>
<td>85.0</td>
<td>51.0</td>
<td>161.0</td>
<td>58.0</td>
<td>101.0</td>
</tr>
<tr>
<td>Chemical properties</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Holocellulose, %</td>
<td>76.5</td>
<td>78.1</td>
<td>77.8</td>
<td>77.0</td>
<td>76.6</td>
<td>81.0</td>
<td>70.0</td>
</tr>
<tr>
<td>Hemicellulose, %</td>
<td>32.4</td>
<td>24.1</td>
<td>27.9</td>
<td>18.0</td>
<td>19.5</td>
<td>40.0</td>
<td>27.0</td>
</tr>
<tr>
<td>Lignin, %</td>
<td>16.2</td>
<td>18.4</td>
<td>20.8</td>
<td>26.0</td>
<td>25.6</td>
<td>19.0</td>
<td>29.0</td>
</tr>
</tbody>
</table>
* dimensions for whole kenaf from bark and core in the ratio of 35 and 65 respectively.

Table 2: Comparison of pulp properties of kenaf with that of other fibers.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Kenaf (37)</th>
<th>Straw (38)</th>
<th>Bagasse (38)</th>
<th>Eucalyptus (37)</th>
<th>Bamboo (37)</th>
<th>Birch (33)</th>
<th>Spruce (39)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSF, ml</td>
<td>300</td>
<td>257</td>
<td>282</td>
<td>300</td>
<td>300</td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>Bulk, cm³/g</td>
<td>1.5</td>
<td>1.4</td>
<td>1.5</td>
<td>1.4</td>
<td>1.5</td>
<td>1.3</td>
<td>1.4</td>
</tr>
<tr>
<td>Breaking length, Km.</td>
<td>6.8</td>
<td>6.5</td>
<td>4.9</td>
<td>7.0</td>
<td>6.4</td>
<td>12.5</td>
<td>14.9</td>
</tr>
<tr>
<td>Tear Index, mN.cm²/g</td>
<td>6.0</td>
<td>3.9</td>
<td>4.3</td>
<td>7.5</td>
<td>7.5</td>
<td>9.4</td>
<td>12.0</td>
</tr>
<tr>
<td>Burst Index, kPa.cm²/g</td>
<td>4.1</td>
<td>4.2</td>
<td>2.5</td>
<td>4.0</td>
<td>3.9</td>
<td>8.2</td>
<td>12.3</td>
</tr>
</tbody>
</table>

*Tensile index (N.m/g)=Breaking length (km)x9.80665.  
=Burst index (kPa.cm²/g)=Burst factorx0.0980665.  
=Tear index (mN.cm²/g)=Tear factorx0.0980665.
mechanical pulp and 18% spruce-balsam fir kraft pulp (57). Later, 72,000-copies of 'The Bakersfield Californian' were printed without any break and linting on the plates (57).

In earlier attempts at producing whole kenaf thermo-mechanical pulp (TMP), Bagby et al. (10) faced problems with the large number of fiber bundles and broken fibers appearing in the sheet and thus affecting the strength properties. However, the cause of the presence of fiber bundles and broken fibers appearing in the sheet was not analyzed. In this study, efforts have been made to produce refiner mechanical pulp (RMP) from whole kenaf (core and bark mixed in the ratio of 65 to 35). RMP was also produced from kenaf stem by cutting it into 25.4-mm size. This experiment has also examined whether the refining of separated bark and core mixed in the ratio of 65 to 35 will improve pulp properties.

2.6 Mechanical pulping

2.6.1 Refining of fibrous raw material

Mechanical pulping is a rapidly growing industrial process for the manufacture of variety of papers, particularly newsprint. Mechanical pulps are characterized by the quality of fibers and fines. In the production of mechanical pulp, chips fed into a refiner are broken down into randomly oriented matchstick-like particles with circulation in the refiner zone (58, 59). The fibers mostly located tangentially on the refiner bars move outwards (60, 61). If the fibers are shorter than the width of the grooves, they will tend to be in the grooves causing a considerable fractionation of the pulp (61). Fibers lying in the grooves are generally intact, but since they escape the refining action of the bars, they yield poor bonding abilities (61, 62). Researchers found that the fiber length and fiber bonding abilities are prerequisites for the good strength properties of mechanical pulps (62-64). Fiber length distribution is also an important factor in predicting the strength, optical and surface properties (65) of the mechanical pulps. It is necessary that mechanical pulps have suitable fiber and fines ratio (62, 66) for optimal pulp quality. However, the sheet properties are considerably dependent on the bonding abilities of fine ribbons and long fibers as well (62, 63, 66-68).
2.6.2 Breakdown mechanism of wood fiber matrix

Schematically, refiner mechanical pulping (RMP) and thermo-mechanical pulping (TMP) essentially consist of three phases: fiberization of chips/fiber bundles to convert them to intact single or broken fibers, the fibrillation of single or broken fibers to develop bonding ability, and finally the creation of fines (69).

Kano et al. (70) proposed a model as given below of the refining process involving four stages. The experimental results show that the breakdown constants, $k_1$ and $k_2$, had higher values as compared to $k_3$. It means that major portion of the energy input during refining is consumed in the refining of fibers (fibrillation) while a little is utilized in the fiberization of chips or fiber bundles.

Model for the refining of chips/fiber bundles; Phase I and II indicate the fiberization, while III and IV show the refining (fibrillation) of fibers. $x$, $y$, and $z$ are weight fractions; $k_1$, $k_2$, and $k_3$ are defined as the breakdown constants (70).

If the temperature is below the lignin glass transition temperature, the fracture during refining is expected to occur in the outermost layer i.e. $S_1$ layer (71), the weakest point of the secondary wall of the wood matrix (72). It may be the larger shear stress being created in the $S_1$ layer due to its having cross fibriller structure (73). Higher fiberization energy required by RMP as compared to TMP could be due to the thermal softening of hemicellulose and lignin during fiberization (70).
Koran (74) found that more broken fibers are created during RMP as compared to TMP. which may be due to the higher refining temperature during TMP. The higher temperature during TMP may also cause the loosening of S$_1$ layer, thus requiring less fiber fibrillation energy in comparison to RMP. In refiner mechanical pulping, brittle fracture through the fiber wall is a dominant reason for the wood failure, causing fiber shortening. The failure also occurs along the length of fiber in the outer wall (75).

Wood, subjected to rapid and repeated shear and compressive forces within the plates of a refiner, experiences a crack formation in the wood matrix by fatigue failure (58, 59, 61, 76). Viscoelastic deformations will raise the temperature of the raw material, while the plastic deformations will cause the bond failure and crack opening of raw material structure (77).

**2.6.3 Refining intensity and pulp quality**

Residence time of pulp determines the number of impacts experienced by a fiber in a chip refiner (78). At constant energy input, the average energy transferred at each impact is defined as the refining intensity (79). Controlling refining consistency and the rotational speed during refiner mechanical pulping can change refining intensity in a refiner. Miles et al. (80) reported that in multi stage refining, the refining intensity is independent of the refining stage because the nature of the material to be refined is different for each stage.

Various pulp properties including tensile strength, shives content, and fiber length are mainly dependent on the refining intensity and specific energy. Miles et al. (80) further reported that the refining intensity is independent of number of stages employed for a given specific energy. Fig. 2 shows that tensile index and scattering coefficient increase with an increase in refining intensity in the first stage TMP (80).

**2.6.4 Flow of fibers in a refiner**

Attack et al. (58) found that pulp, motivated by the centrifugal force, flows radially outward of a coarse and fine bar refiner along the groves of rotating plates besides a fraction of the pulp flowing across the stationary plates. Immobilized fibers, stapled tangentially across the
bars of stationary plates, experience shear and compression forces along their length, as the rotating plate passes over them. Similar shear and compression forces are also experienced by the fibers stapled on the bars of rotating plates.

![Graphs showing refining intensity and quality of pulp](image)

**Figure 2: Effect of refining intensity on the quality of pulp (80).**

Miles and May (78) reported that the nature of each impact experienced by the fibers during refining would depend on the number of impacts for a given specific energy. The number of impacts will depend on the residence time of fiber within the refiner. Thus, the residence time, which is dependent on the radial component of the velocity, will be an important factor in determining the quality of pulp. Using the same analysis, Miles and May developed an equation for the radial velocity of fibers in a chip refiner. The equation is as follows:

\[
\frac{dv}{dr} = \frac{\omega^2}{v} - a \frac{\mu_r}{\mu_u} E_c(r) + \frac{b}{2} C_r \rho_s(r) U(r)^2 A_p(r) \frac{c(r)}{v} \]

(1)

Where,

- \( \frac{dv}{dr} \) = Pulp acceleration
- \( r \) = Radius at a point in the refining zone
- \( \omega \) = Specified rotational speed
- \( v \) = Radial velocity of pulp at radius \( r \)
\( a = \) Constant, \( a = 4 \) for a single-disc refiner, 
\( a = 2 \) for a double disc refiner
\( \mu_l = \) Tangential friction coefficient
\( \mu_r = \) Average of \( \mu_{r1}, \mu_{r2} \), the radial coefficient of friction between pulp and the discs
\( E = \) Total applied specific energy
\( c = \) Pulp consistency at radius \( r \)
\( r_1, r_2 = \) Inner and outer radius of refining zone
\( b = \) Constant defining the radial direction of the flow of steam at any points (+1 for flow towards periphery, -1 if towards inlet)
\( C_f = \) Frictional drag coefficient of steam on pulp
\( \rho_s(r) = \) Density of steam at radius \( r \)
\( U(r) = \) Radial velocity of steam at radius \( r \)
\( A_p(r) = \) Aerodynamic specific surface of pulp at radius \( r \)

In developing this equation, Miles and May (78) assumed that the dilution water during refining remains in the network. The important finding of this analysis was that the coefficient of friction between the plates and the pulp was independent of the pulp consistency in a refiner. They simplified the equation by dropping the last term called ‘steam term’ and solved it for the velocity. Thus, equation 1 now reduces to:

\[
v = \frac{\mu_l \cdot r \cdot \omega \cdot (r_2^2 - r_1^2)}{\mu_r \cdot aEC}
\]

(2)

The same equation can be integrated further to calculate the residence time, \( \tau \) (79).

\[
\tau = \frac{\mu_r}{\mu_l} \cdot \frac{aEc}{\omega \cdot (r_2^2 - r_1^2)} \cdot \ln\left(\frac{r_2}{r_1}\right)
\]

(3)

The above equation has two operating parameters, the inlet consistency and the specific energy applied, while the design parameters included are the refiner speed, size and type of refiner, and the frictional coefficients. The equation is independent of parameters like throughput, plate gap, plate taper, and plate pattern.
2.6.5 Energy consumption during refining

Energy consumption is an important factor during mechanical pulping. Emphasis is always on reducing the specific energy consumption in refining without affecting the quality of pulp (82). Energy consumption will depend on various factors such as consistency, rotational speed, plate gap, plate pattern, type of refiner, and morphological characteristics of the raw material. High-density fibers i.e. fibers with thick cell walls require a greater input of energy to bring about a reasonable fiber collapse (83).

As the energy input is increased during refining, the pulp CSF decreases while sheet density, strength and optical properties will increase (76). This increase may be attributed to an increase in fiber flexibility as well as quality of fines generated during refining. It may also be due to reduction in the mean fiber length. The continuous input of energy will expose the S2 layer of the fibers (66, 67, 84). Cort (82) found that specific refining energy is independent of refining consistency. He concluded that at low speed, using higher consistency can save 10-15% energy.

Researchers (86, 87) have pointed out that a significant portion of the applied energy is converted to heat due to the Viscoelastic deformations of the raw material during refining.

2.6.6 Effect of fiber morphology on the quality of mechanical pulp

Various researchers (88-90) studied the effect of wood density but were unable to correlate it to the pulp properties. Morphological parameters play an important role in determining the mechanical pulp quality and specific energy consumption. In general, low-density wood is preferred in the production of a mechanical pulp having good quality (91). However within a tree species, high-density wood, late wood, is preferred over the low-density wood, early wood (92, 93). The fiber conformability, an important factor influencing the bonding abilities is dependent on the cross sectional dimensions including wall thickness (94). Mohlin (94) and Karnis (95) mentioned that the bonding abilities will also depend on the flexibility of the
fibers, which could be brought about by the internal delamination or the microcracks in the fiber wall. The behavior of the wall structure during mechanical stresses of refining will be greatly influenced by the nature of the fibriller orientation (96).

Pearson (97) reported that the thinner cell walled fibers (low density) will produce a pulp of superior quality than that of thick cell walled fibers (high density). However, Corson (92) found it otherwise for the mechanical pulps manufactured from the corewood and slabwood from radiata pine. Mechanical pulp from slabwood produced sheets with higher density and tensile strength as compared to that of corewood. He concluded that this could be due to the fact that the slabwood mechanical pulp had superior quality and higher quantity of the fibriller fines. This is in agreement with the findings of Montmorency (88) who mentioned that spruce wood density in the range of 300-500 kg/m$^3$ did not show any effect on the quality of mechanical pulping potential of spruce.

Corson (98) has argued that the fiber network developed within a sheet from a particular pulp is dependent on the morphological characteristics of the raw material it has been prepared from. Fiber length will influence fiber packing. Fiber compliance or flexibility will be affected by the fiber diameter. He further reported that fiber length is of prime importance in controlling the pulp quality as compared to the basic wood density.

2.6.7 Effect of refining consistency on mechanical pulps

Miles and May (78) concluded if refiner speed is maintained the same, with an increase in the pulp consistency, the pulp residence time will increase. Thus, the energy per impact will decrease as the number of bar impacts on each fiber increases. This is expected to increase the fiber length but decrease fines content. Pulp freeness and bulk increase, while the scattering coefficient will decrease. Cort (85) found that refiner speed has a more pronounced effect on the residence time than the refining consistency (Table 3). He indicated that at higher speed such as 1,800 rpm, the effect of consistency is negligible.
Table 3: Effect of speed and consistency on the residence time of pulp in a pulp refiner (85).

<table>
<thead>
<tr>
<th>Series #</th>
<th>Rotational Speed, rpm</th>
<th>Refining consistency, %</th>
<th>Residence time, s</th>
<th>Energy per impact x 10^2 (KWh)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.200</td>
<td>22</td>
<td>1.23</td>
<td>44.9</td>
</tr>
<tr>
<td>2</td>
<td>1.200</td>
<td>30</td>
<td>1.68</td>
<td>36.0</td>
</tr>
<tr>
<td>3</td>
<td>1.800</td>
<td>22</td>
<td>0.22</td>
<td>118.3</td>
</tr>
<tr>
<td>4</td>
<td>1.800</td>
<td>30</td>
<td>0.30</td>
<td>83.4</td>
</tr>
</tbody>
</table>

2.6.8 Effect of throughput on the pulp quality

Since E, motor load/throughput, appearing in equations 1, 2, and 3, is dependent on the throughput and motor load, throughput should have an effect on the operation of the refiner. An increase in throughput will increase the motor load, thus maintaining the same residence time. Therefore, Miles and May (78) predicted that change in throughput would not have any effect on the residence time of the pulp if the refining consistency and specific energy are constant. Thus there may not be any change in the pulp quality. But the literature reveals that throughput affected pulp quality which may be due to a change in the residence time (99, 100).

2.6.9 Effect of refiner speed, size, and plate pattern

The rotational speed is an important factor in controlling refining intensity (78). It can be seen from equation 2 that an increase in rotational speed will decrease the residence time of fibers in the refiner if refiner size, plate pattern, refining consistency, and specific energy are kept the same. Thus the number of bar impacts will decrease; however, energy per impact i.e. the refining intensity will be increased. Hence, the rotational speed has a considerable effect on the pulp quality.

The energy consumption is mainly reduced by increasing the rotational speed; however, some pulp properties will be affected (80, 82 101-105). The use of a double disc refiner instead of a single disc refiner will also have a considerable effect in reducing the energy consumption while maintaining pulp quality (105). Single disc refiners can be operated at an efficiency of a double disc refiner by increasing the rotational speed.
Miles and May (78) mentioned that the plate pattern with higher bar density will have higher impacts on the fibers as compared to the plate pattern with lower bar density, provided the inlet consistency and refiner speed are maintained the same. The pulp/fiber radial velocity equation may not have any term for the plate pattern, but it will have an effect on the pulp quality. Pearson (106) showed that almost 10% of energy required can be reduced by the removal of dams from the refining plates without affecting the quality of pulp.

2.6.10 Quality of fiber/fines in mechanical pulps

The quality of mechanical pulps for various grades of writing and printing papers is mainly due to the unique characteristics of their fines which influence the strength, optical, and surface properties of a sheet (107).

The fines generated from wood during mechanical pulping are heterogeneous in nature and typically contain fiber wall fragments, fibrillar material, and ray cells (76). Fines are generated from the peeling of fiber surface from the lignin rich middle lamella to mostly cellulosic secondary walls (108-110). With the peeling of compound middle lamella (middle lamella and primary wall) in the defibration stage, secondary walls are exposed with increased specific energy consumption in the fiber developmental stage; thus fibrillar material starts appearing in the fines (76, 109, 111). The fibrillar content continues to increase with an increase in refining and hence their bonding abilities also increase (112, 113).

Corson (76) asserted that fines generated during refining fill the void spaces within the fiber network and improve the printing characteristics of the mechanical pulps. It is important that the papermaking qualities are developed for the fiber and fines while achieving an optimum fiber length distribution and fiber-fine ratio. However, this would depend on the raw material quality, process, and the design parameters.

The researchers (63, 114) observed that with an additional refining of intact fibers generated during fiberization, good quality fines will be created as a result of the unraveling of the $S_2$ wall of the ‘intact’ fibers. Moreover, a portion of the fines will originate from the removal
of primary and S₁ fiber walls. Fines with high bonding abilities are mainly created from long slender fibers (69). Additional refining will cause considerable fiber development through internal and external fibrillation that assists in improving the bonding abilities (76, 115). Controlling the fines content of mechanical pulp can optimize desired strength and optical properties (116).

Numerous studies were carried out to determine the role of fines on various paper properties (66, 117). The nature and morphological characteristics of the raw material (62, 67, 108, 118-120) govern the structural role of fines. Depending on the grade, fines content of a mechanical pulp varies from 25-50% (118).

Silveira et al. (121) proposed that fines fill up the interstices and bridges the gaps in paper structure. The fines adhere to the fiber surface and form a sort of coating on it (76). These fines thus assist in bonding and improve the fiber compaction in a sheet and the surface properties. Karnis (122) described fines as not only improving the bonding of long fibers but also behaving as fibers. These fines will also tend to increase the scattering coefficient because of their large surface area. However, ribbon-like fines enhance the contact between the fibers and thus the bonding but not the scattering coefficient. This could be due to the fact that in adhering to the fibers the advantage of large specific surface may be lost (121).

Miles et al. (123) indicated that fines generation during refining is proportional to the applied energy, but it does not depend on the nature of raw material. On the other hand, Stationwala et al. (110) stated that the quantity and quality of the fines generated at a particular specific refining energy would depend on the wood species. The quantity and quality of fines significantly affect apparent density, scattering coefficient, and drainage properties. Refining produces long and slender fibers (110).

The low intensity refining produces less fibriller material at a given refining energy (117). With continuous increase in refining energy, the average particle length of the fines
content of mechanical pulps also increases because of more peeling of material from the fiber surface. At low refining energy, fibrils seem to be originating from the primary walls. The same can be confirmed from the lignin rich fines (+100 and +200 fractions) that are generated from the peeling of compound middle lamella, which has approximately 85% lignin concentration (109). However with more energy input, fibrils are expected to originate from S₁ and S₂ walls as the specific energy is increased (76, 109).

2.6.11 Strength, optical, and surface properties of mechanical pulps

The focus in producing mechanical pulps is on improving surface, optical, and strength properties while minimizing the specific energy consumption (124). Lee (125) concluded that fiber coarseness, a measure of fiber stiffness, is proportional to the tear strength but negatively related to the tensile strength. Hence, it is necessary that fiber coarseness be reduced to an optimum level during refining to maximize tear and tensile strength of the pulps.

As per Page’s (126) equation, the tensile strength of a sheet is dependent on the fiber strength and the number and strength of fiber bonds. The fiber strength, however, is dependent on the fibril angle (127). Shallhorn and Karnis proposed (128) that the tensile strength of paper is the sum of the tensile strength due to fiber pull out and breakage.

The tear strength is the sum of measures of the energy required in propagating an initial cut given to a sheet through to a standard length. As the fiber bonding increases, the pull out becomes more difficult, and the fiber breakage dominates. Page (129) proposed that the tear strength of a sheet be mainly due to fiber breakage. Page et al. (130) concluded that tear and tensile strengths of softwoods were inversely related under certain conditions.

Corson (67) showed that tear index is a result of increased fiber length. However, tensile index and elongation are independent of fiber length. Increase in longer fibers will reduce the
reduction of fibers in the web, dry sheet density, and scattering coefficient. He further mentioned that stiff fibers not fibrillated properly will appear in the sheet and cause a break at that point, thus reducing the strength properties of paper. Therefore, it is necessary that the mean fiber length be maintained to enhance wet web and tear index.

The fines content of a mechanical pulp contributes to the bonding of fibers by bridging the gap between the network of long fibers. The improved bonding will enhance the strength properties of the paper. Karnis (122) pointed out that fines in mechanical pulp form stronger bonds as compared to fibers.

The wood density is argued to be inversely proportional to the sheet density and inter-fiber bonding (131). The sheet density may also be improved if a reduction in mean fiber length is brought about by refining. However, sheet density is realistically dependent upon the “synergistic contribution” made by the pulps fines content which will assist the consolidation of fiber network and thus improve the sheet density. The sheet density is also improved by the presence of fines, which enhance fiber-to-fiber interaction (98). Stiffness of fibers is related to the sheet density and surface properties. Karnis (132) reported that an improvement in fiber flexibility would increase the sheet density and surface properties as well.

The specific surface of fines and fibers of the pulp will influence the optical properties of pulps (118). Fines content significantly contributes to the light scattering coefficient and absorption coefficient of sheets. Mohlin (118) showed that light scattering coefficient and sheet density are linearly related. She further noted that light absorption coefficient, proportional to the amount of chromophores present in the pulp, increases with an increase in white water recycling. In another study, she (133) showed that half of the light scattering coefficient is contributed by the presence of fines (+200 mesh).

2.7 Understanding fiber development by surface analysis using X-ray photoelectron spectrophotometer

The fiber development is an important step in the refining. The fiber development can be understood by evaluating pulps for various strength, optical, and surface properties or analyzing the fibers microscopically. However, strength, optical or surface properties do not provide much fundamental knowledge about the peeling of fiber surfaces, while microscopic studies involve
only very few fibers. It is anticipated that the use of X-ray photoelectron Spectrophotometer (XPS), which characterizes a large sample can be useful in understanding fiber development during refining.

XPS developed by Siegbahn and coworkers (134) is used in the chemical analysis of surfaces. Electrons are ejected from atoms or molecules following the bombardment by monochromatic photons. The surface composition, the chemical states (bonding and oxidation), and the location of types of atoms can be determined with the detection and subsequent analysis of the ejected electrons. The technique has been very successful in analyzing the surface composition of polymer substances (135).

Dorris and Gray (136, 137) used XPS in examining the surfaces of cellulose and lignin, different pulps such as kraft, stone ground wood (SGW), TMP, and RMP, and papers such as Whatman filter. Electron spectrophotometer for chemical analysis (ESCA), similar to that of XPS, application was used by Hon (138) in studying the surface of wood, lignin, and cellulose. Barry (139) used XPS application in studying the surfaces of treated Chemi-thermomechanical pulps (CTMP).

The above literature (136-139) reveals that wood or wood fiber contains three C₁₄ peaks i.e. C₁ at approximately 285.0 eV, C₂ at 286.5 eV, and C₃ at 288.0 eV, and a single O₁₄ peak at 533.0 eV. The C₁ peaks represent the carbon atoms bonded only to carbon and/or hydrogen (C-C and/or C-H), C₂ is linked to carbon atoms bonded to a single non-ketonic oxygen atom (C-O-), while C₃ corresponds to carbon atoms bonded to a ketonic, non carbonyl oxygen (C=O) or two non-ketonic oxygen atoms (O-C-O). The presence of C₄ has also been reported at 289.5 eV which has been assigned to the carbon atoms attached to a carbonyl (O-C=O) or non-carbonyl group (140).

The C-H and C-C bonds are dominant in the lignin and extractives, C-O bonds are attributed to primary and secondary alcohol groups in lignin, cellulose, hemicellulose, and extractives, while C=O and/or O-C-O are linked to lignins and extractives. The atomic ratio of
Oxygen-to-carbon (O/C) in wood cellulose based on the general formula \((\text{C}_6\text{H}_{10}\text{O}_5)_n\) has been reported to be 0.83 while for lignin it is 0.33 (135, 137). \(\text{C}_1:\text{C}_2:\text{C}_3\) ratios for cellulose and lignin have been reported as 0.00:0.83:0.17 (136) and 0.49:0.48:0.03 (138) respectively.

2.8 Conclusion

From the literature review, it is clear that there is an imbalance of forests all over the world. Developing countries have exploited their forests heavily for fuel, building and agricultural land, and whatever is left is in poor shape. However, forests in the developed world are by and large well managed, but may not meet the global demand particularly when the environmentalists are actively arguing for a restricted use of forests. In the given scenario, the use of alternative fibrous raw material and technological advancements become imminent. The pulp and paper industry would need to enhance the use of non-woods and mechanical pulps for papermaking to meet the global pulp and paper demand. Attempts have been made to conceptualize the process of the softwood refining. However, no progress has been made in optimizing the refining process for non-woods, which are mainly used for chemical pulping, because of their fiber characteristics. Kenaf could be a potential fibrous raw material because of its fiber quality, which could provide a good quality mechanical pulp for newsprint manufacture.
Chapter 3

Objectives and Rationale of the Study

The literature review reveals that optimization studies for mechanical pulp production were directed towards wood. The conceptual models have been developed for various species of softwoods including black spruce and jack pine (80, 96, 98, 117). On the other hand, non-woods, mainly used in the commercial production of chemical pulp (1, 22), and semichemical pulps, have, so far, remained practically untouched as far as mechanical pulping research is concerned. In fact, mechanical pulping of non-woods is a challenge because of their having morphological (fiber length, parenchyma cells, and vessels) and anatomical characteristics different from wood. Appropriate structural properties of the fibers are necessary for them to withstand the severity of shear and the compressive forces of refining required to develop good papermaking properties. Recently, bagasse has been used in the commercial production of newsprint grade chemi-mechanical pulp (141). The literature review reveals that considerable efforts have been made to optimize the process of mechanical and chemi-mechanical pulps from kenaf (10, 11, 142, 143). Apparently it can be seen that kenaf has the potential of producing mechanical pulp because of its having high quality fiber.

The whole kenaf TMP produced at USDA by Bagby and co-workers (10) had a large number of fiber bundles and broken fibers giving lower strength properties. However, in this work no comment was made on the optical properties of TMP from whole kenaf. In the evaluation of kenaf TMP by Touzinski and coworkers (11), no reason was given for the large amount of fiber bundles and lower strength properties, which could be due to the under-refining of kenaf. The higher amount of broken fibers could be due to the stiffer kenaf fiber that is expected to induce increased fiber breakage under the shear and compressive forces during refining. The presence of fiber bundles in handsheets are expected to cause a failure at that point.
under the tensile forces giving low tensile/burst strength. The quality of fiber and fines must be another reason for the lower strength properties; therefore, the refining process needs to be optimized to improve kenaf pulp quality. A detailed study of the morphological, physical and chemical characteristics of kenaf fiber (bark and core part) would provide important input to optimize the refining process for a better quality pulp from kenaf. The fundamental study of the fiber would be vital in selecting the process parameters.

Keeping in view the problems faced by Bagby (10) and Touzinski (11), in the refining of kenaf, and the demand of the pulp and paper industry, particularly in developing countries, for a raw material, which could produce newsprint from non-woods, this study is intended to optimize the process of refiner mechanical pulp (RMP) from kenaf, which has not been studied so far.

Refining was carried out mainly for two different proportions of core and bark. In the refining of whole kenaf, core content was approximately 65%, while in a second experiment, bark was refined in presence of approximately 22% core. In this study, the effect of low-density core fibers in the presence of high-density bark fibers is analyzed with respect to the quality of pulp.

Fibers with thick secondary walls may be able to preserve their length better, but may require raw material soaking in water at an elevated temperature to loosen the bonds between lamellae (116). To observe the effect of pre-swelling in refining, kenaf was soaked for four hours at different temperatures. It is expected that the swelling of kenaf fiber would make it more flexible, loosening the cell to cell bonding and facilitating the intact separation of fiber from the core/bark fiber matrix. Moreover increased swelling of fiber would help develop the specific surface area of kenaf fiber during refining which would contribute to higher strength properties. The swelling of the fiber is also expected to require less energy during refining.

Bark and core fibers have strength properties similar to those of softwood and hardwood respectively. However, the morphological, anatomical, and chemical properties of kenaf fibers are different to those of wood fibers. Therefore, an important question is whether the bark and core fibers behave similarly from those of softwood and hardwood during refining.

During the refining of kenaf which consists of core, low density thin walled fibers, and
bark, high density thick walled fibers, emphasis is placed on optimizing a conceptual model for the simultaneous and separate refining of two different fibers. This study provides details on how two fibers, core and bark, will behave when refined separately and simultaneously. Kenaf bark lignin, having a simple structure (144) compared to wood lignin, may have a lower glass transition temperature. Therefore, it is expected that the fiberization energy for the whole kenaf and bark will be different to that of wood during RMP. Moreover, since bark has a 'strand' type structure, the fracture in the fiber matrix could be difficult to bring about as compared to wood or core chips, thus affecting the specific refining energy requirement.

The stiffness of bark fibers will be higher because of their having thick cell walls, hence their collapsibility is expected to affect the bonding properties. Therefore, increased refining will be needed to reduce the coarseness of these fibers to make the fibers appropriately flexible. On the other hand, core fibers having large lumen diameter and thin cell walls will be more flexible and collapse readily to give higher bonding abilities. However, a stronger secondary wall will ensure greater external fibrillation and preserve their length better than thin cell walled fibers (63, 116-118, 145). However, higher microfibril angle of fibers may induce higher fiber cutting during refining (69). Hattula and coworkers (146) indicated that the flexibility of thin-walled fibers in chemical pulps has been found higher than the flexibility of intact, uncollapsed tracheids.

It may be expected that the core fibers should require less energy during refining to give reasonably good pulp quality. Conceptually, thin walled core fibers will flex easily and, therefore, will undergo less fiber length reduction as compared to the thick walled bark fibers during refining (76, 98). Thus it can be expected that the core fibers will require less specific refining energy. The objective during refining is to maintain the fiber length while maximizing the specific surface area. Hence, more core fibers will be beneficial as it will help to preserve the fiber length when RMP is produced from whole kenaf. Easy compliance of refined thin walled fibers such as from core will increase fiber-fiber interaction and therefore, the bonding. Thus, more fiber plies can be expected in the fiber network giving higher sheet density (76). The presence of refined long bark fibers in the sheet will improve fiber networking and thus the tear
strength of the sheet. However, bark fibers having thick cell walls will require extensive refining and thus a higher amount of specific energy to reduce the coarseness. Reduced coarseness will enhance fiber flexibility, thus their compliance for improved bonding. Mohlin (94) expected that the collapsibility of thin walled fibers would be easy; thus the bonding ability of these fibers will be higher than those of thick walled fibers (94). However, she expected that the unraveling in the outer layers would be dominant in the thick cell walled fibers compared to the thin walled fibers. However, Corson (76) revealed that at the same freeness value, the specific energy requirement of thin walled core fibers was the same as that of thick walled fibers. Moreover, the sheet density of thin walled fibers was less than that from the thick walled fibers.

The quality of any mechanical pulp is dependent on the relative properties of the raw material it is being manufactured from (92, 94, 99). Pulp properties will depend on the interaction of long, medium, and short fibers. It would be interesting to analyze the effect of bark and core fractions from kenaf fibers with respect to fines and fiber quality.

In mechanical pulps, primary walls with a high share of lignin may restrict swelling and thus external fibrillation will be a prerequisite for internal fibrillation (147). Because kenaf has a low lignin content (144), it would be interesting to analyze the fibrillation of kenaf fiber during refining in relation to the removal of lignin from the fiber surface. Moreover, a comparison between the behavior of the core and bark part would be emphasized as the core has a higher lignin content than the bark.

Since design parameters such as plate pattern and refiner speed are beyond the scope of this study, the focus will be on optimizing the process variables. Four process variables—temperature (45-85 °C) of soaking of kenaf in water, consistency of refining (10-20%), residence time, and refining intensity were. The residence time at constant rotational speed and refining consistency was controlled by plate gap. The pulp was produced from core, bark, and whole kenaf using the Sprout-Bauer pilot refiner at Abitibi-Consolidated Inc. The pulp quality control variables evaluated were freeness (Canadian standard freeness), fiber and fine ratio (Bauer-
McNott classification) and shives content. The kenaf was to be refined to a targeted pre-screened pulp freeness of 100-150 ml. giving an initial understanding of development of fiber and generation of fine content. The shives content was minimized for improvement of the economics of the process: reduced shives content ensures an optimized use of energy.

Based on the mechanism of refining mechanical pulping, the effect of different process variables, and the morphological, physical and chemical characteristics of fiber on the quality of pulp, this study had the following objectives:

1. To develop a theoretical predictive model for improving the pulp property of non-wood fibers during refining;
2. To optimize the process parameters of refiner mechanical pulping for whole kenaf and its components bark and core;
3. To examine the effect of physical, chemical and morphological properties of kenaf on the quality of refiner mechanical pulp;
4. To understand fiber development during refining of core and bark refined separately and simultaneously;
5. To study the role of lignin removal in the kenaf fiber development during refining.
Chapter 4

Materials and Methodology

4.1 Raw material preparation

The crushed whole kenaf (bark and core), bark containing 20-30% core, and kenaf stems with more than 85-90% dryness content were received from Mississippi State University. The raw materials were kept in a cold storage at 4°C. The kenaf contained 4-5% soil, stones, and other extraneous matter. The crushed whole kenaf and bark with 20-30% core were screened on a vibratory screen to remove foreign matter and to separate core and the bark. However, approximately 20 to 22% core still entangled with the separated bark was removed manually for bark refining, but the bark still contained 1-2% core. The larger bark pieces were cut by scissors into 25 to 38 mm sizes. After cutting bark, screening was done manually on a 4.7-mm mesh screen to remove any fiber smaller than 15.0 mm. Finally; all remaining longer bark pieces were sorted out by inspection. Main experiments were carried out for bark containing 22% core (mentioned as bark22 henceforth).

Core, which contained approximately 7 to 8% bark fibers after screening, was re-screened manually to remove bark. Core after screening still contained 1 to 2% bark which was difficult to remove.

Whole kenaf core (referred to as kenaf hereafter) for refining experiments represented a mixture of bark and in 35±1 and 65±1 ratio. Kenaf stems (referred to as stem henceforth) having approximately the same core and bark ratio as in whole kenaf were cut into 25.4-mm long pieces by a guillotine cutter. The reason for pulping stem and kenaf with the same ratio of core and bark was to analyze if the separated core and bark will produce better mechanical pulp and save refining energy. Stems with a diameter more than 20 mm were either discarded or crushed prior to refining. Before soaking various raw materials for refining, kenaf, stems, bark, bark22, and core were washed with warm water to remove any residual soil.
4.2 Refiner mechanical pulping

4.2.1 Refining of whole kenaf, bark, and core

The refiner mechanical pulp (RMP) from different raw materials was prepared in a 300 mm single disc Sprout-Bauer (Model 12 LAB) open discharge laboratory refiner equipped with a type C 2976A plate pattern (Fig. 3) at the then Research and Development Center of Abitibi-Consolidated in Mississauga, ON, Canada. The refiner was operated by a three-phase 575-Volt motor of 55 kW at a speed of 1777 rpm.

Since the refiner available for the refining of kenaf could be operated only at a single speed (1800-rpm), the refining intensity was varied by changing inlet pulp consistency and plate gap while keeping refiner speed and plate pattern the same. The change in consistency and plate gap brought about the change in the residence time of fiber in the refiner and, thus the number of impacts experienced by each fiber. At low consistency, the residence time was reduced substantially, as was the number of bar impacts. Hence, the energy per impact increased, and the cutting of fiber might be expected to be higher.

Table 4 gives the maximum and minimum temperature and consistency for which an experimental design carried out on the SG Plus Statistical Software gave 11 different combinations (Table 5) of soaking temperature and refining consistency. However, the first pass was carried out at 35±1-% consistency for all the experiments. For all the raw materials, refining was carried out in several passes so as to get a CSF between 100-150 ml. For each pass, plate gap was reduced gently and maintained as given in Table 6. Optimization studies were carried out for the kenaf and bark.

No dilution water was introduced in the refiner during the processing of raw materials. After each pass, refined material was scraped off the refiner and the discharge chute, and weighed. Assuming that the o.d. fiber weight remained the same, any loss in weight was made up with the addition of water. For each raw material, feed rate was maintained at 600 g/min for all the passes and each refining consistency.
Figure 4: Plate pattern as used in the refining of whole kenaf is embedded with almost 2/3\textsuperscript{rd} coarser and medium zones.

Table 4: variables to be controlled for the optimization of refining of kenaf and bark22

<table>
<thead>
<tr>
<th>Variables</th>
<th>Minimum</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Consistency, %</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>Temperature, °C</td>
<td>45</td>
<td>85</td>
</tr>
</tbody>
</table>

Table 5: Experimental design for the optimization of the refining of bark22.

<table>
<thead>
<tr>
<th>Run/Variable</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>Consistency, %</td>
<td>15</td>
<td>15</td>
<td>8</td>
<td>15</td>
<td>20</td>
<td>15</td>
<td>10</td>
<td>20</td>
<td>10</td>
<td>22</td>
<td>15</td>
</tr>
<tr>
<td>Temperature, °C</td>
<td>65</td>
<td>93</td>
<td>65</td>
<td>37</td>
<td>85</td>
<td>65</td>
<td>45</td>
<td>45</td>
<td>85</td>
<td>65</td>
<td>65</td>
</tr>
</tbody>
</table>

Table 6: Plate settings for each pass of refining at 15\% and 22\% consistency

<table>
<thead>
<tr>
<th>Pass</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plate gap, mm</td>
<td>1.52</td>
<td>1.27</td>
<td>1.02</td>
<td>0.76</td>
<td>0.51</td>
<td>0.38</td>
<td>0.254</td>
<td>0.127</td>
</tr>
</tbody>
</table>
After optimization studies for soaking temperature and refining consistency, refining was further carried out for kenaf, bark 22, bark, stems, and core soaked in water at 35°C for 4 hours in sealed plastic bags. The refining was carried out at two different consistencies of 15 and 22% for each raw material. The first pass was carried out at 35\pm 1\% consistency (since it was difficult to maintain the required consistency for the first pass) for all the raw materials, as it was difficult to maintain consistency at 15\% or 22\%. Remaining passes was carried at 15\% or 22\% consistency as the case it was. Plate gap for each pass was maintained as given in Table 6. All the passes were carried out on the same refiner using same refiner plates.

4.2.2 Specific energy consumption in the refining

Power consumption was recorded for each refining stage by using a Power Hi Tester wattmeter. The running time of the refiner was recorded through a stopwatch which was started at the same time as the refiner. For each stage, the raw material feeding was started 15 seconds after starting the refiner. The net power applied to the raw material during refining was calculated for each pass by subtracting the refiner's idle power. The net power consumption was measured in kWh per metric ton. The total specific refining energy to refine a raw material to the required CSF is the sum of the net power consumption for all the passes.

4.3 Hot disintegration of mechanical pulps

Beath et al. (148) found that the latency of ground wood and, in general all the mechanical pulps, can be removed by hot disintegration. Karnis (122) reported that latency removal through hot disintegration will eliminate curl, kinks, and microcompressions from the mechanical pulp fibers and is expected to increase the fiber length by 3-5\% while increasing the fiber flexibility by 60\%. Removal of these deformations and a substantial increase in fiber flexibility will tend to increase strength properties significantly. Increased fiber flexibility will increase the sheet density. Fines retention will be maximum when fines and fibers are delatent. Since fines retention is higher, drainage will decrease considerably (122, 132). The point of zero-
span breaking strength improves for the delatent pulp as compared to the latent pulp; however, it is independent of the amount of fines present in the sheet (122, 132).

The RMP pulps from whole kenaf, bark22, kenaf stems, bark, and core, were hot disintegrated separately according to the CPPA standard C.8P (Domtar Method) at 90 °C for two minutes prior to screening using the Noram’s pulp hot disintegration unit.

After the hot disintegration, the pulps were tested for the CSF as per CPPA standard method C.1.

4.4 Pulp shives content

The shives analysis for different pulps was done on a Sommerville screen (slot size 0.15 mm) after the hot disintegration of pulps. Residue left over on the screen after screening of pulp slurry (25 g of o.d. pulp) for 20 minutes was collected and oven dried. Pulp shives content was calculated from the formula as given below:

\[
\text{% Pulp shives content} = 4 \times \text{o.d. weight of shives}
\]

4.5 Pulp washing and screening

The pulps were washed and screened on a Sommerville screen having slot size of 0.15 mm. The screen-accept was collected on a linen cloth to retain all the fines.

4.6 Fiber characterization of pulps

The pulp fractions used in the chemical analysis, fiber length determination, handsheet formation, and curl, kink indices and coarseness measurements were collected on 16, 28, 48, 100, and 200 mesh screens of Bauer-McNett classifier as per Tappi standard T 233 cm-95.

4.7 Evaluation of mechanical pulps

4.7.1 Handsheets formation

For the evaluation of various pulps, handsheets were made in a British Handsheet former as per CPPA test method C.4 for each pulp. White water was circulated so as to maximize the
retention of fines. For each set, 12 handsheets, each having an area of 200-cm² and basis weight of 60g/m², were made by taking 400 ml of pulp slurry at 0.3% consistency. Two stage pressing was carried out on the sheets before air drying them in rings at 50±2 % relative humidity and 23±1 °C.

4.7.2 Pulp drainage time

The pulp drainage time was measured as per Tappi standard T 221 om-93. In calculating standard drainage time, the empirical constant, k, was taken as 25.

4.7.3 Handsheet testing

The handsheets were conditioned at 50±2 % relative humidity and 23±1 °C temperature according to CPPA standard A.4 for 2-4 hours before various tests for each pulp were carried out on them. Non destructive basis weight and thickness measurements were carried out as per CPPA test method CPPA D.4 prior to strength measurements. Handsheets were cut as per CPPA test method D.12 for tear, tensile, and burst measurements.

4.7.3.1 Strength properties

Tensile index (N.m/g), and stretch (%) were carried out as per CPPA standard D.6H, while test method CPPA D.7H for was used for the tensile energy absorption on ten 15 mm wide samples by using Lorentzen and Wettre (L&W) horizontal tensile tester at the Abitibi-Consolidated, Research and Development Center, Sheridan Technology Park, Mississauga, ON.

Tear index (mN.m²/g) was measured on a L&W Elmendorf tear tester as per CPPA standard D.9 at the Pulp and Paper Center, University of Toronto, Toronto, ON.

Burst index (kPa.m²/g) was measured on a L&W Mullen burst tester according to CPPA standard D.8 at the Abitibi-Consolidated Research and Development Center, Sheridan Technology Park, Mississauga, ON.
4.7.3.2 Stiffness test

The stiffness tests for handsheets made from different pulps and pulp fractions were carried out on the Taber stiffness tester (Taber V-5 Model 150-D) from Teledyne Taber, NY, USA at 15° as per CPPA test method given in D.28P at the paper testing lab of Donohue Inc., Thorold, ON.

4.7.3.3 Optical properties

Scattering coefficient and pulp brightness were measured using a Technidyne brightness tester as per CPPA test methods.

4.8 Furnish optimization analysis

The handsheets were also made by furnishing kenaf and bark pulps with the addition of different percentages (5, 10, 15, and 20%) of unbeaten kenaf bleached chemical pulp received from Phoenix Pulp and Paper, Thailand. Handsheets were tested for various strength and optical properties.

4.9 Pulp Bleaching

For bleaching, RMP whole kenaf was pretreated with 0.5% DTPA at 1% consistency for 30 min. Pulp slurry, filtered to a consistency of 13.6%, was placed in plastic bags and preheated before adding bleach liquor. The bleach liquor was prepared by mixing chemicals in the order of sodium hydroxide to maintain the required alkalinity, 5.0% sodium silicate, 0.05% magnesium sulfate, and the required hydrogen peroxide (H₂O₂) and the volume was raised to 100 ml. The sodium hydroxide to be added in 100 ml of bleach liquor was calculated as per the following formula-

\[
\text{Total alkalinity} = \frac{\text{NaOH in sodium silicate} \times 5 + \text{NaOH mass}}{100} \quad (4)
\]
The sodium silicate used in the experiment, contained 11.5% NaOH. So for example if alkalinity was to be maintained at 1%, the mass of sodium hydroxide added to 100 ml of bleach liquor was 0.425g.

10 ml of the bleach liquor was added to the pre-heated pulp and the final consistency was brought to 12%. The bags were sealed and kneaded to mix the bleach liquor completely. Bags were put in a water bath at 60°C for two hours. Filtrate was squeezed from the bleached pulps before diluting them to 1%-consistency and bringing pulp pH to 5.5. Pulp pads, formed on a Buchner funnel, were dried overnight at 20°C before testing for the brightness by Technibrite Brightness Tester.

Filtrate extracted from each pulp sample was titrated to determine the quantity of H₂O₂ used in the bleaching of pulps.

Bleaching efficiency was calculated as the relative "decoloration number" [DC] as provided in (149) using the following formula:

\[
[DC] = \frac{(k/s)_{\text{unbleached}} - (k/s)_{\text{bleached}}}{(k/s)_{\text{unbleached}}} \times 100
\]  

(5)

(k/s) for bleached and unbleached pulps was calculated using the following formula:

\[
k / s = \frac{(1 - R_e)^2}{R_e}
\]  

(6)

Where,

\( R_e = \) reflectance factor with sheets of the same pulp pads as backing used as decimal fraction.

This is the R(y) component at 557 nm (150).

\( k = \) light-absorption coefficient

\( s = \) light-scattering coefficient

In bleaching, the color or the light-absorption coefficient is reduced while having little or no effect on the light-scattering coefficient of the pulp (149).
4.10 Chemical Analysis

4.10.1 Extraction of lignin

The lignin content for core, bark, whole kenaf and various pulp fractions was determined as per Tappi standard T 222 os-54.

4.10.1.1 Acid insoluble lignin

'Tea bags' (pulp wrapped in kimwipes) were prepared from ground whole kenaf (core and bark mixed in 65 to 35 ratio), bark, core, and different pulp fractions (+16, +28, +48, +100, and +200 fractions of Bauer-McNett Classification) for extraction with ethanol-benzene (2 volume of benzene and 1 volume of ethanol (95%)) as per TAPPI standard T 204 om-88.

The 'tea bags' were air-dried following extraction of various samples. For soluble and insoluble lignin, extractive free whole kenaf, bark, core, and pulp fractions were treated separately with 72% sulfuric acid. 0.5 g of each extractive free sample was treated separately with 72% sulfuric acid in 50 ml beakers placed in a water bath at 20±1 °C. The samples were continuously macerated with a glass rod while adding acid and were kept for 2 hours under the same conditions. The material was stirred constantly at intervals of 15 minutes to ensure the proper reaction of whole kenaf, bark, core, and different pulp fractions with sulfuric acid.

At the end of 2 hours reaction at room temperature, the complete material was transferred to marked Erlenmeyer flasks and the volume in each flask was raised to 250 ml by adding distilled water so as to maintain an acid concentration at 3%. The solution was boiled for 4 hours while maintaining the volume at 250 ml by frequently adding distilled water.

The solution was filtered after 4 hours of boiling on the marked; oven dried and weighed medium fritted crucible. Filtrate was collected for a quantitative determination of soluble lignin. Insoluble lignin in the crucible was washed with 400-500 ml of hot water to remove all the remaining acid.
The lignin and crucible were dried overnight in an oven at 105 ± 2 °C to determine acid insoluble lignin.

4.10.1.2 Acid soluble lignin

When pulp or 40 mesh-powdered wood is treated with 72% sulfuric acid, a part of the lignin is dissolved in acid, termed acid soluble lignin. The total lignin in wood or pulp is the sum of acid soluble and insoluble lignin.

The first filtrate collected in the determination of acid insoluble lignin was used for calculation of acid soluble lignin. An ultraviolet spectrophotometer from Shimadzu, Model 160, was used to measure the UV absorbency of the filtrate. Ultraviolet light at 205 nm was passed through the filtrate in a cuvette and the ultraviolet absorbency was noted. Filtrate was diluted if the absorbency was above 0.7. Three-percent sulfuric acid was used as a blank or reference.

The acid soluble lignin of different fractions was calculated by using the following formula (204):

\[
\% \text{ Soluble lignin} = \frac{(A/110)DV}{1000W}
\]

Where,
- A = Absorbence
- D = Dilution
- V = Total volume of filtrate i.e. 400 ml in our case
- W = Oven dried weight of each pulp fraction

4.10.2 Determination of holocellulose content

Holocellulose and α-cellulose contents of core, bark, whole kenaf and various pulp fractions were determined by the method given by Zobel et al. (151).

A sample of 0.7 g of each extractive free core, bark, whole kenaf and various pulp fractions was placed into a 250 ml Erlenmeyer flask. Three replicates were prepared for each sample. Ten ml of solution A (60 ml glacial acetic acid and 20 g NaOH per liter of distilled water) was added to each flask and was followed by an immediate addition of solution B (200 g
NaClO₂ per liter distilled water). Before putting the flasks in a water bath maintained at 70 °C, they were swirled to ensure a thorough mixing of chemicals.

The flasks were swirled frequently for better penetration of chemicals. 1 ml of solution B was added after 45 minutes, 90 minutes, and 150 minutes after placing the flasks in the water bath. After keeping the flasks in the water for a total of 4 hours, flasks were placed into cold tap water and 15-20 ml of chilled distilled water was added to each flask to stop the reaction. Treated samples were filtered under mild suction on a predried and weighed crucibles. Flasks were washed with 100 ml of 1-% acetic acid and transferred to the crucible. Suction was stopped and the filtered material was washed with a series of two 5-ml acetic acid and drained under the gravity.

After applying full suction at the end of acetone washing to extract the excess acetone, crucibles were placed in a conditioning chamber for at least 4 days. The weight of each crucible was recorded after conditioning. One of these crucibles was placed in an oven to remove the moisture and determine the oven dry weight of holocellulose in the other two crucibles.

This was the holocellulose content of extracted free samples. The holocellulose from these two crucibles was used to determine α-cellulose in each fraction.

4.10.3 Determination of α-cellulose content

Two crucibles containing holocellulose for each sample species were placed in a Syracuse watch glass containing water up to a height of 1 cm. 3 ml of 17.5% NaOH solution was added to each crucible and stirred with a glass rod to ensure thorough mixing. After 5 minutes, another 3 ml of 17.5% NaOH was added and mixed thoroughly. 35 minutes after the second NaOH addition, 6 ml of distilled water was added to each crucible to stop the reaction.

The crucibles were filtered under mild suction. The content in the crucible was rinsed with 60 ml of distilled water and filtered under mild suction. 5 ml of 10% acetic acid was poured in to the crucible and allowed to drain under gravity. The crucible content was then washed under
mild suction with 60 ml of distilled water. Finally, the content was rinsed with 10 ml of acetone and allowed to drain under gravity. This step was repeated with another 10 ml of acetone. Crucibles were dried overnight in an oven at 105±2 °C. The oven dry mass in each crucible i.e. α-cellulose content was reported as a percentage of the oven dry weight of each sample species.

4.11 Fiber maceration for length and coarseness determination

Core and bark, cut into small pieces, were boiled in separate beakers containing water to remove all the air from the raw material. The boiling continued until core and bark sank.

As per the modified Franklin method, pieces of the air free bark and core were placed in separate test tubes containing an equal amount of glacial acetic acid and 30-35% hydrogen peroxide. Test tubes were placed in a boiling water bath until core and bark pieces were uniformly white.

Thorough washing of these fibers was done with a series of distilled water on a mild fritted crucible. Washed pieces of bark and core were collected in separate test tubes and shaken in an ethanol and distilled water mixture.

4.12 Use of Fiber Quality Analyzer (FQA) for fiber length, coarseness, and curl and kink indices

FQA from OpTest Equipment Inc. was used to determine fiber length, coarseness, and curl and kink indices for various pulps and +16, +28, +48, +100, and +200 fractions from kenaf and bark22 pulps at the Pulp and Paper Center, University of Toronto, ON. All the test were carried out on a pulp slurry at 0.001% consistency to give a fiber count between 5 and 20 fibers per second. If needed, dilution was carried out to bring the fiber count to the required level.

Out of the three average fiber lengths, arithmetic (Lₐ), length-weighted (Lₕ), and weight-weighted (Lₘₕ), provided by the FQA, arithmetic length unless mentioned otherwise was used for
analysis in this study. The length-weighted average is affected by the long fibers while the weight-weighted average is affected by the presence of fines (FQA Manual).

Coarseness (mg/m) is defined as the o.d. fiber mass per unit length. The $L_n$ is used to calculate coarseness by FQA. Coarseness is given by the formula:

Coarseness (mg/m) =

\[
\frac{\text{Mass of oven dried fiber tested (mg)}}{\text{Fiber Total} \times L_n \text{ (for fibers 0.07 to 10.0 mm in length)} \times \frac{1 m}{1000 \text{ mm}}}
\]

(8)

Where

Total fiber length,

\[
L_T (m) = \text{Fiber Total} \times L_n \text{ (for fibers 0.07 to 10.0 mm in length)} \times \frac{1 m}{1000 \text{ mm}}
\]

(9)

Fiber counts, as provided by FQA and used to calculate the fiber length, is the number of fibers tracked correctly during a particular run. However, fiber total is defined as the total number of fibers, which were detected (tracked and untracked fibers) as they passed through the flow cell during the coarseness test.

Curl and kink indices will be higher for the mechanical pulp fibers because of their repeated compression within a refiner (122). Curl index (%) as used in the analysis of different pulps in this study is the result of multiplying curl index calculated by FQA by 100. So,

\[
\text{Curl Index, \%} = \left( \frac{\text{Contour length, } L}{\text{Projected length, } l} - 1 \right) \times 100
\]

(10)

For straight fibers, contour length, $L$, and the projected length are more or less the same. However, for curled fibers such as mechanical fibers, $L$ and $l$ are very different (152).
4.13 X-ray Photoelectron Spectrophotometer (XPS)

The XPS spectra for different fractions were obtained by using an X-ray photoelectron spectrophotometer from Leybold Max-200 (presently owned by Specs, Germany), using an unmonochromated magnesium Kα (binding energy 1253.6 eV, width 0.7 eV) X-ray radiation source operated at 15kV and 20 mA. Samples 6 mm x 6 mm were mounted on a holder and kept in a chamber maintained at a vacuum of approximately 10⁻⁷ bar. An X-ray beam was applied at an angle of 54.7°; it penetrated the sample to a depth of 75-100 Å. Photoelectrons emitted from the sample as a result of the X-ray bombardment were analyzed at a 90° take-off angle relative to the detector. An schematic diagram of surface analysis by an XPS is shown in Fig. 4. ESCA Tools™ package compatible with MatLab™ was used for data analysis (153).

4.14 Statistical analysis

Experimental design was carried out to optimize raw material soaking temperature and refining consistency for the production of refiner mechanical pulps from bark 22. The design was carried out using response surface design of the SG Plus Statistical Software compatible with the DOS operating system. Controlled variables were shives content and CSF value, while independent variables were sheet density, scattering coefficient, and tensile, tear, and burst indices. Eleven different combinations (Table 5) for soaking temperature and refining consistency were obtained for the temperature range of 45-85°C and refining consistency range of 10-20%.

The Multiple regression analysis was carried out for the data obtained from different experimental runs. While, the simple sum, average and other data analysis including analysis of variance (ANOVA) was carried out using Microsoft Office Excel version 7.0.
Figure 4: Schematic diagram of fiber surface analysis by X-ray photoelectron spectrophotometer (XPS) (153).
Chapter 5

Optimization of Process Parameters For the Refiner

Mechanical Pulping of Bark

5.1 Effect of raw material soaking temperature and consistency on pulp properties

5.1.1 Introduction

In the production of mechanical pulps, the goal is always to optimization of various pulp properties and reduction of specific refining energy. Thermal and chemical softening has been used to soften the lignin in the raw materials prior to refining, which is expected to reduce the energy consumption while maintaining the fiber length (154-158).

Atack (71) indicated that wood breakage in a refiner is highly temperature dependent. At low temperature, 80-90°C, fiber separation is in the fiber wall while at high temperature it is preferentially in the middle lamella, possibly causing lignin coating of the fibers. Salmen (154) reported that this process is responsible for an increased flexibility of the fibers. However, the energy consumption at lower temperature is greater as compared to that at the higher temperature.

Miles and Karnis (159) has likened the thermal treatment of wood chips compared to the chemical treatment, which helped to maintain the long fiber content even at smaller plate clearances. In addition, it also helps fibers to separate preferentially in the middle lamella rather than in the secondary walls. In TMP, wood is heated to a temperature below its lignin glass transition temperature, which causes a failure in the weak transition layers and thus reduces the breakage of fibers during refining as compared to RMP. The random distribution of fibers is expected to contribute to the fiber shortening. Therefore, to reduce the extent of fiber shortening, a thermal treatment prior to refining can be useful, as is done in the TMP process (160).
The objective of this study, carried out on bark22, is to determine if the refining consistency and temperature of raw material soaking in water prior to refining affect specific energy consumption of refining and various pulp properties. Different combinations of soaking temperature (between 37 and 93°C) and refining consistency (between 8 and 22%) obtained using Experimental Design of Statistical Graphics Plus (Table 5) were evaluated in this study.

5.1.2 Results and discussion

Eleven combinations (Table 5) of the temperature (range 37-93°C) of raw material soaking in water and refining consistency (range 8-22%) were obtained using response surface model of experimental design of Statistical Graphics Plus. Bark22, soaked in water at various temperature, was refined on a small 300 mm refiner in several passes to get a pulp with a prescreened CSF of 100-150 ml. Detailed description of the refining process is given in Chapter 4, Materials and Methodology. Pulps were tested for various properties and multiple regressions were carried out for the data obtained from the evaluation of bark22 RMP. Details of the multiple regression analysis are given in the Appendix 1-10. The non-significant variables have not been dropped from the multiple regression equations, discussed below, because in this case the coefficients of the variables not dropped will be modified, hence will provide biased values (161). However, if a graph has been plotted, it is between the significant independent and response variables.

Multiple regression analyses of pulps' shives content, sheet density, scattering coefficient and tensile, tear and burst indices indicate that the relationship between the controlled variable and the response variable is not statistically significant at the 5% significance level (F-values of the regression analysis and t-values for the coefficients of both the control variables (consistency and temperature) are higher than 5%) in all the equations. The statistical details of regression equations are given in Appendix 1-6. These results show that the soaking temperature of raw material and the refining consistency do not have any significant effect at the 5% confidence level on pulps' shives content, sheet density, scattering coefficient and tensile, tear and burst indices. This could be due to the fact that these properties are mainly dependent on the fiber
morphological properties, specific energy applied, plate gap and to some extent, on the plate pattern.

It is possible that the temperature effect was lost due to the refining of fibers in several passes to obtain a pulp with a specific CSF. The temperature within the refiner is expected to be more than 100°C as the temperature of the discharged material after each pass was observed in the range of 85-95°C. The material was continuously subjected to thermal effect in each pass, which enhanced the softening of the material significantly. On the other hand, the consistency also did not show any significant effect on various pulp properties discussed here. As found by Cort (85), at high speed (1,800 rpm in the present case), refining consistency hardly had any impact on the fiber residence time and thus on the pulp strength properties. Moreover, use of a small refiner too had large effect on the residence time of fibers in the refiner.

5.1.3 Effect of raw material soaking temperature and refining consistency on specific energy consumption

Energy, kWh/t = 4371.2 + 5.98 Consistency - 7.45 Temperature

\[ t = 1.040 \quad (t = -5.737) \]

Adjusted \( R^2 \) = 0.76

The statistical summary (Appendix 7) of the above equation for refining energy consumption indicates that the relationship between the controlled variables, raw material soaking temperature and refining consistency, and energy consumption is significant at the 5% confidence level (significance level of 'F' 0.00132). The adjusted \( R^2 \) for the above equation is 0.76.

The t-values indicate that the coefficient of consistency is not statistically different from zero at the 5% level of significance (for 8 degrees of freedom, critical value of t-statistic at the 5% significance level is 2.31) while the temperature effect is statistically significant at the same significance level. Thus, refining energy consumption is dependent on the raw material soaking temperature but not on the refining consistency.
Figure 5: Calculated and experimental specific energy consumption against the raw material soaking temperature. Calculated refining energy is for a given refining consistency of 15%.
The soaking temperature might have had an initial effect on kenaf defiberation as is seen from the refining energy equation. It may be because of an increase in raw material soaking temperature enhances loosening of bonds between lamellae, which possibly reduces the energy requirement in the defibration stage. Therefore, it can be concluded that an increase in the soaking temperature will decrease the refining energy requirement. It is worth mentioning here that the specific energy does not include the energy needed to soak the raw material at different temperatures.

Fig. 5, shows a trend of estimated (from regression models) and observed specific energy consumption against the raw material soaking temperature for the refining of bark22. Though the energy consumption in the defibration stage is less than that of refining (fiber development stage) energy, still the overall energy consumption will reduce by approximately 11% if the raw material soaking temperature is raised from 35°C to 95°C. However, the effect of temperature on the energy consumption is expected to be higher if the refining is carried out on a large refiner. On the other hand, data analysis also indicates that soaking of bark at higher temperature did not produce any effective results on the CSF, sheet density, scattering coefficient, and tensile, tear, and burst indices because of its strand type physical structure.

5.1.4 Effect of soaking temperature and refining consistency on CSF, and fiber and fines content of bark22 RMP

\[
\text{CSF. ml} = 115.98 + 1.39 \text{ Consistency} - 1.15 \times 10^{-1} \text{ Temperature} \\
(\text{t} = 3.206) \quad (\text{t} = 1.175) \\
\text{Adjusted } R^2 = 0.49
\]

\[
\text{Fiber. %} = 61.4 - 4.01 \times 10^{-1} \text{ Consistency} + 2.86 \times 10^{-2} \text{ Temperature} \\
(\text{t} = -2.602) \quad (\text{t} = 0.821) \\
\text{Adjusted } R^2 = 0.35
\]

\[
\text{Fines, %} = 38.60 + 2.8 \times 10^{-1} \text{ Consistency} + 3.36 \times 10^{-2} \text{ Temperature} \\
(\text{t} = 2.921) \quad (\text{t} = 1.553) \\
\text{Adjusted } R^2 = 0.47
\]
The above equations for the bark22 RMP's CSF, fiber and fines content show that their respective regression models are statistically significant at the 5% confidence level except for the fiber content, which is significant at the 10% confidence level. Analyses for the controlled variables (t-values at the 5% confidence level) indicate that the coefficients of temperature are not statistically different than zero, while coefficients of consistency are different from zero at the 5% significance level in all the three equations. Hence, it can be concluded that temperature plays no role in determining the CSF and fiber and fines content of the bark22 RMP, while consistency significantly affects these properties.

Sundholm and co-workers (162) reported that the pulp prepared by skipping chip preheating prior to pressurized refining produced as strong pulp as was produced from TMP, which involves chip preheating. It indicates that the chip preheating has no significant effect on the pulp quality. The present study also confirms that the raw material soaking temperature did not have any significant effect on the pulp properties. However, an increased temperature will certainly decrease specific refining energy, as the defibration of the softened material will be easier and may be a vital factor in retaining the fiber length provided the refining is carried out in 3-4 passes.

For the present study, it was decided that in the production of RMP from core, whole kenaf, bark and bark22, the various raw materials would be soaked at 35°C for four hours prior to refining.

5.2 Refiner mechanical pulping of bark with 22% core

5.2.1 Specific energy consumption during refining of bark22 and bark fibers

The quality of kenaf bark RMP in the present experiment should not be viewed in terms of the energy consumption required refining bark22 and barking to a CSF of 100-150 CSF. Nor should the energy be compared with that required in two or three-stage wood refining. In fact, each refining stage in the commercial process involves large refiners with different plate patterns. Second stage refining is carried out between refiner plates embedded with mostly fine
Figure 6: Tissues (120X) of shives from bark indicate that shives contain vessels, Parenchyma cells, and fibers from core part of the raw material.

Figure 7: Tissues (120X) indicate that on occasion the fibers from bark were entangled causing higher shives content.
bar zones. Hatton et al. reported that the energy consumption in small refiners is higher than in large refiners (165). The stability of small refiners at higher consistencies, 22% in the present case, is also an important factor in the energy consumption during refining.

As mentioned earlier, fiber morphology plays an important role during refining (78, 98). The higher energy consumption in the refining of bark22 and bark could be due to the bark fibers having thick cell walls (166), which is expected to require more energy to refine to a reasonable coarseness.

5.2.2 Properties of bark22 mechanical pulps

5.2.2.1 Pulps’ shives content

The amount of shives was reduced with the continuous input of specific refining energy. The final shives content of bark22 and bark RMP refined at 15 and 22% consistencies is in the range of 2-3%, which is slightly higher than the shives content reported for most of the softwoods (170). The presence of 22% core fibers in bark22 could be a reason for the higher shives content. Tissues of shives seen by light microscopy (Fig. 6) show the presence of a fair amount of core fibers, vessels, and parenchyma cells, indicating that the presence of 22% core in the raw material was contributing to the higher shives content. Bark pulp can be refined to a shives content of less than 1% and is compatible to that of wood RMP. It confirms that the presence of core fibers in the case of bark22 increased the pulp shives content (Table 7). The other reasons for a higher shives content could be fiber entangling (Fig. 7) mainly from bark fibers. Some of the shives mainly core fiber bundles, passed through the Somerville screen (0.15-mm slots) and appeared in the sheet. A weight-weighted length average of tissues from bark22 shives also confirms that the shives were mainly coming from core fraction of the kenaf raw material.

The screened yield of RMP bark22 and bark refined at 15% and 22% consistency was more than 91%.
Figure 8: Relationship between pulp CSF and fines (-48 fraction) for bark refined at 15% and 22% consistencies.

Figure 9: Relationship between pulp fines content (-48 fraction) on tensile index for bark22 refined at 15% and 22% consistencies.
Figure 10: The tear index for the pulps increases with an increase in the specific refining energy.

Figure 11: Tensile-tear index relationship for bark22 refined at 15% and 22% consistencies.
5.2.2.2 Strength properties of bark22 mechanical pulps

The handsheets were formed by circulating white water, which contained many fines. The first five handsheets were rejected to stabilize the quality of white water and maintain a constant drainage time for each sheet. It was expected that this would help mobilize fines within the sheet and increase the compactness of the fibers.

Figs. 8-10 indicate that the fines content, tensile index, and tear index all increase with an increase in the refining energy. For bark22 refined at 15% and 22% consistency. With an increasing fines content, the pulp CSF value decreased continuously; the pulp was refined in several passes to attain a CSF in the range of 100-150 ml. Changes in the Bauer-McNett long fiber (+48 fraction) and fines (-48 fraction) with increased refining are illustrated in Fig. 8. The long fiber fraction decreases from a high of 67.9% to 56.2% for refining at 15% consistency and 63.5% to 54% for refining at 22% consistency. The fines' fraction increased from 32.1% to 43.8% and from 36.5% to 46% for refining at 15% and 22% consistency respectively. The data analysis indicates that fiber cutting (which increases middle fiber fraction) is more prominent in the initial stages of refining at 15% consistency. The increased fines content enhanced the consolidation of the fiber network in a sheet and will increase the light scattering coefficient. However, the sheet density and strength properties are expected to be controlled by the stiffness or flexibility of long bark fibers. The bark fiber collapsibility, due to their thick cell walls, is equally important not just from the point of view of energy consumption, but also for achieving better strength properties. However, presence of unrefined core fibers certainly affected the bonding of fibers and thus the strength properties.

The fines content was higher for the bark22 and bark refined at 22% consistency as compared to the bark22 refined at 15% consistency. This could be due to the fact that increased fiber-to-fiber interaction at 22% consistency caused more peeling of the fiber surface, which included the middle lamella, and the primary walls and a part of secondary walls. This peeling of fiber surface will reduce the coarseness and make the fibers more flexible. This will increase
Figure 12: Relationship between sheet density and tensile index of bark22 mechanical pulps.
the compliance of the fibers and enhance the bonding. Hence, the percentage of long fibers (+48 fraction as per weight) will be lower for the pulps refined at 22% consistency as compared to refining at 15% consistency. At the same time, it may be expected that the fiber length will be preserved for the pulp/raw material refined at 22% consistency. However, because of the higher length of the fiber and more fiber-to-fiber interaction, kink and curl have shown higher values than the pulp refined at 15% consistency (Table 7), therefore nullifying the effect of retaining the longer fiber length during refining. Fig. 11 shows that the tensile and tear indices are almost linearly related and continue to improve with refining.

Fig. 12 shows that, with an increase in sheet density, the tensile index increases linearly for both consistencies. It indicates that refining increased the consolidation of fibers as the conformity of fibers increases, which also indicates that the quality of fines increases as the refining is carried out at lower plate gaps. The sheet density is slightly lower when compared to that of the spruce RMP (170). This could be due to the lower collapsibility of bark fibers having thick cell walls. The other reason could be the higher stiffness of partially refined or unrefined core and bark fibers, which might have resisted fiber compaction. Moreover, the stiff core fibers would resist fiber bonding, which might have caused lower sheet density. The hand sheets made from bark22 refined at 22% consistency has slightly higher sheet density than the pulp refined at 15% consistency. This could be due to the fact that pulp refined at 22% has a higher fines content, which assists the consolidation of fiber network and improves sheet density (98).

Table 7 shows that there is no significant difference in the various properties of bark22 refined at 15% and 22% consistency when compared at the same CSF. However, bark has shown much better properties than bark22, which contains 22% core fibers. The strength properties of RMP bark22 (22% core and 78% bark) are much better than has been reported by Hatton and Johal (165) for RMP from the simultaneous refining of aspen and spruce in a mixture of 25% and 75% respectively. This comparison has been made in relation to core fibers having strength similar to that of hardwood while bark fiber has strength similar to that of softwood (9).
Figure 14: Relationship between light scattering coefficient and tensile index for bark.

Figure 15: A typical relation between the sheet density and scattering coefficient for bark.

Scattering coefficient, m²/kg

Sheet density, Kg/m²

Scattering coefficient, m²/kg

Tensile index, N/m²

Shear modulus, Kg/cm²
Table 7: Properties of RMP bark (with 22% core) refined at 15% and 22% consistency.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Bark with 22% core</th>
<th>Norwegian spruce PRMP (162)</th>
<th>Douglas fir MW RMP (167)</th>
<th>Jack pine MW RMP (167)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refining Energy, kWh/t</td>
<td>4099</td>
<td>4110</td>
<td>1755</td>
<td>3000</td>
</tr>
<tr>
<td>CSF, ml</td>
<td>120</td>
<td>120</td>
<td>148</td>
<td>-</td>
</tr>
<tr>
<td>Shives, %</td>
<td>1.8</td>
<td>1.7</td>
<td>0.72</td>
<td>-</td>
</tr>
<tr>
<td>Density, kg/m³</td>
<td>347</td>
<td>350</td>
<td>520</td>
<td>-</td>
</tr>
<tr>
<td>Tensile Index, N.m/g</td>
<td>42.7</td>
<td>40.2</td>
<td>38.9</td>
<td>36</td>
</tr>
<tr>
<td>Stretch, %</td>
<td>2.1</td>
<td>2.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TEA, J/m²</td>
<td>35.9</td>
<td>37.7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Tear Index, mN.m²/g</td>
<td>9.2</td>
<td>9.4</td>
<td>7.92</td>
<td>8.4</td>
</tr>
<tr>
<td>Burst Index, kPa.m²/g</td>
<td>2.5</td>
<td>2.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Scattering Coefficient, m²/kg</td>
<td>66.8</td>
<td>66.5</td>
<td>-</td>
<td>49.1</td>
</tr>
<tr>
<td>Fibers (+ 48 fraction), %</td>
<td>55.5</td>
<td>54.3</td>
<td>58.9</td>
<td>57.0</td>
</tr>
<tr>
<td>Fines (-48 fraction), %</td>
<td>44.5</td>
<td>45.7</td>
<td>41.1</td>
<td>43.0</td>
</tr>
<tr>
<td>Weight-weighted fiber length, mm</td>
<td>1.79</td>
<td>1.87</td>
<td>-</td>
<td>2.16</td>
</tr>
<tr>
<td>Kink Index</td>
<td>0.81</td>
<td>0.92</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Coarseness, mg/m</td>
<td>0.25</td>
<td>0.22</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* 1MJ = 3.6 kWh
Further, the bark22 RMP quality is better than that of the mature wood RMPs from Douglas fir and jack pine (167) and is comparable to that of Norwegian pressurized refiner mechanical pulp (PRMP) (162).

5.2.2.3 Optical properties of bark22 RMP

The scattering coefficient is dependent on the fiber length distribution and the quality and quantity of fines in a pulp (98). Hence, with an increase in fines content the scattering coefficient of the sheet will increase with an increase in refining energy. It was observed that white water recycling had a significant effect on the scattering coefficient of the bark and bark22 pulps and improved the same by 5-10%. The lignin and holocellulose content of +100 and +200 fines of the bark22 RMP indicated that these fines contained a considerable amount of fibrils (107). This increased the specific surface area of fines and contributed positively to the pulp's scattering coefficient. With an increase in the fines content of pulps, bonded and unbonded area increases and the same is reflected from an increase in the tensile strength and collapsibility of bark fibers having thick cell walls. The other reason could be the higher stiffness of partially refined or unrefined core and bark fibers, which might have resisted fiber scattering coefficient (Fig. 9, Fig. 14). As seen in Fig. 13, the light scattering coefficient and sheet density is linearly related which is similar to the reports in the literature (118).

Fig. 14 shows a linear relationship between tensile index and scattering coefficient for the pulps both refined at 15% and 22% consistency. This shows that an increase in the specific surface of fibers and the quality fines increased fiber-fiber interaction and thus the bonding. The scattering coefficient for bark22 was higher than that of RMP bark, which could be due to a higher fines content contributed by the presence of 22% core in the raw material.
5.3 Conclusion

- Increase in the raw material soaking temperature reduces the fiberization energy, however its effect on pulp properties was minimal.

- Using a 300 mm small refiner, kenaf bark has to be refined in several passes before it can produce a pulp with a reasonable CSF of 100-150 ml.

- A large amount of energy is wasted as the refined material in each pass goes through the coarser and medium refining zone that, in fact, does not contribute to the development of fiber after two- or three-passes. However, more energy is required to refine bark fibers because of their having thicker cell walls.

- Bark22 RMP has better strength properties than softwood RMP.

- RMP bark 22 can be used for high quality newsprint, super calendered newsprint, and various lightweights coated applications. However, core bundles appearing in the sheet have to be removed by improved or modified screening.
Chapter 6

Production of Newsprint from 100% Kenaf Pulp

6.1 Refiner mechanical pulping of kenaf

6.1.1 Introduction

Over the last few decades, various studies have been carried out to develop conceptual models for the refining of softwood and hardwood. In a single sample of such raw materials, the fibers are all, more or less, of uniform size and nature (58, 64, 69, 76, 80). In this study, the fundamental knowledge of these conceptual models is intended to be applied to the mechanical refining of kenaf, consisting of two morphologically, anatomically and chemically different fibres (9, 27). This study is expected to develop an approximate design of kenaf refining, elucidating how the combination of two fibers, core and bark, will behave under similar conditions of refining.

In earlier attempts at producing whole kenaf TMP, researchers (10, 11) at the U.S. Department of Agriculture had problems with the large number of fiber bundles and broken fibers appearing in the sheet and thus affecting the strength properties. In the work, the cause of fiber bundles and broken fibers appearing in the sheet were not analyzed adequately. Hence in the given scenario of raw material supplies for papermaking, there is a need for optimizing the refining process for this most promising raw material, kenaf. In this study, efforts have been made to produce RMP from whole kenaf (core and bark mixed in the ratio of 65 to 35) and from the kenaf stems having the same ratio of core and bark as in the case of whole kenaf. The other objective was to determine if the separated core and bark mixed in 65 and 35 ratio would produce better pulp quality and save the refining energy.
6.1.2 Results and discussion

6.1.2.1 Refining intensity, plate clearance, and residence time

Specific energy (E) per bar impact (n) is known as the refining intensity (e) depending on the rotational speed, bar density, and the residence time of the pulp in the refining zone (163). Refining intensity has an important role in determining the quality of refiner mechanical pulp. Refining intensity can be changed by varying either refining consistency, or the rotational speed, or by the size and pattern of the refiner plates or by a combination of these factors. However, refining intensity in each pass is changed independently of the other because of a difference in the nature of the material to be refined. Miles and May (78) have shown that the radial velocity of the pulp in a refiner is given by –

\[
\frac{dv}{dr} = r \omega^2 - a \frac{\mu_r}{\mu_d} \frac{E \cdot c}{\omega (r_2^2 - r_1^2)}
\]

In the present experiment, refining intensity was controlled by a change in the refining consistency while keeping rotation speed and the refiner plates constant. The residence time, playing an important role in determining the quality of pulp, defines the number of bar impacts received by the raw material in the refiner zone. The residence time was changed by controlling the plate gap and by the number of passes. The plate gap was reduced from 1.52 mm to 0.127 mm (Table 6) to approximate the refining action of the present refiner on the fibers to that of commercial refiners. Total residence time for kenaf and stem refining in 8 passes (reducing the plate gap from 1.52 mm to 0.127 mm) is the sum of the residence time of fibers in each pass. Hence, total residence time for the fibers in the refiner will be-

\[
\tau = \tau_1 + \tau_2 + \tau_3 + \tau_4 + \tau_5 + \tau_6 + \tau_7 + \tau_8
\]
Where, \( \tau_1, \tau_2, \tau_3, \tau_4, \tau_5, \tau_6, \tau_7, \tau_8 \) are the residence time of the material in an individual pass for the plate gaps decreasing from 1.52 mm to 0.127 mm respectively. Miles (163) reported that the residence time was proportional to the plate gap. Hence, the residence time for each pass will decrease with a decrease in the plate gap from 1.52 mm to 0.127-mm time for each refining at an inlet refining consistency of 15% and 22%. So, we have:

\[ \tau_1 > \tau_2 > \tau_3 > \tau_4 > \tau_5 > \tau_6 > \tau_7 > \tau_8 \]  

Hence, the number of impacts on the fiber will decrease with a decrease in plate gap for each refining at 15% and 22% consistencies, and thus less fiber cutting may be expected. As all the passes were carried out on a single refiner, it should be mentioned that the plate bar density and rotational speed were maintained the same throughout this experiment. Hence from Equation 1. it can be said that the radial velocity of pulp fibers in a refiner will be a function of inlet consistency, and the ratio of frictional coefficients which will be primarily dependent on plate gap.

### 6.1.2.2 Effect of consistency on refining

The consistency is argued to be an important parameter in determining the quality of pulp for a particular specific energy (78). Keeping the plate gap constant, residence time was changed by varying inlet consistency to the refiner used in this experiment. With a change in the consistency from 15% to 22%, the lubricating effect of water will influence the mobility of fibers; hence the frictional forces within plates are expected to increase with an increase in the consistency (164). Miles and May (78) indicated that the axial thrust and the motor load showed a linear relationship indicating that the tangential frictional coefficient \( \mu_a \) was independent of the consistency. However, at a constant plate gap, specific energy increases with an increase in consistency. Moreover, for a given consistency, a decrease in the plate gap will increase the specific refining energy. It can be argued that the nature of the material will have a considerable
impact on the frictional forces within a refiner. With continued refining of fibers, the specific surface of the fibers will increase, thus enhancing their flocculating tendency. At an increased fiber flocculation, the mobility of fibers will be greatly reduced, hence retaining the fibers for a longer time in the refiner.

The centrifugal force, \( dM(r) \cdot \omega^2 r \), as given by Miles and May (78) is controlled by the wet mass of pulp, \( dM(r) \). i.e. the consistency that in turn will determine the residence time of the material between the refiner plates. Therefore, for a particular plate gap if the consistency is changed from 15% to 22%, the residence time will increase.

The volume between the two plates will decrease with a reduction in plates’ gap. Hence for a given consistency, the volumetric flow rate of the material being refined will increase with a decrease in the plate gap if the throughput is kept constant. This means that the corresponding residence time of the material within the refiner will decrease while reducing the number of bar impacts experienced by the fiber on a refiner. Therefore, from Equation 1, the energy per impact will increase. Thus for a given consistency, refining intensity is increased while reducing the plate gap from 1.52 mm to 0.127. It should be mentioned that with an increase in the refining intensity, the fiber length could be controlled while expecting enhanced fibrillation.

In keeping feed rate (o.d. weight) the same for each 15% and 22% consistency, more incoming water with a raw material at 15% consistency will work as a lubricant causing less fiber-to-plate friction, thereby decreasing the residence time of the material between refining plates. Reduced residence time will correspond to reduced bar impacts, but more energy per impact, which causes more fiber cutting. However, refining at 22% consistency, localized de-watering induces more fiber-to-fiber interaction reducing the shortening of fibers. As a result, kink and curl of fiber will increase due to higher axial compression and abrasion. The fiber-fine ratio (by weight) of pulp refined at 15% consistency is higher than the pulp refined at 22% consistency (147).
6.1.2.3 Number of passes and specific energy consumption in a 300 mm Sprout-Bauer refiner

A small refiner as has been used in this study needs a high amount of energy to refine kenaf/stem to a CSF of 100-125 ml compared to a larger refiner (165). The plate pattern had an influence on the quality of pulp and specific energy required for refining the fibers (78). Equation 1 developed by May and Miles (76) indicates that fiber residence time in a refiner is independent of plate pattern. However, keeping refiner speed, plate gap, refining consistency and the feed rate the same, plate pattern will certainly affect fiber residence time. The final stage refining in two-stage refining is necessarily done on a refiner equipped with plates of higher bar density. Thus, fibers experience an increased residence time ensuring a higher number of bar impacts. By maintaining the aforesaid process parameters the same, the size of refiner plate will play a vital role in determining the residence time of fiber in a refiner. Fibers will experience a residence time at least six times higher in a 600 mm refiner equipped with high bar density plates as compared to a 300 mm refiner as used in this study.

It may be worth mentioning that refiner plates used in this study were originally designed for softwood refining. The kenaf and stem had to be refined in several passes to get a required CSF, which resulted in higher energy consumption. Fig. 3 shows that the plate area is mostly covered with medium and coarse bar zones. After defiberization of kenaf/stem, coarse and medium sections did not contribute anything to the fiber development. The core fibers were stuck in the bar grooves particularly in the coarse and medium zone because of the grooves being wider than the core fibers, leaving a substantial portion of the core fibers unrefined. Moreover, the coarse refining zone may not have caused any defiberization to bark because of its strand type morphological structure. The coarse zone, on the other hand, consumed a significant portion of the energy applied in transporting the material to a section of the plate with higher bar density. On occasions, the fibers got embedded in the coarse refining zone after 3-4 passes causing serious problems in the flow of material to be refined.
As a consequence of the repeated compressive and shearing actions during refining, a large portion of the electrical energy will be converted into thermal energy through hysteresis losses due to the viscoelastic nature of the fiber material (77, 98). West (86) also claimed that most of the electrical energy is converted to heat during refining. In this experiment, the temperature of the material discharged from the refiner rose to 85-95°C (temperature within the refiner plates is expected to be more than 100°C) after refining which indicated that a substantial amount of power was dissipated as heat after each pass. A possible reason for this could be higher tangential friction between pulp and plates, which was expected to increase with a reduction in plate gap.

Bark and core fiber matrix, which is different from that of wood fiber (9, 27), will also affect energy consumption. Bark fibers having thick cell walls (166) were difficult to refine, and hence needed higher specific energy to give the required CSF and to improve fiber flexibility. On the other hand, core fibers having thin cell walls were expected to refine easily under the compressive refining action and to contribute to the pulp quality. However, it seems that core fibers escaped refining actions in the presence of long and thick cell walled bark fibers and did not produce expected fibrillation, thus not contributing to bringing down the pulp CSF to a required level and enhancing pulp quality. Hatton (167) reported that the thin walled fibers, being more flexible than the thick walled fibers, might absorb a substantial amount of energy before getting appropriately fibrillated. Moreover, he asserted that the specific energy consumption would be higher for the refining of thin walled fibers since one metric ton would have more thin walled fibers (core) as compared to the thick walled fibers (bark) in one metric ton. Since kenaf and stem contain approximately 65% thin walled core fibers, the specific energy consumption will be higher to refine the material to a CSF in the vicinity of 100-125 ml. This may be one of the reasons that the refining energy requirement for kenaf is higher than that required to refine bark or bark with 22% core (bark22) to a similar pulp CSF (168).

Moreover, the higher energy consumption could be due to the thermal softening of lignin and hemicellulose. Goring (169) has reported that the lignin softening temperature is decreased
considerably in the presence of water. Kano and co-workers (70) also reported that energy consumption is higher in RMP, which may be attributed to the thermal softening of hemicellulose and lignin during refining. Lignin thermal softening may be expected to be higher because of the simple lignin structure of kenaf/bark (144).

Another reason could be an inefficient use of energy in the fiber-to-fiber rubbing induced at 22% consistency (147). The fiber cushioning between refiner plates causing higher plate-fiber friction also seems to have affected the specific energy requirement.

The sharpness of bar edges and their angles, which are expected to become rusted and pitted over the time of this study and earlier experiments, might have also affected refining energy consumption. The energy consumed to refine whole kenaf is comparable to what has been reported by Kano et al. (70) in the refining of Todomatsu (Abies sachalinenis).

6.1.2.4 Shives content of kenaf and stem RMP

Mechanical pulps are needed to refine to the lowest possible freeness level so as to minimize pulp shives content (170). As shown in Fig. 15, the amount of shives decreased with an increase in specific energy for all the raw materials refined at 15 and 22% consistencies. Shives analyzed for kenaf and stem RMP at different energy levels indicates that the percentage of bark fibers in shives decreases with refining. The average shives content for the pulps at a CSF level of 100–125 ml is approximately 2.5–4%. Tissue analysis of shives indicated that shives constituted mainly bundles of core fibers (Fig. 16). Fig. 17 indicates the presence of paranchyma cells, vessels and short fibers, indicating that the shives are mainly coming from the core part of kenaf raw material. Hence, it can be concluded that the shives were mainly the core bundles of core fibers which being short might have escaped the impact of the refiner bar plates and were flowed outward through the bar grooves. The other reason for higher shives content could be the plate pattern, originally designed for softwood.

Some small and broken bundles of core fibers passed through the screen and, as shown in Fig. 18, appeared in the hand sheets. The presence of fiber bundles might have a negative impact
Figure 15: Shives of whole kenaf and kenaf stem RMP decrease continuously with refining. (Legends for all the graphs, 'S' stands for stem, WK stands for kenaf, Cy. stands for consistency. Therefore, e.g. S@15%Cy. stands for refining of stems at 15% consistency.)

Figure 16: It indicates that the shives content (120X) from kenaf and stem RMP contained core bundles, which also appeared in the sheet.
Figure 17: Tissues (120X) of shives show the presence of vessels and paranchyma cells in kenaf pulp shives.

Figure 18: This figure shows that unrefined core fibers or bundles are present on the surface of the handsheet prepared from the whole kenaf RMP.
on the strength, surface and optical properties.

### 6.1.2.5 Fiber-fine ratio of kenaf/stem RMP

The fines content of the mechanical pulps contributes significantly to the mechanical (63, 118) and optical properties (171) and also affects the drainage characteristics. White water, which contained high fines content, was recycled during handsheets formation from kenaf and stem RMP to retain them in the fiber network. The first five handsheets were discarded to stabilize the quality of white water to be recycled. The drainage time (calculated by Tappi standard T 221 om-93) as mentioned in the literature (172) was almost constant after five sheets, though it was noted that the drainage time increased significantly after the first white water circulation. Fig. 19 gives the drainage time of various pulps having different CSF values. In summary the drainage time increases considerably with a decrease in pulp CSF and the white water recycling. Filtration resistance at higher fines particles present in the pulp will be higher because of the void space between the fiber network filled up by the fines is expected to be reduced, which will increase the drainage time.

The quality and quantity of fines generated during refining depend on the morphological nature of fibers. The chemical analysis of various fractions of kenaf and bark22 RMP shows that lignin removal was slower for the core fibers as compared to bark fibers (109), which could be due to more flexible nature of the thin walled core fibers as compared to the thick walled bark fibers. The kenaf and stem RMP analyzed for fiber (+48 fraction) and fines (-48 fraction) as per weight by the Bauer-McNett classifier indicate that fiber-to-fine ratio decreases with an increase in the refining energy (Fig. 20). The raw materials refined at 22% consistency produced slightly more fines compared to the refining at 15% consistency. Increased fiber-to-fiber interaction at 22% will peel off more material from the fibers surface which contributes to increased fines content. Therefore, fibers as determined by the Bauer-McNett Classification will be lower as per weight for the raw materials refined at 22%.

The fines content of pulp essentially contributes to sheet consolidation, as the networking
Figure 19: The drainage time (with recycling of white water) of whole kenaf and bark RMP increases exponentially with a decrease in pulp CSF value.

Figure 20: Effect of specific refining energy on pulps' fines content (~48 fraction).
of long fibers is enhanced (172). An increase in pulp fines content will tend to increase the scattering coefficient and air resistance of a handsheet (172). However, the fines content for different pulps are affected by the plate pattern, residence time and raw materials fiber matrix (67. 78). Hence, it is necessary that an optimum fiber-to-fine ratio be maintained for the RMP kenaf to improve various pulp properties. However, the quality of fines is equally important in determining the pulp quality (147. 67).

The white water circulation for handsheet making certainly increases the drainage time because of the fines possibly plugging the pores in the web through which the water was expected to pass (172). Fines are expected to behave as small fibers or filler during drainage depending on their size. Higher retention of fines will tend to increase sheet consolidation and its strength. Fiber compactness in a sheet improves with white water circulation as compared to the hand sheets prepared without white water circulation. During this experiment, it was noticed that strength properties improve by 5-10% with the recycling of white water during hand sheet formation. The white water circulation increases the drainage time due possibly to enhanced mobilization of fines. However, it improves some strength and optical properties of paper by a possible increase in fiber bonding or more fiber-to-fiber interaction in a sheet.

6.1.2.6 Properties of the kenaf mechanical pulps

Fig. 21 indicates that the pulps' CSF decreases with an increase in refining energy. CSF values can be reflected from the fines content of the pulp and the stiffness of the long fibers. This shows that stiff fines are developing considerable papermaking potential i.e. contain more flexible fibriller and ribbon like material. With increased specific refining energy, however, it has been argued that the fines content and fiber fibrillation is not necessarily a prerequisite to improve strength properties of mechanical pulps.

Figs. 22-24 show the trend of tensile index, burst index, and tear index for whole kenaf and stem refined at 15 and 22% consistency with respect to the specific energy consumption. CSF drops linearly with refining energy for both the raw materials because of increased fines
Figure 21: Effect of specific refining energy on pulp CSF.

Figure 22: Relationship between tensile index and CSF values of various pulps.
Whole kenaf and stem refining at 15% and 22% produce almost the same results for tensile, burst and tear indices (Figs. 22-24, Table 8). It could be due to the fact that the difference in residence time for the fibers refined at 15% and 22% consistencies was negligible at the refiner speed of 1,800 rpm. Cort (85) mentioned that the high rotational speed such as 1,800-rpm has more significant control over the residence time than the refining consistency.

As is seen in Figs. 22-24, additional refining tends to increase fiber fibrillation due to internal and external fibrillation and, hence the fiber-fiber bonding in a sheet; thus, the sheet tensile index of whole kenaf RMP may be expected to be higher (Fig. 22). As per Page (126), fiber length and the degree of fiber bonding determine the sheet bonding. Thus, cutting of fiber will be a crucial factor for an optimum tensile strength of whole kenaf and stem RMP.

The tear index for all the raw materials refined at 15% and 22% increases initially with refining energy but drops with more energy input. The tear index is dependent on the fiber length, the fibers participating in rupture (intrinsic fiber strength), and the fiber-fiber bonding. During a tear test, the work involved is either against the pulling of fibers from the fiber network or against fiber rupturing or against the combination of both (173). As can be noted from Fig. 22, tensile index increases linearly for all the pulps with refining. It indicates increase in an inter-fiber bonding with refining. Thus, work done in pulling the fibers from a sheet of fiber network increases with an increase in refining energy. However, with more refining inter fiber bonding is further enhanced but tear strength starts to drop which could be due to fiber length and degree of bonding exceeding the critical value (128).

Fig. 25 shows that with more refining energy, tensile index continues to increase while tear index starts to drop. This could be because, under the conditions of tightly bonded fibers, more fibers are ruptured with the propagation of the initial cut, thus giving lower tear strength.

It may be worth noting that fiber rupture requires less energy than pulling of fibers from the fiber network (173). Moreover, Seth and Page (174) have shown that for the highly bonded sheets, the tear index is less dependent on the fiber length.
Figure 23: Tear index of different pulps increases initially with an increase in refining, however declines with continued refining.

Figure 24: Burst index of various pulps increases with the decreasing pulp CSF.
Figure 25: Typical relationship between tear and tensile index of whole kenaf and stem mechanical pulps.

Figure 26: Sheet density and tensile index relationship of various pulps.
The tear index of RMP is dependent on the refining consistency (78). The tear index was higher for the material refined at 22% consistency for both kenaf and stem. It may be because of the fact that the fiber cutting is less at higher consistency while the fiber bonding improved with refining. Table 8 and Fig. 20 indicates that there is no significant difference in +48 fraction (which is by weight) for the pulps refined at 15% and 22%.

The tear and tensile indices could be improved further using a screen with 0.1-mm slots will reduce the core fiber bundles coming with the kenaf and stem RMP which appeared in the sheets (Fig. 18). Higher stiffness of these bundles affected the conformity of fibers and hence the fiber bonding. Under tension, failure in the fiber network could have occurred at a point of the presence of these bundles, lowering the tensile and tensile energy absorption. The sheet density (Table 8) indicates that the fibers are coarser which reflects lower fiber flexibility causing reduced inter fiber bonding.

Fig. 26 shows a linear relationship between the sheet density and tensile index indicating that the inter-fiber bonding improved with increased refining. The core fibers having thin cell walls were expected to flex more during refining and produce a sheet of high density. However because of the stiff core bundles appearing in the sheet, the sheet density is lower than that of the bark fibers refined with 22% core fibers (168).

Table 8 shows various properties of RMP from kenaf and stem extrapolated to a common CSF from their corresponding best fit curve equations. Because of a small size refiner used in this study, the over all residence time of the material refined at 15% and 22% consistencies may not be significantly different as the refining is controlled more by the refiner speed. This could be one of the reasons that the pulps properties refined at two different consistencies are not significantly different.

The tear and burst indices of RMP whole kenaf show an improvement over the whole kenaf TMP (10, 11) and are comparable to that of whole kenaf CTMP (52) as reported by the U.S. Department of Agriculture.
Table 8: The data in the table show the extrapolated properties of refiner mechanical pulps from kenaf and stem refined at 15 and 22% consistencies. The Table also provides a comparison of pulp properties with those of whole kenaf TMP (10) and CTMP (52), produced by USDA.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Refining at 15%</th>
<th>Refining at 22%</th>
<th>Whole Kenaf</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Stalk</td>
<td>Whole kenaf</td>
<td>Stalk</td>
<td>Whole kenaf</td>
<td>TMP(10)</td>
</tr>
<tr>
<td>Refining energy, kWh/t</td>
<td>4320</td>
<td>4303</td>
<td>4509</td>
<td>4760</td>
<td>-</td>
</tr>
<tr>
<td>CSF, ml</td>
<td>108</td>
<td>108</td>
<td>108</td>
<td>108</td>
<td>-</td>
</tr>
<tr>
<td>Shives, %</td>
<td>3.7</td>
<td>5.2</td>
<td>3.5</td>
<td>4.0</td>
<td>-</td>
</tr>
<tr>
<td>Tensile Index, N.m/g</td>
<td>28.0</td>
<td>28.1</td>
<td>28.0</td>
<td>28.1</td>
<td>32.6</td>
</tr>
<tr>
<td>Tear Index, mN.m²/g</td>
<td>4.8</td>
<td>5.5</td>
<td>4.7</td>
<td>4.9</td>
<td>5.4</td>
</tr>
<tr>
<td>Burst Index, kPa. m²/g</td>
<td>1.3</td>
<td>1.4</td>
<td>1.3</td>
<td>1.3</td>
<td>1.0</td>
</tr>
<tr>
<td>Fiber (+48 fraction), %</td>
<td>41.7</td>
<td>41.5</td>
<td>40.7</td>
<td>40.8</td>
<td>-</td>
</tr>
<tr>
<td>Fines (-48 fraction), %</td>
<td>58.3</td>
<td>58.5</td>
<td>59.3</td>
<td>59.2</td>
<td>-</td>
</tr>
</tbody>
</table>
6.2 Blending of kenaf and bark22 RMP with varying percentages of whole kenaf soda pulp

In commercial newsprint production, the wet and dry strength properties of mechanical pulps are improved by reinforcing them with an appropriate amount (though as low as possible) of refined chemical pulps. However, the two pulps behave independently of each other in the furnish. Mohlin and co-workers (176) reported that the bonding potential of chemical pulps cannot be utilized in a furnish of mechanical and chemical pulps because of weak bonding between chemical and mechanical fibers.

In an effort to produce newsprint from the 100% whole kenaf, the effect of addition of whole kenaf soda pulp, supplied by Phoenix Pulp and Paper, Thailand, to the kenaf and bark22 RMP in various proportions was analyzed in this study. The kenaf soda pulp was beaten to a CSF of approximately 300 ml prior to its 5%, 10%, 15%, and 20% addition to the kenaf and bark22 mechanical pulps.

Handsheets were prepared from the kenaf and bark22 RMP furnished with the various proportions of beaten kenaf soda pulp and evaluated for the tensile, tear, and burst indices. The results as shown in Figs. 27 (a), (b) and (c) indicate that 5% and 10% addition of chemical pulp do not have any significant effect on the properties of bark22 pulps, while kenaf RMP shows an improvement in the properties. A further increase in the chemical pulp content has a positive effect on the various properties except the tear index for bark22 pulp. Kenaf soda pulp’s tear index (7.4 mN.m²/g) is lower than that of the bark22 RMP (9.1 mN.m²/g) which may be because of higher long fiber content in the latter pulp. As the chemical pulp content is increased, the tear index continues to drop for the bark22 pulp. It can be observed from the results that the sheet properties for all the proportions of chemical pulps are not additive but are mainly determined by the mechanical pulp. This is in line with the observations made by Mohlin and Wennberg (176). The results also indicate that the improvement was more pronounced for the kenaf RMP as compared to bark22. This could be due to the soda pulp...
Figure 27: Effect of reinforcement of kenaf and bark22 RMP with kenaf soda pulp. (Chemical pulp's tensile index = 64.5 N.m/g, tear index = 7.4 mN.m2/g, while the burst index is 3.7 kPa.m2/g).
containing more short fibers (whole kenaf contains 65% core fiber). Mohlin et al. (176) suggested that the shorter the fibers of chemical pulp the smaller will be its effect on the final sheet properties, particularly on strength.

6.3 Bleaching study of kenaf and bark22 mechanical pulps

6.3.1 Introduction

Because of the wood-fiber supply constraints, the use of mechanical and high yield pulps is increasing as a suitable substitute for expensive bleached chemical pulps in the manufacture of various printing grades besides their traditional use in newsprint. In addition to improving the strength and optical properties of mechanical pulps, the focus is on increasing their brightness at a reasonable cost and without affecting the yield and strength properties. Hydrogen peroxide and hydrosulphide, which preserve the lignin during brightening, are the two most common chemicals used in bleaching mechanical pulp commercially. However, hydrogen peroxide is more effective than the hydrosulphide in improving the pulp brightness. Normally, a single stage hydrogen peroxide bleaching can raise the brightness by 10-15%, but the raise is dependent on initial pulp brightness, sodium hydroxide dose, and some other bleaching variables such as retention time, temperature.

Cunningham et al. (177) tried to optimize a single stage hydrogen peroxide bleaching of kenaf TMP. However, the final brightness was just above 50% despite applying 3 per cent hydrogen peroxide for three hours at 3 percent consistency. The low initial brightness (39.1%) of kenaf pulp indicates that the pulp contained a considerable amount of soil or other foreign matter and seems to be one of the reasons for the poor response to hydrogen peroxide during bleaching.

In this study, initial optimization studies of bleaching have been carried out for kenaf and bark22 mechanical pulps with various percentages of hydrogen peroxide and sodium hydroxide. The other process conditions such as time, temperature and consistency were taken from the literature (178).
6.3.2 Results and discussion

The kenaf and bark22 RMP with an initial brightness of 52.2 and 45.6% ISO respectively were well below the acceptable brightness level (normally in the range of 60-65% ISO) for newsprint manufacture. Therefore, the two pulps, chelated with 0.5% DTPA for half an hour at 1% pulp consistency, were bleached in the laboratory under varying chemical applications of hydrogen peroxide and sodium hydroxide. To achieve a certain level of brightness, the peroxide requirement is dependent on the unbleached pulp brightness level. Figs. 28(a) and (b) show a plot between the hydrogen peroxide charged and the pulp brightness achieved after two hours of bleaching at 60 °C. The figures indicate that the pulp brightness increases in each case as the bleaching severity is increased. It can also be noted that the pulp brightness improves for a given dosage of peroxide as the alkalinity is raised. An increase in H₂O₂ will increase the bleaching rate by enhancing the chromophores removal (179).

The results show that the kenaf and bark22 pulps can be bleached efficiently with small peroxide and sodium hydroxide dosages. Both pulps can attain the brightness to an acceptable newsprint level with a small dose of 1% of each peroxide and alkalinity. However, if pulps, particularly bark22, are to be used for lightweight-coated (LWC) or any other speciality grades, they have to be bleached to a brightness range of 72-74%, meaning that an increased chemical application during bleaching will be required. However, the brightness starts levelling off for any addition of peroxide beyond 3% irrespective of the alkalinity level.

Figs. 29(a) and (b) are plots of peroxide consumed versus the pulp brightness at various alkalinitities for kenaf and bark22 RMP respectively. The results indicated that if the alkalinity were maintained the same, the percentage of residual H₂O₂ would increase with an elevated dosage of bleaching chemical. Moreover, H₂O₂ consumption is increased for both kenaf and bark22 RMP as the alkalinity is increased for a given H₂O₂ dosage. This could be due to increased brightening reaction and increased consumption at higher alkalinity levels (180). As a result of this, the bleaching efficiency for both kenaf and bark22 is increased considerably.
Figure 28: The figure shows that the pulp brightness for (a) kenaf, and (b) bark22 RMP increases with increasing sodium hydroxide and hydrogen peroxide dosages.
Figure 29: The graphs shows that the pulp brightness of (a) kenaf, and (b) bark22 RMP increases with an increased consumption of hydrogen peroxide. Hydrogen peroxide consumption increased with an increase in sodium hydroxide (alkalinity) dosage.
However, the darkening reaction, which is also dominant at higher alkalinity levels had a negative impact on the bleaching efficiency as defined in section 4.9 of Chapter 4 on page 36-37. It increases considerably as the alkalinity is increased for a given peroxide dosage as shown in Figs. 30(a) and (b) for kenaf and bark22 RMP, however the impact on brightness gain is less as compared to that at 1% $H_2O_2$ and 1% alkalinity level. At higher alkalinity levels, darkening prevails over the brightening reaction. At higher alkalinity levels, the darkening reaction becomes faster than the brightening, once the maximum in pulp brightness is reached comparatively sooner but lower and is further affected by the darkening reaction. Hence to achieve higher bleaching efficiency, it is necessary that an optimum alkali level be maintained during peroxide bleaching.

The bleaching results show that the peroxide consumption in the case of kenaf RMP is higher than that of bark22, which could be due to higher extractive content of core fibres (whole kenaf constitute 65% core fibers while bark22 contains 22% core fibers). The extractives seem to interfere with the bleaching performance of kenaf RMP by consuming a significant portion of the peroxide charged, which otherwise would have contributed to the pulp brightening. This could be one of the reasons that the bleaching efficiency is lower for the kenaf RMP as compared to that of bark22 RMP. However, higher lignin content (Table 12) means higher chromophoric compounds of kenaf fibers compared to that of bark22, which could possibly be another reason for an increased consumption of peroxide during kenaf RMP bleaching. It can be seen from Fig. 30(b) that the increasing alkalinity did not have any considerable effect on the bark22 RMP bleaching efficiency, which could be that at high alkalinity levels, a large portion of $H_2O_2$ dosage was consumed in working against the darkening reaction.

It is noticed from the results that the initial pulp brightness had a large effect on the bleaching efficiency. The bark22 RMP having almost 6 points lower brightness than that of kenaf RMP shows higher bleaching efficiency as compared to that of kenaf RMP for each combination of the $H_2O_2$ and NaOH dosages. For example, the bleaching efficiency for bark22
Figure 30: It shows that the bleaching efficiency for (a) kenaf RMP, and (b) bark22 RMP increases with an increased consumption of hydrogen peroxide during bleaching at any sodium hydroxide (alkalinity) dosage.
at 1% H₂O₂ and 1% alkalinity is 78.1% while for kenaf RMP, the bleaching efficiency is 60.4%. However, as the H₂O₂ and alkalinity increased the bleaching efficiency for bark22 RMP approached to that of bark22 RMP e.g. 89.4% for kenaf RMP vs 92.9% for bark22 RMP at 4% H₂O₂ and 3% alkalinity levels.

It can be seen that both the pulps can be bleached to a brightness level of more than 75% ISO with an application of 4% H₂O₂ and NaOH while keeping other process variables constant.

6.4 Conclusion

- Raw material screening and washing prior to refining improved final pulp brightness which will save considerable amount of chemicals.
- Kenaf and stem have to be refined in several passes to produce pulp with a freeness of 100-125 ml.
- The specific energy consumption was higher to refine kenaf/stem. This could be due to a small refiner having plates, which were originally designed for softwood, and possibly due to the morphological and anatomical characteristics of kenaf fibers. There is no significant difference in the energy consumption of the raw materials refined at two consistencies.
- Core fibers expected to be refined easily were protected during simultaneous refining of core and bark fibers.
- The shives content was higher for kenaf/stem RMP that could be due to unrefined core bundles. Some of these bundles also appeared in the sheet and affected its surface, optical and strength properties.
- White water recycling retained the fines and improved the strength and optical properties by approximately 5-10%.
- There is no significant difference in the properties of kenaf/stem refined at 15 and 22% consistencies respectively. The refiner speed seems to have minimized the effect of difference in the residence time for the refining at 22% consistency. However, kenaf RMP properties are comparable to that of kenaf TMP produced in the literature.
The pulp brightness for the pulp produced from kenaf is significantly lower than that of the kenaf RMP which could be due to less amount of core, which has higher initial brightness.

Blending of kenaf and bark22 RMP with kenaf soda pulp has a positive effect on the strength properties except on the bark22 tear index. The effect on the bark22 RMP properties will be much greater if it is blended with the long-fibered bark chemical pulp. However, it seems possible that newsprint can be produced from the whole kenaf RMP if blended with an appropriate amount of kenaf chemical pulp.

The results indicate that the bleachability of kenaf and bark22 RMP with H₂O₂ is high.

At a given alkalinity, H₂O₂ consumption is higher for the kenaf RMP as compared to bark22 RMP. However, the bleaching efficiency of bark22 pulp is higher than that of kenaf RMP.

Both the pulps can be bleached to a desired brightness with an appropriate chemical application. A small dose of 1% each of H₂O₂ and NaOH is enough to bleach the pulps to a newsprint level.
Chapter 7

Development of Core and Bark Fibers during Refining

7.1 Interaction of core and bark, refined simultaneously and separately on the pulp properties

7.1.1 Introduction

Kenaf consists of two fibers, core and bark, which differ morphologically and anatomically. Bark, long with thick cell walls but a small lumen diameter, has strength similar to that of softwood, while core, short with thin cell walls but larger lumen diameter, has a strength similar to that of hardwood fibers. Core also contains approximately 10% pith material, mainly parenchyma cells and vessels, which is not considered useful for papermaking. Because of the differences in the morphological, anatomical, chemical and physical characteristics of the bark and core fibers, the two fibers are expected to behave differently under the compressive and shear actions of refining. Hence, in optimizing the refining process, the process and design parameters will be different for the two fibers. However, in this study, the focus will be to optimize the refining process parameters only, as the design conditions are beyond the scope of this project. The objective of this study is to analyze the behavior of bark and core fibers refined separately and simultaneously.

Core and bark, soaked in water at 35° C for four hours were refined separately at 15 and 22% consistencies. As mentioned earlier, in case of kenaf and bark22, core and bark were refined simultaneously at 15% and 22% consistencies.

7.1.2 Interaction of core and bark fibers when refined separately and simultaneously

When refined separately, the core fibers, having thin cell walls and larger lumen diameters, will be expected to flex easily, and under the refining action, a desired fiber collapsibility and fibrillation may be achieved. Hence, it may be expected that the core fibers will require less energy to develop reasonable papermaking properties. However, as shown in Table
9. Core fibers required the same amount of specific energy as is the bark fibers to be refined to the same CSF level. This may be because of the thin-walled fibers, having flexible structure, absorbed substantial amount of energy before developing appropriate papermaking properties (167). Hatton (167) further asserted that the energy consumption for the thin cell-walled fibers would again be greater as the number of fibers per metric ton are higher as compared to that of the thick cell-walled fibers in one metric ton.

Core fibers, being thin-walled, may be expected to collapse easily and form a well-bonded sheet with a smooth surface. But the core RMP strength properties indicate that the fibers and fines do not possess the requisite papermaking properties (Table 9). Stiff and unrefined core RMP fibers inhibited proper bonding while the fines, in the presence of more unrefined fibers and fiber bundles, contained mainly broken fiber ends or pith, which do not contribute to the fiber-fiber compliance.

Unlike the core (or wood chips), the bark component has a strand type physical structure. Thus the coarse zone in the refiner will have little or no effect on the bark and needs to be refined at lower plate gaps. It can be expected that the fiber cutting will be reduced substantially, while the fibrillation will be enhanced as the plate gap is reduced. The plate gap also seems to play an important role in reducing the coarseness of bark fibers with thick cell walls by making fibers flexible enough to contribute to the papermaking properties. Stationwala and coworkers (181) have indicated that in refiner mechanical pulping, the pulp quality is largely determined by the plate gap, plate condition, and the specific energy. The pulp properties have improved significantly as a result of improved fiber and fines quality. As compared to bark22 RMP (168), the tensile, tear and burst indices of bark RMP have increased by approximately 10%, 30%, and 20% respectively. The pulp properties of bark refined at 15 and 22% consistencies are given in Table 9. Kenaf bark refined at 15% and 22% consistencies have shown better pulp properties as compared to those of the black spruce TMP reported in literature (170).
Table 9: Properties of core refined at 15% consistency and bark refined at 15 and 22% consistencies.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Core refined at 15% Consistency</th>
<th>Core refined at 15% Consistency</th>
<th>Bark refined at 22% consistency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refining energy, kWh/t</td>
<td>3854</td>
<td>3944</td>
<td>4081</td>
</tr>
<tr>
<td>CSF, ml</td>
<td>147</td>
<td>150</td>
<td>141</td>
</tr>
<tr>
<td>Shives, %</td>
<td>5.7</td>
<td>0.8</td>
<td>0.4</td>
</tr>
<tr>
<td>Density, kg/m³</td>
<td>215</td>
<td>314</td>
<td>320</td>
</tr>
<tr>
<td>Tensile Index, N.m/g</td>
<td>11.8</td>
<td>47.3</td>
<td>44.5</td>
</tr>
<tr>
<td>Stretch, %</td>
<td>2.2</td>
<td>2.2</td>
<td>2.2</td>
</tr>
<tr>
<td>TEA, J/m²</td>
<td>7.2</td>
<td>40.8</td>
<td>39.3</td>
</tr>
<tr>
<td>Tear Index, mN.m²/g</td>
<td>2.1</td>
<td>12.7</td>
<td>12.3</td>
</tr>
<tr>
<td>Burst Index, kPa. m³/g</td>
<td>0.4</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Scattering coefficient, m²/kg</td>
<td></td>
<td>58.0</td>
<td>59.8</td>
</tr>
<tr>
<td>Fiber (+48 fraction), %</td>
<td>36.8</td>
<td>62.6</td>
<td>60.2</td>
</tr>
<tr>
<td>Fines (-48 fraction), %</td>
<td>63.2</td>
<td>37.4</td>
<td>39.8</td>
</tr>
<tr>
<td>Weight-weighted fiber length, mm</td>
<td>1.08</td>
<td>1.91</td>
<td>1.96</td>
</tr>
<tr>
<td>Kink index</td>
<td>0.15</td>
<td>0.99</td>
<td>1.03</td>
</tr>
<tr>
<td>Coarseness, mg/m</td>
<td>0.412</td>
<td>0.25</td>
<td>0.24</td>
</tr>
</tbody>
</table>
It was expected that the handsheets formed by mixing 65% core RMP and 35% bark RMP would give the same results as were obtained from the handsheets made from kenaf RMP in which core (65% by weight) and bark (35% by weight) were refined simultaneously. However, the strength properties for the two pulps were significantly different (Fig. 31). The tensile, tear and burst indices of handsheets made from mixing 65% core RMP and 35% bark RMP dropped by 20%, 11%, and 29% respectively as compared to those from the simultaneous refining of bark and core in 65 to 35 ratio. The results indicate that the average fiber length of the mixture pulp may be the same (since tear reduces only by 10%); however bonding properties are poorly affected as seen from the higher losses for tensile and burst indices.

Similarly, strength properties for the core and bark RMP mixed in the ratio of 22% to 78% respectively were significantly different to those of bark22 RMP (168), 22% core and 78% bark refined simultaneously. However, the losses are less as compared to those from mixing 65% core and 35% bark. This shows that the core fibers refined separately could not stand the severity of bar actions during refining and did not produce the expected papermaking properties. The core fibers seem to have become damaged more than they were fibrillated during refining. The fines' quality from core RMP is also affected considerably and does not contribute to the sheet consolidation. Therefore, it can be summarized that the core fibers, when refined with the bark fibers, were protected by the long bark fibers and were not exposed to severe bar impacts during refining but eventually developed reasonable better pulp properties. This finding is similar to that observed by Ohls (182) during simultaneous refining of hardwood and softwood fibers. However, Hatton and Johal (165) reported that the hardwood (similar to core fibers) and softwood (similar to bark fiber) behave independently of each other during their simultaneous refining. The present experience shows that the core fibers refined with the bark fibers have improved properties of the core over the core refined separately. Significant changes have to be made in the process or design
Figure 31: Comparison of (a) tensile, (b) tear, and (c) the burst indices of sheets made from the bark and core refined simultaneously (e.g., kenaf and bark22 RMP) to those made from the equal proportions of bark and core fibers refined separately.
parameters to achieve an optimal pulp quality from the core fibers refined separately.

7.2 Fiber coarseness, flexibility and sheet stiffness

7.2.1 Development of core and bark fibers during refining: microscopic study

A series of photographs taken on a light microscope for the different fibers fractions from kenaf and bark RMP provided a useful insight in understanding the fiber development during refining. It can be noted from the photographs that the fibrils were liberated from their secondary walls with refining. Fibrillation is more prominent for the bark fibers having strong cell walls while the core fibers are either unexposed to refining or the intense refining action detached their fibrils. Some of the cases e.g. +16, +28, and +48 fibers from bark22 RMP as shown in Figs. 32 A, C and D respectively indicate the unraveling of the fibers’ surface and the removal of outer walls in most of the cases, thus leaving the $S_2$ wall exposed. However, in some cases, particularly for the kenaf and core RMPs, the various fractions still contain unrefined fibers or fiber bundles.

For the kenaf RMP fibers, it can be seen that core fibers are either not exposed to bars (as unrefined bundles can be noticed from Fig. 33 D) or they have only outer layers partially removed. However, the core fibers are not as fibrillated as are bark fibers in the simultaneous refining of these two fibers. It may be expected that most of the core fibers, being short, not only channeled through the bar grooves (bar plates were originally designed for the softwood refining and the grooves are wider than the core fiber length) but also interfered in the development of bark fibers as the bark fibers from kenaf RMP are not as refined as in the case of bark22 RMP. Moreover, the ‘gentle refining’ (reducing plate gap slowly from a high of 1.52 mm to 0.127 mm in several passes) seems to have its positive impact on the fiber during refining as the fibrils and even microfibrils are attached to the fibers and can be noticed all along the fiber length. As observed from Fig. 33 E, +28 fibers from the core RMP are under refined or mainly contain fiber bundles. The fines’ fraction from core RMP also indicates that it contains chunky material having broken ends of fibers or fiber bundles. Fig. 33 C shows typical fibrils and microfibrils.
Figure 32: Photographs (taken by a light microscope by enlarging them to 120X) of various fibrillated fibers (A) and (B)+16 fraction, (C) +28, (D) +48, (E) +100 fractions from the bark22 RMP refined at energy level 4, while (F) +16 fraction from the bark22 RMP refined at energy level 1.
Figure 33: Microscopic photographs (taken on a light microscope by enlarging them to 120 times) of various fiber (A) +16 fraction from the bark22 refined at energy level, (B) +100 fraction from the bark22 refined at energy level 1, (C) entangled fibrils of +16 fraction of bark22 refined at energy level 4, (D) +100 fraction of finally refined kenaf RMP, (E) fiber bundle from the +16/28 fraction of Core RMP.

(Specific energy consumption for the bark22 refining increases from energy level 1 to 4. Energy levels are different for kenaf, bark and core refining.)
entanglement for the bark22 RMP+16, which indicates the intensity of delaminating the fiber walls particularly for the bark fibers. The bar impacts seem to have better effect on the stiff and thick cell-walled bark fibers as compared to that of the flexible core fibers with thin cell walls in unraveling of the fiber surface.

As can be noticed from Fig. 32 (E), bark22 RMP +100 fractions contain mostly fibrils and microfibrils detached from the bark fibers' surface, mainly from the bark fibers during refining. On the other hand, the +100 fraction from the kenaf RMP (Fig. 33 (E)) contains a significant amount of parenchyma cells and vessels mainly from core fibers besides some detached fibrils and microfibrils from the bark fibers' surface.

7.2.2 Fiber coarseness of refined and unrefined fibers

Coarseness is defined as the weight of oven dried fiber per unit length and is expressed in mg/m or decigrex (mg/100 m). If all other factors are equal, the pulp with less coarse fibers will give a stronger, smoother and better folding paper (147). Fiber coarseness calculated by Tappi Test Method T234 cm-84 is a somewhat lengthy and tedious procedure and is based on microscopic study, which involves the study of few fibers. Moreover, it is only good for the pulped fibers as it does not provide any detail as to how to calculate the coarseness of an original unpulped fiber. Hence, there is a need for a simple and quick method to calculate the coarseness of the fiber in its original form in order to provide a basis for a comparison of coarseness during various pulping processes. The objective of this study is to analyze the coarseness reduction carried out during separate and simultaneous refining of two kenaf fiber types.

Ten replicates of core and bark with known o. d. weight were pulped as per the modified Franklin method described in Section 4.11 of Chapter 4 at page 41. The core and bark pulps' yield (by modified Franklin Method) as calculated from five replicates are 38.4% (range 35% to 41.3%) and 60.6% (range 56.9% to 64.5%), respectively. The remaining five samples of bark and core pulps were diluted to 0.001 percent consistency for FQA analysis.
Table 10: Analysis of bark (A) and core (B) fibers, prepared by the modified Franklin Method, by the Fiber Quality analyzer for different parameters.

(A)

<table>
<thead>
<tr>
<th>Sample</th>
<th>#1</th>
<th>#2</th>
<th>#3</th>
<th>#4</th>
<th>#5</th>
<th>Average</th>
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<tbody>
<tr>
<td>Fibers</td>
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<td>6206</td>
<td>6065</td>
<td>9823</td>
<td>9698</td>
<td>9960</td>
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<td>Length, Arithmetic, mm</td>
<td>1.34</td>
<td>1.35</td>
<td>1.37</td>
<td>1.44</td>
<td>1.48</td>
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<td>Length weighted, mm</td>
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<td>2.05</td>
<td>2.02</td>
<td>2.11</td>
<td>2.11</td>
<td>2.09</td>
</tr>
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<td>Weight-weighted, mm</td>
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<td>2.45</td>
<td>2.56</td>
<td>2.56</td>
<td>2.57</td>
</tr>
<tr>
<td>Coarseness, mg/m</td>
<td>0.197</td>
<td>0.200</td>
<td>0.213</td>
<td>0.182</td>
<td>0.187</td>
<td>0.185</td>
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<tr>
<td>Kink index</td>
<td>0.38</td>
<td>0.37</td>
<td>0.40</td>
<td>0.49</td>
<td>0.42</td>
<td>0.39</td>
</tr>
<tr>
<td>Total kink angle</td>
<td>4.12</td>
<td>1.01</td>
<td>1.09</td>
<td>5.10</td>
<td>5.10</td>
<td>5.10</td>
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<tr>
<td>Curl index, Arithmetic</td>
<td>0.039</td>
<td>0.036</td>
<td>0.040</td>
<td>0.042</td>
<td>0.045</td>
<td>0.049</td>
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<td>0.041</td>
<td>0.051</td>
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(B)

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<th>Sample</th>
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<th>#4</th>
<th>#5</th>
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<td>0.56</td>
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<td>Weight-weighted, mm</td>
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<td>0.97</td>
<td>0.89</td>
<td>0.99</td>
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<tr>
<td>Coarseness, mg/m</td>
<td>0.278</td>
<td>0.273</td>
<td>0.270</td>
<td>0.281</td>
<td>0.268</td>
<td>0.241</td>
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<tr>
<td>Kink index</td>
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<td>0.05</td>
<td>0.07</td>
<td>0.07</td>
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<tr>
<td>Total kink angle</td>
<td>1.11</td>
<td>1.12</td>
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<td>1.11</td>
<td>1.08</td>
<td>1.08</td>
</tr>
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<td>0.02</td>
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Table 11: Values of various fiber fractions, retained on the +16, +28, and +48 Bauer-McNett mesh.
(Specific energy consumption increases from energy level 1 to 4. Bolded values are the averages of the other two sub columns for each energy level).

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<th>Sample</th>
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<th>Energy level 2, +16</th>
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<td>1.55</td>
<td>1.46</td>
<td>1.50</td>
<td>1.37</td>
</tr>
<tr>
<td>Length wtd. mm</td>
<td>2.33</td>
<td>2.27</td>
<td>2.30</td>
<td>2.28</td>
</tr>
<tr>
<td>Weight-weighted. mm</td>
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<td>2.60</td>
<td>2.65</td>
<td>2.67</td>
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<tr>
<td>Coarseness, mg/m</td>
<td>0.177</td>
<td>0.165</td>
<td>0.17</td>
<td>0.207</td>
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<tr>
<td>Kink index</td>
<td>0.82</td>
<td>0.81</td>
<td>0.82</td>
<td>0.76</td>
</tr>
<tr>
<td>Total kink angle.°</td>
<td>28.3</td>
<td>27.2</td>
<td>28.8</td>
<td>25.5</td>
</tr>
<tr>
<td>Curl index, Arithmetic</td>
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<td>0.06</td>
<td>0.06</td>
<td>0.06</td>
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<tr>
<td>Curl index, Length wtd.</td>
<td>0.07</td>
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<table>
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<tr>
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<td>1.42</td>
<td>1.45</td>
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<td>Length wtd. mm</td>
<td>1.95</td>
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<td>1.95</td>
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<td>Coarseness, mg/m</td>
<td>0.166</td>
<td>0.193</td>
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<td>Kink index</td>
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<tr>
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<td>0.06</td>
<td>0.06</td>
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<tr>
<td>Curl index, Length wtd.</td>
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<td>0.06</td>
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</table>

<table>
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<th>Energy level 1, +48</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length, Arithmetic. mm</td>
<td>1.06</td>
<td>1.10</td>
<td>1.08</td>
<td>1.10</td>
</tr>
<tr>
<td>Length wtd. mm</td>
<td>1.40</td>
<td>1.40</td>
<td>1.40</td>
<td>1.43</td>
</tr>
<tr>
<td>Weight-wtd. mm</td>
<td>1.59</td>
<td>1.57</td>
<td>1.58</td>
<td>1.63</td>
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<tr>
<td>Coarseness, mg/m</td>
<td>0.211</td>
<td>0.213</td>
<td>0.21</td>
<td>0.235</td>
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<tr>
<td>Kink index</td>
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<td>0.8</td>
<td>0.81</td>
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<tr>
<td>Total kink angle.°</td>
<td>19.5</td>
<td>18.5</td>
<td>19.0</td>
<td>18.8</td>
</tr>
<tr>
<td>Curl index, Arithmetic</td>
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<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Curl index, Length wtd.</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
</tr>
</tbody>
</table>
Detailed results are provided in Table 10. The coarseness of the unpulped fibers was calculated as per the following equation:

\[
\text{Coarseness of unpulped fiber, } \frac{\text{mg}}{\text{m}} = \frac{\text{Pulped fiber coarseness calculated by FQA}}{\text{Franklin Method pulp yield}} \tag{1}
\]

Results show that the core fibers, being short, have less curl and kink indices, while the kink angle for the bark fibers is significantly higher than the core fibers (13.9 vs. 1.1). Fig. 34(a) indicates that there is little change in the coarseness of various fiber fractions with refining, which could be due to the large amount of fines created during refining. This is more significant in the case of pulps having a higher proportion of core fibers in the raw material (e.g. kenaf).

When the pulp fines content is low (<20%) and the pulp is from long fibered-pulp (e.g. bark or bark22), the fibers contribute more to the total fiber length, while there is little to no impact of fines on the total fiber length (149). Therefore, fines have no to little impact on the coarseness. However, when the fines content is increased (~45%) and the pulp is from the short fibers e.g. core and kenaf RMP, the fiber length is significantly affected by the fines and so is the fiber coarseness. However, the average fiber length is preserved during refining as shown in Fig 34 (b). It is observed that the coarseness of core and bark mechanical pulps is significantly affected by the presence of fines generated during refining. This is the reason that the coarseness of core and bark mechanical pulped fibers is higher than the original fibers (pulped by the Modified Franklin Method), Table 10 and Fig. 34 (a). Thus, the coarseness values for bark and core RMP fibers as given in Table 10 may not be fibers true values because of the high amount of fines present in the pulps.

In addition to flaky and fibril fines, there are also thick-walled fines such as ray cells, pith cells, parenchyma cells, which are more prominent in very short core fibers but can have a very high coarseness. One assumption, in the case of core RMP fibers, could be that possibly a few ray, pith and parenchyma cells contribute enough to the mass that they balance out many laky fines which are not contributing much to the mass but are significantly contributing to the fiber...
Specific energy consumption, kwh/t

Figure 34: Relationship of (a) fiber coarseness and (b) fiber length to specific refining energy. (Legends: A-Unrefined bark fiber, B-unrefined core fiber, C-refined core fiber, D-kenaf fiber refined at 15% consistency, E & F-bark22 refined at 15% and 22% consistencies respectively, while G & H represent bark refined at 15% and 22% consistencies respectively.)
As per Tappi Test Method T234, this problem can be avoided if all the fines are washed and removed from the sample before weighing and testing for the coarseness. Therefore, to have a true sense of the fiber coarseness of different RMP produced in this study, coarseness was calculated for various fiber fractions (retained on +16 to +48 mesh) from bark22 RMP. As can be seen from Fig. 35, the coarseness of different fractions of bark22 RMP decreases with an increase in refining. The reason for the higher coarseness of +28 and +48 bark22 RMP fractions as compared to that of the +16 fibers could be due to the presence of core fibers, which being short are expected to be in the medium fraction of the pulps, or it may be due to chunky fibers or broken ends of the fibers.

7.2.3 Effect of plate gap and refining on fiber length

Table 11 and Fig. 36 suggest that the plate gap and refining energy did not have any significant effect on fiber length of different fractions of bark22 RMP. May (203) also found that the fiber length is preserved during refining even at lower plate gaps. One of the reasons for the same could be that over the time, the sharpness of the bar edge is changed (gets rounded), thus reduces fiber cutting but enhances fibrillation. However, more work and explanation need to be carried out for the length preservation during refining.

7.2.4 Coarseness, sheet density and sheet stiffness made from different fractions from bark22 RMP

The stiffness of paper is an important property for printing grade papers. The stiffness of paper is proportional to the cube of its thickness while keeping its density constant. Smith (173) reported that the 'rigidity' of paper and board is proportional to the first power of the density provided the thickness is kept constant.

In thick papers, stiffness depends on the fiber bonding, while in thin papers the effect of the individual fiber rigidity is more pronounced (173). Thus, for the newsprint grade, the stiffness of paper will decrease as the specific energy is increased to refine the fibers. In other
Figure 35: Coarseness of different fiber fractions at different energy levels.
(Legends: Specific energy consumption increases from Energy level 1 to 4)

Figure 36: Fiber length of different fiber fractions at various energy levels.
(Legends: Specific energy consumption increases from Energy level 1 to 4)
Words a decrease in the stiffness of fibers or paper will correspond to enhanced fiber flexibility with an increased refining. Thus, as the fiber coarseness decreases with refining, it can be concluded that the wet fiber flexibility will increase, which will enhance the consolidation of fibers. Similarly, Fig. 37 shows that the sheet density increases as the fiber coarseness is reduced. Sheet density of +28 and +48 fractions is higher because of a significant amount of unrefined core fibers and bundles present in these two fractions.

Further, it has been noticed that the smaller fibers are stiffer than the long fibers, which is due to the higher force required to deflect them to a particular angle. If we consider the case of two cantilevered fibers, a short fiber (e.g. core) in Fig. 38 (A), and a long fiber (e.g. bark fiber) in 38 (B), the force ‘F’ required to deflect/bend the short fiber by ‘θ’ will be more compared to that of the long fiber if the two fibers have the same cell wall thickness and diameter. The moment (force times the fiber length) generated by force ‘F’ will be less in the case of the short core fiber as compared to that required by long bark fiber. However, the sheet made of short core fibers or kenaf fibers will have high bulk and poor bonding as is observed by its strength properties (Table 9). On the other hand, sheet formed by the long bark fibers is dense and has good strength properties indicating that the fibers are well bonded. Thus the stiffness of the sheet formed by stiff fibers will be lower than the fibers, which are less stiff. Therefore, it may be concluded that stiff fibers would oppose fiber bonding. However, cell wall thickness of bark fibers may also affect the stiffness (elasticity multiplied by the cross-sectional moment of inertia) as the cross-sectional moment of inertia depends on annular (fiber cell wall) thickness of the pipe (in our case fiber).

![Figure 38: Cantilevered (A) core and (B) bark fibers.](image-url)
Figure 37: Relationship between sheet density and fiber coarseness of various fractions.

Figure 39: Relationship between fiber coarseness and the sheet stiffness (Taber).
The fiber rigidity or flexibility will be dependent on the morphological characteristics of fiber and the pulping process used to separate them from the fiber matrix. Thick cell-walled bark fibers with small lumen diameter will be more rigid as compared to thin cell-walled core fibers having large lumen diameter. Mechanical pulp fibers are expected to be stiffer than the chemical pulp fibers because of the considerable lignin content still attached to fibers' surface (109).

Thus, to enhance the flexibility of bark fibers, more material needs to be peeled off from their surface and at the same time they must be unraveled appropriately. The peeling of fibers' surface reduces their coarseness and enhances their flexibility. Reduced coarseness may be expected to increase the conformity of fibers in a network and thus the sheet density. Therefore, it will be interesting to investigate if a correlation can be established between the sheet density and fiber coarseness as was done for the wet fiber flexibility and sheet density by Steadman and Lunar (183). In a study of sheet density of the sheets made from various fractions from bark22 RMP and their coarseness, it can be seen that the sheet density (or fiber compliance) increases with a reduction in the fiber coarseness. It shows that the fiber compliance during sheet formation improves as the fiber coarseness goes down. In other words, wet fiber flexibility improves with the reduction in fiber coarseness. Thus, it may be expected that the fiber coarseness would provide a good measure of its flexibility or rigidity.

In a typical relationship between sheet stiffness and the fibers' coarseness, Fig. 39 highlights that the sheet stiffness increases with a decrease in the fiber coarseness. This may be due to improved fiber bonding, which increases the stiffness (173). In an interesting relationship between sheet density and sheet stiffness, Fig. 40 shows a positive relationship, which is an increase in the sheet density with an increase in the sheet stiffness, since these two properties are related to the fiber consolidation and their compliance during fiber networking. This observation will depend on the fiber morphological properties and the type of pulp. However, more investigations are needed to arrive at any final conclusion. The objective of this study was to investigate if any relationship exists between the sheet density and stiffness, which will help to
Figure 40: Sheet density increases as the sheet stiffness increases for different fractions of bark2 RMP.
avoid the lengthy and tedious determination of wet fiber flexibility as suggested by various researchers (183-185).

Higher wall thickness of bark fibers will affect their wet compactability and their elasticity. The collapsibility of the thick-walled bark fibers may also be in question if they are not properly developed. Hence, it is necessary that these fibers be well fibrillated externally, which will help to make surface tension of the water effective and to bring these fibers together to form a good fiber network. The stiffness of the fibers in a sheet will depend on their ability to collapse into flattened ribbons at the time of pressing and drying of paper. As the refining continues, bark fibers will tend to collapse from the circular cylinders to flattened ribbons when made into paper. "Clark (147) has mentioned that the stiffness of a circular tube depends on the difference between the fourth power of the outside and inside diameters, or if flattened, directly on the resulting width and on the cube of the thickness of each of the two walls." Thin-walled core fibers, even partially fibrillated, may collapse to flatten to twice the wall thickness and the stiffness would be eight times or more. Thus, the fiber wall thickness of bark and core is an important factor in determining various sheet properties.

However, unrefined core fibers and their bundles were too stiff to collapse, hence affected the bonding area and interlocking and forming a soft, weak and bulky sheet particularly from core RMP. This is also one of the possible reasons why the kenaf sheet has lower density (higher bulk) than that of the bark22 RMP because of its higher core fiber (65% by weight) content than in the bark22 RMP.

7.2.5 Curl index of core and bark RMP fibers

Curl is an important property of fibers, which is said not only to increase the stretch in dry state (186) but also the wet-web extensibility (187-190). Hence, it is necessary that the fibers be moderately curled. The length and shape change of fibers during refining is species dependent. Thick-walled fibers have a lower curl index as compared to those of the thin-walled fibers. The curl index may indicate fiber flexibility or its stiffness (96). Therefore, bark fibers having thick cell walls will be expected to have a lower curl index as compared to the thin cell-
walled core fibers after refining. However, the results indicate that the bark fibers refined at 15% consistency have a higher curl index than that of the core fibers refined at the same consistency (0.057 v. 0.024). The results also indicate that there is no significant change in the curl and kink indices of unrefined core fibers over those of refined core fibers e.g. comparing pulped fibers with the +28 fraction of core RMP, the curl (0.03 v. 0.04) and kink (0.06 v. 0.06) indices are more or less the same. It shows that the fibers are stiff and have not been appropriately exposed to the refining bars.

On the other hand, there is a significant change in the curl index for the refined bark fibers. Because of the lower curl of the core fibers, the sheet formation was difficult, indicating that the wet web extensibility of these fibers was low. Moreover, stretch in dry state for the sheets made from RMP having higher core content decreased, showing that the lower curl index of core fibers was one of the reasons. The dry stretch for the sheets made from core was significantly lower than the sheets made from bark. The sheet stretches in dry state for the handsheets made from kenaf and bark22 RMP were observed to be 1.43 and 2.12% respectively.

7.2.6 Kink index of core and bark RMP fibers

Similar to the curl index, the kink index is also a measure of fiber curvature or shape. As per Kibblewhite (96), kink index is defined as the number of kinks, N_x, within a range of ‘x’ kink angles. Kink and curl indices provide important information on the behaviour of fibers during refining. Bark fibers are expected to have a lower kink index as compared to the core fibers. However with increasing refining, coarseness of the bark fibers is reduced gradually, thus making the fiber more flexible. For the finally refined pulps, the fibers, being long are expected to provide a higher kink index, which is comparable to that of core fibers. This indicates that core fibers, being smaller, were subjected to less refining showing that the fibers were protected during refining. The kink index of core fibers refined at 15% consistency is significantly lower than that of the bark fibers refined at the same consistency (0.16 v. 0.99). The kink angle is also smaller for the core fibers as compared to that of bark fibers (3.1° v. 22.1°). The lower kink index and angle of core fibers further indicates that the fibers, despite having thin cell walls, escaped
the refining actions or simply could not stand up to intense refining bar actions and just created a ‘debris’ which is not good for papermaking.

7.3 Conclusion

- Refiner bars seem to show more damaging effect on the core fibers when they are refined separately. From the pulp evaluation, it is clear that the fiber and fines do not possess appropriate papermaking properties.

- The pulp quality from the bark fibers, refined separately, is fairly good and the pulp quality is better than the black spruce TMP as given in the literature.

- The properties indicate that bark RMP may be a good substitute for expensive softwood kraft pulps for their use in the value-added products manufactured from mechanical pulps.

- Properties of the handsheets made from the two pulps, core and bark mixed in the ratio of 65 and 35%, are inferior to those made from kenaf (65% core and 35% bark refined simultaneously). Similarly, the pulp furnish prepared from the mixing of 78% bark and 22% core RMPs showed lower values as compared to that of core and bark refined simultaneously in the ratio of 22% and 78% respectively. It reinforces the finding that an optimum pulp quality is obtained when the two fibers are refined simultaneously.

- The results confirm the earlier observation that the core fibers are protected during simultaneous refining of core and bark.

- Fiber development has shown that slowly reducing the plate clearance helped develop fibers better. However, the core fibers did not develop appropriately during refining. During simultaneous refining of core and bark, core fiber was not only underdeveloped but also seems to have interfered with the refining of bark fibers.

- Original fiber coarseness can be calculated using the modified Franklin Method and FQA.

- Stiffness is higher for the sheet made of core fibers; however as the bonding tendency of bark fibers increased with refining, stiffness also increased for the sheet made of bark fibers.
The relationship between coarseness, stiffness, and sheet density could provide a good explanation for the wet fiber compactability and flexibility.

- The curl and kink indices for the core fibers further indicate that the core fibers escaped the bar refining actions and, hence, were not appropriately refined.
Chapter 8

Lignin Removal and Fiber Development during Refiner Mechanical Pulping of Kenaf

8.1 Introduction

Refining is a complex process in which a large number of physical and chemical changes occur to the fibrous components (63, 110, 191, 192). When producing mechanical pulp, the emphasis is always on maintaining the fiber length while maximizing fiber surface development. It is necessary that raw material structure, fiber properties, and the breakdown mechanism of the fiber matrix be understood properly. The fiber/raw material breakdown mechanism is mainly dependent on residence time, which in turn is dependent on several other factors including refiner plate pattern, refiner speed, plate gap, and refining consistency (80). Fiber separation and fibrillation are dependent on the morphological, chemical, and physical characteristics of the raw material being refined (69, 91, 98). An important factor affecting fibrillation, both external and internal, is the presence of lignin and hemicellulose between the cellulosic crystallites and the various laminae of the fiber (147).

The objective of this study is to understand the pattern of lignin removal during refining which is expected to throw light on the development of the fiber during refining and the relationship between the raw material structure and the generation of fines. An attempt has been made to understand the quality of fines, which controls many properties of paper. An X-ray photoelectron spectrophotometer (XPS) was used to analyze the fiber surfaces to support the result obtained from the chemical analysis of various fiber fractions. It may be interesting to note how the two morphologically and chemically different fibers, core and bark, behave during their simultaneous refining.
8.2 Fiber morphology

Wood or kenaf fibers consist of the middle lamella, primary wall, and secondary walls ($S_1$, $S_2$, and $S_3$). These layers are chemically and morphologically different from one another. The middle lamella (0.1-1.0 μm) is highly lignified. The primary wall (0.1-0.2 μm) is mainly comprised of cellulose and hemicellulose as well as some extractives 'glued' to each other by lignin. The compound middle lamella comprising of primary wall and middle lamella has an average lignin concentration of having more than 85% (151), and contains approximately 25% of the total lignin, while the secondary walls consists of microfibrils comprising cellulose, hemicellulose and lignin. Kenaf and bark fibers as shown in Figs. 41 (a) and 41 (b) respectively indicate that the bark fibers are long while the core fibers are short and contain a significant portion of parenchyma cells and vessels. Kenaf lignin has been reported to be different from any other lignin that has been characterized as it has a high syringyl content, moreover the side chain hydroxyls are relatively highly acetylated (144). Chemical composition of whole kenaf, bark, core and bark22 is given in Table 12. Some differences in the kenaf chemical composition as compared to that reported in the literature (94, 95) result from various factors including the growing conditions.

8.3 Results and discussion

8.3.1 Chemical analysis of whole kenaf, bark (with 22% core) and various RMP fractions

Chemical composition of whole kenaf, bark, core, and bark22 as given in Table 12, was determined as per the methods provided in section 4.10 of Chapter 4 at page 37. Some differences in the kenaf chemical composition as compared to what has been reported in the literature (27, 194) are probably because of the differences in growing conditions or due to an impurity of bark in core and core in bark fibers. Bark lignin is rich in a highly etherified syringyl component, which is unbranched and contains high temperature base-cleavable β-aryl ether units (144).
Table 12: Chemical composition of whole kenaf, bark fibers used for the production of refiner mechanical pulp.

<table>
<thead>
<tr>
<th>Chemical/Raw material</th>
<th>Whole kenaf</th>
<th>Core</th>
<th>Bark</th>
<th>Bark22*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose, %</td>
<td>42.7</td>
<td>35.2</td>
<td>49.6</td>
<td>47.0</td>
</tr>
<tr>
<td>Holocellulose, %</td>
<td>75.4</td>
<td>73.3</td>
<td>80.3</td>
<td>77.8</td>
</tr>
<tr>
<td>Lignin, %</td>
<td>18.2</td>
<td>21.1</td>
<td>12.5</td>
<td>15.3</td>
</tr>
<tr>
<td>Extractives, %</td>
<td>3.1</td>
<td>5.4</td>
<td>4.4</td>
<td>4.8</td>
</tr>
</tbody>
</table>

*bark and core mixed in the ratio of 78 and 22.

Table 13: Various percent weight fractions of whole kenaf and bark22 refiner mechanical pulps. However for various fractions, it may be difficult to find out the ratio of core and bark fiber in each fractions.

<table>
<thead>
<tr>
<th>Pulp Fraction</th>
<th>Whole kenaf</th>
<th>Bark with 22% core</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Energy level 1</td>
<td>Energy level 2</td>
</tr>
<tr>
<td>+16</td>
<td>7.7</td>
<td>4.4</td>
</tr>
<tr>
<td>+28</td>
<td>19.3</td>
<td>18.9</td>
</tr>
<tr>
<td>+48</td>
<td>20.9</td>
<td>19.9</td>
</tr>
<tr>
<td>+100</td>
<td>13.2</td>
<td>16.4</td>
</tr>
<tr>
<td>+200</td>
<td>9.7</td>
<td>12</td>
</tr>
<tr>
<td>Fiber/fine</td>
<td>47.9/52.1</td>
<td>43.2/56.8</td>
</tr>
</tbody>
</table>
Figure 41: Tissues of (a) core and (b) bark fibers.

Figure 42: Fines (-48 mesh) and fiber (+48 mesh) fractions of bark with 22% core and whole kenaf (WK) refined at 15% consistency.
Fig. 42 shows various fiber (i.e. material retained up to +48 mesh) and fine (i.e. material passed through -48 mesh) fractions, by weight, of bark22 and whole kenaf at various energy levels. With increased refining (more specific energy input) the fines fraction continued to increase while the long fibers fraction declined for both bark22 and whole kenaf RMP. Mohlin (94) mentioned that unravelling was pronounced for the thick cell walled fibers while thin cell walled fibers did not unravel during refining. Thus thick cell-walled bark fibers will be expected to unravel more than the thin cell-walled core fibers. The fines fraction increased primarily because of peeling of the fiber outer layer comprising middle lamella, primary and S1 walls. Pulps fines content may also include broken ends of fibers. The weight distribution for various fractions of whole kenaf and bark22 RMP are given in Table 13. However, it may be difficult to comment upon the core to bark ratio in +16, +28, and +48 fractions of different pulps.

Since whole kenaf contains 65% core, short fibers while bark22 constitutes 78% bark, long fibers. it may be expected that the various pulp fractions will contain different proportions of the core and bark fibers. In either case, core fibers being short are expected to appear in the +28 and +48 fractions. Hence, it may be expected that the chemical composition of various fractions from bark22 and whole kenaf will be different because of a difference in the chemical composition of core and bark fibers (Table 12). Lignin from different fractions of bark22 and whole kenaf refined at various energy levels was isolated to understand the pattern of its removal in relation to the fiber development.

8.3.1.1 +16 fraction of bark22 RMP

Though it is difficult to quantify the proportions of core to bark ratio of any fraction, visual and tissue analysis confirm that the +16 fraction of the bark22 RMP consists of mainly slender and long fibers supposedly coming from bark. Depending on the core component of +16 fraction, initial lignin content of the +16 fractions will vary between 12.5% for 100% bark and 15.3% for bark22. As shown in Fig. 43 (b), the lignin content of +16 fractions (i.e. longest fiber
Figure 43: Total lignin content (soluble and insoluble) of various fiber fractions of (a) whole kenaf, and (b) bark22 refined at different energy levels.

(Energy levels increased from level 1 to 4. However, energy levels are different for whole kenaf and bark22.)
fraction in a pulp) of RMP bark22 decreases continuously with increased refining. It indicates that lignin is gradually removed from the fiber surfaces. The lignin content of finally (after energy level 4) refined bark22 RMP +16 fractions indicate a drop by more than 25% (reduces to 9.9%) of the total lignin in bark22 unrefined fibers (Fig. 43 (b)). This indicates that a part of the S₁ wall along with the middle lamella and primary wall have been peeled off (middle lamella and primary wall contains approximately 25% of the total lignin). Thus, it may be expected that in some cases the S₂ wall will be stressed to lift the embedded fibrils, as has been reported in literature (95).

This is expected to increase the flexibility of fibers. The flexing and micro-cracking of these fibers will continue with continued specific refining energy input. However, S₂ layer exposure during refining will depend upon the nature of raw material, plate pattern, and the refining intensity. It is noticed that an optimum plate gap setting is needed to enhance lignin removal from the fiber surface and increased fiber fibrillation. It shows that the plate gap plays a vital role in the opening of the fiber structure. The micro-compressions developed in the fiber wall as a result of axial compression of the fibers will enhance the elongation properties of the fiber network (195).

8.3.1.2 +28 and +48 fractions of bark22 and kenaf RMP

+28 and +48 fiber fractions in a pulp primarily include broken long fibers (mainly bark) or otherwise medium sized fibers (core fibers). These fractions for either of the two pulps will constitute a significant portion of the core fibers, thus affecting the lignin content considerably. Fig. 43 (b) shows that the lignin content of +28 and +48 fractions for bark 22 decreases continuously indicating a gradual lignin removal from the fibers' surface. However, it indicates that the lignin content of these fractions is higher as compared to +16 fibers. This may be due to the fact that the +28 and +48 fractions are expected to constitute short and thin walled core fibers along with bark fibers. The core fibers having high lignin content would have increased the total lignin content of these fractions. It could also be due to the fact that the longer bark fibers would be subjected to greater mechanical stress and fatigue by the bars of the refiner. This will scrape off the outer layer lignin more than for the shorter core fibers. Moreover, the longer fibers would
be a part of the middle lamella or primary wall, which still seems to be attached to the fibers. The other reason may be that larger pieces of peeled middle lamellae and primary walls from +16 fibers are retained in these fiber fractions. This proposal will be confirmed in the latter part of the paper, when XPS data are analyzed.

From Fig. 43 (a), it can be seen that lignin removal is generally slow during refining of whole kenaf fibers. Even after final stage refining at 0.127 mm plate gap, a significant amount of lignin (16-18%) is still associated with the whole kenaf fibers. Thin walled (1-2 μm) core fibers (65% of whole kenaf) seem to have ruptured under the intense mechanical action of refiner bars before the splitting of middle lamella at the fiber interface, thus making fibrillation difficult. Kure (196) reported that thin-walled wood fibers (similar to that of core fibers) undergo only a small reduction in wall thickness with increasing refining energy compared to thick cell wall fibers. Hence, it can be expected the fiber surface peeling was less in the case of thin walled core fibers as compared to thick walled bark fibers. Another reason for the higher lignin content of these fractions could be that the short core fibers escaped refining action in presence of long bark fibers. It may be worth mentioning that the refiner plate pattern used in this study was originally designed for softwood (long fibers) refining, hence plate pattern may also be another possible reason for this.

8.3.1.3 +100 and +200 fractions of bark22 and kenaf RMP

The morphology and physicochemical properties of the fines (-48 to -200 fractions) are different from those of the fiber fractions. However, the fines content is vital for any mechanical pulp and, in fact, determines the pulp quality. The degree of swelling of fines is higher while the crystallinity, as determined by X-ray, is lower (197). Most of the fines created during refining are expected to originate from the fiber surface (198) such as fibrils detached from the stressing of $S_1$ and $S_2$ walls.

In the initial phases of refining, lignin primarily removed from the surface (middle lamella) of individual fibers or fiber bundles appears in the +100 to -200 pulp fractions. Figs. 44
(a) and (b) shows that +100 and +200 fractions are lignin rich. Hoffman et al. (199) reported that kraft pulp fines, which are also lignin rich, contained some ray cells and fibrils. Under the shear action of refiner bars, fibrils (~40 Å) embedded in lignin in the primary and secondary walls open up and sometimes get detached from the fibers. Fibrils' cleavage is expected to be more intense during refiner mechanical pulping which is carried out at lower temperatures as compared to thermo-mechanical pulping. The increased fibriller content of the +100 and +200 fractions will enhance the fiber network, thus improving sheet density, strength, and optical properties.

Fig. 43 (b) shows that lignin concentration drops once these fibrils begin appearing in +100 and +200 fractions of bark22 RMP. Heikkurinen et al. (111) also observed that the lignin content of fines fraction decreases while the cellulose content increases with an increase in specific energy. On the other hand, lignin concentration continued to increase for the +100 and +200 fractions of whole kenaf (Fig. 43(a)) further indicating that the middle lamella and primary walls are not yet peeled off completely. Figs. 43 (a) and (b) show a considerable difference in the chemical composition of +100 and +200 fractions from whole kenaf and bark22. Hence, it can be expected that whole kenaf and bark22 fines will behave differently during papermaking and may influence various paper properties, including sheet density, accordingly. Specific surface area by turbidity method could be used to determine fines quality from whole kenaf and bark22 (200).

8.3.1.4 Holocellulose content of bark22 and kenaf RMP fractions

Holocellulose content in various fiber fractions (+16 to +200 from bark22 and +28 to +200 from whole kenaf RMP) are shown in Figs. 44 (a) and (b). The two figures reflect that the holocellulose content increases as the lignin is removed from the surface of +16 to +48 fiber fractions of bark22 and whole kenaf refined at various energy levels. However, holocellulose content for +100 and +200 bark22 fractions decreases initially with increased refining until it begins to increase with the arrival of fibrils and other cellulosic material. On the other hand, holocellulose content continued to decrease for the whole kenaf +100 and +200 fractions as the lignin
Figure 44: Holo-cellulose content of various fiber fractions of (a) whole kenaf, and (b) kenaf22 refined at different energy levels.

(Energy levels increase from level 1 to 4. However, energy levels are different for whole kenaf and bark22.)
was still being removed from the fibers' surface. It further indicates that the $S_1$ layer is not yet exposed for these fibers.

### 8.3.2 Fiber surface analysis: X-ray photoelectron spectra

Examples of broad range XPS spectra of +48 fractions (retained on +48 mesh) from bark22 RMP are presented in Figs. 45 (a) and (b) which is drawn with the number of electrons counted (Y-axis) versus binding energy (eV) (X-axis) from 600 eV to 0 eV.

The high-resolution XPS spectra of RMP fractions for oxygen and carbon were recorded at an approximate binding energy of 533 eV and 285 eV, respectively. Elemental analysis (oxygen and carbon) with O/C ratio and carbon peaks with differing binding energies are shown in Table 14 and Figs. 46 (a) and (b) respectively. Data analysis shows that high-resolution spectra of C$_{1s}$ consists of 3 different peaks, C$_1$ (C-C/C-H) from 284.6-285.1 eV, C$_2$ (C-OH, C-OCH$_3$) from 286.4-286.8 eV, and C$_3$ (-O-C-O, C=O) from 288.4-289.0 eV, respectively.

The theoretical oxygen-to-carbon (O/C) atomic ratio in cellulose with a general formula of (C$_6$H$_{10}$O$_5$)$_n$ has been reported as 0.83 (136, 137), while for lignin it is 0.33 (136, 138). C$_1$:C$_2$:C$_3$ ratio for cellulose was reported 0.00:0.83:0.17 in the literature (199) indicating that the C-OH bond dominates in cellulose's linear structure (201). For lignin, C$_1$:C$_2$:C$_3$ ratio is 0.49:0.48:0.03, showing that C-H, C-C, C-OH and C-OCH$_3$ are the dominating bonds in a complex and branched lignin structure (202).

The presence of extractives (O/C ratio 0.11) on the fiber surface might have reduced the O/C ratio measured by XPS. O/C ratio of extractive free pulps has been reported to increase from its original O/C ratio (136). Thus, the O/C ratio for different fibers analyzed in this study indicates that the fibers surface comprises material other than extractives. The analysis of data generated (Table 14) from various XPS spectra indicates that O/C ratio is significantly lower than 0.83 for all bark22, whole kenaf, and core RMP fractions (+16 to +48). Hence, it can be summarized from the O/C ratio that the fiber surfaces contain a significant portion of lignin.

However, as shown in Table 14, the O/C ratio continues to increase for all the corresponding pulp
Figure 45: Examples of broad range XPS spectra of +48 fractions from bark22 RMP.
Figure 46: C1 (C-C/C-H), C2 (C-OH), and C3 (-O-C-O, C=O) peaks from the curve fit analysis at differing binding energies of 285.0 eV, 286.5 eV, and 288.5 eV respectively for +48 fractions from bark (with 22% core) refined at (a) energy level 1, and (b) energy level 4.
fractions with increased refining (energy level 1 to energy level 4). It indicates that the lignin concentration on the fibers' surface is decreasing with refining.

It is clear from the C₁:C₂:C₃ ratio (Table 14) that the C₁ component is significantly higher than zero, which is expected for pure cellulose, indicating the presence of impurities (mainly lignin and hemicellulose) on the surface of fiber. With increased refining, C₁ continues to decrease for all the fractions of bark22 pulp, indicating a continuous lignin removal from the fibers' surface through middle lamella and primary wall peeling.

The C₁:C₂:C₃ and O/C ratios for +16, +28 and +48 fractions of bark22 refined at various energy levels are statistically the same, indicating an equal amount of lignin present on the fibers' surface. The same trend was noticed from the lignin content of +28 and +48 fiber fractions as shown in Figs. 43 (a) and (b). However, the +16 fiber fraction contains less lignin, which could be due to several reasons mentioned earlier. A gradual increase in the O/C ratio and a gradual decrease in the C₁ component of C₁:C₂:C₃ ratio for the various fiber fractions show that lignin is being removed continuously with refining energy. Hence, given these values, we can rule out the possibility that the lignin removed during refining coated the fibers. Higher lignin content of +28 and +48 fibers is due to the larger lignin pieces removed from the fiber surfaces being retained in these fractions.

XPS spectra analysis indicates that there is no significant change in the C₁:C₂:C₃ and O/C ratios (Table 14) of +28 fiber fractions from the whole kenaf refined at two different energy levels. It shows that the rate of lignin removal from fiber surface was slow despite a considerable energy input (193). It also shows that the core fibers, 65% of the whole kenaf, being short in length (168, 193) escaped bar actions in presence of long bark fibers during refining.

8.4 Conclusion

- Lignin removal is comparatively slower for the thin walled core fibers during refining despite refining at small plate gaps.
Table 14: O/C ratio and analysis of high resolution C$_{15}$ peaks for various fractions of bark (with 22% core), whole kenaf, and core refiner mechanical pulps.

<table>
<thead>
<tr>
<th>Pulp fraction</th>
<th>O/C ratio</th>
<th>C$_1$:C$_2$:C$_3$ ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Energy Level 1$^*$</td>
<td>Energy level 4$^*$</td>
</tr>
<tr>
<td>Bark (with 22% core)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>+16</td>
<td>0.46</td>
<td>0.51</td>
</tr>
<tr>
<td>+28</td>
<td>0.49</td>
<td>0.58</td>
</tr>
<tr>
<td>+48</td>
<td>0.49</td>
<td>0.55</td>
</tr>
<tr>
<td>Whole kenaf</td>
<td></td>
<td></td>
</tr>
<tr>
<td>+28</td>
<td>0.52</td>
<td>0.55</td>
</tr>
<tr>
<td>Core</td>
<td></td>
<td></td>
</tr>
<tr>
<td>+16</td>
<td>-</td>
<td>0.46</td>
</tr>
</tbody>
</table>

*Energy levels are different for the refining of bark (with 22% core), whole kenaf, and core.

Note: The theoretical ratio for various components of fibers are:

<table>
<thead>
<tr>
<th>Component</th>
<th>O/C ratio</th>
<th>C$_1$:C$_2$:C$_3$ ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>0.83</td>
<td>0.00 : 0.83 : 0.17</td>
</tr>
<tr>
<td>Lignin</td>
<td>0.33</td>
<td>0.49 : 0.48 : 0.03</td>
</tr>
<tr>
<td>Extractives</td>
<td>0.11</td>
<td>-</td>
</tr>
</tbody>
</table>
• Lignin removal is faster for the thick walled bark fibers with increasing energy. However, plate gap and plate pattern are also equally important in lignin removal.

• +100 and +200 fines of whole kenaf and bark22 RMP are lignin rich. Lignin percentage continues to increase with refining energy for whole kenaf fibers indicating that S1 is not exposed yet and a part of the middle lamella/primary wall is still attached to fibers.

• Lignin percentage in the +100 and +200 bark22 RMP fractions decreases with increased refining indicating that middle lamella and primary walls are removed completely for most of the fibers while exposing S1 and S2 layers.

• It can be expected that presence of fibrils removed from the surface of bark fibers will enhance bark22 RMP fines quality, thus improving various pulp/paper properties. It can be summarized that whole kenaf RMP fines quality may be inferior to that of bark22 RMP fines.

• Since the chemical analysis of various fractions involves a wide population of pulp fibers, it can provide better understanding of the fiber development as compared to microscopic studies in which only few fibers are analyzed.

• X-ray photoelectron spectrophotometer (XPS) provides an excellent tool to study fiber development during refining by analyzing the surface of various fiber fractions. It simulates the findings from the chemical analysis of various fractions. XPS analysis can also be used to detect if the lignin removed during refining is coating the fibers.
Chapter 9

Conclusions, Implications of Research, and Recommendations for Future Work

9.1 Summary of findings of this research and its implications

9.1.1 Introduction

Because of sharp decline in the forest area in developing countries, some inexpensive and quality non-wood fibers like kenaf will be required for pulp and paper manufacture. Hardwood pulps have always been blended with the softwood pulps to improve runnability on paper machine and strength properties. Use of kenaf, which has a natural blend of two fibers, core and bark having strength similar to that of hardwood and softwood fibers respectively, will avoid the use of expensive wood (particularly in developing countries) for papermaking.

Besides many other objectives (as listed in Chapter 3), the main aim of this study was to develop a theoretical conceptual model for an optimal refiner mechanical pulping process for the simultaneous and separate refining of core and bark fibers. The results have shown that a ‘good quality’ pulp can be produced from the combination of core and bark fibers for newsprint manufacture particularly in countries where wood, mainly softwood, is either expensive or in short supply. In the absence of softwood, newsprint manufacture has been a challenge in these countries. Hence, it is expected that the findings of this study will provide a solution to this problem.

The use of a small refiner in this study dictated that the raw material be refined in several passes to obtain a required pulp freeness level. Moreover, the morphology of core and bark fibers had a significant effect on pulp quality. Based on the results and discussion carried out in Chapter 5-8, conclusions can be made which are summarized below:
9.1.2 Energy consumption during refining of core and bark fibers

Specific energy consumption in the refining of core and bark was considerably higher than was needed in the commercial refining of wood. However, the pulp properties should not be viewed in terms of the energy applied to refine the raw material to a required CSF value. The main reason for higher specific energy consumption was the small size refiner, fiber morphology and plate pattern. Energy consumption for kenaf refining was higher because it contained a higher amount of core, which had a flexible structure and had a tendency to absorb energy. Higher energy consumption was also required to peel off the material from the thick cell-walled bark fibers' surface to reduce coarseness and to lift the fibrils embedded in lignin in secondary walls.

9.1.3 Effect of fiber morphology on pulp quality

The fiber morphology of core and bark fibers had a significant affect on the quality of mechanical pulps. Conceptually, it was expected that the thin cell walled core fibers would be refined easily and provide a good quality pulp. However, the pulp properties indicated that bark fibers having thick cell walls managed to withstand the shear bar impacts, while the core fibers either escaped the compressive refining actions or their cellular structure was torn apart due to severity of bar impacts. The microscopic studies, surface analysis by X-ray photoelectron spectrophotometer and lignin analysis indicated that strong cell wall of fibers was a prerequisite for the fibers to fibrillate appropriately and develop papermaking properties. It was observed that thin-walled core fibers did not develop adequately during refining, while thick cell-walled bark fibers had their fibrils and microfibrils lifted up from their being embedded in lignin in the S1 and S2 walls with refining. Thick cell walls of kenaf fibers may affect their collapsibility but had a significant effect in their fibrillation. Lignin nature and amount also had an effect on the refining of fibers. If lignin distribution in bark is assumed to be in the same proportion as in the various walls of a wood fiber, S1 and S2 wall layers of bark fiber will have less lignin and more cellulose as compared to wood or core fiber. Hence, once the compound middle lamella of bark fibers is
removed, fibrillation is easier as compared to wood or core fibers. The fibrillation may be affected by the simple structure of kenaf lignin as proposed in the literature.

9.1.4 Effect of process parameters on the refining of kenaf

Results indicated that the raw material soaking temperature had a minimal effect on various pulp properties. It was observed that the specific refining energy consumption decreased due to easy defiberization of the softened raw material at an elevated soaking temperature. But the advantage of energy saving was minimized because of raw material refining in several passes to get a required pulp freeness. Specific energy consumption for bark refining revealed that the soaking temperature did not have any significant effect on bark fiber development probably due to its having strand type structure.

Effect of refining consistency, which controls the number of bar impacts and residence time was minimized due to refining of raw materials in several passes. The other reason was higher refiner speed at which the difference in residence time was negligible for the raw material refined at 15% and 22% consistencies.

Plate gap played an important role in kenaf refining particularly for that of bark. Lower plate gaps were needed to cause a failure in the bark matrix and to separate intact bark fibers during refining.

Plate pattern, though beyond the scope of this study, had an impact on the pulp quality particularly when core and bark fibers were refined separately. The bar breaker (coarse refining) zone had no effect on the development/fibrization of bark because of its physical structure. It was unable to cause any failure in the bark matrix but consumed considerable energy to transport the raw material to the medium and fine refining bar zones. For core refining, the groove width is required to be smaller than the core fiber length to achieve reasonable papermaking properties, particularly when core fibers are refined separately.
9.1.5 Interaction of bark and core fibers during their simultaneous refining

In this experiment, bark and core fibers were refined separately (RMP production from core and bark) as well simultaneously (kenaf RMP, stem RMP, and bark22 RMP). The results indicated that the two fibers behaved differently, particularly the core fibers, when refined separately. The core fibers were protected by the long bark fibers when the two fibers were refined simultaneously. Core fibers seem to have been damaged when refined separately and could not develop appropriate papermaking properties. The strength properties of sheets made from mixing core and bark RMP in the ratio of 65% and 35% respectively were significantly inferior to that of kenaf RMP (65% core and 35% bark refined simultaneously). Similarly, the strength properties of sheets made from the blend of 22% core RMP and 78% bark RMP are significantly lower than that of bark22 RMP (22% core and 78% bark refined simultaneously). This analysis clearly showed that the core fibers refined with the bark developed much better papermaking properties as compared to when they were refined separately. Thus, to achieve reasonable papermaking properties of core fibers, it is necessary that the core fibers are refined in presence of the bark fibers.

9.1.6 Quality of fines in the refining of core and bark

Chemical analysis of fines content of kenaf and bark22 RMP indicated that there was a significant difference in the quality and quantity of fines generated from the refining of two fibers, core and bark. +100 and +200 fractions of kenaf and bark22 RMP are lignin rich but the lignin content decreases with the arrival of fibrillar material, which is pronounced in case of bark22 and bark RMP. Kenaf RMP had higher fines content as compared to bark22 RMP but it mainly contained parenchyma cells, vessels and broken fiber ends, which were detrimental to the papermaking properties. On the other hand, fibrillar content of +100 and +200 fractions of bark22 and bark RMP increased with refining, which enhanced the consolidation of fibers, thus the strength and optical properties.
White water circulation increased the drainage time, hence the mobilization of fines. The fiber consolidation improved with white water recycling, which subsequently increased strength and optical properties by 5-10% for both kenaf and bark22 RMP as compared to that made without white water recycling.

9.1.7 Properties of mechanical pulps

Pulp properties indicated that newsprint with acceptable strength could be made from kenaf and bark22 RMP. Pulp properties can be improved if unrefined core fibers and bundles are reduced by modifying the plate pattern or process parameters particularly for the refining of core fibers e.g. soaking core fibers in presence of alkali prior to refining. Kenaf and bark22 RMP shives, containing mainly unrefined core fibers and bundles, appeared in the sheet and affected fiber compliance during sheet formation. Shives appearing in the sheet caused a failure at the point of their presence under stress, resulting in lower tensile and tear values. The bark22 RMP properties were better than those of spruce RMP and were comparable to those of spruce TMP. Bark RMP showed strong papermaking properties and could be used for the value-added applications; thus the use of expensive softwood pulps can be avoided.

Furnishing of kenaf and bark mechanical pulps with whole kenaf soda pulp, improved kenaf RMP properties, but for bark22 and bark pulps, blending with the kenaf soda pulp did not yield any significant improvement in their strength properties. However, the properties of bark22 and bark RMP reflect that newsprint can be produced from 100% furnish of either of these two pulps. More precisely, with improved pulp properties as were obtained in this study, newsprint manufacture from 100% kenaf is a reality now.

9.1.8 Response of core and bark22 RMP during bleaching with H₂O₂

Kenaf and bark22 RMP were very receptive to H₂O₂ bleaching. Kenaf and bark22 RMPs can be bleached to the newsprint brightness level with a small dose of H₂O₂ (1%) and NaOH (1-2%). For value added applications (e.g. lightweight coated), brightness can be increased with increased dosages of NaOH and H₂O₂ depending on the brightness level required. Bleaching
efficiency for kenaf RMP was observed to be lower than that of the bark22 RMP, which was due to kenaf containing more core fibers having higher lignin and extractive content as compared to bark fibers. Moreover, bleaching efficiency was also dependent on the initial brightness of the pulp to be bleached showing that the bleaching efficiency would be higher for the pulp having lower initial pulp.

9.1.9 Development of core and bark fiber during refining

Lignin removal from the fibers' surface with refining was more pronounced for bark fibers as compared to that from the core fibers. Plate pattern and gap, and specific energy played an important role in the stripping off compound middle lamella and gradual exposure of $S_1$ and $S_2$ walls of core and bark fibers. More materials being removed from surface of thick cell-walled bark fibers reduced their coarseness and enhanced the collapsibility. With continuous energy input, fibrils were detached from the fibers surface and appeared in the $+100$ and $+200$ fraction, which was prominent for the bark fibers and the process continued all along the fiber surface. Lignin and XPS analysis provided a better understanding of the fiber development during refining as it involved a wide population of fibers, while in microscopic studies, only a few fibers were analyzed.

9.1.10 Fiber length, coarseness and wet fiber flexibility of bark22 RMP fibers

It was interesting to note that fiber length was preserved during refining and was independent of plate gap and specific refining energy. Hence, it can be summarised from this finding that lower plate gaps (e.g. 0.38 mm, 0.254 mm and 0.127 mm) had a positive effect in the lifting of fibrils from the fibers surface while maintaining the fiber length, which would increase tensile and tear indices. This was the reason that the tear and tensile of bark22 RMP continued to improve with refining (Fig. 12). However, for the new plates, the sharp bar edges might enhance fiber cutting particularly at low (10–12%) refining consistencies.

Modified Franklin method and FQA could be used to determine the coarseness of original fibers, which was otherwise difficult to find. Reduction in the fiber coarseness with
increased refining indicated that the wet fiber flexibility increased, which in turn improved fiber-fiber interaction during bonding. A correlation amongst fiber coarseness, sheet density and stiffness provided an indication of wet fiber flexibility. This correlation would provide a better understanding of wet fiber flexibility, which could avoid the determination of this parameter by the long and tedious methods as provided in the literature.

Comparison of kink and curl indices of core refined and unrefined fibers further showed that the core fibers escaped the refining actions when refined in presence of bark fibers.

9.2 Recommendation for future work

A proper method should be developed to cut the bark fibers to an optimal size to reduce the shives content and energy consumption. If possible, study on designing the plate pattern for bark and core refining may be carried out, which may save energy and to develop appropriate papermaking properties.

To investigate the effect of raw material soaking temperature on refining energy, refining should be carried out in two stages on a large refiner as is carried out in commercial refining.

Structure of the fiber surface lignin may be studied by XPS and FTIR to provide information on if the lignin was just deposited or was chemically bonded to the fiber surface. This analysis will also provide a valuable information on the change in lignin structure during refining, if there is any. C\textsuperscript{13} NMR could be a good tool for this study.

RMP core fibers have shown poor papermaking properties, hence to develop appropriate papermaking properties of core fibers, some process modifications need to be carried out. Since soaking temperature had a minimal effect on the pulp properties, core fibers may be refined separately after soaking them in 1-2% NaOH or sulphite, while addition of H\textsubscript{2}O\textsubscript{2} could be an added advantage.
Two stage bleaching studies may be carried out to analyze if it will improve the brightness or bleaching efficiency. Bleaching with peracetic acid may also be studied prior to hydrogen peroxide bleaching.

More detailed study should be carried out for various fibers to develop a correlation amongst fiber coarseness, sheet density and stiffness before arriving at any firm conclusion.
References


62. W. Brecht, and K.H. Klemm, the mixture of structures in a mechanical pulp as a key to the knowledge of its technological properties, Pulp and Paper Can. 54(1): 72-80 (1953).


152. Patricia Sutton, Personal communication, OpTest Equipment Inc., Hawkesbury. ON (July 1999).


203. W.D. May, Personal communication (Sept. 1999).

Appendix
Appendix 1

SUMMARY OUTPUT - Shives, %

Regression Statistics
Multiple R       0.434559
R Square         0.188841
Adjusted R Square -0.013947
Standard Error   0.17454
Observations     11

ANOVA

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Legends:

$R^2$ value of any multiple regression equation explains a variation in the dependent variable.

Adjusted $R^2$ is the value of $R^2$ adjusted to account for the degrees of freedom. It means if degrees of freedom changes, $R^2$ will be adjusted accordingly.

Adjusted $R^2 = R^2 - (k-1)(1-R^2)/(T-k)$, where $k$ - No. of independent variables
$T$ - No. of observations

'df' stands for degrees of freedom.

'SS' stands for the sum of squares.

'MS' stands for the mean of sum of squares, which is given by sum of squares divided by degrees of freedom.

'F' is the Fisher's value.

Coefficients are defined as the coefficients of explanatory variables i.e. soaking temperature and consistency.

P-value' indicates the significance of 't-statistic'. In this study, coefficients of soaking temperature and consistency are significant if the p-value is less than 0.05 or 5% e.g. p-value of the coefficients of temperature in Appendix 1 is 0.59. It means that the coefficients is different from zero at 59% significance level. In this study, significance has been checked at 5% significance level.
## Appendix 2

### SUMMARY OUTPUT - Density, kg/m³

**Regression Statistics**
- Multiple R: 0.54078
- R Square: 0.292443
- Adjusted R Square: 0.115554
- Standard Error: 19.44873
- Observations: 11

### ANOVA

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### SUMMARY OUTPUT - Scattering coefficient, m²/kg

| Multiple R | 0.649353 |
| R Square   | 0.421659 |
| Adjusted R Square | 0.277074 |
| Standard Error | 2.051332 |
| Observations | 11 |

### ANOVA

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Appendix 4

SUMMARY OUTPUT-Tensile index, N.m/g

Regression Statistics
Multiple R  0.611212
R Square    0.37358
Adjusted R Square  0.216975
Standard Error  0.720862
Observations   11

ANOVA

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### SUMMARY OUTPUT - Tear index, mN.m²/g

**Regression Statistics**
- Multiple R: 0.339021
- R Square: 0.114935
- Adjusted R Square: -0.10633
- Standard Error: 0.12843
- Observations: 11

**ANOVA**

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### SUMMARY OUTPUT - Burst index, kPa.m²/g

**Regression Statistics**
- Multiple R: 0.643702
- R Square: 0.414353
- Adjusted R Square: 0.267941
- Standard Error: 0.062267
- Observations: 11

**ANOVA**

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SUMMARY OUTPUT - Energy, kWh/t

Regression Statistics
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Adjusted R Square 0.761904
Standard Error 80.9354
Observations 11

ANOVA

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- Multiple R: 0.770091
- R Square: 0.593041
- Adjusted R Square: 0.491301
- Standard Error: 6.096123
- Observations: 11

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- Observations: 11

#### ANOVA

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#### Coefficients

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<th>P-value</th>
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SUMMARY OUTPUT-Fines, %

Regression Statistics
Multiple R 0.760028
R Square 0.577643
Adjusted R Square 0.472054
Standard Error 1.34803
Observations 11

ANOVA

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