Processing of Value-Added Textile and Geotextile Products From Sugarcane and Kenaf.

Ovidiu Romanoschi
Louisiana State University and Agricultural & Mechanical College

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UMI
PROCESSING OF VALUE-ADDED TEXTILE AND GEOTEXTILE PRODUCTS FROM SUGAR CANE AND KENAF

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy in The Department of Engineering Science

by

Ovidiu Romanoschi

M.S., Louisiana State University, Baton Rouge, December 1996
B.S. & M.S., Technical University “Gh. Asachi”, Iasi, Romania, June1992
May, 1998
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I would like to express my gratitude and love toward my mother, for whom her sons' happiness is her meaning in life. Finally, my special and deep love to my wife Simona, for being not only an extraordinary friend, but also a great colleague and research mate. I dedicate this work to my wife and my mother.
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**NOMENCLATURE**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Explanation</th>
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</thead>
<tbody>
<tr>
<td>A</td>
<td>geometrical constant for the semi-hyperbolic die, mm</td>
</tr>
<tr>
<td>A</td>
<td>cross sectional area, m²</td>
</tr>
<tr>
<td>B</td>
<td>geometrical constant for the semi-hyperbolic die, mm³</td>
</tr>
<tr>
<td>F</td>
<td>Gibbs free energy, J/m³</td>
</tr>
<tr>
<td>fm</td>
<td>mixing factor, dimensionless</td>
</tr>
<tr>
<td>g</td>
<td>force necessary to orient the material, m/s³</td>
</tr>
<tr>
<td>H</td>
<td>enthalpy, J/m³</td>
</tr>
<tr>
<td>k</td>
<td>consistency of a power-law fluid, dimensions depend on n</td>
</tr>
<tr>
<td>L</td>
<td>length of the die, mm</td>
</tr>
<tr>
<td>Li</td>
<td>initial length of fibers, mm</td>
</tr>
<tr>
<td>Lf</td>
<td>final length of fibers, mm</td>
</tr>
<tr>
<td>n</td>
<td>power-law index of a power-law fluid, dimensionless</td>
</tr>
<tr>
<td>p, P</td>
<td>isotropic or hydrostatic pressure, Pa</td>
</tr>
<tr>
<td>q</td>
<td>energy flux, cal/(g-mole K)</td>
</tr>
<tr>
<td>R</td>
<td>radius of the flow channel, mm</td>
</tr>
<tr>
<td>S</td>
<td>entropy, J/(m³·K)</td>
</tr>
<tr>
<td>t</td>
<td>time, s</td>
</tr>
<tr>
<td>v</td>
<td>velocity, m/s</td>
</tr>
<tr>
<td>T</td>
<td>temperature, K</td>
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**Greek Symbols**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ</td>
<td>shear arte, s⁻¹</td>
</tr>
<tr>
<td>Δ</td>
<td>gradient operator</td>
</tr>
<tr>
<td>ε</td>
<td>strain rate, s⁻¹</td>
</tr>
<tr>
<td>εₜₜ</td>
<td>Henckey strain, dimensionless</td>
</tr>
<tr>
<td>ρ</td>
<td>density, Kg/m³</td>
</tr>
<tr>
<td>Φ</td>
<td>potential function, mm²/s</td>
</tr>
<tr>
<td>Ψ</td>
<td>stream function, mm³/s</td>
</tr>
<tr>
<td>δ</td>
<td>phase angle, rad</td>
</tr>
<tr>
<td>η</td>
<td>viscosity, elongational or shear, as defined in the text, Pa·s</td>
</tr>
<tr>
<td>τ</td>
<td>stress tensor, Pa</td>
</tr>
</tbody>
</table>

**Subscripts**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td>x, y, z</td>
<td>axis in rectangular coordinates</td>
</tr>
<tr>
<td>z, r, θ</td>
<td>axis in cylindrical coordinates</td>
</tr>
<tr>
<td>0, ex</td>
<td>entrance and exit positions in the die</td>
</tr>
<tr>
<td>vector</td>
<td></td>
</tr>
<tr>
<td>tensor</td>
<td></td>
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ABSTRACT

Utilization of agricultural crops as alternate raw materials for many industries was investigated for both sugar cane and kenaf. Value-added products with textile and geotextile applicabilities were developed and their properties assessed in direct correlation with their final use.

Bundles of fibers were extracted from the rind of sugar cane in three distinct steps: mechanical separation (using a Tilby separator), chemical extraction, and steam explosion. The process of fiber extraction was optimized for an atmospheric pressure alkali delignification, taking into account different factors such as: alkali concentration, reaction time, mixing, and steam explosion. Statistical techniques were used to study the effect of different process variables on the final characteristics of the fiber bundles.

The same process was adapted for different types of kenaf. The kenaf rind containing the outer bast fibers was separated from the inner core material, and the separated rind was submitted to a hot alkali partial delignification followed by steam explosion. The length and fineness of the fibers obtained were relatively sensitive to the sodium hydroxide concentration, but were influenced by the presence of steam explosion. The differences in kenaf harvesting, processing, and storage affected the final physical characteristics of the fiber bundles.

Lyocell solutions of sugar cane, kenaf, recycled cotton, and dissolving pulp in N-methyl morpholine-oxide (NMMO) were obtained at moderate temperature (80-95 °C).
Rheological behavior of these lyocell solutions was studied in both shear and elongational flow, pertaining particularly to the spinning process. A liquid crystalline pattern was noticed in polarized light, by differential scanning calorimetry, and by both shear and elongational rheology. Power-law shear thinning behavior was noticed for all the lyocell systems.

The lyocell solution effective elongational viscosities were measured by a novel method, observing the flow characteristics in a hyperbolic die. These measurements correlated with shear-flow determinations were used to estimate the enthalpy and entropy changes as functions of processing conditions. Also, the flow through a converging die provoked cellulose/lignocellulose phase separation and crystallization, microfiber formation, and orientation.
CHAPTER 1  JUSTIFICATION OF RESEARCH

Current research in the U.S. agricultural and forestry industry is concerned with the development of new uses and added value to farm and forestry products for greater economic benefits. The processing and recycling of the natural products is done in an environmentally responsible manner, using these resources efficiently. Utilization of agricultural crops as alternate raw materials for many industries is more a necessity than an option. Sugar cane bagasse is established as the future fiber of tropics and subtropics for pulp and paper making (Atchinson, 1995). Also, kenaf is a very promising material for paper pulps and textile applications (KP Products Inc., 1993).

Sugar cane (*Saccharum Officinarum*) is grown in large amounts for the production of cane sugar. The sugar cane stalk is composed of an outer rind and an inner pith. The pith contains small fibers and the majority of the sucrose, while the rind contains longer and finer fibers, arranged randomly throughout the stem and bound together by lignin (18%) and hemicellulose (30%) to form fiber bundles (Paturau, 1989). In most current processing, the cane stalks are crushed to extract the pith containing most of the sucrose, and the bagasse (crushed stalks and pith residue) is then used for fuel, minor products, or discarded (Paturau, 1989).

Kenaf (*Hibiscus Cannabinus*) is another annual plant considered to be an alternative fiber crop. The kenaf plant has two fiber types: the outer bark or bast portion (40% of the plant) and the inner woody core material (60%) (Sellers et al., 1993). As
was determined, for kenaf to be a viable source for chemical pulping, it would be necessary to separate and to process the bast and core fibers independently. Kenaf has been investigated for use in pulp, paper, twines, ropes and fishing nets, and in apparel and interior furnishings (Kalgren et al., 1989).

Prior studies conducted by Collier et al. (1995), showed that by extracting controlled amounts of lignin and hemicellulose from the rind of sugar cane, thin fiber bundles can be obtained. These bundles have properties appropriate for geotextile (in erosion control) and textile applications. High temperature and pressure alkaline extraction, followed by steam explosion were used in a batch process to obtain sugar cane fiber bundles with the required characteristics (length and tex). The sugar cane fiber bundles from this process have been investigated as value-added agricultural waste by-products in textile and geotextile applications (Elsunni & Collier, 1995).

Similar treatments involving low alkaline concentration extractions and steam explosion were also used in other studies to improve the solubility of wood substrates in an amine-oxide system. These studies came from the desire to spin cellulosic fibers directly from solutions. The cellulosic and lignocellulosic solutions in an amino-oxide type solvent are generically called lyocell solutions. Thus, it was possible to obtain high quality fibers from an abundant and renewable raw material, in a process that is environmentally friendly (Chanzy et al., 1986).
1.1 Research Objectives

The specific objectives of this work were the following:

1) To optimize the extraction process of fiber bundles from sugar cane rind and to determine the effects of extraction conditions (alkaline concentration, time of reaction, mixing, presence or absence of steam explosion, reactor volume, valve opening, rind type) on fiber properties. The alkaline extraction was conducted at atmospheric pressure. This modification had a beneficial economic and technological impact on the process. Different statistical techniques were used to diagnose and to model the effect of extraction conditions, and, ultimately, to optimize the process.

2) To adapt the extraction process for kenaf rind in a similar process to the sugar cane extraction. Different types of kenaf were investigated. The alkaline extraction was conducted at high pressure, followed by steam explosion. A study of different extraction conditions was statistically analyzed.

3) To form lyocell solutions from the extracted sugar cane and kenaf fiber bundles. Lyocell solutions from partially pulped kenaf and sugar cane were prepared in a concentration range of 2-20%. These solutions were compared with similar cellulosic solutions from dissolving pulp and recycled cotton.

4) To characterize the sugar cane and kenaf based lyocell solutions, pertaining particularly to the spinning process. Formation of a liquid crystalline phase and shear and elongational properties of the lyocell solutions were studied. A novel technique for measuring elongational flow properties of polymer melt and solutions through
converging dies was developed and implemented for the lyocell systems. The formation of microfibers due to phase separation was demonstrated.

Parts of this dissertation have been already published (Romanoschi et al. 1996, 1997, 1998). Four articles are to be published (Collier et al., in press, Romanoschi et al., in press).

1.2 Arrangement of This Report

This dissertation is organized in two parts. The first deals with the experimental aspects of developing textile and geotextile value-added products from sugar cane and kenaf rind. A literature review of different applications of sugar cane and kenaf, with direct implications in the textile and geotextile fields, is presented in Chapter 2. Chapter 3 presents the methods and material, experimental results, and conclusions for optimization of the atmospheric pressure delignification process from sugar cane rind. Successively, the same organization is presented separately in Chapter 4 for the kenaf extraction process. Finally the first part of this dissertation ends with recommendations (Chapter 5).

The second part is related by the formation and characterization of sugar cane and kenaf lyocell solutions. A literature review on lyocell solutions is presented in Chapter 6. Methods and materials are given in Chapter 7 followed by results and discussions in Chapter 8. Finally conclusions are presented in Chapter 9. The second part of this dissertation ends with recommendations in Chapter 10.
PART I

TEXTILE AND GEOTEXTILE VALUE-ADDED PRODUCTS FROM SUGAR CANE AND KENAF
CHAPTER 2. LITERATURE REVIEW

2.1 Value-added Products from Sugar Cane Bagasse

In view of the gradual depletion of traditional fibrous raw materials and the expected global energy crisis, sugar cane byproducts (bagasse, molasses, and press-cake) can be used profitably in the manufacture of valuable products. This would also partially alleviate the seasonal nature of the sugar industry. Bagasse could provide the cellulosic material for the pulp and paper industry or in manufacture of erosion control mats, ceiling tiles, boards, and livestock feeds, or chemicals such as furfural. Molasses is used mainly in the distilling industry for the manufacture of ethanol, but also for manufacture of oxalic and citric acids. Uses for press-cake include extraction of sugar cane wax and manufacture of balanced fertilizers (Atchinson, 1995).

Bagasse is a fibrous residue that remains after crushing of the stalks, and contains short fibers. It is essentially a waste product that causes mills to incur additional disposal costs. According to Atchinson (1995), bagasse will be ahead of all other crops as a source of fiber for the pulp and paper industry. It is estimated that the worldwide amount of bagasse produced annually is about 80,000,000 metric tons (MT), from which 25,000,000 metric tons will be used for pulping (equal to 13% of the total paper-making pulp capacity). As a result of the favorable economics of bagasse pulp production, it is expected that its uses will spread especially in the cane sugar producing countries more than the use of other non-wood fibers. The fibers from bagasse are

Bagasse pulps are used for all grades of paper: writing, toilet tissue, toweling, glassine, and others (Table 2.1). Bagasse newsprint paper is a low grade and low priced sheet appropriate for high-speed printing presses, with resistance to deformation, quick oil absorption, high opacity, and smooth printing surfaces. Bagasse newsprint paper is a commercially successful product (India. Indonesia. Mexico. USA) and can be made from depithed and properly stored bagasse to prevent loss in fiber properties due to uncontrolled fermentation. A formulation for very good quality newsprint includes: 50% bagasse mechanical and chemi-mechanical pulp bleached with peroxide. 35% bleached bagasse, and 15% bleached eucalyptus pulp (Atchinson, 1995).

Research has showed that some key factors should be considered in the production of bagasse newsprint. These relate to the use of a high content of mechanical pulp, all or part of which can be produced from bagasse, the use of highly efficient depithing systems for the bagasse, and the use of a storage method that assures excellent preservation of the bagasse properties, including color and brightness.
In addition, the well depithed bagasse is used in various types of reconstituted panel board, such as insulation board, wet- and dry-process hardboard, particle board, and medium-density fiberboard. The key factors in this field are (Atchinson, 1995):

- bagasse has to be depithed for use in all these products (except insulation board);
- bagasse has to be very well stored.

Table 2.1 Uses of Bagasse Pulps in Various Grades of Paper and Paperboard

<table>
<thead>
<tr>
<th>Pulp type</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Bleached bagasse mechanical</td>
<td>Newsprint</td>
</tr>
<tr>
<td>chemi-mechanical and/or</td>
<td>Mechanical-type printing papers</td>
</tr>
<tr>
<td>thermo-mechanical pulps</td>
<td>Tissue</td>
</tr>
<tr>
<td>B. Unbleached bagasse</td>
<td>Wrapping paper</td>
</tr>
<tr>
<td>chemical pulp</td>
<td>Multi-wall bag paper</td>
</tr>
<tr>
<td></td>
<td>Glassine and greaseproof paper</td>
</tr>
<tr>
<td></td>
<td>Test linerboard</td>
</tr>
<tr>
<td>C. High yield unbleached</td>
<td>Corrugating medium</td>
</tr>
<tr>
<td>bagasse chemical pulp</td>
<td></td>
</tr>
<tr>
<td>D. Bleached bagasse</td>
<td>Printing and writing papers</td>
</tr>
<tr>
<td>chemical pulp</td>
<td>Glassine and greaseproof paper</td>
</tr>
<tr>
<td></td>
<td>Fruit wraps and tissues</td>
</tr>
<tr>
<td></td>
<td>White-lined combination board</td>
</tr>
<tr>
<td></td>
<td>Food, milk bottle, and Bristol board</td>
</tr>
</tbody>
</table>
These bagasse boards have been produced from: bagasse and PVC (Moldas & Kokta, 1991), acetylated bagasse fibers (Rowell & Keany, 1991), bagasse and gypsum (Thole et al., 1993), bagasse and phenol-formaldehyde or urea-formaldehyde resins (Serantes et al., 1990, Singh & Singh, 1993). In Indonesia, sugar cane bagasse and rice straw are sometimes used as growing media for mushrooms; the wastes remaining after the mushroom harvest are alkali treated and 10% adhesive (urea-formaldehyde or phenol-formaldehyde) is added. The mat formed is pressed to give fiberboards of medium density (Hortoyo & Sutigno, 1993).

The lignin obtained from the spent liquor from the soda pulping of bagasse has been used in preparation of thermosetting adhesives by reacting the lignin with formaldehyde and optionally with a crosslinking agent such as phenol or urea. These techniques are applied to the preparation of wood adhesives for particleboards and veneer boards (Pizzi et al., 1989, Singh & Joshi, 1990, Singh & Singh, 1993). Also molding resins were obtained using direct condensation of lignin with phenol and formaldehyde or by introduction of phenol-formaldehyde pre-condensate to lignin (Ysbrandy et al., 1994). The hemicellulose from the spent liquor from the soda pulping of bagasse can be used as a paper strengthener, a briquette binder, and an adhesive for corrugated boards (Venter et al., 1989).

Bagasse has been used also as a raw material for a modified viscose process to obtain rayon fibers. The successful manufacturing of the textile fibers obtained from prehydrolysis sulfate pulp of bagasse by the viscose process was studied including the effect of variation of chemical and technical parameters (Paul et al., 1993).
Bagasse can be a source of ethanol. Ethanol is not just a good replacement for fossil fuels, but it is also an environmentally friendly fuel. Apart from this, ethanol is a very versatile chemical raw material from which a variety of other chemicals such as ethylene, acetic acid, acetaldehyde, and others, can be produced (Sharma, 1989).

2.1.2 Sugar Cane Rind and Bagasse for Textiles and Geotextiles

Research at Louisiana State University (LSU) has been conducted to determine the feasibility of sugar cane rind fibers for textile and geotextile applications (Elsunni & Collier, 1996). Sugar cane is grown in large amounts in several southern states (Louisiana, Florida, and Texas) and in Hawaii for the production of cane sugar. The sugar cane stalk is composed of an outer rind and an inner pith. The pith contains small fibers and the majority of the sucrose, while the rind contains longer and finer fibers, arranged randomly throughout the stem and bound together by lignin (18%) and hemicellulose (30%) to form fiber bundles (Patarau, 1989). In most current processing, the cane stalks are crushed to extract the pith containing most of the sucrose, and the bagasse (crushed stalks and pith residue) is then used for fuel, minor products, or discarded. However, a patented process has been developed to produce the fiber bundles from the rind of the cane stalk (Collier & Collier, 1998). Part of the process is also applied to bagasse. The fiber bundles from this process have been investigated as value-added agricultural waste by-products in textile and geotextile applications.

The total process includes a mechanical separation, a specific chemical extraction, and a steam explosion process when necessary. In the first step, sugar cane
stalks are processed through the Tilby separation process (Figure 2.1) that mechanically splits the cane stalk longitudinally, and routs out the inner pith, leaving the rind pieces containing the longer fibers. In the chemical treatment, the rind is treated with low NaOH concentrations (0.1 to 3 N), while agitating or tumbling, causing a removal of controlled amounts of lignin and hemicellulose. This results in a reduction of cross section of the cane rind pieces, while the length is maintained (Elsunni & Collier, 1995) (Figure 2.2). Two reactors have been used: a 20 L laboratory scale autoclave reactor.
still in use at LSU, and a 200 L autoclave reactor used primarily at the Cinclaire Sugar Mill. The extraction processes initially were conducted under high pressure. It was observed in the autoclave reactors that the agitation and tumbling are critical factors when finer fiber bundles are needed for some applications. Both reactors operate in a batch process and are provided with quick opening valves that allow them to discharge by steam explosion when further separation is necessary.

Figure 2.2 Directional Splitting and Delignification of Sugar Cane Rind
The wet fiber bundles obtained are washed, then formed into various products. One product is a nonwoven mat formed by suspending the fiber bundles on a screen in water, then dewatering and drying. The mats have been tested as geotextiles for soil erosion control in civil engineering applications.

The purpose of erosion control is to identify potential or existing erosion problems and to define effective and economical measures that can prevent, or at least, control erosion. A suitable natural fiber geotextile can perform this function and will biodegrade as vegetation grows to permanently control soil movement and erosion loss. Certain requirements are necessary. The geotextiles must be penetrable by growing plants, be capable of permitting interaction between air and soil, and allow rain to penetrate the soil and drain excess water (Collier et al., 1995). Thus, a low cost biodegradable geotextile can be produced in local sugar mills, providing an economic benefit to both the transportation industry and to the sugar cane industry.

A field test was conducted in summer 1995 in cooperation with the Louisiana Transportation Research Center (LTRC) and the Louisiana Department of Transportation and Development (LADOTD) to compare the cane erosion control mats with currently available natural fiber geotextiles of wood shavings, coconut, and straw (Thames, 1997). The mats performed as well as the commercial products and were superior in critical characteristics while being less expensive. They exhibited grass propagation and slope protection equivalent to other products, but were superior in conformation to the slope. Because of the long fiber entanglements, short fiber matting, and the retained lignin which acted like an adhesive, the sugar cane mats did not need
yarn stitching to maintain their shape and bulk properties and they conformed better to the slope, retaining cohesion even after heavy rains. Also, they completely biodegraded. In the case of stitched mats, bridging allowed undercutting and small channel formation, while the synthetic stitching interfered with mowing and did not biodegrade (Collier et al., 1996. Thames. 1997).

Recently, good erosion control mats have been produced from bagasse. The bagasse use as a raw material for mats has economic advantages, and also decouples the production of by-product fibers from the cane harvesting season. Otherwise, the cane must be processed quickly after harvesting to prevent loss of sugar quality. Thus, if the step of separating the rind from the pith can be eliminated, a more cost efficient production could result.

Processed bagasse will be used in the future as a spray-on product, to broaden the usage of sugar cane mats to areas where a spray-on application is more appropriate. This will enable the in-situ formation of mats that will be stable, less dependent on weather conditions, and of a lower cost. In addition it is possible to apply fertilizer and seeds at the same time. The spray-on mat of sugar cane presents several advantages over other commercial spray-on products. Because of the adhesion due to longer fibers entangling, short fiber matting, and retained lignin, another additive should not be needed. In short wood fiber products, a guar gum additive is used as an adhesive and processing aid. Also, the absence of any additive in the case of the sugar cane spray-on product will reduce the time following the application for the development of stability (Collier et al., 1995).
Fiber bundles will still be extracted for textile applications. Sugar cane fibers will be carded, and then formed into a yarn, bleached and dyed to determine their applicability for textile purposes. Spinning and blending of sugar cane fibers with cotton has been tried earlier at the US Department of Agriculture (USDA) Southern Regional Research Center (SRRC) in New Orleans. A 34% cane fiber / 66% cotton blend yarn was produced from a 50/50 mixture and compared with a 100% cotton yarn. The evenness and tensile properties of the blended yarn were lower than of the control yarn because of the irregularity of the yarn and the poor fiber cohesion (Chen, 1993). Difficulty in yarn spinning was due to the fact that cotton equipment was used, and the cane fibers tended to be rejected, since they are much coarser and longer than cotton fibers. However, recently at LSU a card designed for long bast fibers was purchased and used for sugar cane, and a spinning machine will also be designed to accommodate such long ligno-cellulosic fibers like sugar cane and kenaf. LSU studies were also conducted on hydrogen peroxide bleaching as well as on dyeing of sugar cane fibers. Direct dyes traditionally used for cellulosic fibers and basic dyes used for jute, were applied to sugar cane fibers (Romanoschi, 1997).

2.2 Value-added Products from Kenaf

Kenaf (Hibiscus Cannabinus) is an annual plant grown in areas with temperate or tropical climate within 35 degrees North and South of the Equator. At present it is grown in the sunbelt region of US, southern Russia, China, Thailand, Indonesia, Bangladesh, India, and in some Latin American countries. Also it can be potentially grown throughout South and Southeast Asia, Australia, and Africa, as well as in
Southern Europe, or wherever there are not sufficient or suitable forest resources (Kalgren et al., 1989). It is a very hardy plant that requires few fertilizers, herbicides, or pesticides, with low water requirements. Kenaf annually produces six to ten tons of raw fiber per acre. USDA field trials showed that kenaf can yield three to five times more fiber per acre per year than southern pine (KP Products Inc., 1993).

The kenaf plant has two fiber types: the outer bark or bast portion (40% of the plant) and the inner woody core material (60%). The refined outer bast fibers measure 2.6 mm and are similar to the best softwood fibers in strength and burst tests. The refined inner core fibers measure 0.6 mm (Kaldor, 1992). The plant's 60/40 composition is well suited for making newsprint. As was determined, for kenaf to be a viable source for chemical pulping, it would be necessary to separate and to process the bast and core fibers independently (Jeyasingam, 1990). The two kinds of fibers can be blended in different proportions to produce nearly any grade and quality of paper.

The process of separating the long and short fibers depends upon the method of harvesting. In frost free regions, the kenaf stalk is cut while green with special equipment. In cooler regions, the plant is typically frost killed and a natural drying of the stalk occurs, making harvesting with conventional farm equipment possible. The separation equipment is designed to accommodate the raw material in either whole stalk or chopped (KP Products Inc., 1993).

Laboratory trials on the chemical pulping of long and short fiber components of kenaf have been conducted in Australia, Japan, and Canada. The pulping of the whole stalk was also performed in a continuous chemical process on a commercial scale in

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Thailand. In North America, mill scale trials were conducted on the chemithermomechanical pulping of the entire stalk. Results indicated the technical feasibility of pulping kenaf fiber on the commercial scale (Kaldor, 1992). Also, at a mill in Sri Lanka it was shown that by blending kenaf pulp with straw pulp, the required physical properties and printing characteristics for good quality printing can be achieved (Jeyansingam, 1990).

From an economic point of view, a kenaf pulp mill would require a higher investment for raw material storage and fiber separation than a regular wood pulp mill, however this is offset by lower costs in raw material preparation (Kalgren et al., 1989). Because of the lower lignin content than wood (7.7%), fewer chemicals are required for pulping, and in addition the fibers require less bleaching. Thus, the waste water contamination is also reduced, and fewer chemical by-products are produced in the paper making process. Another factor that distinguishes kenaf bast material from wood materials is the orientation of the fibrils. In bast fibers, the fibrils lie parallel to the plant axis, whereas in wood the fibrils are spirally wound. Thus, the kenaf, as well as other bast fibers, can be split lengthwise by mechanical action, to yield fine and long fibrous bundles. The high hot-water solubility and the 1% NaOH solubility of kenaf explain also the loss of yield after any thermal or chemithermomechanical pulping process, as compared with wood. The fungal treatment of kenaf followed by pressurized mechanical pulping results in enhancement of strength properties. The controlled fibrillation that restricts the formation of fines is responsible for this behavior (Sabharwal et al., 1994).
Finally, kenaf can compete in cost, quality, and availability, if suitable conditions and land areas exist. In the US, kenaf is also a complementary crop for soy beans, cotton, and sugar cane. In Australia kenaf can replace wheat or rice, depending on location. In Thailand kenaf is an alternative to plantation eucalyptus and cassava. Also there is land availability in most of the countries that rely on the import of long fiber pulps for which they need foreign currency. Opportunities exist also in South America and Africa (Kaldor, 1992).

As was stated earlier, for kenaf to become a viable source for pulp paper, it is necessary to separate the bast and core fractions. As a result, the core fibers generated have been investigated as sources for low density composites (Sellers et al., 1993). Panels of core material were constructed and tested for strength properties, dimensional stability, water absorbance properties, and acoustical properties. Phenol-formaldehyde, urea-formaldehyde, and polymeric diphenylmethane diisocyanate resins were used as binders. The results showed that the panels would be suitable for sound adsorption type products. Also, kenaf core panels were produced for ceiling tiles, decorative panel substrates, floor tile substrates, and certain structural components (Sellers et al., 1995). Kenaf can be used as reinforcing fibers in the formation of synergistic property enhanced fiber/thermoplastic composite materials. A compatibilized blend of kenaf/polypropylene has good tensile properties (Sanadi et al., 1994, Rowell et al., 1994).

Research has determined also that kenaf plant fines and kenaf milled fines are excellent oil sorbent materials and also prevent the oil from leaking after absorption. All these properties will be beneficial in minimizing industrial waste (Goforth, 1994).
can play a significant role in fluid/particle separation operations such as oil adsorption, coalescence, deep-bed filtration (cartridges), and as filter aids for decreasing the resistance of filter cakes. Fibers can be used to improve filtering characteristics of municipal wastewater (Tiller & Zhon. 1995).

The misuse or improper disposal of preservatives used in the wood treatment industry is another environmental concern. Large areas of soil can be contaminated, and usually are cleaned by nature's own bacteria and fungi. However, research by the Environmental Biotechnology Group of the Mississippi Forest Products Laboratory (MFPL) to identify microorganisms and methods through which soil contaminants can be converted to harmless byproducts (CO₂, H₂O) is progressing. This process is called bioremediation. To date scientists at MFPL have found that kenaf is an excellent enhancer of this process because of its absorption properties, biodegradability, high protein content, and large number of natural microorganisms. Kenaf can remove the pollutants from soil particles, making them more available to the microorganisms. Also kenaf itself provides more microorganisms to help biodegradation of the contaminants (Borazjani & Diehl, 1994).

2.2.1 Kenaf Rind for Textiles and Geotextiles

Scientists at the Mississippi Agricultural and Forestry Experiment Station have developed nonwoven kenaf and textile fibers mats impregnated with turf seed (Robinson, 1995). The mat is composed of equal amounts of kenaf bast fiber and by-product from a mote gin operation. The components are mixed, then a biodegradable, low melt bonding fiber is added to it, and it is run through a 350 degree oven to kill any
weed seed and to bind the fibers. After the mat is cooled, it is sprinkled with seed. A rayon scrim is laid, then the mat is needled to hold the fibers and the seeds in place. Commercially, the mats are used in home constructions, highway erosion control, and are being manufactured by Mississippi Mat Line, of Charleston, MS, a subsidiary of Agro-Fibers, Inc. The mat functions like an insulator over an area where turf is needed. If it is watered, the seeds germinate and grass growth occurs. Also, the mat serves two important purposes: it gives the seed a good medium in which to germinate (since water is retained in the mat) and it helps hold the seed in place. After the grass develops, the mat biodegrades (Robinson, 1995).

Kenaf fibers have been incorporated into various types of nonwoven textiles, like kenaf/PP blends or kenaf/cotton/PP blends, that may be used for products such as fabric softener sheets, furniture underlays, coverstocks, and barrier textiles for medical and agricultural protective clothing (Ramaswami & Boyd, 1994). Kenaf fibers were also bleached to a good white with hydrogen peroxide, and then dyed with direct and basic dyes (Romanoschi, 1997). Kenaf fibers treated with sodium hydroxide have been carded and needle punched into 100 % kenaf and kenaf/cotton blended mats. These mats are also biodegradable and have potential in the prevention of soil erosion, the control of weeds, and the cleanup of waste liquids (Tao & Moreau, 1994). Kenaf bast fibers, cleaned of core fibers, have been mixed with refined wood, synthetic and other natural fibers to make various nonwoven needle punched products: lightweight seeded grass mats, wild flower mats, vegetable strips, erosion control mats, oil absorption mats, pads and pillows, substrates for molded automobile parts, and composites (Fisher, 1994).
The feasibility of kenaf for yarns and fabrics was also evaluated. Since jute and pineapple fibers have been used to make coarser fabrics, it was expected that kenaf's good tensile properties and its resistance to mildew and rot may make kenaf an alternative crop for industrial textiles. The fibers were retted both chemically and bacterially, followed by a degumming process (either with alkali or with an enzyme). Then the fibers were blended with cotton, successfully spun into yarns, and knitted (Ramaswami & Boyd, 1994).

The process developed for the extraction of fiber bundles from the rind of sugar cane has been adapted for kenaf. Green whole stalk kenaf, semi-dry frost killed whole stalk kenaf, field harvested in bales kenaf rind, and field harvested and two year field stored kenaf have been used with positive results. Various weights of kenaf erosion control mats were produced using normal field harvested kenaf. The mats were tested with other sugar cane mats for erosion control and roadside turf grass establishment, in collaboration with the Horticulture Department from LSU. The surface was pretreated with Roundup® weed killer three times during June and July 1994, rototilled, leveled for seedbed preparation, seeded, and fertilized. Bermudagrass was sowed and covered with mats of sugar cane and kenaf on August 4, 1994, and later was covered by mats of wood fiber and coconut (on August 25, 1994). Plots were rated for density of grass growth weekly. It was found that there were no significant differences between any of the mats with respect to grass plant propagation. Also, the kenaf and cane mats completely biodegraded after seven months, while some of the coconut and the stitching of the commercial mats remained in place. The medium weight kenaf mats allowed more
growth than the thinner or thicker mats (Collier et al., 1994, 1994, 1997, Romanoschi et al., 1997).

Another conducted test was a slope stability test on a 23° slope that was rototilled but not chemically treated, nor seeded or fertilized. Six sugar cane and three kenaf 2.24 ft² nonwoven mats were placed on the slope. All the mats survived and conformed to the irregularities of the soil, even though a heavy rain occurred during that time. Grass shoots quickly developed and after seven months the mats completely biodegraded and the slope was covered with grass.

Another use of the cellulosic mats is for reinforcement in structural reaction injection molding (SRIM). The cellulosic reinforcement included: cheesecloth and nonwoven mats from kenaf and sugar cane rind, and sweet gum wood. Excellent adhesion between the reinforcement and the matrix phases results from chemical bonds between the cellulosic hydroxyl groups and the isocyanate groups in one of the component used to form the polyurethane matrix. Therefore, the modulus of elasticity and tensile strength were doubled with as little as 3 to 7 per cent cellulose (Collier et al., 1995, Fahrurrozi, 1997).
CHAPTER 3. ALKALI DELIGNIFICATION OF SUGAR CANE AT ATMOSPHERIC PRESSURE

Fibers were extracted from sugar cane rind and investigated as a new source for the textile and geotextile industries. Structurally, the cane stalk from which the fibers were extracted consists of an outside rind and an inner pith. The longer and finer fibers that are the focus of this research are in the rind, while the pith contains shorter fibers and most of the sucrose (Collier et al., 1998).

Previous studies indicated that the key to the extraction processes is an alkaline treatment at high pressure (100-150 psi) with appropriate mechanical action. In later work the best fibers were produced by an alkaline extraction followed by steam explosion. This process has been simplified by performing the alkaline extraction at atmospheric pressure (Elsunni & Collier, 1996).

3.1 Materials and Methods

Three distinct steps were used to obtain the fiber product: mechanical separation, chemical extraction (retting), and steam explosion. Sugar cane stalks from the 1994 harvesting season were used as raw material. In the first step the sugar cane rind was separated from the pith immediately after arriving at the sugar mill using the Tilby technology. The separated rind pieces having lengths between 50-280 mm were subjected to different processing times, drying and storage methods:

1) Fresh harvested sugar cane rind (FHR), which was sun-dried after Tilby separation, and processed immediately;
2) Dried sugar cane rind (DR), which was sun-dried after Tilby separation, and then stored for four months at atmospheric conditions;

3) Frost killed sugar cane rind (FR), which was sun-dried after Tilby separation, stored in bags and then frozen for about seven months until needed for extraction. Every frost sugar cane rind piece was individually measured in length (mm) and weight (g). Weight averaged length was computed for every batch.

Lignin extractions were conducted in a 20-L autoclave reactor. The autoclave vessel is equipped with an oscillatory agitator powered with a 30-watt DC motor to provide mechanical action by tumbling the reactor contents, and a rapid discharge valve at the bottom. The extractions were performed at different concentrations, reaction times, tumbling frequencies, initial mass of rind, and volume of alkali solution. After delignification, sodium hydroxide consumption was measured by titration of black liquor and expressed as g of NaOH consumed/100 g rind. The lignin concentration in the extract (black liquor) was measured by a spectrophotometric method based on adsorption of ultraviolet radiation at 280 nm (Alen & Hartus, 1988).

In the steam explosion step, saturated steam at a pressure of about 760 kPa at 168 °C was injected into the autoclave reactor containing the product from the previous step. After a period of one minute while the reactor was maintained at high pressure, the discharge valve at the bottom of the reactor was opened. The sudden release of pressure expelled the reactor contents and blew the fibers apart, resulting in relatively dry separated fiber bundles.
After extraction, 0.1 g of fibers were randomly selected from the fibers extracted under each condition. The number of fibers in a sample varied from 20 to 50, depending on the fineness of the fibers. The fiber bundles were characterized in terms of weight, length and linear density to determine their suitability for textile and geotextile applications. The linear density, i.e. the mass per unit length, was reported as tex. Tex, a standard measure, represents the weight in grams of one thousand meters of fiber.

3.2 Experimental Design

Seven process variables were analyzed as possible factors of influence for the sugar cane fiber bundle characteristics (weight, length, and tex). These process variables were: alkali concentration in solution (expressed as normality), reaction time, frequency of tumbling (expressed as the time interval between two successive tumbling sessions), volume of alkali solution, initial rind mass, type of rind, and presence of steam explosion.

Nine initial experiments were conducted using 250 g of FHR rinds, a time of reaction of 60 min. and the interval between tumblings of 30 min. The normalities for the NaOH solutions were: 0.30, 0.40, 0.50, 0.60, 1.00, 2.00 and 3.00 N. Three experiments were conducted using different volumes of solution: 8, 10, and 16 L for the same 1.00 N concentration. Fiber characteristics for the experiments using 0.40 N and 0.50 N solution concentrations were measured before and after steam explosion.

Thirteen experiments were performed using DR rinds. Batches of 250 g of rind were delignified using 8 L of NaOH solution with different normalities (0.30, 0.40, 0.50, 0.70, 1.00, 1.50, 1.80, 2.20, 3.00, 3.30, 4.00, 4.50, and 5.00), a reaction time of 60 min.
with an interval between tumblings of 30 min. After delignification all these batches were steam exploded.

3.2.1 Central Composite Rotatable Experimental Design

The next eighteen experiments were organized in a central composite rotatable experimental design with just three input process variables: concentration of NaOH solution, time of reaction, and frequency of tumbling (Cohran & Cox, 1957). These experiments were done for FR rind, using a volume of solution of 8 L, 100 g of rind, and presence of steam explosion. The first step of this design was to locate the appropriate experimental region for each parameter. The values of the variables were coded so that the lower and upper levels of each dimensionless factor were \(-1.68\) and \(+1.68\). For every parameter five coded levels were chosen: \(-1.68, -1, 0, 1, 1.68\) and every real interval of values for the three parameters was coded based on Equations 3.1, 3.2 and 3.3:

\[
\begin{align*}
    x_1 &= \frac{3.36(C - 0.5)}{2.5} - 1.68 \\
    x_2 &= \frac{3.36(T - 30)}{210} - 1.68 \\
    x_3 &= \frac{3.36(I - 10)}{50} - 1.68
\end{align*}
\]

where \(C\) is the normality of NaOH solution, \(T\) is the time of reaction expressed in minutes, \(I\) is the time interval in minutes between two consecutive tumblings, and \(x_1, x_2, x_3\) are the corresponding coded variables for the parameters: concentration, time of reaction, and time interval between agitation (Table 3.1).
Table 3.1 Coded and Experimental Values of Process Variables

<table>
<thead>
<tr>
<th>Coded level</th>
<th>Normality</th>
<th>Time of operating [min]</th>
<th>Frequency of tumbling*[min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1.68</td>
<td>0.50</td>
<td>30</td>
<td>10</td>
</tr>
<tr>
<td>-1.00</td>
<td>1.00</td>
<td>72</td>
<td>20</td>
</tr>
<tr>
<td>0.00</td>
<td>1.75</td>
<td>135</td>
<td>35</td>
</tr>
<tr>
<td>1.00</td>
<td>2.50</td>
<td>198</td>
<td>50</td>
</tr>
<tr>
<td>1.68</td>
<td>3.00</td>
<td>240</td>
<td>60</td>
</tr>
</tbody>
</table>

*interval between two consecutive tumbling sessions

The experimental design was obtained from the combination of the five levels for each of the three parameters (first 14 experiments) and the repetition of the central experiment (from 15 to 18) (Table 3.2). The regression analysis of this succession of eighteen experiments gave quadratic response surfaces characterized by the general equation:

\[ y = a_0 + \sum_{i=1,2,3} a_i x_i + \sum_{i,j=1,2,3} a_{ij} x_i x_j \]  \hspace{1cm} (3.4)

where the \( a \) values are the polynomial coefficients computed by RSReg Procedure from SAS.

Another eleven experiments completed the design in order to introduce the delignification process characteristics without any agitation. The real and coded variables for these eleven experiments are presented in Table 3.3. The obtained model for the alkali delignification was optimized using MINOS® 5.4. The objective function

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was tex with the experimental intervals for our three parameters and lower limits for length as constrains.

<table>
<thead>
<tr>
<th>No. exp.</th>
<th>Coded variables</th>
<th>Real variables</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$x_1$</td>
<td>$x_2$</td>
</tr>
<tr>
<td>1</td>
<td>-1.00</td>
<td>-1.00</td>
</tr>
<tr>
<td>2</td>
<td>1.00</td>
<td>-1.00</td>
</tr>
<tr>
<td>3</td>
<td>-1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>4</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>5</td>
<td>-1.00</td>
<td>-1.00</td>
</tr>
<tr>
<td>6</td>
<td>1.00</td>
<td>-1.00</td>
</tr>
<tr>
<td>7</td>
<td>-1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>8</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>9</td>
<td>-1.68</td>
<td>0.00</td>
</tr>
<tr>
<td>10</td>
<td>1.68</td>
<td>0.00</td>
</tr>
<tr>
<td>11</td>
<td>0.00</td>
<td>-1.68</td>
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<tr>
<td>12</td>
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<td>1.68</td>
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<td>0.00</td>
</tr>
<tr>
<td>18</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

*interval between consecutive tumbling sessions
Table 3.3 Experiments without Agitation

<table>
<thead>
<tr>
<th>No. Experiment</th>
<th>Normality</th>
<th>Time of reaction [min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.00</td>
<td>72</td>
</tr>
<tr>
<td>2</td>
<td>2.50</td>
<td>72</td>
</tr>
<tr>
<td>3</td>
<td>1.00</td>
<td>198</td>
</tr>
<tr>
<td>4</td>
<td>2.50</td>
<td>198</td>
</tr>
<tr>
<td>5</td>
<td>0.50</td>
<td>135</td>
</tr>
<tr>
<td>6</td>
<td>3.00</td>
<td>135</td>
</tr>
<tr>
<td>7</td>
<td>1.75</td>
<td>30</td>
</tr>
<tr>
<td>8</td>
<td>1.75</td>
<td>240</td>
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<tr>
<td>9</td>
<td>1.75</td>
<td>135</td>
</tr>
<tr>
<td>10</td>
<td>1.75</td>
<td>135</td>
</tr>
<tr>
<td>11</td>
<td>1.75</td>
<td>135</td>
</tr>
</tbody>
</table>

3.3 Results and Discussion

Table 3.4 presents the results from the T-Tests between fiber replicates extracted under identical conditions. Except for the tex values for 1.00 N extraction concentration, there are no significant differences between fiber replicates, which suggests that the results are repeatable and reliable. The difference detected for the tex is due to the marginal difference in weight (p=0.07).

The characteristics for each individual fiber from each sample, and the process variables were considered input for a Multivariate Analysis of Variance (MANOVA). The MANOVA procedure used a high number of observations (1454) and it shows
Table 3.4 T Test Results for Replicates of Sugar Cane Fibers from the Same Extraction Conditions

<table>
<thead>
<tr>
<th>Extraction condition</th>
<th>Mean weight (mg)</th>
<th>P value</th>
<th>Mean length (mm)</th>
<th>P value</th>
<th>Mean tex</th>
<th>P value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00N</td>
<td>3.12</td>
<td>0.07</td>
<td>89.32</td>
<td>0.12</td>
<td>31.52</td>
<td>0.03</td>
</tr>
<tr>
<td>1.00N*</td>
<td>2.21</td>
<td></td>
<td>97.45</td>
<td></td>
<td>22.79</td>
<td></td>
</tr>
<tr>
<td>2.20N</td>
<td>2.01</td>
<td>0.95</td>
<td>78.85</td>
<td>0.87</td>
<td>23.75</td>
<td>0.72</td>
</tr>
<tr>
<td>2.20N*</td>
<td>2.02</td>
<td></td>
<td>78.14</td>
<td></td>
<td>24.62</td>
<td></td>
</tr>
<tr>
<td>3.00N</td>
<td>2.95</td>
<td>0.36</td>
<td>100.26</td>
<td>0.10</td>
<td>28.15</td>
<td>0.77</td>
</tr>
<tr>
<td>3.00N*</td>
<td>2.58</td>
<td></td>
<td>91.93</td>
<td></td>
<td>27.32</td>
<td></td>
</tr>
<tr>
<td>4.50N</td>
<td>2.02</td>
<td>0.99</td>
<td>79.67</td>
<td>0.92</td>
<td>23.79</td>
<td>0.95</td>
</tr>
<tr>
<td>4.50N*</td>
<td>2.02</td>
<td></td>
<td>79.53</td>
<td></td>
<td>23.56</td>
<td></td>
</tr>
</tbody>
</table>

* - replicates of fibers

whether or not the process variables affected the final fiber bundles characteristics.

Table 3.5 presents the MANOVA matrix for any possible process variable-fiber characteristic association, using a 90% confidence interval. The probability from Table 3.5 represents the probability for a null hypothesis $H_0$: "No effect of X process variable on Y fiber characteristic." These probabilities should be less than 0.10 to consider an effect of the process variable on the fiber characteristic.

Concentration of the alkaline extraction solution was a significant variable for length, weight and tex. Figure 3.1 presents the dependencies of these fiber
Table 3.5 MANOVA Matrix for the Process Variables vs. Fiber Characteristics
(p probabilities of significant differences)

<table>
<thead>
<tr>
<th>Process variable</th>
<th>Weight</th>
<th>Length</th>
<th>Tex</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Time of reaction</td>
<td>0.02</td>
<td>0.00</td>
<td>0.05</td>
</tr>
<tr>
<td>Interval between tumblings</td>
<td>0.02</td>
<td>0.00</td>
<td>0.01</td>
</tr>
<tr>
<td>Volume of alkali solution</td>
<td>0.16</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Mass of rind</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Type of rind</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Steam explosion</td>
<td>0.73</td>
<td>0.07</td>
<td>0.17</td>
</tr>
</tbody>
</table>

characteristics on concentration. The Duncan groupings showed no significant differences for length, weight, and tex for concentrations between 0.50 N and 4.00 N. For lower concentrations (0.30 and 0.40) weight and tex are statistically different from other concentrations. Length is different for upper limits of concentrations, around 5.00 N. The lowest tex is obtained for concentration around 2.00 N.

The effects of reaction time and interval between two successive tumbling sessions on fiber characteristics were complex. *Post hoc* analysis showed a slight variation with these two process variables. Figure 3.2 presents the variation in length, weight and tex with reaction time. A time of 135 minutes produced the longest and coarsest fiber bundles. Fibers extracted at 240 minutes were finer while maintaining similar lengths. The dependency of final fiber bundle characteristics on time interval
Figure 3.1 The Weight, Length, and Tex Dependencies on Concentration (for dried sugar cane rinds (DR), reaction time of 60 min, interval between tumblings of 30 min, steam explosion, and initial rind mass of 250 g)
between two successive tumbling sessions is presented in Figure 3.3. As observed, agitation was a critical factor, with frequent agitation yielding finer and shorter fibers.

The influence of **volume of solution** (8, 10 or 16 L) was also assessed (Figure 3.4). Between 10 L and 16 L, and 10L and 8 L there were significant differences in length and tex. However, there were no significant differences between 8 L and 16 L. Fibers extracted in 10 L of solution were longer and finer.

The **steam explosion** process also significantly affected fiber size (length and weight at 0.40 N and length at 0.50 N NaOH concentration). However, tex was not significantly different. Steam explosion may be a source of variability for length of fibers, but does not appear to affect the mean weight and tex (Figure 3.5).

**Rind type** was an important variable in the system for all three fiber characteristics. A comparison between the FHR and DR rinds showed some differences for length, tex and weight (Figure 3.6), especially for low concentrations. For a NaOH concentration of 0.40 N these differences were larger. Also, some statistical differences in weight were observed for a concentration of 0.3 N. Tex was different for 0.30 N, 0.4 N and 1.00 N. Therefore, it would be assumed that the time between harvesting of the cane and actual extraction of fibers, and the storage method, have some influence on the final fiber characteristics. Also, this difference suggests chemical transformations of the lignocellulosic substrate which affect the severity of the extraction process and, finally, the fiber length, weight and fineness. These chemical transformations exert a stronger influence on the kinetics of the extraction at the lowest concentrations.
Figure 3.2 Influence of Time of Reaction on Fiber Characteristics (for 100 g of FR sugar cane rind reacted with 8 L of 1.75 N solution with a time interval for tumbling of 35 min. and then steam exploded)
Figure 3.3 Influence of Interval between Tumblings on Fiber Characteristics (100 g of FR sugar cane rind were first reacted with 8 L of 1.75 N NaOH solution for 135 minutes, and then steam exploded)
Figure 3.4 Influence of Volume of Solution on Fiber Characteristics (250 g of FHR rind at the same concentration of 1.00 N, time of reaction of one hour, and interval between tumblings of 30 min)

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Figure 3.5 The Influence of the Steam Explosion on Weight, Length, and Tex of FHR Sugar Cane Fibers (continuos line for presence of steam explosion, dashed line for absence of steam explosion)
Figure 3.6 The Effect of Rind Type on Fiber Length, Weight, and Tex for a Reaction Time of 60 min and an Interval between Tumblings of 30 min (continuos line for FHR sugar cane rinds, dashed line for DR sugar cane rinds)
A possible linear correlation between the fiber characteristics and the process variables was tested using the Canonical Correlation Procedure (Proc CanCorr). The results showed that there is not a significant direct linear correlation between the dependent and independent variables.

**Variances of length and tex** for a sample are a very important feature for a possible textile application of the product. In the case of geotextile mats it is desirable for the product to have a combination of short and long fibers, because short fibers have good matting properties, while long fibers provide good entanglement. The obtained tex range for all the reaction conditions is acceptable for geotextile applicability. For textile applicability, however, less dispersity of length and a certain range of tex are necessary conditions for carding and spinning processes. Therefore, length and tex variances are important considerations in the process.

The influence of the type of sugar cane rind on the variance of tex can be explained mainly by an inherent variability in the fibers or possible nonuniform chemical transformations in the lignocellulosic material that will modify the quality and quantity of the extracted lignin. Also, steam explosion can be an important source of variability for fiber length. This process step is difficult to control, because of variation in the pressure of the heating and explosion agent (steam), variation in the opening of the discharge valve, or variation in the inherent moisture of the fibers before the explosion.

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3.3.1 Response Surface Modeling and Optimization

Table 3.6 summarizes vector responses for: weight, length, tex, ratio of final fiber length (Lf) to initial weighted average length of starting rind pieces (Li), consumption of NaOH, lignin concentration in the liquor extract, and mixing factor. The mixing factor, fm is the ratio between lignin extracted with mixing and lignin extracted with no mixing. Responses were analyzed using the RSReg from SAS, and the lack of fit option was performed. Table 3.7 presents the response surface coefficients for all the response vectors.

Process yield was measured as the ratio (expressed in percent) of the mass of the final fiber bundles and the initial mass of rind. The yield was in the range of 40-60% with an average of 48.69% for all experiments. These values indicate that lignin was removed, as well as some hemicellulose probably, since these constituents are soluble (hemicellulose with low degrees of polymerization) in strong alkali.

The correlation between tex and length of the final fiber bundles is an important property in the carding and spinning processes for textile applications. Tex is found to have a near linear relationship with length for higher reaction times. For textile purposes, the tex of the final fibers should be minimized. In using MINOS 5.4, tex was chosen as an objective function with a lower limit for the averaged length of the final fibers as a main constraint. Table 3.8 gives the values of the imposed lower limits for length, the minimized tex, and the optimized real parameters that give this minimized
Table 3.6 Vector Responses for the Atmospheric Pressure Delignification of Sugar Cane Rinds

<table>
<thead>
<tr>
<th>No.</th>
<th>Weight [mg]</th>
<th>Length [mm]</th>
<th>Tex</th>
<th>Lf/Li</th>
<th>g NaOH consumed/1 kg rinds</th>
<th>g extracted lignin/100 g rinds</th>
<th>Mixing factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.02</td>
<td>71.21</td>
<td>19.79</td>
<td>0.62</td>
<td>78.93</td>
<td>2.84</td>
<td>0.65</td>
</tr>
<tr>
<td>2</td>
<td>3.01</td>
<td>105.10</td>
<td>26.58</td>
<td>0.69</td>
<td>95.29</td>
<td>3.55</td>
<td>0.64</td>
</tr>
<tr>
<td>3</td>
<td>2.48</td>
<td>88.71</td>
<td>26.23</td>
<td>0.60</td>
<td>100.00</td>
<td>2.51</td>
<td>0.45</td>
</tr>
<tr>
<td>4</td>
<td>2.51</td>
<td>99.48</td>
<td>24.70</td>
<td>0.67</td>
<td>389.77</td>
<td>2.51</td>
<td>0.53</td>
</tr>
<tr>
<td>5</td>
<td>1.95</td>
<td>72.31</td>
<td>26.31</td>
<td>0.54</td>
<td>79.00</td>
<td>3.09</td>
<td>0.71</td>
</tr>
<tr>
<td>6</td>
<td>2.43</td>
<td>93.47</td>
<td>24.41</td>
<td>0.69</td>
<td>178.27</td>
<td>4.25</td>
<td>0.76</td>
</tr>
<tr>
<td>7</td>
<td>2.77</td>
<td>108.37</td>
<td>23.91</td>
<td>0.81</td>
<td>24.18</td>
<td>4.08</td>
<td>0.74</td>
</tr>
<tr>
<td>8</td>
<td>1.98</td>
<td>82.50</td>
<td>24.43</td>
<td>0.55</td>
<td>146.29</td>
<td>4.17</td>
<td>0.89</td>
</tr>
<tr>
<td>9</td>
<td>2.04</td>
<td>89.08</td>
<td>22.79</td>
<td>0.59</td>
<td>41.66</td>
<td>3.76</td>
<td>0.75</td>
</tr>
<tr>
<td>10</td>
<td>2.23</td>
<td>83.97</td>
<td>26.19</td>
<td>0.56</td>
<td>232.16</td>
<td>4.37</td>
<td>0.89</td>
</tr>
<tr>
<td>11</td>
<td>1.77</td>
<td>82.46</td>
<td>20.46</td>
<td>0.68</td>
<td>146.44</td>
<td>4.06</td>
<td>1.00</td>
</tr>
<tr>
<td>12</td>
<td>1.62</td>
<td>82.28</td>
<td>19.11</td>
<td>0.58</td>
<td>124.38</td>
<td>4.38</td>
<td>0.90</td>
</tr>
<tr>
<td>13</td>
<td>1.61</td>
<td>82.21</td>
<td>18.76</td>
<td>0.51</td>
<td>43.14</td>
<td>4.17</td>
<td>0.65</td>
</tr>
<tr>
<td>14</td>
<td>3.38</td>
<td>111.72</td>
<td>27.24</td>
<td>0.69</td>
<td>12.83</td>
<td>5.02</td>
<td>0.79</td>
</tr>
<tr>
<td>15</td>
<td>2.26</td>
<td>93.09</td>
<td>21.34</td>
<td>0.56</td>
<td>110.90</td>
<td>4.96</td>
<td>1.08</td>
</tr>
<tr>
<td>16</td>
<td>2.43</td>
<td>97.23</td>
<td>23.84</td>
<td>0.62</td>
<td>132.41</td>
<td>4.29</td>
<td>0.94</td>
</tr>
<tr>
<td>17</td>
<td>2.61</td>
<td>96.94</td>
<td>25.23</td>
<td>0.66</td>
<td>63.79</td>
<td>4.48</td>
<td>0.98</td>
</tr>
<tr>
<td>18</td>
<td>2.39</td>
<td>98.56</td>
<td>23.97</td>
<td>0.74</td>
<td>90.00</td>
<td>4.25</td>
<td>0.93</td>
</tr>
</tbody>
</table>
value. An indirect linear dependency between the optimized concentration and the lower limit for length was observed.

3.4 Conclusions

Analysis of process variables for extraction of sugar cane fibers showed a complex effect on the characteristics of the fiber bundles. Normality, reaction time, and frequency of tumbling were the primary factors influencing length, weight, and tex. Time of processing and method of rind storage also affected the properties of final fiber bundles. Steam explosion affected fiber length, but had no statistically significant effect on tex. Variances of length and tex were influenced mainly by concentration and type of rind.

Response surface models for effects of lignin extraction, NaOH consumption, and agitation on characteristic properties of sugar cane fibers were obtained for the

Table 3.7 Polynomial Response Surface Coefficients

<table>
<thead>
<tr>
<th>Response surface</th>
<th>$a_0$</th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$a_3$</th>
<th>$a_{11}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight [mg]</td>
<td>2.42</td>
<td>0.70</td>
<td>0.00</td>
<td>0.15</td>
<td>-0.40</td>
</tr>
<tr>
<td>Length [mm]</td>
<td>96.35</td>
<td>2.29</td>
<td>2.68</td>
<td>3.05</td>
<td>-3.10</td>
</tr>
<tr>
<td>Lf/Li</td>
<td>0.64</td>
<td>0.00</td>
<td>0.00</td>
<td>0.02</td>
<td>-0.01</td>
</tr>
<tr>
<td>Tex</td>
<td>23.48</td>
<td>0.70</td>
<td>0.00</td>
<td>1.17</td>
<td>0.80</td>
</tr>
<tr>
<td>g NaOH consumed/1 kg rind</td>
<td>97.46</td>
<td>97.46</td>
<td>14.04</td>
<td>-21.05</td>
<td>21.23</td>
</tr>
<tr>
<td>g extracted lignin/100g rind</td>
<td>4.54</td>
<td>0.37</td>
<td>0.00</td>
<td>0.69</td>
<td>-0.98</td>
</tr>
<tr>
<td>Mixing factor</td>
<td>0.99</td>
<td>0.00</td>
<td>-0.20</td>
<td>0.07</td>
<td>-0.09</td>
</tr>
</tbody>
</table>

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<tr>
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</tr>
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<td>0.64</td>
<td>0.00</td>
<td>0.00</td>
<td>0.02</td>
<td>-0.01</td>
</tr>
<tr>
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</tr>
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<td>4.54</td>
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<td>0.69</td>
<td>-0.98</td>
</tr>
<tr>
<td>Mixing factor</td>
<td>0.99</td>
<td>0.00</td>
<td>-0.20</td>
<td>0.07</td>
<td>-0.09</td>
</tr>
</tbody>
</table>
process of fiber extraction at atmospheric pressure. The parameters for the models were normality of the NaOH solution, reaction time, and the interval between two consecutive agitations. The experimental design used was a central composite rotatable design. Based on the models obtained, the tex was optimized having the lower limit of length as a constraint. A short time of reaction (30 min.), with a high frequency of tumbling (once at every 10 min.), gave the lowest tex. A solution of NaOH of 0.89 N also produced fibers with the lowest tex, but the shortest length.
CHAPTER 4 KENAF ALKALI PROCESSING

4.1 Introduction

A process developed for the extraction of fiber bundles from the rind of sugar cane has been adapted to kenaf. The process consists of four distinct steps: mechanical separation, chemical extraction, steam explosion, and product formation. Through this process it is possible to obtain fiber bundles reduced in cross section, but with sufficient length for textile applications. By changing the extraction parameters, the final properties of the fiber bundles can be controlled.

The mechanical separation is accomplished with the Tilby cane separator that separates the pith from the rind by longitudinal splitting and rotating actions (Figure 2.1). The Tilby was developed for the sugar cane industry to separate rind for use in paneling and building materials and to simplify the steps necessary to obtain brown sugar or to produce a starting material for rum production (Tilby et al., 1976).

The second process step is chemical retting using low concentration alkaline solutions, high temperature, and pressure. This process is different from the usual pulping actions since the intent is to extract controlled length fiber bundles from rind strips, with minimal reduction of the fiber bundle length while reducing its cross section. The chemicals used make the process environmentally friendly and the slightly alkaline discharge, or black liquor (BL), can be easily neutralized. The key to this controlled extraction is the synergistic action of chemical removal of controlled amounts of lignin and hemicellulose with
mechanical action in the reaction system. This mechanical action, that can be an oscillatory agitation and/or a tumbling motion, is responsible for a preferential reduction of cross section rather than the length of the fiber bundles. The splitting of the kenaf rind pieces is parallel to the long axis of the stalk. This axis is also the direction in which the cellulosic fibers are aligned. The mechanical action creates new surfaces for chemical penetration into the lignocellulosic substrate.

In the optional third step the kenaf fiber bundles are steam exploded to further reduce bundle cross sections. In this process live steam is injected into the reactor and then the pressure is quickly released. The moisture in the fibers evaporates suddenly, blowing them apart into relatively dry separated fiber bundles.

The final step in this process is specific to the potential application. The obtained fiber bundles can be spun into yarns after they are dried and pneumatically conveyed to a bag house for collection. For nonwoven applications a slurry of the fiber bundles is manually deposited on a screen, dewatered, and dried. As an alternative to this manual process the fiber bundles can be carded, needle punched, and if necessary have a rayon scrim applied.

4.2 Method and Materials

Four different types of kenaf were used in this study:

1) Field harvested kenaf, full stalks with an average strand length of 60 cm obtained after two years of field storage from the Iberia Research Station of the Louisiana Agricultural Experiment Station; (LSU kenaf)
2) Field harvested kenaf obtained from Mississippi State University in bales with average fiber length of 9 cm (MSU kenaf)

3) Semi-dry, frost killed kenaf stalks obtained from Mississippi State University in the form of full stalks (SD kenaf)

4) Green kenaf received from Agro-Fibers, a commercial producer.

The kenaf stalks were processed through the Tilby separator resulting in a clean and complete separation between the pith and the rind. The entire 60 cm long rind stems of the LSU kenaf were used, with an average separation yield of 18.75% (mass of fibers after Tilby separation/mass of kenaf stems). The SD fiber kenaf stalks were too thin to handle through the Tilby separator and, therefore, the fiber strands were peeled by hand.

Two series of experiments were performed under different conditions to determine the effects of extraction conditions and steam explosion on properties of the resulting fibers. All the extractions were conducted in a 20 L laboratory scale reactor, except for one experiment conducted in a 200 L reactor. These reactors had rapid discharge valves at the bottom. and the 20 L reactor was equipped to provide continuous mechanical action either by tumbling or with an oscillatory agitator. Constant conditions for all experiments were: 160 °C. elevated pressure (0.7 MPa), and one hour.

Alkaline consumption during extraction was measured by titration of the initial solution and the BL and expressed as grams of alkali consumed/100 g kenaf fibers. Lignin concentration in the extracts was measured by a spectrophotometric method based on absorption of UV radiation at 280 nm (Alen & Hartus, 1988). In one experiment, a higher concentration of NaOH (1.0 N), a higher treatment time (ten hours), as well as a continuous
tumbling of the reactor. were used to determine the total lignin content in the LSU kenaf. Due to the severe treatment conditions, fibers obtained from this experiment were completely decomposed and discarded.

For the steam exploded samples, steam at a pressure of about 0.7 MPa was injected into the autoclave reactor following the alkaline extraction. After a period of one minute, with the reactor maintained at high pressure, the reactor was rotated to a horizontal position, and then the discharge valve provided at the bottom of the reactor was opened. The fibers ejected from the reactor were collected for analysis and product formation. For two experiments steam explosion was done by opening the valve partially to determine the effect of a gradual decrease of pressure on the fibers.

For fiber characterization, 0.1 g of fibers from each experiment were randomly selected. The length (mm) and weight (mg) of each fiber in the sample was then measured. Suitability for textile or geotextile applications can be assessed by fiber linear density values, which are reported in tex (weight in grams/thousand meters of fiber). The results were statistically analyzed.

Five process variables were analyzed as possible factors of influence for the kenaf fiber bundle characteristics (length and tex). These process variables were: alkali concentration in solution (expressed as normality), type of rind, valve opening, presence of steam explosion, and reactor volume. Type of rind, valve opening, and presence of steam explosion were considered fixed effects with two levels each. The reactor volume was considered a random effect.
Proc MIXED from SAS® was used to fit the mixed linear models (i.e. fixed and random effects models) for both length and tex. A mixed model is a generalization of the standard linear model, the generalization being that the model analyzes data generated from several sources of variation instead of one. The inferential statistics are based for this analysis on the restricted maximum likelihood method. One of the main advantages of the mixed model approach is the capability of including missing cells in the experimental design.

4.3 Results and Discussions

The first series of experiments are listed in Table 4.1, and the physical characteristics of fibers extracted at different conditions are presented in Table 4.2, with results grouped according to type of kenaf and valve opening during the steam explosion. The data show that LSU kenaf fibers are longer and coarser than MSU kenaf. The finest fibers were produced from the MSU kenaf using 0.1 N NaOH extraction solutions and steam explosion. The manner of valve opening during explosion affected the appearance of the fibers. The fibers steam exploded with the partially open valve were wetter, had a woolen appearance, and were difficult to remove from the reactor. Extracted fibers from Experiments 11 (Green kenaf) and 12 (SD kenaf) maintained the starting strand length, were smaller in diameter, flexible, and darker in color than both LSU and MSU fibers. Fibers from green kenaf were much darker than that of SD kenaf.

Table 4.3 presents the alkali consumption for Experiments 1-3 and 5-9. The data show a similar delignification severity for LSU and MSU kenaf. Also, in Experiment 8 potassium hydroxide (KOH) was used instead of NaOH, but no visual difference in fibers
Table 4.1 Extraction Conditions for Kenaf Fibers

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Type of kenaf</th>
<th>Alkali solution: volume (L), normality (N) and type of base</th>
<th>Fiber mass [kg]</th>
<th>Steam explosion</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MSU</td>
<td>16 L, 0.1 N NaOH</td>
<td>0.5</td>
<td>yes</td>
</tr>
<tr>
<td>2</td>
<td>MSU</td>
<td>16 L, 0.2 N NaOH</td>
<td>0.5</td>
<td>yes</td>
</tr>
<tr>
<td>3</td>
<td>MSU</td>
<td>16 L, 0.3 N NaOH</td>
<td>0.5</td>
<td>yes</td>
</tr>
<tr>
<td>4</td>
<td>MSU</td>
<td>16 L, 0.1 N NaOH</td>
<td>0.5</td>
<td>yes</td>
</tr>
<tr>
<td>5</td>
<td>LSU</td>
<td>16 L, 0.1 N NaOH</td>
<td>0.5</td>
<td>yes</td>
</tr>
<tr>
<td>6</td>
<td>LSU</td>
<td>16 L, 0.2 N NaOH</td>
<td>0.5</td>
<td>yes</td>
</tr>
<tr>
<td>7</td>
<td>LSU</td>
<td>16 L, 0.3 N NaOH</td>
<td>0.5</td>
<td>yes</td>
</tr>
<tr>
<td>8</td>
<td>LSU</td>
<td>16 L, 0.1 N KOH</td>
<td>0.5</td>
<td>yes</td>
</tr>
<tr>
<td>9</td>
<td>LSU</td>
<td>16 L, 1 N NaOH</td>
<td>0.5</td>
<td>no</td>
</tr>
<tr>
<td>10</td>
<td>MSU</td>
<td>160 L, 0.2 N NaOH</td>
<td>4.0</td>
<td>no</td>
</tr>
<tr>
<td>11</td>
<td>Green</td>
<td>16 L, 0.1 N NaOH</td>
<td>0.5</td>
<td>yes</td>
</tr>
<tr>
<td>12</td>
<td>SD</td>
<td>16 L, 0.1 N NaOH</td>
<td>0.5</td>
<td>yes</td>
</tr>
</tbody>
</table>

was observed. The consumption of KOH is higher, however, making NaOH a more efficient base for lignin extraction from the kenaf fibers.

Ten additional experiments were conducted in the 20 L reactor, using LSU kenaf, under the same reaction conditions but at different alkaline concentrations (Table 4.4) in the range 0.035 to 0.35 N (Figure 4.1). An increase in concentration has results in an apparent increase in tex. This is mainly due to the increase in length and weight variability. The average yield of the delignification process (mass fibers after delignification /
Table 4.2 Kenaf Fiber Bundle Characteristics

<table>
<thead>
<tr>
<th>Type of kenaf</th>
<th>Extraction Conditions</th>
<th>Weight (mg)</th>
<th>Length (mm)</th>
<th>Tex</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSU 0.1 N</td>
<td>2.80</td>
<td>39</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>MSU 0.3 N</td>
<td>0.73</td>
<td>38</td>
<td>19</td>
<td></td>
</tr>
<tr>
<td>MSU 0.1 N</td>
<td>3.00</td>
<td>41</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>LSU 0.1 N</td>
<td>0.76</td>
<td>61</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>LSU 0.2 N</td>
<td>1.76</td>
<td>97</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>LSU 0.3 N</td>
<td>1.23</td>
<td>78</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>MSU 0.2 N, 200L reactor</td>
<td>3.14</td>
<td>193</td>
<td>15</td>
<td></td>
</tr>
</tbody>
</table>

*totally open valve; b partially open valve; A,B,C,D,E Duncan groupings

Table 4.3 Alkali Consumption for Delignification Process

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Type of kenaf</th>
<th>Alkali solution: volume (L), normality (N) and type of base</th>
<th>g consumed base/l kg kenaf fibers</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MSU 0.1 N NaOH</td>
<td>16 L. 0.1 N NaOH</td>
<td>75.78</td>
</tr>
<tr>
<td>2</td>
<td>MSU 0.2 N NaOH</td>
<td>16 L. 0.2 N NaOH</td>
<td>124.16</td>
</tr>
<tr>
<td>3</td>
<td>MSU 0.3 N NaOH</td>
<td>16 L. 0.3 N NaOH</td>
<td>32.11</td>
</tr>
<tr>
<td>5</td>
<td>LSU 0.1 N NaOH</td>
<td>16 L. 0.1 N NaOH</td>
<td>72.71</td>
</tr>
<tr>
<td>6</td>
<td>LSU 0.2 N NaOH</td>
<td>16 L. 0.2 N NaOH</td>
<td>113.92</td>
</tr>
<tr>
<td>7</td>
<td>LSU 0.3 N NaOH</td>
<td>16 L. 0.3 N NaOH</td>
<td>33.92</td>
</tr>
<tr>
<td>8</td>
<td>LSU 0.1 N KOH</td>
<td>16 L. 0.1 N KOH</td>
<td>89.38</td>
</tr>
<tr>
<td>9</td>
<td>LSU 1 N NaOH</td>
<td>16 L. 1 N NaOH</td>
<td>313.23*</td>
</tr>
</tbody>
</table>

* to determine total delignification

mass fibers before delignification) was 74%. Fibers extracted at 0.1 and 0.125 N were also characterized prior to the steam explosion to see how this process affected the properties of the fibers (Table 4.4). Fibers not subjected to a steam explosion process were reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
Figure 4.1 The Effect of NaOH Normality on Fiber Characteristics LSU Kenaf

Table 4.4 Characteristics of LSU Kenaf Fibers Extracted at Different Conditions

<table>
<thead>
<tr>
<th>Normality</th>
<th>Steam explosion</th>
<th>Weight [mg]</th>
<th>Length [mm]</th>
<th>Tex</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.035</td>
<td>Yes</td>
<td>0.72&lt;sup&gt;E&lt;/sup&gt;</td>
<td>70&lt;sup&gt;D&lt;/sup&gt;</td>
<td>10&lt;sup&gt;BCD&lt;/sup&gt;</td>
</tr>
<tr>
<td>0.050</td>
<td>Yes</td>
<td>0.72&lt;sup&gt;E&lt;/sup&gt;</td>
<td>71&lt;sup&gt;D&lt;/sup&gt;</td>
<td>10&lt;sup&gt;BCD&lt;/sup&gt;</td>
</tr>
<tr>
<td>0.075</td>
<td>Yes</td>
<td>1.28&lt;sup&gt;DC&lt;/sup&gt;</td>
<td>100&lt;sup&gt;C&lt;/sup&gt;</td>
<td>11&lt;sup&gt;CBD&lt;/sup&gt;</td>
</tr>
<tr>
<td>0.100</td>
<td>Yes</td>
<td>0.59&lt;sup&gt;E&lt;/sup&gt;</td>
<td>91&lt;sup&gt;C&lt;/sup&gt;</td>
<td>6&lt;sup&gt;E&lt;/sup&gt;</td>
</tr>
<tr>
<td>0.125</td>
<td>Yes</td>
<td>0.47&lt;sup&gt;BC&lt;/sup&gt;</td>
<td>62&lt;sup&gt;D&lt;/sup&gt;</td>
<td>8&lt;sup&gt;DE&lt;/sup&gt;</td>
</tr>
<tr>
<td>0.150</td>
<td>Yes</td>
<td>1.47&lt;sup&gt;BC&lt;/sup&gt;</td>
<td>153&lt;sup&gt;A&lt;/sup&gt;</td>
<td>9&lt;sup&gt;CDE&lt;/sup&gt;</td>
</tr>
<tr>
<td>0.200</td>
<td>Yes</td>
<td>1.71&lt;sup&gt;ABC&lt;/sup&gt;</td>
<td>117&lt;sup&gt;B&lt;/sup&gt;</td>
<td>14&lt;sup&gt;B&lt;/sup&gt;</td>
</tr>
<tr>
<td>0.250</td>
<td>Yes</td>
<td>1.94&lt;sup&gt;AB&lt;/sup&gt;</td>
<td>144&lt;sup&gt;A&lt;/sup&gt;</td>
<td>12&lt;sup&gt;BC&lt;/sup&gt;</td>
</tr>
<tr>
<td>0.300</td>
<td>Yes</td>
<td>1.63&lt;sup&gt;ABC&lt;/sup&gt;</td>
<td>117&lt;sup&gt;B&lt;/sup&gt;</td>
<td>13&lt;sup&gt;BC&lt;/sup&gt;</td>
</tr>
<tr>
<td>0.350</td>
<td>Yes</td>
<td>0.88&lt;sup&gt;DE&lt;/sup&gt;</td>
<td>67&lt;sup&gt;D&lt;/sup&gt;</td>
<td>12&lt;sup&gt;BC&lt;/sup&gt;</td>
</tr>
<tr>
<td>0.100</td>
<td>No</td>
<td>2.04&lt;sup&gt;A&lt;/sup&gt;</td>
<td>117&lt;sup&gt;B&lt;/sup&gt;</td>
<td>17&lt;sup&gt;A&lt;/sup&gt;</td>
</tr>
<tr>
<td>0.125</td>
<td>No</td>
<td>1.49&lt;sup&gt;BC&lt;/sup&gt;</td>
<td>119&lt;sup&gt;B&lt;/sup&gt;</td>
<td>11&lt;sup&gt;BCD&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

A, B, C, D, E Duncan groupings

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longer and coarser (Figure 4.2). The NaOH consumption and the lignin concentration in the extract are presented for all 10 experiments. There does not seem to be a systematic relationship between consumption of alkali and amount of lignin extracted.

Proc MIXED was used to analyze the dependency of tex and length by the five process variables considered for study. Linear models for tex and length were obtained. Third order polynomial dependencies on the alkali normality of the natural logarithms of length and tex, were selected to reduce the variability in the model. The rind type (MSU or LSU), steam explosion (presence or absence), and valve opening (total or partial) were considered as fixed effects in the model and treated as sources of variability. Table 4.5 presents the significant linear model coefficients for the natural logarithms of tex and length.

The influence of the fixed effects was analyzed based on the combined models of tex and length. MSU kenaf gave a finer but shorter fiber at low concentrations, while at higher concentrations LSU kenaf acted similarly. Steam explosion affected both the tex and the length of the obtained kenaf fibers. At low and moderate values of concentration, a decrease in the tex of the exploded fibers is mainly due to a significant decrease in cross-section, indicating that for low alkali concentrations the kenaf rind is “weakened” by a preferential controlled delignification. This is why in the steam explosion process the fiber bundle cross-section is reduced, while keeping the fiber length essentially unaffected. Under severe delignification at higher concentrations however, the length is strongly affected. Valve opening has a main effect on length and tex. The higher the alkali concentration, the more intensive the delignification, and so a weaker fiber is obtained. At the moment of steam
Figure 4.2 Effect of Normality on NaOH Consumption and Lignin Extracted

Table 4.5 The Mixed Model Coefficients

<table>
<thead>
<tr>
<th>Variable</th>
<th>Ln(Length)</th>
<th>Ln(Tex)</th>
</tr>
</thead>
<tbody>
<tr>
<td>intercept</td>
<td>0.166</td>
<td>1.723</td>
</tr>
<tr>
<td>normality</td>
<td>6.479</td>
<td>-6.333</td>
</tr>
<tr>
<td>(normality)^2</td>
<td>62.936</td>
<td>84.955</td>
</tr>
<tr>
<td>(normality)^3</td>
<td>-140.369</td>
<td>-149.561</td>
</tr>
<tr>
<td>type of rind *</td>
<td>1.872</td>
<td>0.685</td>
</tr>
<tr>
<td>type of rind * × normality</td>
<td>-12.002</td>
<td>-5.356</td>
</tr>
<tr>
<td>steam explosion **</td>
<td>0.719</td>
<td>3.472</td>
</tr>
<tr>
<td>steam explosion ** × normality</td>
<td>NSS</td>
<td>-26.824</td>
</tr>
<tr>
<td>valve opening ***</td>
<td>1.374</td>
<td>NSS</td>
</tr>
<tr>
<td>valve opening *** × normality</td>
<td>-13.606</td>
<td>-4.553</td>
</tr>
</tbody>
</table>

* for LSU kenaf; ** for absence of steam explosion; *** for partial valve opening; NSS -not statistically significant
explosion, due to the rapid discharge and contact with the partially open valve, the fibers will be mechanically broken because of their lower strength. This may also explain the woolen appearance of the exploded fibers.

The mixed model is especially important because it includes the influences of the fixed effects. These influences combined with the polynomial dependency on alkali normality, show that a concentration between 0.10 and 0.15 N, presence of steam explosion, and a total opening of the discharge valve, are the best conditions for LSU kenaf fiber extraction.

4.4 Conclusions

Kenaf, harvested with different techniques and ranging in age from fresh to at least two years old, can be converted to fiber bundles using processes developed for sugar cane. A Tilby type processor for splitting sugar cane stalks and then routing out the core was effective on kenaf due to the physical similarity of kenaf to sugar cane. Furthermore, the partial delignification process developed to convert sugar cane rind pieces to fiber bundles using low concentration alkali and mechanical action was also effective for kenaf.

The experiments conducted showed that LSU kenaf fibers were longer and coarser than MSU kenaf fibers, probably due to differences in processing. The length and fineness of the fibers obtained was relatively sensitive to the concentration of the alkaline extraction solutions within the 0.035 to 0.35 N range. The mean length was about 10 cm in a range of 7 to 15 cm and the mean tex was 9 in a range of 6 to 17. The lowest tex fibers were produced with 0.10 to 0.15 N NaOH extractions, followed by steam explosion. This length is comparable to the 9 cm length of the MSU kenaf. Steam explosion affected the physical
characteristics of the fibers, because those not subjected to this process were coarser and longer. Also, the way in which the valve was opened during the steam explosion affected the appearance and the length of fibers.
CHAPTER 5 RECOMMENDATIONS

Several areas for future work may be:

1) Apply the atmospheric pressure delignification process to both kenaf and bagasse. The implementation of atmospheric pressure delignification simplifies the fiber bundle extraction process, reducing the process cost because of equipment requirements, usually necessary for a high pressure delignification. For sugar cane the process may be further simplified using bagasse, eliminating the mechanical separation step, and/or the steam explosion procedure. Thus, bagasse use as a raw material for mats has economic advantages, and also decouples the production of by-product fibers from the harvesting season.

2) Investigate the correlations between the properties (e.g., lignin content) of the extracted solid substrate (sugar cane or kenaf) and different extraction parameters. An optimization of the extraction process parameters has to take in consideration the amount of lignin left into the lignocellulosic material after extraction, and its intimate correlation with the length, tex, strength of the fiber bundles, pertaining particularly to further processing, such as, bleaching, dyeing, carding, and spinning.

3) Optimize the extraction parameters for a continuous delignification process. The optimization has to be correlated with the final applicability of the obtained fiber bundles: geotextile mat, spray-on, or yarn. The advantages of the continuous
processing are not only related to the cost reduction, but also to the properties of the final product. A continuous mixing and a relatively constant available alkali in the extraction liquor is expected to give a lower variability in the length and tex of the final fiber bundles obtained. This low variability is required in future processing steps, as carding and spinning.
PART II

LYOCELL SOLUTIONS FROM SUGAR CANE AND KENAF
6.1 Advanced Fibers from Cellulose Solution

The regenerated cellulose fibers (rayons) were the earliest man-made fibers. Nitrocellulose and viscose, followed by the acetate and cuprammonium rayons are the main classes of regenerated cellulose fibers (Summers et al., 1993).

Viscose rayon, which came to be the most important cellulosic fiber, is produced by treating wood chips (or almost any lignocellulosic material) with CS₂, dissolving the cellulose derivative (named xanthate) in NaOH, and regenerating the cellulose in an acid medium (usually H₂SO₄). Certain physical characteristics of hand and comfort for the rayon are superior to those of the petrochemical based textile fibers. Another big advantage is that rayons are derived from an abundant and renewable raw material, and are biodegradable (Summers et al., 1993).

A major aspect of the viscose process has always been the pollution and the accompanying smell caused by the use and escape of hydrogen sulfide gas (H₂S) in the process. This and other environmental problems have driven the search for an environmentally friendly process to substitute for the viscose technologies, while keeping or enhancing the product properties (Summers et al., 1993).

A new trend in cellulosic fibers are the fibers made from processes involving direct dissolution of cellulose. The efforts to dissolve cellulose directly have taken into account the dual chemical behavior of cellulose, which can act chemically in the
dissolution mechanism as a basic or an acidic compound. Also, cellulose can form a complex (such as with a metal ion) or a chemical derivative (Woodings, 1996). Cellulose as a base was dissolved directly using protonic acids (sulfuric, nitric, and phosphoric) or Lewis acids (zinc chloride, thiocyanates, iodides and bromides). Solutions of cellulose were obtained when cellulose was acting as an acid, with an inorganic basic solvent (sodium zincate, sodium hydroxide, hydrazine) or an organic basic solvent (quaternary ammonium hydroxides, amines, amine oxides). For some of these systems there are limitations in the retained degree of polymerization of the dissolved cellulose and degradation problems, and almost all of them form solutions from which regenerated cellulosic fibers can not be spun. So far, the amine oxide route is the best for spinnability purposes (Johnson, 1969, 1985, Franks, 1979, Woodings, 1996).

The potential of the amine oxide group was first realized by Johnson who used cyclic mono N-methyl morpholine-N-oxide (NMMO) (4-methyl morpholine-4-oxide, hereafter called N-methyl morpholine-oxide) as a solvent for strengthening paper by partially dissolving the cellulose and lignocellulosic fibers (Figure 6.1) (Johnson, 1995). NMMO emerged as the best of the amine oxides. Two of the biggest rayon producers, Courtaulds and American Enka set up pilot plants in the early 1980s with the objectives of developing the fiber spinning and recovery operations. In 1992, Courtaulds (British based company) proceeded to commercial scale for the new process based upon NMMO. Since then, the plant capacity was increased 150% (now 300 million pounds annually). Plans for new plants in the Far East and Europe are also being considered. The commercial brand name for the Courtaulds fiber is Tencel® (Courtaulds, 1995).
Also a generic name, lyocell, for this non-derivative system (amine oxide with cellulose) produced fiber was largely accepted. The Austrian viscose producer Lenzing studied different systems and started pilot operations on an NMMO system at the end of 80s. and it announced a commercial plant in the June 1997 (Lenzing, 1997). The commercial name for the Lenzing produced fiber is Lyocell®.

\[
\begin{array}{c}
\text{O} \\
\text{N} \\
\text{CH}_3 \text{^O}
\end{array}
\]

Figure 6.1 N - methyl morpholine-oxide (NMMO)

NMMO is an environmentally friendly solvent which is also used as an ingredient in hair care products. The solvent is completely recovered and recycled in the lyocell process (Fele, 1994). The efficiency of NMMO recovery in the production of lyocell fiber has been developed to the point where the consumption is now down to a few kilograms per ton of fibers (Lenox-Kerr, 1994). Also, with increased scale of fabrication, the manufacturing costs for the solvent should decrease. The regenerated fibers, like the vegetation from which they arise, are totally biodegradable by common, ubiquitous soil bacteria to the final breakdown products: carbon dioxide and water. By fiber disposal it is possible to liberate energy by burning or by anaerobic biodegradation.
(source of methane). As a recognition for reducing the environmental impact to a minimum in its Tencel plant, Courtaulds was awarded the "United Nation Fashion Industry and Environmental Award" (Courtaulds, 1995).

Introduced as an environmentally friendly replacement for viscose, lyocell fiber was finally marketed as a new-premium-quality clothing cellulosic fiber, because of the amazing textile features. Lyocell fibers are: stronger than rayons and other cellulosic fibers (especially when wet), easy to blend with natural and synthetic fibers, easy to process alone (yarns and fabrics) and in blends, easy to spin, easy to dye, stable to washing and drying, and thermally stable (Courtaulds, 1995).

The usual Courtaulds semi-commercial production is a sequence of steps: formation of the solution (mixing and hot dissolution), filtration, spinning, washing with water and drying. The amine oxide solvent from the liquid effluents is recovered and recycled. The spinning process is a dry-jet wet spinning type process (Woodings, 1996).

A research group from the Plant Macromolecules Research Center (CERMAM-CNRS) in Grenoble has studied the cellulose/NMMO system in depth. Chanzy et al. showed that the solvent system can be extended to other polysacharides and lignin systems. This makes possible the direct use of different lignocellulosic substrates (wood, annual plants) as cellulose sources for dissolution in NMMO (Chanzy et al., 1982).

6.2 Solution Formation. Phase Equilibrium

Regarding the mechanism of cellulose dissolution with different solvents, a clear discrimination between "derivatizing systems", acting via formation of a cellulose derivative, and "nonderivatizing systems", acting via intermolecular forces only, was done.
(Johnson, 1985). In correlation with this distinction, several mechanisms for the cellulose dissolution were proposed. So far, the concepts sustaining these mechanisms are: electron donor/acceptor (EDA) concept, acid-base concept and the cryptoionic concept (Berger et al., 1988).

The EDA concept considers the participation in a donor-acceptor complex of both solvent and cellulose. The H-atoms of the hydroxylic groups and the O-atoms from the monomer unit (ring and bridge) participate in a donor-acceptor interaction with the solvent (Berger et al., 1988). For the solvent, the donor and acceptor must not necessarily be located within one molecule, but may be provided by different components of the solvent system. The advantages of this mechanism are that it explains the solvent action without derivatization and the fact that the swelling of cellulose can be correlated much better to a function of the sum of donor and acceptor strength of the medium. The model has some limitations related to the role of cellulose physical structure in the mechanism, and energy considerations on cellulose-cellulose interactions via H-bonds to be overcome by the cellulose-solvent interactions (Berger et al., 1988).

The acid-base concept is based on the amphoteric behaviour of cellulose. The idea that cellulose can act, depending on its environment, as a base or as an acid, takes into account different acidities for hydroxylic cellulosic groups and makes a bridge between aqueous and non-aqueous solvents. For both EDA and acid-base concepts, only the polar forces of interaction between solvent and cellulose are considered, while non-polar forces have been generally neglected (Berger et al., 1988).
Berger et al proposed an extended mechanism which takes into account the cellulose-cellulose and cellulose-solvent interactions via H-bonds, in addition to the acid-base type interactions (Berger et al., 1988). They introduced the concept of a "cryptoionic" H-bond between cellulose and solvent. The formation of this complex was supported experimentally using non-aqueous solvents, especially in O-basic systems, as NMMO. The concept sustains the "amplifying effect" of some small molecular salts, such as lithium chloride (LiCl), in formation of the "cryptoionic" structures in which the small molecular salt is included. For a complete understanding of cellulose dissolution, the role of physical structure of cellulose has to be taken also into account (Berger et al., 1988).

The $^{13}$C-NMR studies showed that the dissolution of cellulose in NMMO does not involve formation of a cellulose-derivative. Also, the same studies supported by $^{13}$C spin lattice relaxation time measurements showed a very strong association between solvent and cellulose (Gagnaire et al., 1980, Nehls et al., 1995).

Related to the NMMO-cellulose system, wide angle X-ray and degree of polymerization measurements indicated "stepwise increasing solvent power and wedge-like penetration of the solvent into the ordered regions of the fiber structures prior to a complete separation of the polymer chains". So, an entropic contribution must be added to the enthalpic effect in order to break the H-bonds in the ordered regions of cellulose (Philipp, 1993).

Among all the solvent systems that have been investigated, tertiary amine oxides stand out as very powerful non-derivative solvents. NMMO is the tertiary amine oxide

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most used to dissolve cellulose and other lignocellulosic compounds. Because of its melting point (184 °C), anhydrous NMMO leads to extensive degradation of the cellulose molecule. NMMO monohydrate is actually the industrial solvent used in the fiber industry due to its high capacity to dissolve even high molecular cellulose quickly, irrespective of physical structure (Lenox-Kerr, 1994, Woodings, 1996). However, when the content of water for hydrates becomes greater than two moles water per mole of NMMO the material no longer behaves as a solvent, but simply swells the cellulose. With a water content smaller than two molecules of water per one molecule of NMMO, NMMO and cellulose form true solutions with a mesomorphic phase at high concentration and low water content (Chanzy et al., 1982).

The melting points of NMMO hydrates are inversely related to their water content. The melting point of anhydrous NMMO is observed at 184 °C, whereas it occurs at 74 °C and 3 °C for monohydrate, and NMMO with 2.5 water molecules respectively (Chanzy et al., 1982). The decrease in both the melting point and the solvent capacity of increasing water content NMMO hydrates were explained by equilibrium dissociation vapor-pressure studies for NMMO•H₂O and NMMO•2.5H₂O, which demonstrate that N-O⋅⋅⋅H-O-H hydrogen bonds are stronger in the higher hydrate (Harman et al., 1992). The crystalline structure of both hydrates have been determinated and their phase-diagrams were obtained in the absence of cellulose, but presence of water (Chanzy et al., 1982).

With NMMO, a typically solution was obtained dissolving 10% cellulose in the presence of 15.5% water between 90-100 °C. To obtain a spinning solution, Courtaulds...
proposed a procedure that starts with 60/40 by weight NMMO/water solution with crushed wood pulp. The water excess is removed by evaporation. The cellulose first passes through a swelling stage. At the beginning the swelling is reversible, becoming after this irreversible. The true solution is formed for a water content between 13-19% (Lenox-Kerr. 1994).

Ternary diagrams were developed for achievable cellulose dissolution, taking into account: cellulose concentration, water content, and temperature. Also, solutions having cellulose concentrations greater than 30% have been prepared. The phase diagram was completed by Iovleva et al., including also a broad range of cellulose concentrations. The phase diagram was obtained assuming an almost linear nature of the change of melting temperature of NMMO/water/cellulose system with cellulose concentration for a larger range of concentrations (0-50%) (Iovleva. 1989).

Degradation is a serious problem, affecting both NMMO and cellulose. The thermal limit stability for NMMO is 120 °C, but in the presence of cellulose NMMO is more susceptible to decomposition during heating, resulting in the formation of methylmorpholine, morpholine and carbon dioxide. Consequently, the thermal degradation of cellulose is accompanied by degradation caused by NMMO decomposition, leading to an excessive decrease in the degree of polymerization (Lang et al., 1986). By addition of stabilizing compounds (such as n-propyl gallate), the cellulose degradation and NMMO decomposition can be inhibited but not completely eliminated (Lang et al., 1986).
NMMO-Cellulose solutions form mesomorphic phases similar to other polymers, as observed by optical microscopy between crossed polarizers. The nature of the liquid crystal lyocell solutions is still obscure. Chanzy et al. (1982) were the first to describe the mesomorphic structures of the NMMO-cellulose solutions with a low water content and a high concentration of cellulose (i.e., more than 20% w/w). A possible explanation for this is the formation of ordered structures due to steric hindrance and the decrease of the available chain conformation.

The indirect correlation of the water content with the chain rigidity can be explained by the preference of NMMO to form H-bonds with water, rather than with cellulose. At slightly lower water content a small order extension occurred, a fact which does not contribute to high tensile properties for the fibers spun from this kind of solution. But the presence of water in the system lowers the melting point of the anhydrous NMMO, making the system spinnable and avoiding excessive decomposition (Chanzy et al., 1982).

6.3 Shear and Elongational Rheology

Rheology (term coined in 1929 by E. C. Bingham) is the science of deformation and the flow of matter (Tanner, 1985). The viscosity of a substance may be characterized (depending of the geometry of the flow) by its shear viscosity, its elongational viscosity, or a combination of shear and elongational viscosities. Shear viscosity may be understood as the resistance to flow due to a force that is perpendicular to the normal of the plane on which the force acts. Elongational viscosity is the resistance to flow due to a force parallel to the normal of the plane on which the force
acts. Elongational or extensional viscosity may be thought of as the resistance of the fluid to stretching. Usually, there is little correlation between shear viscosity and elongational viscosity for complex substances. A detailed description of both types of viscosities is presented in Appendix A.

In contrast to shear rheometry, extensional or elongational rheometry is still in its formative stages. Developing rheology measurement techniques for polymer melts and solutions is important not only because shear rheological behavior alone is not sufficient to characterize these materials, but also because elongational flow is the dominant mode of fluid flow when a rapid change of shape such as stretching is involved in an operation. These operations include several important polymer processing operations: fiber spinning, extrusion through converging profiles, film blowing, and injection molding (Barnes et al., 1989).

Different approaches have been used for elongational viscosity measurements (James, 1990, Macosko, 1994). Four main approaches were used in measuring elongational viscosity: (1) use of unconfined flow in stretching devices, (2) spinning, (3) indirect measurements, involving entry effects, using data from shear rheology, and (4) lubricated flow. A more detailed review of these four techniques and others can be found in literature (James, 1990, Macosko, 1994).

The main difficulties in studying elongational rheological properties were reported to be that (1) it is difficult to generate a steady and controlled elongational flow field, and (2) it is difficult to prevent, compensate, or even measure the shear effects that typically occur simultaneously with the elongational flow. Also, the commercially
available elongational rheometers are useful only at elongational rates at least an order of magnitude lower than those encountered in typical industrial processes (Ferguson & Zemblowski, 1991).

In prior studies accomplished by this research group, a unique technique for characterization of the elongational rheology of polymer melts at processing strain rates was developed. It was initially demonstrated that an essentially pure elongational flow could be obtained in the core of core/skin coextrusion; this was accomplished experimentally using a core/skin viscosity ratio in the range of 30 to 100, and a core/skin flow rate ratio of about 10. The high viscosity ratio (core-to-skin) causes the skin layer to act as a lubricating layer (Collier 1994, 1997, Kim et al., 1994, Pendse & Collier. 1995, 1996). Experimental measurements on a pilot scale coextrusion system in a planar slit die using tracer particles and an image analysis system confirmed the predicted behavior and demonstrated the ability to achieve a constant elongational strain rate in the core layer (Kim et al., 1994). One of limitation of this rheometer was that the analysis of the core polymer melt behavior requires the choice of an appropriate lubricant or skin (Collier, 1994).

6.3.1 Rheological Characterization of Lyocell Solutions

Previous rheological investigations of cellulose solutions have mainly dealt with dilute solutions, due to the lack of an appropriate solvent for more concentrated solutions. NMMO•H₂O-cellulose was the first system studied rheologically for concentrated solutions. The flow studies of dilute and concentrated solutions were done in correlation with spinning processes, taking into account the mesomorphy of the
solution and degradation of the solution during processing. In depth studies of the shear rheology of NMMO•H₂O-cellulose systems were done by Navard et al (Navard & Haudin, 1980, 1985, 1986). No elongational rheology studies for the lyocell solutions were published.

Optical observations with microscopy between crossed polarized light revealed the formation of a mesomorphic phase for the NMMO system. These results were completed with rheological measurements, especially around the transition temperature, enabling characterization of the transition between anisotropic and isotropic phases. The cellulose-NMMO solutions are different from other mesomorphic polymer solutions in that they form viscoelastic solutions with high viscosities. Also, the transition temperature range for these solutions is dependent on the degree of polymerization of cellulose and the solution concentration. The NMMO-cellulose solutions are subject to the same rules as those of the viscoelastic molten polymers (time-temperature superposition, strength dependence, and time of relaxation) (Navard & Haudin, 1980, 1985, 1986).

High molecular weight cellulose forms lyocell solutions with very high viscosities. These solutions require high spinning temperatures which are higher than the anisotropic-isotropic temperature transition and for which the degradation is enhanced. The flowability of the lyocell solutions is strongly influenced by the existence of high molecular weight fractions. Special distributions of cellulose molecular weight will give preferred spinning qualities (Schrempf et al., 1995). Also, the viscosity is strongly increased when antioxidants (n-propylgallate) are added to the NMMO/cellulose/water
system. This difference is due to the rapid decrease of the molecular weight of cellulose when no antioxidant is present in the solution (Navard & Haudin, 1980, 1985, 1986).

From the shear flow characterization of the system, a pseudoplastic power-law behavior was noticed for the NMMO-cellulose system. The non-Newtonian behavior is due to chain entanglements, which are a result of frictional interactions between adjacent molecules. An increase in cellulose concentration gives a higher density of entanglements and, therefore, a higher shear flow activation energy (the difference between the shear flow activation energies of the two phases at the transition temperature) (Navard & Haudin, 1980, 1985, 1986).

6.4 Spinning from Lyocell Solutions

Cellulose regenerated fibers are produced by a dry-jet wet spinning technique. After leaving the spinneret orifice, the lyocell fiber is deformed in an air gap, and then passed through a water bath, wound up on a bobbin at selected speeds and dried. A take-up system draws the filament, improving the mechanical properties. The spinning temperature is a controlled function of lyocell viscosity and the presence of antioxidants which increase the viscosity (Philipp, 1993, Lenox-Kerr, 1994, Woodings, 1996).

Dube & Blackwell (1983) detected by X-ray that the cellulose regenerated from NMMO/cellulose/water systems is a cellulose II polymorph. The oriented cellulose fibers produced from lyocell systems possess a fibrillar structure in which microfibrils are arranged parallel to the fiber axis. The fibers have the tendency to fibrillate, because of the high orientation and especially because of the apparent lack of lateral cohesion. This effect is desirable for nonwoven applications, but is a drawback in woven textile
applications because it affects launderability (Lenz et al., 1988, 1990, 1990). Also, in the manufacturing of composite materials such as low density polyethylene (LDPE)/cellulose, the surface fibrillation of regenerated cellulose fibers spun from lyocell solutions improves the adhesion between the LDPE matrix and cellulose fibers (Karlsson et al., 1996).

In order to obtain high strength fibers, uncoiling of the macromolecular chain is necessary. This orientation is done successively in the spinning process, by passing through an air gap, a coagulation bath and by drying.

The air gap is an important part of the spinning process because of the drawing that takes place, in which the final orientation and linear density of the polymer are obtained. Mortimer and Peguy (1996, 1996, 1997, 1997) showed that several processes occur in the air gap: filament temperature reduction, water mass transfer across the filament surface, acceleration of the material, reduction of the filament diameter, strong polymer chain orientation, and possibly crystallization of cellulose. The length and the conditioning of the air gap can affect the formation of the filament. The strongest fibers were spun in either a short and humid air gap, or a long, dry air gap. Air conditioning did not affect the structure of the fibers (as measured by X-ray diffraction or birefringence), but had a strong influence on fiber properties.

Precipitation of cellulose from amine oxide solutions was done by contact with a cellulose nonsolvent, such as water or methanol. If water is present in the system, the amine oxide molecules are more attracted to it than to cellulose. The removal of the NMMO from the system will allow intra- and inter-molecular bonds to reform between
the macromolecular cellulose chains. Since water is not a solvent for cellulose but a very
good one for NMMO, dissolution and precipitation of cellulose occurs. A strong gel-
like material is formed even after short contact times with water. Cellulose
concentration, water temperature, presence of additives, contact time and drying
procedure will affect the precipitation kinetics (Dube & Blackwell, 1983, Mortimer &

The presence of certain additives in the bath coagulation, such as CaCl₂ and
especially NH₄Cl, will increase the mechanical properties (tensile strength, Young’s
modulus), and will strongly influence the internal morphology of the fibers (Chanzy et
al., 1990). The inner structure of a fiber coagulated in a water bath containing NH₄Cl as
an additive appears as packets of microfibrils aligned parallel to the fiber axis, because of
the high orientation of the polymer structure (Chanzy et al., 1990). To reduce
fibrillation, Mortimer and Peguy (1996) proposed 25% NMMO in water as a
coagulation bath. The bath composition was correlated with its temperature and length
in order to control the diffusion of NMMO into the bath. Lower spinning temperatures
will give fibrillation but a higher tenacity and extension at break.

The drying procedure also causes a further increase in fiber crystallization, with a
decrease in the fiber diameter. When samples with initially poor crystallinity were
treated with hot water, Dube and Blackwell (1983) observed that the cellulose IV
polymorph appeared. Also, a significant improvement of the crystallinity can be
obtained when the cellulosic samples are pretreated with sodium hydroxide (5% and
20%), when a loss of material less than 4% occurs for both pretreatment concentrations.
Mortimer and Peguy (1996, 1997) optimized the process in order to decrease the fibrillation and to increase the orientation of the macromolecular chains, and consequently, to improve the mechanical characteristics of the spun fibers. The input variables considered were: the air gap length and conditioning, line speed, draw ratio, polymer solution cellulose and water contents, and the temperature and composition of the spin bath. Their optimized process to obtain non-fibrillable lyocell fibers is "a solution of 10% dissolving pulp in a mixture of 85.5% NMMO and 14.5% water, spun at 115°C into an air gap of 100 mm conditioned to 30°C and 100% relative humidity, with a draw ratio of 5. The fiber is coagulated in a solution of 25% NMMO in water" (Mortimer, 1997). The draw ratio is the ratio between take-up velocity of the material and the velocity as the extrudate exits the spinneret (Mortimer, 1997).

6.5 Lyocell Solution from Lignocellulosic Substrates

Lynn Johnson from Eastman Kodak Company patented in 1969 the application of aminoxides as solvents for various substrates which he named "fibrous materials". He said: "the term 'fibrous material' is used in describing my invention in a broad sense to comprise any woven or nonwoven fabric containing a substantial proportion of fibers that are soluble or swellable in the amine oxide, including natural cellulosic fibers such as wood, pulp, cotton, linen and the like, animal fibers such as wool, fur and the like, and synthetic fibers such as nylon, rayon, polyester fibers, etc. and mixtures of such fibers. These fibers may be aggregate, as in papers of various kinds, felted and non-woven fabrics and the like, or may be woven fabrics. A particularly preferred embodiment of the invention is the strengthening of papers comprising cellulosic fibers, by means of
amine oxides” (Johnson, 1969). Thus, NMMO, a cyclic amine is not only a very good solvent for cellulose dissolution, but also a solvent for other bio-polymers and synthetic polymers.

A research team from Cedex, France, was the only one to develop the concept further. Chanzy et al. showed in 1982 that the NMMO/water solvent can be applied to a large number of underivatized polysaccharides with the exception of chitin. The obtained solutions present liquid crystalline order depending on the stiffness of the molecules. Some of the anisotropic solutions could be spun or extruded easily, and upon regeneration well oriented films or fibers were obtained. The orientation was also a distinct function of the linkage type in the polysaccharide molecules. Materials such as mannan, and galactomannan (type 1-4 beta linked molecules), gave the best oriented fibers (Chanzy et al., 1982). Also, the fact that hemicellulose and small amounts of lignin can be dissolved easily in the NMMO-water system, oriented the research towards the solubilization of lignocellulosic substrates (Johnson, 1969, Chanzy et al., 1982). In order to broaden the NMMO solvent applications, most of the work was done using wood directly or a series of pulps of lower purity. Different physico-chemical or chemical treatments were considered in order to improve the solubility of wood in NMMO. Such treatments used to enhance the solubility in NMMO were: delignification with alkali or acid solutions and steam explosion (Katrib et al., 1988, Chanzy et al., 1982).

Katrib et al. (1988) studied the component separation of a hard-wood type lignocellulosic substrate, based on dissolution in NMMO. They stressed the importance of the structure of the biological substrate for the solubilization in NMMO, and the
importance of chemical or physico-chemical treatments. An alkaline or acid
delignification will enhance the solubility of the wood substrate. Also, steam explosion
proved to be the technique that gave the best improved solubility. Thus, a wood
substrate, previously steam exploded, was dissolved in NMMO-water system and spun at
temperatures between 70°-100°C, with linear speeds between 50 and 100 m/min
(Chanzy et al., 1986). The obtained fibers were homogeneous and compact. Their
structure was an evenly distributed blend of cellulose with lignin. It was observed that
the cellulose chain orientation decreased with the relative increase of the lignin amount
present and with the relative increase of the cellulose degree of polymerization. The
mechanical properties were comparable with those of rayon, but a decrease of the
elongation at break was observed because of the lignin presence. In addition, it was
observed that the spinning of exploded wood regenerated fibers from lyocell solutions
requires the use of a filtration system and a high draw ratio (Chanzy et al., 1986).

6.6 Microfibers

The term “microfiber” may be thought of as referring to a fiber about 1 decitex (1
decitex = 1 g/10,000 m) or less. The only commercially available microfibers are certain
polyester microfibers. Nylon microfibers were also reported, but they are not
commercially available. A microfiber of cellulose would be about 7-10 μm in diameter or
less (Tortora & Collier, 1997).

Because of the diameter of microfibers is an order of magnitude smaller than that
of regular fibers, fabrics made from polyester microfibers feel like a soft brushed cotton
fabric and have the flexibility of fine silk. The main disadvantage of this type of synthetic
fabric is the lack of comfort due their reduced water absorbency. Fabric made of cellulosic microfibers, if available, would have the very soft feel of polyester microfiber fabric, together with the water absorbency and comfort of other cellulosic fabrics.

However, no one has previously reported cellulosic microfibers suitable for textiles. Both Courtaulds and Lenzing produced cellulosic fibers from solution in NMMO. The produced fibers tend to fibrillate, due to lack of lateral cohesion. These fragments would not be useful in textiles because they are too tangled and short.

The manufacturing of polyester or nylon microfibers is based on spinning "sea and island" type composite fibers, in which the microfibers are embedded in a sea of another component. The two phases are immiscible under spinning conditions. The "sea" component is removed by a combination of mechanical action and solvation, although usually not until the microfibers have been converted to yarns or fabrics to protect the microfibers. These techniques are not applicable to cellulose (Tortora & Collier, 1997).
7.1 Preparation of Lyocell Solutions

Lyocell solutions with concentrations between 2% and 20% (by weight) were obtained by the dissolution of various cellulosic and lignocellulosic materials in the NMMO monohydrate system (Table 7.1). Different pretreatments were used to enhance the lignocellulosic materials’ ability to form solutions.

Table 7.1 Cellulosic and Lignocellulosic Materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissolving pulp</td>
<td>- softwood pulp (degree of polymerization (DP) ~800).</td>
</tr>
<tr>
<td>Recycled cotton</td>
<td>- a low molecular weight (DP ~1000) cotton was separated through a novel method from a blend of polyester-cotton, after treatment with strong alkali solution (Kwon, 1997).</td>
</tr>
<tr>
<td>Sugar cane</td>
<td>- the lignocellulosic material rich in cellulose (DP ~1100) was extracted from sugar cane rind using an alkali partial delignification (two hours atmospheric pressure extraction with a 1.75 N NaOH solution, and under continuous mixing), followed by steam explosion.</td>
</tr>
<tr>
<td>Kenaf</td>
<td>- mechanically separated EV-41 kenaf was partially delignified (three hours atmospheric pressure extraction with a 5 N NaOH solution, and under continuous mixing).</td>
</tr>
</tbody>
</table>
The lyocell solutions were prepared as follows: a 50% NMMO-water solution was mixed with the finely powdered cellulosic or lignocellulosic material, and with the antioxidant (n-propyl-gallate), in order to control the degradation of both cellulose and NMMO (Chanzy et al., 1982). The monohydrate lyocell system was obtained by distilling water under continuous mixing and vacuum at a moderate temperature range between 80 -95 °C. A more detailed description of the procedure is presented in Appendix B for the example of a 15% lyocell solution.

7.2 Methods and Instrumentation for Lyocell Solutions Characterization

As reported in the literature, liquid crystalline phases appear for both cellulose and lignocellulose systems under certain conditions of concentration and temperature. The lyocell solutions obtained were optically observed using an Olympus optical microscope between crossed polarizers. A Seiko 220 differential scanning calorimeter (DSC) was used to measure the enthalpic effect around the transition temperatures.

Shear rheological properties were determined with a Rheometric Scientific Advanced Capillary Extrusion Rheometer (ACER), a Seiko 110 dynamo mechanical spectrometer (DMS), and a Haake RS 150 rheometer in a parallel-plate setting. All rheological measurements (including elongational flow measurements) were performed between 75°C (the melting point for the NMMO monohydrate is 74°C) and 110°C (above this temperature it is difficult to control the water content).
7.2.1 The Advanced Capillary Extrusion Rheometer (ACER)

Shear and elongational rheological measurements were done using the ACER manufactured by Polymer Laboratories Ltd., UK (now part of Rheometric Scientific Inc., USA). A schematic of the ACER is presented in Figure 7.1. The polymer or the viscous polymer solution was packed in the heated cylindrical barrel and a capillary die was fitted on the end of the barrel. The pressure drop across the die was measured with a pressure transducer attached flush with the wall of the barrel 5 mm above the die. The transducer used for these studies had a range of 0 to 70MPa.

A well-controlled drive section at the top moved the ram through the length of the barrel pushing the polymer melt or solution through the die at the programmed...
parameters (volumetric flow rate and temperature). The ram could be detached from the holder to allow packing of the material in the barrel. The range of the ram speed was 0.05-3000 mm/min and the maximum travel length was 300mm.

Good control of flow rate and temperature makes possible the use of ACER not only as a measurement device, but also as a mini-extruder for fiber spinning. Samples of some of the extrudates were collected immediately after the ACER die in a cold water bath. In addition, a Cambridge StereoScan 260 scanning electron microscope (SEM) was used to observe the fibers obtained from the collected extrudates.

For shear rheology measurements, the ACER functions as a regular capillary rheometer, in which the lyocell solution from a barrel is pushed out by a ram through a regular cylindrical capillary die such as the 20 L/D die shown in Figure 7.2. For the die used in the experiments, the range of apparent shear rates achieved was $5.33 \times 10^5$ s$^{-1}$ to $1.6 \times 10^5$ s$^{-1}$.

![Figure 7.2 Capillary Die used in ACER for Shear Rheometry](reproduced_with_permission_of_the_copyrtight_owner_further_reproduction_prohibited_without_permission)
The determination of the uniaxial elongational rheological properties of polymer melts and concentrated solutions was done by replacing the capillary cylindrical die with semi-hyperbolic converging asymmetric dies. These electrodischarge machined (EDM) semi-hyperbolic convergent conical dies were designed to generate a constant elongational strain rate throughout the core; to accomplish this, the flow channel decreases as $R^2(z + A) = B$, where $z$ is the flow direction, $R$ is the radius of the flow channel, $A$ is offset entrance $z$ from asymptotic, and $B$ defines streamline of surface (Figure 7.3). Two conical dies were used, having Hencky strains $\epsilon_h$ of 6 and 7: $\epsilon_h = \ln$ (area reduction). Their geometrical design parameters $A$ and $B$ are presented in Table 7.2. Elongational strain rates up to 533 sec$^{-1}$ for polypropylene (PP) melts have been achieved in this rheometer (the range includes processing rates). The elongational (or shear) strain rates were achieved in steps of ram speeds, each strain rate corresponding to a fixed ram speed.

Figure 7.3 Semi-hyperbolic Conical Die ($\epsilon_h = 6$)

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Table 7.2 Geometrical Constants for the Semi-hyperbolic Dies

<table>
<thead>
<tr>
<th>Hencky strains, $\epsilon_h$</th>
<th>Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\epsilon_h = 7$</td>
<td>$A = 0.0228$ mm</td>
</tr>
<tr>
<td></td>
<td>$B = 2.2727$ mm$^2$</td>
</tr>
<tr>
<td>$\epsilon_h = 6$</td>
<td>$A = 0.0621$ mm</td>
</tr>
<tr>
<td></td>
<td>$B = 6.1875$ mm$^2$</td>
</tr>
</tbody>
</table>

7.2.2 Materials. Procedure and Data Acquisition

PP and lyocell solutions were used as test materials for the determination of the uniaxial elongational rheological properties. Polyethylene (PE) was used as the skin material for the core-skin PP determinations.

The PP used for the experiments was obtained from Phillips (Grade HGX 030). The zero-shear viscosity of the PP was 77,382 Pa-s at 200 °C, and the molecular weight was 300,000 with a polydispersity index between 4 to 6. For the skin-core measurements of elongational viscosities of PP, low density DOWLEX PE (with a zero-shear viscosity of 63 Pa-s at 200 °C) was used for the outer layer. The melting points obtained using DSC were 164 °C for PP and 135 °C for PE.

When the ACER is used to measure the shear viscosities and for the skinless elongational viscosities, the barrel is filled with the polymer or polymer solution directly into the preheated barrel. For skin-core elongational viscosity measurements, the preheated barrel is filled with a specially prepared billet, with the outer diameter exactly matching the inside diameter of the barrel. The billet is a two-layer concentric cylinder.
(with the polymer to be analyzed in the core completely encapsulated by the skin). The billets were prepared as described in a previous study (Pendse, 1995).

For the skinless and skin-core PP determinations, a 20 min heat soak was allowed for the samples to reach a thermal steady state prior to experiments’ start. This period was reduced to 5 min in the case of lyocell solutions, to prevent possible degradations.

Temperature was kept constant for each run and the pressure drop across the die was recorded. Elongational viscosities were determined separately on a spreadsheet (Quattro Pro®), after pressure and ram speed smoothing. For the shear viscosities measurements, direct data were extracted using the ACER software capabilities.

7.2.3 Theoretical Development for Measuring Elongational Flow Characteristics

Analysis of this flow was accomplished using the measured pressure and volumetric flow rate data, and mass, momentum and energy balances. The die shapes (Figure 7.4) were defined realizing that since the interface between the polymer melt or solution and either the die wall for skinless, or if used, a lubricating skin must be a stream tube, i.e. a set of streamlines all experiencing the same conditions including the same value of the stream function, \( \Psi \), and forming a two dimensional surface. The stream function in turn must satisfy the continuity equation and the potential function, \( \Phi \), which for shear free flows must be orthogonal to \( \Psi \) and satisfy the irrotationality equation. Constant values of the potential function should define surfaces of constant driving force in the systems, i.e. constant pressure surfaces. As given below the stream function and potential function that satisfy these conditions in converging cone geometries and give a constant elongation strain rate are semi-hyperbolic and mutually orthogonal. A parallel
Development has been accomplished for the converging slit geometry (the appropriate $\Psi$ and $\Phi$ are given by Collier (1994)), but since it results in the same viscosity equations, the slit development is not given in detail although specific key aspects are mentioned.

For cylindrical coordinates, the stream function:

$$\Psi = \frac{\dot{\varepsilon}}{2} r^2 z \quad (7.1)$$

and the potential function,

$$\Phi = \dot{\varepsilon} \left( \frac{r^2}{4} - \frac{z^2}{2} \right) \quad (7.2)$$

Figure 7.4 Semi-hyperbolic Convergent Die

describe the system with the pressure being directly proportional to $\rho \dot{\varepsilon} \Phi$, where $\dot{\varepsilon}$ is the elongational strain rate, and $\rho$ is the density. The velocities are:

$$v_z = -\frac{1}{r} \frac{\partial \Psi}{\partial r} = -\frac{\partial \Phi}{\partial z} = \dot{\varepsilon} z \quad (7.3)$$

$$v_r = \frac{1}{r} \frac{\partial \Psi}{\partial z} = -\frac{\partial \Phi}{\partial r} = -\frac{\dot{\varepsilon}}{2} r \quad (7.4)$$,
and the non-zero velocity gradients are:

\[
\frac{\partial v_z}{\partial z} = \dot{\varepsilon}, \quad \frac{1}{r} \frac{\partial (r v_r)}{\partial r} = -\dot{\varepsilon}, \quad \frac{\partial v_r}{\partial r} = -\frac{\dot{\varepsilon}}{2} \tag{7.5}
\]

The basic equations describing the flow are the scalar equations of continuity (i.e., mass balance) and a form of energy balance expressed in terms of enthalpy per unit mass, \( \dot{\mathcal{H}} \); the first order tensor (i.e. vector) momentum balance, and for potential flow the irrotationality equation. (In the following, it should be noted that unless otherwise indicated, the analysis applies to both the skinless flow and to the core material in the skin/core lubricated flow.) Mass, momentum and energy are conserved separately.

These equations in tensor notation are (Bird et al., 1969):

**Continuity Equation (Mass Balance)**

\[
\frac{D\rho}{Dt} = -\rho \left( \nabla \cdot v \right) \tag{7.6}
\]

**Momentum Balance**

\[
\rho \frac{Dv}{Dt} = -\left( \nabla \cdot P \right) - \left[ \nabla \cdot \tau \right] + \rho g \tag{7.7}
\]

**Energy Balance**

\[
\rho \frac{D\dot{\mathcal{H}}}{Dt} = -\left( \nabla \cdot q \right) - \left( \tau : \dot{v} \right) + \frac{DP}{Dt} \tag{7.8}
\]

**Irrotationality Equation**

\[
\nabla \times v = 0 \tag{7.9}
\]

where \( \frac{D}{Dt} = \frac{\partial}{\partial t} + v \cdot \nabla \) and in cylindrical coordinates:
\[ \nabla = \delta_r \frac{\partial}{\partial r} + \delta_\theta \frac{1}{r} \frac{\partial}{\partial \theta} + \delta_z \frac{\partial}{\partial z} \quad (7.10) \]

\( \tau \), a second order tensor, is the stress, and the first order tensor (i.e. vector) quantities \( V \) and \( q \) are the velocity and energy flux respectively. The body force term, \( g \), a first order tensor, primarily represents the force necessary to orient the material; this term would include a gravitational force if that were significant. The scalar terms \( P \), \( \rho \), and \( \dot{H} \) are the pressure, density, and enthalpy per unit mass, respectively.

The geometry of the hyperbolic dies used in this research was chosen to force the elongational strain rate (noted earlier as \( \dot{\varepsilon} \)) to be a constant value determined by the geometry and the volumetric flow rate. The only velocity gradients in this essentially pure elongational flow are in the flow and transverse directions; therefore, the only non-zero components of the deformation rate second order tensor, \( \Delta \), are the normal components. Since the fluid is assumed to be incompressible then \( \nabla \cdot \mathbf{v} = 0 \); therefore the components of \( \Delta \) are defined in Cartesian coordinates and for \( i \) and \( j \) being \( r \) and \( z \) in cylindrical coordinates as:

\[ \Delta_{ij} = \left( \frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right) \quad (7.11) \]
\[ \Delta_{\theta \theta} = 2 \left( \frac{1}{r} \frac{\partial v_\theta}{\partial \theta} + \frac{v_r}{r} \right) \quad (7.12) \]

in cylindrical coordinates. The "extra" term, \( \frac{v_r}{r} \), in the \( \Delta_{\theta \theta} \) term arises due to the dependence of the unit vector in the \( r \) direction upon position. As a result in Cartesian coordinates the only non-zero components are the flow and transverse components, \( \Delta_r \) and \( \Delta_\theta \), respectively; \( \Delta_r = -\Delta_\theta = 2 \dot{\varepsilon} \). The corresponding non-zero components in cylindrical coordinates are \( \Delta_z \), \( \Delta_r \), and \( \Delta_{\theta \theta} \); where \( \Delta_z \) is the flow direction;
\[ \Delta_z = -2 \Delta_r = -2 \Delta_{\theta \theta} = 2 \dot{\varepsilon} . \]
(Note that \( \Delta_{\theta \theta} \) and the corresponding stress tensor component \( \tau_{\theta \theta} \) are both non-zero.)

The basic assumptions in this analysis and the related implications are:

1. The stress state in the fluid is uniquely determined by the strain rate state, e.g. the fluid could be described by a generalized Newtonian constitutive equation (not a Newtonian fluid), such as a Herschel-Bulkley material, etc. Since the geometry dictates that the only non-zero deformation rate components in the essentially shear free flow region are the normal components and further that the deformation rate components are not a function of position, then the only non-zero stress components are the normal components and the stress components are not a function of position. Therefore \( \nabla \cdot \tau = 0 \).

2. The fluid is incompressible; therefore, \( \nabla \cdot v = 0 \).

3. The system is isothermal; therefore, \( \nabla \cdot q = 0 \).
4. The flow is steady; therefore \( \frac{\partial}{\partial t} = 0 \).

5. The inertial terms are negligible, therefore, \( \mathbf{v} \cdot \nabla \mathbf{v} = 0 \), and \( \nabla \left( \frac{\nu^2}{2} \right) = 0 \).

Since the convergence of the flow channel was designed to force a constant
elongational strain rate, the longitudinal and transverse normal components of the stress
tensor, i.e. \( \tau_z \) and \( \tau_r \), are also constant with their values controlled by \( \dot{\varepsilon} \). If the
analysis were for lubricated flow the shear stress gradients in the core would be
assumed to be negligible. It is shown below, by the experimental data, that the body
force, \( \mathbf{g}_z \), is dominant and causes the shear stress gradient to also be negligible in
skinless flow. Therefore, the stress gradient terms, \( \nabla \cdot \tau \) for both lubricated and
skinless flow, in the momentum balance equation are negligible, and the inertial terms,
\( \rho \frac{D \mathbf{v}}{Dt} \), are also negligible (the pressure gradients calculated from them alone were
two to three orders of magnitude lower than observed and were independent of fluid
character). Using these assumptions the solution to the momentum balance reveals that
the body force \( \mathbf{g}_z \) is equal to \( \nabla P \); i.e. in cylindrical coordinates:

\[
g_z = \frac{\partial P}{\partial z} \quad \text{and} \quad g_r = \frac{\partial P}{\partial r}
\]

(7.13).
The pressure should be directly proportional to the potential function, $\Phi$. Since the pressure is the driving force, then the proper form, to be dimensionally correct, must have the same form as indicated above, i.e. $P$ is directly proportional to $\rho \dot{\varepsilon} \Phi$, and should have the form:

$$P = A \rho \dot{\varepsilon} \Phi + B = P_o \left[ \frac{(r^2 - z^2)}{2} + \left( L^2 - \frac{r_e^2}{2} \right) \right]. \quad (7.14)$$

The variables $r_o$ and $r_e$ are the entrance and exit radius values respectively, $L$ is the centerline length of the die, and $P_o$ is the entrance pressure.

The stress term in the energy balance equation is,

$$\tau : \nabla \mathbf{v} = 3 \frac{\tau}{2} = \dot{\varepsilon} \quad (7.15)$$

for cylindrical coordinates, and for Cartesian coordinates is:

$$\tau : \nabla \mathbf{v} = 2 \tau = \dot{\varepsilon} \quad (7.16).$$

Using the above basic assumptions, the other two possibly non-zero terms in the energy balance are $\rho \frac{D\dot{H}}{Dt}$ and $\frac{DP}{Dt}$ which with the steady flow assumption become $\rho \dot{\mathbf{v}} \cdot \nabla \dot{\mathbf{H}}$

and $\mathbf{v} \cdot \nabla P$. In cylindrical coordinates
\[ \mathbf{v} \cdot \nabla P = v_r \frac{\partial P}{\partial r} + v_z \frac{\partial P}{\partial z} \quad (7.17). \]

The effect of this can be shown by realizing that \( P \) is directly proportional to \( \Phi \) and then integrating from \( r = 0 \) to \( r_i \) (\( r_i \) is the value of \( r \) at the interface either between the polymer and the die wall in skinless or between the polymer and the skin in lubricated flow, and is a function of \( z \) although \( r \) is not) and then from \( z = 0 \) to \( L \). The result is that the first term is negligible since it is proportional to \( r_i^3 \) and the second term is proportional to \( L^2 \) (the first term is three orders of magnitude lower than the second).

The same result occurs in Cartesian coordinates.

In cylindrical coordinates

\[
\rho \mathbf{v} \cdot \nabla \hat{H} = \rho v_r \frac{\partial \hat{H}}{\partial r} + \rho v_z \frac{\partial \hat{H}}{\partial z} \quad (7.18).
\]

By doing a similar double integration it can be shown that the \( v_r \) value is two orders of magnitude lower than \( v_z \); furthermore, \( \frac{\partial \hat{H}}{\partial r} \) should be significantly lower than \( \frac{\partial \hat{H}}{\partial z} \) since these terms are related to orientation development in a stretching plug flow and possible heat transfer. Since the flow is occurring inside the temperature controlled die, the heat transfer in the transverse direction would be negligible and the fluid is being stretched as a plug in the flow direction, therefore the gradient in the transverse direction would be significantly smaller than in the longitudinal. The same results occur for these pressure and enthalpy terms in Cartesian coordinates. As a result of these simplifications, the energy balance expressed in terms of enthalpy becomes
\[
\rho \, v_\varepsilon \, \frac{\partial \hat{H}}{\partial z} = -\frac{3}{2} \tau_\varepsilon \, \dot{\varepsilon} + v_\varepsilon \, \frac{\partial P}{\partial z} \quad (7.19)
\]

Since \( v_\varepsilon = \dot{\varepsilon} \, z \quad (7.20) \)

and \( \varepsilon_h = \ln \left( \frac{z}{\varepsilon_0} \right) = \ln \left( \frac{r_0}{r_\varepsilon} \right) \quad (7.21) \),

the energy balance can be integrated from the entrance to the exit. Therefore the stress component in cylindrical coordinates is

\[
\tau_\varepsilon = + \frac{2}{3} \frac{\Delta P}{\varepsilon_h} - \frac{2}{3} \frac{\rho \Delta \hat{H}}{\varepsilon_h} = + \frac{2}{3} \frac{\Delta P}{\varepsilon_h} - \frac{2}{3} \frac{\Delta H}{\varepsilon_h} \quad (7.22)
\]

where \( \Delta H \) is the enthalpy change per unit volume and \( \rho \Delta \hat{H} = \Delta H \) where \( H \) is the enthalpy per unit volume, and in Cartesian coordinates this term is

\[
\tau_\varepsilon = + \frac{1}{2} \frac{\Delta P}{\varepsilon_h} - \frac{1}{2} \frac{\rho \Delta \hat{H}}{\varepsilon_h} = + \frac{1}{2} \frac{\Delta P}{\varepsilon_h} - \frac{1}{2} \frac{\Delta H}{\varepsilon_h} \quad (7.23)
\]

The elongational viscosity term, \( \eta_e \), in cylindrical coordinates is defined and results in this geometry as:

\[
\eta_e = \frac{\tau_{zz} - \tau_{rr}}{\dot{\varepsilon}} = \frac{3}{2} \frac{\tau_{zz}}{\dot{\varepsilon}} \quad (7.24)
\]

and in Cartesian coordinates

\[
\eta_e = \frac{\tau_{zz} - \tau_{xx}}{\dot{\varepsilon}} = \frac{\tau_{zz}}{\dot{\varepsilon}} \quad (7.25)
\]

Therefore in both Cartesian and cylindrical coordinates the elongational viscosity is:
\[ \eta_e = \frac{\Delta P}{\dot{e} \varepsilon_h} - \frac{\rho \Delta H}{\dot{e} \varepsilon_h} = \frac{\Delta P}{\dot{e} \varepsilon_h} - \frac{\Delta H}{\dot{e} \varepsilon_h} \quad (7.26) . \]

The enthalpy term would represent either a real or apparent phase change that may be induced by the imposed orientation on the polymer melt or solution.

The definition of the effective elongational viscosity, \( \eta_{ef} \), and its relation to \( \eta_e \) in both Cartesian and cylindrical coordinates is as follow:

\[ \eta_{ef} = -\frac{\Delta P}{\dot{e} \varepsilon_h} \quad (7.27) , \]

\[ \eta_e = \eta_{ef} + \frac{\Delta H}{\dot{e} \varepsilon_h} \quad (7.28) . \]

This definition of \( \eta_{ef} \) assumes that any enthalpy change is included in this and except for the term \( \varepsilon_h \) is similar to the 'instantaneous elongational viscosity' for the spin-line rheometer where \( \sigma_e = -\Delta P \) viscosity term (Ferguson & Zemblowski, 1991). In these expressions \( \Delta P \) is the pressure gradient, \( \Delta H \) is the enthalpy change per unit volume, \( \dot{e} \) is the elongational strain rate and

\[ \dot{e} = (v_o /L)(\exp \varepsilon_h + 1) \quad (7.29), \]

where \( \varepsilon_h \) is the Hencky strain and \( \varepsilon_h = \ln (A_o/A_{ex}) \). \( A_o \) is the initial area, \( A_{ex} \) is the exit area, \( L \) is the centerline length, and \( v_o \) is the initial velocity.

The enthalpy change associated with what can at least be considered a flow induced transformation to a metastable liquid crystalline form in various polymer systems can be estimated as follows. If the assumption is made that the non-Newtonian character of the fluid in excess of that reflected in \( \eta_e \) (at an equal shear rate) is due to the resistance to orientation, then the actual Trouton ratio would be \( \eta_e/\eta_b = 3 \). By
measuring \( \eta \), then \( \eta_e = 3\eta \), and substituting \( 3\eta \) into the above equations, enthalpy per unit volume, \( \Delta H = \rho \Delta \dot{H} \), can be calculated from the resultant equation,

\[
\Delta H = -\epsilon_h \dot{\epsilon} (\eta_{ef} - 3\eta_u)
\]

(7.30).

The entropy change, \( \Delta S \), indicating the degree of orientation that develops can be determined from \( \Delta F = \Delta H - T\Delta S \), where \( \Delta F \) is the Gibbs free energy and \( T \) is the absolute temperature. If it is assumed that due to the flow induced orientation, the transition to the metastable state is at equilibrium then \( \Delta F = 0 \) and \( \Delta S = (\Delta H/T) \).
CHAPTER 8  LYOCELL RESULTS AND DISCUSSIONS

8.1 Transition Temperature Determination and Shear-Flow Characterization

As shown in literature, liquid crystalline phases appear for both cellulose and lignocellulose systems under certain conditions of concentration and temperature. A transition temperature range from the mesomorphic phase to the isotropic phase becomes important for the final properties of the spun fibers, because the liquid crystalline phase is characterized by more oriented macromolecules (Chanzy et al., 1982. Navard & Haudin, 1980, 1985, 1986).

The lyocell solutions were examined with an optical microscope under polarized light. Figure 8.1 presents a micrograph of a 30% dissolved pulp lyocell solution, in which the anisotropic phase can be observed. Therefore, the transition temperature can be determined optically for relatively high concentrations. The same findings were strengthened using the DSC technique, in which a small enthalpic change ($\Delta H = 0.5-3.0$ J/g) was noticed around the transition temperature. A transition temperature range between 85 - 95 °C was noticed by both optical microscopy and DSC.

The dynamic measurements with DMS showed a sudden change in both dynamic viscosity and tan $\delta$, for both cellulosic and lignocellulosic materials, including kenaf (Figure 8.2). These changes indicate the same transition temperature domain.
The rheological measurements do not require the use of relatively high concentrations as the optical microscopy does. The transition between phases being noticed for lower concentrations (starting with 2% concentration, as opposed to the lower limit around 20% in the case of optical measurements).

The phase transition was indicated also in the steady-state viscosity variation. For a lower range of shear rates between 1-100 s⁻¹, the parallel-plate rheometer was used. Figure 8.3 shows steady-state viscosity dependency by temperature for a 4% kenaf lyocell, with different shear rates. For a higher range of shear rate, pertaining particularly to the spinning processing, viscosity data were collected using the ACER. DMS data before and after ACER measurements showed no change in viscosity, thus no significant degradation occurs. Figure 8.4 presents the viscosity dependency on the
Figure 8.2 Dynamic Viscosities and Tan δ for 12% Sugar Cane Lyocell
Figure 8.3 Steady-state Shear Viscosities for 4% Kenaf Lyocell Solution

Figure 8.4 ACER Determination of Shear Viscosities for 12% Sugar Cane Lyocell Solution

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inverse absolute temperature for a 12% sugar cane lyocell solution, in which a transition around 85 °C is noticed.

The difference in shear viscosities between the two phases implies a difference between the shear flow activation energies at the transition temperatures. An Arhenius type equation defines the shear viscosity \( \eta_s \) as a function of the temperature independent shear flow energy of activation \( E_a \): 

\[
\eta_s = A \exp\left(\frac{E_a}{RT}\right)
\]

where \( T \) is the absolute temperature, \( R \) is the universal constant and \( A \) is a constant. The shear flow energy of activation was obtained from the slope in the graph of \( \ln(\eta_s) \) vs. the inverse absolute temperature.

The energy of activation will increase with the concentration. This trend may be explained by the increased density of macromolecular chain entanglements (as a result of frictional interactions between adjacent molecules), with increased concentrations (Figure 8.5). A decrease in the energy of activation with the shear rate was also noticed.

In both the mesomorphic and isotropic phases the shear rheological behavior of the lyocell solutions may be described by a power-law type dependency:

\[
\eta_s = K \gamma^{n-1}
\]

where \( K \) is the consistency, \( n \) is the power-law index, and \( \gamma \) is the shear rate. The dependency of the power-law index on the nature of the substrate and on temperature is presented in Figure 8.6. A shear thinning effect (pseudoplastic) is noticed, as well as a strong temperature dependency of the flow index.
Figure 8.5 Viscosity Dependency by Concentration for Recycled Cotton Lyocell

Figure 8.6 Power-law Index Dependency on Temperature
8.2 Elongational Flow Rheology through Converging Dies. Polypropylene
Elongational Flow Characteristics

The effective elongational viscosities of skin/core PE/PP and skinless PP melts as a function of strain rate are shown in Figure 8.7 (Data for the skin-core measurements with a Hencky strain of 6 are from Pendse (1995)). Regression analysis results for both Hencky strains of 6 and 7, show that there are not statistically significant differences between the skin-core and skinless data. It should be noted that the PP skin/core data are more scattered than are the skinless data, probably because it is difficult to control the exact ratio of the skin to core layers.

Data from the flow behavior of PP illustrate the calculation of thermodynamic properties. The calculated enthalpy and entropy changes of PP are shown in Figure 8.8 and Figure 8.9, respectively. For PP at 200°C the enthalpy change for the flow induced transformation to a metastable state ranged from $-1.03 \times 10^7$ to $-3.83 \times 10^7$ J/m$^3$, with an increase in magnitude as strain rate ranged from $1.1 \text{ s}^{-1}$ to $128.0 \text{ s}^{-1}$ and higher values for $\epsilon_h = 7$ than for $\epsilon_h = 6$. This can be compared to the enthalpy of fusion for PP of $-2.15 \times 10^8$ J/m$^3$ that is expected to be an order of magnitude higher since the solid crystalline state has a much higher degree of organization than does a low order liquid crystalline form (Collier, 1972). The same trends were noted for the calculated entropy changes in PP which ranged from $-2.18 \times 10^4$ to $-8.09 \times 10^4$ J/(K m$^3$). It should be noted that the shear viscosity for this PP melt at the test temperature of 200°C is Newtonian until the shear rate is around $10^{-1}$ s$^{-1}$ and then it becomes shear thinning, as shown in Figure 8.10.
Figure 8.7 Lubricated and Skinless Polypropylene Effective Elongational Viscosities

![Stress-rate Graph](image)

Figure 8.8 Polypropylene Enthalpy Change from Rheology

![Enthalpy Change Graph](image)
The $\Delta H$ and $\Delta S$ values are essentially zero below $10^{-1}$ s$^{-1}$ and then they develop a dependence upon elongational strain rate.

As a result of the imposed pressures (1.15 to 42.60 MPa at elongational strain rates of 0.02 to 136.00 s$^{-1}$) the momentum balance equation suggested that significant body forces must be necessary to orient the fluid. Furthermore, the energy balance, expressed in terms of enthalpy for this controlled isothermal system, revealed a significant enthalpy change is consistent with transformation to an ordered liquid crystalline form (which may be metastable and induced due to flow). The suggestion of a transformation to an oriented liquid crystalline form by both calculated body forces and the enthalpy change, is consistent with earlier work on PP (Collier et al., 1976). In the previous study, PP flowed through a linearly converging section of a die, then through a constant diameter section. A sharp temperature gradient was imposed on the latter section; thereby crystallizing the PP inside the die (Collier et al., 1976). The die used in this earlier study was a standard Instron capillary die with a 90° linear tapered entrance with $\epsilon_h = 4$ for the machined entrance; if the flow defined wine glass stem entrance pattern to the die from the specially designed reservoir were considered, then an effective $\epsilon_h$ would be approximately 7. These earlier PP samples exhibited 0.03 µm diameter ultra-fine filaments and an extremely high Herman-Stein orientation function (0.996 where 1.000 is perfect alignment in the flow direction, 0.000 is random, and -0.500 is transverse alignment) (Collier et al., 1976).
Figure 8.9 Polypropylene Entropy Change

Figure 8.10 Polypropylene Shear Viscosities

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8.3 Elongational Flow Characteristics For Lyocell Solutions

Elongational viscosity results for lyocell solutions were similar to those for PP but were lower values. These relative high effective elongational viscosities were obtained for the lyocell solutions, probably due to the influence of the entropic contribution.

8.3.1 17 % Recycled Cotton Lyocell Solution

The dependence of the effective elongational viscosity of lyocell solutions upon temperature is shown in Figure 8.11 for a 17% solution of recycled cotton cellulose in NMMO•H₂O in the εₜₐₙ = 7 die. The Trouton ratios (elongational viscosity over the shearing viscosity) for this lyocell solution in this die vary from 3 (theoretical value for Newtonian behavior) at a strain rate of 11.9 s⁻¹ to 40 at a strain rate of 94.0 s⁻¹. A transition, probably related to the liquid crystalline form, occurs in the range of 85 to 105 °C in both ηₑₑₑₑ and the Trouton ratio with a local maximum around 95 °C. The imposed pressures for elongational flow of this lyocell solution and Hencky strain were from 2.58 MPa to 10.7 MPa for strain rates of 11.9 to 94.0 s⁻¹ and temperatures from 80 to 110 °C; the corresponding values for εₜₐₙ = 6 were pressures from 0.75 to 4.33 MPa for strain rates of 4.3 to 34.1 s⁻¹ and temperatures from 80 to 110 °C.

The enthalpy change for the 17% recycled cotton cellulose in an NMMO•H₂O solution at 95°C, corrected for its concentration, ranged from -1.99 x 10⁷ to -4.38 x 10⁷ J/m³, with an increase in magnitude as strain rate ranged from 34.1 s⁻¹ to 94.0 s⁻¹ and higher values for εₜₐₙ = 7 than for εₜₐₙ = 6. The entropy ranged from -4.49 x 10⁴ to -11.9 x 10⁴ J/(K m³) (Figure 8.12). These cellulose values are comparable to results for the same
Figure 8.11 17% Recycled Cotton Cellulose in Lyocell Elongational Viscosities

Figure 8.12 17% Recycled Cotton Lyocell Entropy Change from Rheology ($\epsilon_n=7$)
solution measured by DSC; the measured enthalpy and calculated entropy changes were 
-0.441 x 10^6 to -4.38 x 10^7 J/m^3, and -1.20 x 10^4 to -7.19 x 10^4 J/(K m^3), respectively.

8.3.2 8% Kenaf Lyocell Solution

Figure 8.13 presents the dependency of the effective elongational viscosity of a 8% kenaf lyocell solution in the ε_0 =7 die. A transition temperature range occurs between 85 -100 °C for both Trouton ratios and elongational viscosities. The presence of the lignin in the lyocell system gives higher Trouton ratios. ranging between 57 at a strain rate of 11.9 s^{-1} to 185 at a strain rate of 94.0 s^{-1} in the ε_0 =7 die. For the ε_0 =6 hyperbolical die, the Trouton ratios ranged between 43 at a strain rate of 4.33 s^{-1} to 250 at a strain rate of 17.90 s^{-1}.

A similar trend (Figure 8.14) was noticed for the enthalpy and entropy changes for the 8% kenaf lyocell. The enthalpy range for elongational flow was -3.1 x 10^5 to -9.8 x 10^5 J/m^3 in the ε_0 =7 die for a range of strain rates between 11.90 s^{-1} to 47.02 s^{-1} (the entropy ranged from -0.82 x 10^5 to -2.8 x 10^5 J/(K m^3)). For the ε_0 =6 converging die, the enthalpy range between -3.3 x 10^5 to -9.8 x 10^5 J/m^3 (entropy range is between -0.9 x 10^5 to -2.6 x 10^5 J/(K m^3)) at a strain rate of 4.33 s^{-1} to 17.09 s^{-1}.

8.3.3 6% Sugar Cane Lyocell Solution

A transition related to the anisotropic-isotropic phase change, occured in the range of 90 to 100 °C for the elongational viscosity of a 6% sugar cane lyocell solution. Figure 8.15 presents the effective elongational viscosities for a ε_0 =7 die, with a pressure range between 0.037 to 0.282 MPa, temperatures from 80 to 110 °C, and the strain rates of 64.11, 32.26, and 11.90 1/s. The Trouton ratios for this lyocell solution in this die
Figure 8.13 8% Kenaf Lyocell Elongational Viscosities

Figure 8.14 8% Kenaf Lyocell Entropy Changes from Rheology ($\epsilon_b = 7$)
varied from 6.50 to 30.15. The entropy of orientation (Figure 8.16) ranged from -53.15 to -709.42 J/(K m²).

8.3.4 4% Dissolving Pulp Lyocell Solution

The same strain rates, temperature range, and die as in the case of the 6% sugar cane lyocell were used for a 4% dissolving pulp lyocell solution. Figure 8.17 presents the effective elongational viscosities for this solution. An anisotropic-isotropic transition temperature range occurred between 85 to 95 °C. The pressure drop varied between 0.069 to 0.340 MPa. and the entropy of orientation ranged from -183 to -963 J/(K m³) (Figure 8.18).

The different trends in elongational viscosities, and especially the different trends in the entropy of orientation for all the studied lyocell systems, suggest a complex phase-diagram of the transitions between the liquid crystal phase to the isotropic phase. The presence of lignin in the lyocell solution makes the elongational flow behavior more complex.

8.4 Phase Separation and Microfiber Formation

The lyocell solutions were forced through the hyperbolic converging die to provoke phase separation and lignocellulose/cellulose crystallization, and microfiber formation and orientation. The solutions were transformed to a two-phase regime by the strong entropic effect under stress application, induced by flow through the converging die. One of the two phases contains oriented microfibers (with perhaps some retained solvent), and the other phase is primary solvent (with perhaps some retained cellulose).
Figure 8.15 6% Sugar Cane Lyocell Solution Elongational Viscosities ($\epsilon_h = 7$)

Figure 8.16 6% Sugar Cane Lyocell Solution Entropy Change from Rheology ($\epsilon_h = 7$)
Figure 8.17 4% Dissolving Pulp Lyocell Solution Elongational Viscosities ($\varepsilon_s = 7$)

Figure 8.18 4% Dissolving Pulp Lyocell Solution Entropy Change from Rheology ($\varepsilon_s = 7$)
When phase separation occurs during the flow of the cellulose in a solvent such as NMMO-H₂O, the solvent rich phase becomes a lubricating layer, because this lower-viscosity phase tends to migrate to the shear region near the die interface. Because the skin layer has a viscosity substantially lower than the viscosity of the core, the shearing gradient from the wall is essentially confined to the skin, producing an essentially elongational flow pattern in the core.

Separation of the cellulose-rich phase from the solvent-rich phase may depend in part on the amount of lignin in the solution, which can be controlled as desired by controlling the amount of lignin removed from the cellulose source. The retained lignin may also affect the size of the phase separated regions, and therefore, the size of the resulting microfibers. Future experiments will better define the effect of lignin.

Scanning electron micrographs of the extrudates confirmed orientation in the direction of the fiber axis. The result of this process is an extrudate having two distinct levels of organization, both oriented in the direction of flow. On the larger scale, the extrudate comprises distinct filaments, each filament having a diameter on the order of 10 μm (in the range of microfibers, defined to be 0.1 denier or less), aligned with one another in the flow direction. Each filament has a substructure: each is a bundle of ultrafine fibers with a diameter on the order of 0.5 μm (in the range of ultrafine fibers, defined to be 0.01 denier or less).

Furthermore, a high degree of alignment of cellulosic microfiber bundles formed from lyocell in elongational flow using these same dies is apparent in Figures 8.19 and 8.20. The sugar cane derived lyocell extrudate in Figure 8.20 and the kenaf derived
lyocell extrudate in Figure 8.21. indicate the orientation in the flow direction and organization into 10 μm structures, that are magnified in Figure 8.20 (from a recycled cotton lyocell solution) and indicate 0.5 μm microfibers.

An additional benefit to orienting and forming the microfibers inside a hyperbolically converging channel is that the breakage of the microfibers is greatly reduced compared to the breakage of commercially manufactured polyester microfibers. Flow through the hyperbolically converging channel forms and orients the fibers by pushing rather than pulling, so that the fibers have sufficient strength when they exit the die.

The hyperbolically converging opening not only induced orientation inside the die, but did so at a constant elongational strain rate, thereby enabling high spinning rates. Hyperbolic convergence of flow is preferred because it induces a constant strain and is less likely to produce flow instabilities than linear convergence.
Figure 8.19  Sugar Cane Lyocell Extrudate

Figure 8.20  Lyocell Microfiber Tow

Figure 8.21  Kenaf Lyocell Extrudate
CHAPTER 9 CONCLUSIONS

Lyocell solutions of kenaf, sugar cane, recycled cotton, and pulp with concentrations between 2-20 % (by weight) were obtained at moderate temperatures (80-90 °C) and studied under shear and elongational flow. The presence of a mesomorphic phase was noticed for cellulose/lignocellulose NMMO monohydrate solutions using microscopy under polarized light, differential scanning calorimetry, and shear and elongational rheology. A transition temperature domain was found between 85 - 95 °C, and it depends on the concentration and nature of the substrate in NMMO monohydrate.

A change was noticed in the dynamic and steady-state shear viscosities, and in tan δ around the transition temperature from the mesomorphic phase to the isotropic phase. These steep changes in viscosities increased with concentration and decreased with shear rate. Measurements in shear flow showed shear thinning effects, and a power-law rheological model can be used to characterize the shear flow rheology of lyocell solutions.

Elongational rheology of polymer melts and concentrated solutions using semi-hyperbolically converging conical dies has demonstrated, at least for the PP melts and lyocell solutions tested, that the flow is dominated by the orientation developing in the fluid. Therefore, a skin layer of a lower viscosity fluid is neither necessary nor do measurements require correction for shearing effects; the body forces related to the
developing orientation are sufficiently strong to make the shearing gradient insignificant. The fluids are being transformed from an isotropic state to an, at least metastable, oriented state.

This novel technique was used to measure the lyocell solution effective elongational viscosities. The induced phase separation coupled with the minimization principle caused a solvent-rich low-viscosity lubricating phase formation closed to the wall. The effective elongational viscosities and the corresponding Trouton ratios showed the same transition, related to the liquid crystalline form, in a range of 85 to 105 °C. They were dependent on the applied strain rates, pressure drops, and the die geometry (Hencky ratios).

The enthalpy and entropy changes were estimated as functions of processing conditions, from the elongational and shear viscosity data, assuming a metastable transition. These thermodynamic measurements were comparable with the values measured for the same solution in a differential scanning calorimeter.

The flow through a converging die displayed not only phase separation and cellulose crystallization, but also microfiber formation and orientation. Cellulosic and lignocellulosic microfibers with a high degree of alignment were obtained, having two distinct levels of organization. The first level, formed by filaments having a diameter in the microfiber range (10μm), had a substructure of ultrafine fibers with a diameter on the order of 0.5 μm (the second level).
CHAPTER 10 RECOMMENDATIONS

The present work represents initial lyocell solution studies, from the perspective of lignocellulosic solutions and their properties. The new approach of measuring elongational flow characteristics and microfiber formation are recommended to be correlated with lyocell solution properties.

Several areas for future work may be:

1) Optimize the extraction process for different lignocellulosic materials in correlation with the lyocell solution characteristics, pertaining particularly to the final spun fiber or microfiber properties. The lignin concentration in the substrate is a direct result of different extraction conditions (alkali concentration, reaction time, mixing, and presence or absence of steam explosion), and of the inherited biological nature of the substrate.

2) Investigate lyocell solution formation from the perspective of lignin and cellulose characteristics, such as, molecular weight, molecular weight distribution, and biological origin.

3) Explore the possibility of lyocell solution preparation under shear conditions. Direct formation of solutions in a twin-screw extruder is desirable for better mixing and for continuous processing implementation and optimization.

4) Investigate the elongational flow characteristics of lyocell solutions in relation to the presence or absence of lignin in the system. Establish correlations between
lignin content, entropy of orientation due to flow through converging dies, shear rheological properties, phase separation, and microfiber formation.

5) Explore a possible relationship between the molecular parameters such as molecular weight, polydispersity index and the extent of branching in the polymer, and the elongational viscosity and Trouton ratio behavior of the polymer melts or solutions (including lyocell solutions).

6) Investigate the usage of the elongational rheological measurement technique alone or as part of an on-line process controller, in which elongational viscosities (optionally in conjunction with other properties) are measured as part of a feedback loop that is used to control a process such as polymer manufacture or extrusion. The affinity to orient, and the retention of orientation is important in most polymer processing operations.
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APPENDIX A SHEAR AND ELONGATIONAL FLOW

A.1 Simple Shear Flow

The velocity field in simple shear flow (defined for discussion in a cartesian coordinate system) has only one component, e.g. $v_x$, which changes only in one direction, e.g. $y$ (Figure A.1):

$$v_x = v_x(y), \quad v_y = v_z = 0$$  \hspace{1cm} (A.1)

Such a flow can occur between two parallel plates or in the case of cylindrical geometry, in a tube (Poiseuille flow).

In simple shear flow, the apparent shear viscosity can be defined as the ratio of the shear stress $\tau_{yx}$ and the shear rate:

$$\eta_o = \frac{\tau_{yx}}{\gamma}$$  \hspace{1cm} (A.2)
where this shear rate, $\dot{\gamma}$, is defined as:

$$\dot{\gamma} = \frac{\partial v_x}{\partial y}. \quad (A.3)$$

Generally, for polymer melts, the shear viscosity is a strong function of shear rate at a given temperature. The power-law models the shear viscosity and flow behavior over a large range:

$$\eta = k \dot{\gamma}^{n-1}. \quad (A.4)$$

$m$ is the consistency and $n$ is the power-law index. When $n=1$, the fluid is a Newtonian fluid (Bird et al., 1969).

A.2 Simple Elongational Flow

Figure A.2 (a), (b) and (c) depict three classes of simple elongational flow: planar, uniaxial and biaxial (Barnes et al., 1989). These flows are classified according to the form of the velocity field.

The term uniaxial elongational flow is used in a velocity field of type:

$$v_x = \dot{\varepsilon} x, \quad v_y = -\frac{\dot{\varepsilon}}{2} y, \quad v_z = -\frac{\dot{\varepsilon}}{2} z \quad (A.5)$$

This type of flow is encountered in converging dies and spinning. A major part of this work deals with uniaxial elongational flow in cylindrical geometry. Unless otherwise stated the term elongational viscosity in this work would refer to the uniaxial elongational viscosity.
Figure A.2 Classification of Simple Elongational Flow

The uniaxial apparent elongational viscosity is defined as:

$$\eta(\dot{\varepsilon}) = \frac{\tau_{xx} - \tau_{yy}}{\dot{\varepsilon}}$$  \hspace{1cm} (A.6)

in cartesian geometry. The analysis has been carried out in cylindrical geometry in this work, where the elongational viscosity is defined as:

$$\eta(\dot{\varepsilon}) = \frac{\tau_{zz} - \tau_\sigma}{\dot{\varepsilon}}.$$  \hspace{1cm} (A.7)
Comparing the above equations for elongational viscosity with the shear viscosity it can be concluded that the ratio of the elongational and shear viscosity at similar deformation rates is a scalar parameter. This ratio is called the Trouton ratio. This ratio is constant and independent of the strain rate for Newtonian fluids. The Trouton ratio for uniaxial, planar and biaxial geometries for Newtonian fluids is equal to 3, 4 and 6 respectively (Barnes et al., 1989).

The Trouton ratio is one measure of the deviation of the fluid from the Newtonian behavior. For polymer melts and solutions the value of Trouton ratio has been reported from 3 (at very low strain rates) to up to 200.
A typical preparation of a 15% lyocell solution is as follows. For other concentrations the amounts of water, NMMO, and cellulose were modified.

A mass of 148 g water was mixed with 148 g of 50% aqueous NMMO in a 500 cm$^3$ spherical flask. This flask was heated to a 75 °C by immersion in a water bath. Separately, the cellulosic or lignocellulosic material was cut and ground finely in a coffee grinder. 15 g of dried material and 0.1 g of n-propyl gallate were added into the flask. The flask was connected to a Buchi rotavapor initially operated at 70 °C and atmospheric pressure. The bath temperature was increased to 100 °C and the rotavapor was then connected to a water pump giving a vacuum. After 1 to 2 hours of rapid rotation, a bubble free lyocell solution was obtained. The time to complete the cellulose dissolution and the water removal differs by the substrate concentration, being longer for higher concentrations. After solution formation, the flask was brought to atmospheric pressure, cooled down to room temperature, capped, and refrigerated until further use.
VITA

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DOCTORAL EXAMINATION AND DISSERTATION REPORT

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Major Field: Engineering Science

Title of Dissertation: Processing of Value-Added Textile and Geotextile Products From Sugar Cane and Kenaf

Approved: 

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Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

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Date of Examination:

April 1, 1998