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LIGNIN RECOVERED FROM THE NEAR-NEUTRAL HEMICELLULOSE EXTRACTION PROCESS AS A PRECURSOR FOR CARBON FIBER

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Lignin recovered from the near-neutral hemicellulose extraction process was investigated as a precursor suitable for production of carbon fiber. Crude lignin was precipitated from the wood extract by adding sulfuric acid to lower the pH value to 1.0. The crude lignin extract was then upgraded by using hydrolysis to cleave lignin-carbohydrate bonds and to remove carbohydrates that contaminate the lignin. The precipitated solids were separated by filtration, washed with water, and then dried. Lignin recovered using the hydrolysis method was found to be high in carbon, high in total lignin, low in inorganic contamination, and low in insoluble material, but high in volatile material. The recovered lignin could be thermally spun into lignin fibers, but the spun fibers proved to be brittle, which was thought to be due to its low-molecular mass and the glassy nature of lignin. Micrographs obtained using scanning electron microscopy (SEM) illustrated imperfections on the surface and in the interior microstructure of the carbon fiber when compared to micrographs taken of commercial carbon fiber manufactured using PAN and pitch. These imperfections were thought to be related to the high volatile material content in the samples and the slow rate of heating during the carbonization process. Baker (2011) suggests that increasing the rate of heating during carbonization can reduce the degree of brittleness and improve mechanical properties.

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INTRODUCTION

Carbon fiber is an important engineering material used in the manufacture of advanced composite materials. Carbon fiber is lightweight and has high strength, flexibility, and fatigue-resistance. These excellent properties result from the orientation of a graphite layer along the fiber axis during the production process (Chung 1994). Carbon fiber is manufactured by thermally treating a precursor fiber in the "carbonization" process. Formation of the precursor fiber can be accomplished either by melt spinning or wet spinning. Prior to carbonization, the precursor fiber is often subjected to "thermo-stabilization," or a process leading to cross-linking of the polymer on the fiber surfaces, thus preventing shrinking, melting, and fusing (Chung 1994). Based on its mechanical properties, carbon fiber can be classified as general purpose (GP) or high performance (HP). The precursor materials used to produce carbon fiber are extremely

important in determining the final properties and its classification. Pitch, derived from petroleum or coal, and polyacrylonitrile (PAN) are the most important types of precursor materials used to produce carbon fiber commercially. Almost 80% of commercial carbon fiber is predicated on using PAN as the starting raw material because of its superior properties compared to those of pitch-based carbon fiber. However, carbon fiber produced from PAN is expensive, and thus has application limited to high-performance structural materials. There is a need for a low-cost precursor material that can produce carbon fiber with properties equal to or superior to those of pitch and approaching those of PAN.

Lignin is potentially a precursor material for the production of carbon fiber. Advantages of lignin for the production of commercial carbon fiber are that it is naturally occurring, readily available, inexpensive, and structurally rich in phenyl propane groups that are high in carbon (60%). Lignin, however, possesses several disadvantages, the most notable of which is the difficulty in its recovery in a clean, pure form. The near-neutral hemicelluloses extraction process is being developed for the extraction of acetyl groups and carbohydrates from hardwood chips for conversion into acetic acid and five- and six-carbon sugars, while the residual wood is used to produce market kraft pulp (van Heiningen 2006, 2011). Green liquor is a mixture of sodium carbonate and sodium sulfide and is used as the extraction solvent in the process. In this biorefinery process the extracted lignin is underutilized. Also, the process requires additional revenues from new byproducts to be economically viable. Currently, lignin recovered in the extraction process is separated and returned to the main black liquor stream to be burned as a source of energy. The lignin in the hemicelluloses extraction process thus represents an opportunity to obtain a clean pure lignin feedstock and possibly a new, needed source of revenue.

The objective of this work was to investigate the suitability of lignin recovered from the near-neutral hemicellulose extraction process (van Heiningen 2006, 2011) as a precursor for the production of carbon fibers. "Crude" lignin is defined as lignin that is recovered from the original hardwood source following extraction using green liquor in the "Near Neutral Hemicellulose Extraction Process" (Mao 2010; van Heiningen 2011). "Purified" lignin is defined as lignin resulting from the crude lignin after it has been upgraded by an appropriate technique or process, two of which are described here (Figs. 1 and 2).

PREVIOUS WORK

Lignin as a precursor for carbon fiber production has been studied for more than 50 years. The first lignin–based carbon fiber was produced in Japan in 1964 using thiolignin, alkali lignin, and lignosulfonates (Schmidl 1992). The first commercial lignin-based carbon fiber was manufactured in a small pilot plant operated by Nippon Chemical Co. in the 1970s. The poor mechanical properties of the carbon fiber product forced this project to be abandoned. Recently considerable research has been done on the manufacture of carbon fiber from lignin at the Oak Ridge National Laboratory (ORNL).

Notable among this work are the studies of Baker (2005, 2011), who developed specifications for lignin for use as a carbon precursor (Table 1).

Work at ORNL

Researchers at ORNL investigated lignin blends as a low-cost, high-production volume feedstock for carbon fiber (Griffin 2004). A critical factor in this investigation was the ability of the lignin to be melt-spun into lignin fiber. The ORNL team concluded that carbon fiber can be produced in high yields and can readily be stabilized, carbonized, and graphitized. The physical structure and mechanical properties of lignin carbon fibers, although still below those desired by the automobile industry, indicate the feasibility of using lignin in transportation as a reinforcing agent for composite materials. Contamination is a major problem that must be overcome if commercially produced lignin is to be used as a precursor material. This requires the development of low-cost technology suitable for the removal of contaminants, such as sand, salts used in the pulping process, and entrained carbohydrates. Recently, a fifth specification for precursor lignin has been added, namely that the residual carbohydrates have to be less than 500 ppm (Baker 2011).

Table 1. ORNL Specifications for Lignin as a Precursor Material for the Production of Carbon Fiber (Baker et al. 2005)

Specification	Value
Lignin Content (w %)	99%
Ash Content (w %)	< 0.1%
Volatile Material (w %)	< 5% (at 250°C)
Particulate Matter (w %)	100% Removal of particulate matter > 1µm in diameter

Modified Lignin for Use in Carbon Fiber Production

Hydrogenated lignin precursor

Sudo (1992) described a process for the production of carbon fiber from hardwood lignin in which steam-explosion technology was used to isolate lignin from birch wood. The steam-exploded lignin was hydrogenated using a Raney Nickel catalyst to lower its softening point to 110°C and modify the lignin to improve melt spinning. Sudo compared the chemical structure of the precursor to the crude lignin and concluded that there was a significant elimination of aliphatic functional groups relative to the original starting material.

Phenolated lignin precursor

Sudo (1993) in a continuation of previous work investigated using phenolated lignin as a carbon fiber precursor. This work was done as an alternative to using hydrogenated lignin because of the high manufacturing cost associated with producing

hydrogen. The tensile strength of the carbon fiber was improved, but was not as high as that of the hydrogenated lignin.

Acetylated lignin precursor

Researchers at Weyerhaeuser (Eckert 2008) developed a method for acetylating softwood kraft lignin for use in melt-spinning lignin fiber. The acetylation process was conducted by using acetyl chloride, acetic anhydride, and acetic acid as reagents. Acetylation of the lignin decreases the glass transition temperature and greatly aided spinning lignin fiber. Unfortunately no data were presented for the physical properties and the overall process yield for the carbon fiber product.

Organosolv Lignin as Precursor

Hardwood lignin from acetic acid pulping

Crude lignin was obtained by acetic acid pulping of birch wood and used as a precursor for producing carbon fiber (Uraki 1995). The organosolv lignin obtained by aqueous acetic acid pulping was used without chemical modification outside of that done in the pulping process.

Softwood lignin from acetic acid pulping

Kubo (1998) replicated Uraki's 1995 work but used softwood. Lignin was recovered by atmospheric pressure acetic acid pulping and used in the production of carbon fiber. A major difference existed between Uraki's original work and that done by Kubo. Uraki used the crude hardwood lignin obtained directly from the acetic acid pulping process in the production of carbon fibers. Kubo, by contrast, had to remove the high molecular mass infusible fraction of the crude softwood lignin to permit melt spinning. The high molecular mass infusible lignin was removed by filtering the crude lignin obtained from the acetic acid pulping process. The low molecular weight fractions were dissolved in acetic acid at a lower concentration than that used in the pulping process. This technique preferentially dissolved the lower molecular weight fractions of the crude lignin, which then re-precipitated. By using the above technique, carbon fiber could be prepared by direct carbonization, thus avoiding the thermo-stabilization process.

Hardwood lignin prepared by the Alcell process

In the Alcell process, a 50 weight % ethanol/water mixture is used to produce hardwood organosolv pulp, lignin, and sugars. Alcell lignin is highly hydrophobic, low in ash, and contains no sulfur, and thus is distinctly different from either lignosulfonates obtained from the sulfite process or kraft thiolignin. Attributes of Alcell lignin include its low contamination, low number-average molecular weight, low softening point, low glass transition temperature, and small median particle size.

Kadla (2002) compared Alcell lignin to lignin obtained from hardwood kraft lignin and Indulin AT (softwood kraft lignin). Kadla reported that the Indulin AT could not be spun into lignin fiber because of charring before melting. Both the Alcell and hardwood kraft lignin could be melt-spun into lignin fiber, but the Alcell lignin had a considerably lower spinning temperature.

Carbon Fibers from Lignin–Synthetic Polymeric Blends

Kadla (2002) investigated the applicability of lignin-polyethylene oxide (PEO) blends as precursors for the production of carbon fiber. What is unique about Kadla's (2002) work is that commercially available kraft hardwood lignin was used without chemical modification to produce carbon fibers by thermal spinning followed by carbon-ization. Fiber spinning was facilitated by the addition of the PEO to the commercial hardwood lignin. The lignin-PEO blends could readily be converted into fiber by the addition PEO. Although the addition of PEO into the blend improved fiber spinning, the physical properties of the carbon fiber were not improved.

Kubo (2005A) discusses the applications of a variety of lignin-synthetic polymer blends as precursor materials for the production of carbon fiber. Fiber spun from both unmodified hardwood kraft and organosolv lignin proved to be brittle and difficult to handle. Kubo overcame this problem by using blends of lignin and synthetic polymers of poly (ethylene terephthalate) (PET), polyethylene oxide (PEO), and polypropylene (PP) to reduce the brittleness and improve the physical properties of the spun fiber properties. However, the physical properties of the carbon fiber were not materially improved.

Table 2. Properties of Carbon Fiber

Precursor Materials	PAN[a]	Pitch[b]	Plasticized Indulin AT	Hardwood Lignin	Hydrogenated Lignin
Manufacturer	Zoltek (2009)	Cytec (2009)	Schmidl (1992)	Kadla (2002)	Sudo (1992)
Fiber Diameter (μm)	7.2	11	103±3.5	46±8	7.6±2.7
Elongation (%)	1.71	0.91	0.32±0.11	1.12±0.22	1.63±0.19
Tensile Strength (MPa)	4,137	1,560	150±20	422±80	660±230
Tensile Modulus (GPa)	242	172	49.1±14.4	40±11	40.7±6.3
Density (gm/cm^3)	1.81	1.90	NA	NA	NA
Carbon Content (%)	95	97+	91	NA	NA
Price ($/lb)	10~80	45	NA	NA	NA

(a) Zoltek, PANEX35 typical properties data sheet.
(b) Cytec P25 typical properties data sheet.

Physical Properties of Carbon Fiber from Lignin

Table 2 lists the physical properties of carbon fibers produced from various lignins and commercial materials manufactured from PAN (PANEX35) and pitch (P25). The diameter of carbon fiber produced from hydrogenated lignin was reported by Sudo (1992) to be approximately 7.6 μm, which compares favorably with commercial carbon fiber produced from PAN. The PAN-based carbon fiber has the highest tensile strength (4,137 MPa), while carbon fibers from petroleum pitch is less than half this value (1,560 MPa). For comparison purposes the tensile strength of commercial carbon steel is 324 MPa. Commercial carbon fiber from pitch has 35% of the value of carbon fiber from PAN. The elongation of carbon fiber from hydrogenated lignin reported by Sudo (1992) was about 1.63% and is close to the carbon fiber from PAN, 1.71%. By contrast, the tensile strength of carbon fiber from hydrogenated lignin was only about 16% of the value of carbon fiber from PAN.

EXPERIMENTAL

The experimental methods are described in detail by Luo (2010).

Lignin Extraction

Mixed northeast US hardwood chips were obtained from a local pulp mill and were composed of birch, beech, maple, poplar, and trace amounts of softwoods. The wood was extracted using green liquor, which is a mixture of sodium carbonate and sodium sulfide. The experimental conditions were similar to those previously described (Genco 2008). Extraction experiments were conducted with green liquor application rates of 0, 2, 4, and 6% based upon the mass of oven-dry wood. The 0% green liquor extraction experiment was conducted using pure water. The extraction experiments were performed at a liquor-to-wood ratio (L/W) of 4 to 1. The extraction experiments were conducted for 110 minutes at 160°C in an indirectly-heated, seven-liter circulating digester. The contents of the extraction vessel were heated to the extraction temperature over a 55 minutes period of time using a linear temperature ramp. The time-temperature heating schedule was measured using the H-factor variable applicable to lignin removal for kraft pulping (Sixta 2006). Samples of the wood extract were drained from the extraction vessel following the heating period and were cooled and refrigerated.

Lignin Isolation and Characterization

A comparison was made between two methods of isolating lignin to meet the lignin specifications summarized in Table 1 (Baker et al. 2005). Sun (1999) describes a method in which lignin is separated from carbohydrates by neutralization with phosphoric acid, followed by precipitation with ethanol. Sun's method was compared to a hydrolysis method, developed in this work, which involved simultaneously precip-itating and cleaving lignin carbohydrate bonds by hydrolysis with sulfuric acid.

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Ethanol method (Sun 1999)

Figure 1 illustrates a novel two-step method developed by Sun and co-workers (1999) for separating lignin from carbohydrates. In this method, cooled extraction liquor (A) is first concentrated by evaporation of water. The pH of the concentrated extraction liquor (B) is lowered to pH 6.0 by addition of 9.68 N H_3PO_4. The polysaccharide degradation products (D) are then separated by precipitation from concentrated liquor (B) by extraction with three (3) volumes of ethanol. The ethanol is then evaporated from the liquid fraction (C) and the solid lignin fraction (F) precipitated by reducing the pH of the liquid fraction (C) to 2.0, again by addition of 9.68 N H_3PO_4. The purified lignin fraction (G) is obtained by washing the solid fraction (F) with acidified water (pH 2.0). Lastly, the recovered lignin fraction (G) is air dried.
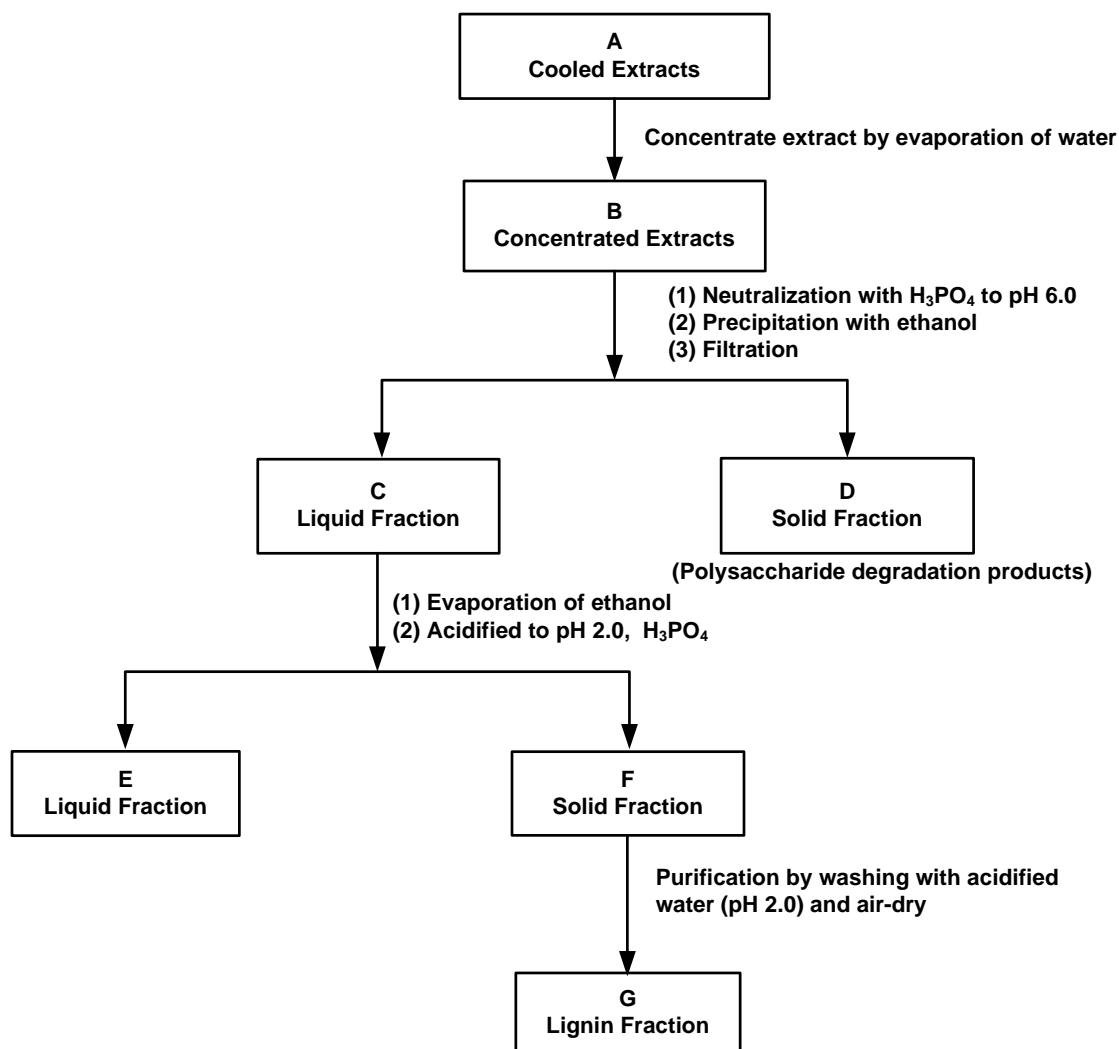
Fig. 1. Protocol for lignin isolation method using ethanol (Sun et al. 1999)

Hydrolysis method

The lignin isolation method developed in the work reported here is shown in Fig. 2. This method is based upon the hydrolysis of the lignin and is similar to what is done when determining Klason lignin. This method was selected because it will hydrolyze lignin-carbohydrate bonds (Lawoko 2005). In this method, the cooled extraction liquor (A) was treated with 72% sulfuric acid to lower the pH to 1.0, and the sample was stored at room temperature overnight. The sample was then hydrolyzed at 121°C for 2 hours to obtain a mixture of solids and liquids, designated as (B). The solids fraction (D) was separated from the mixture (B) by filtration. The solids (D) were then washed with deionized water and air dried to obtain the purified lignin sample (E).
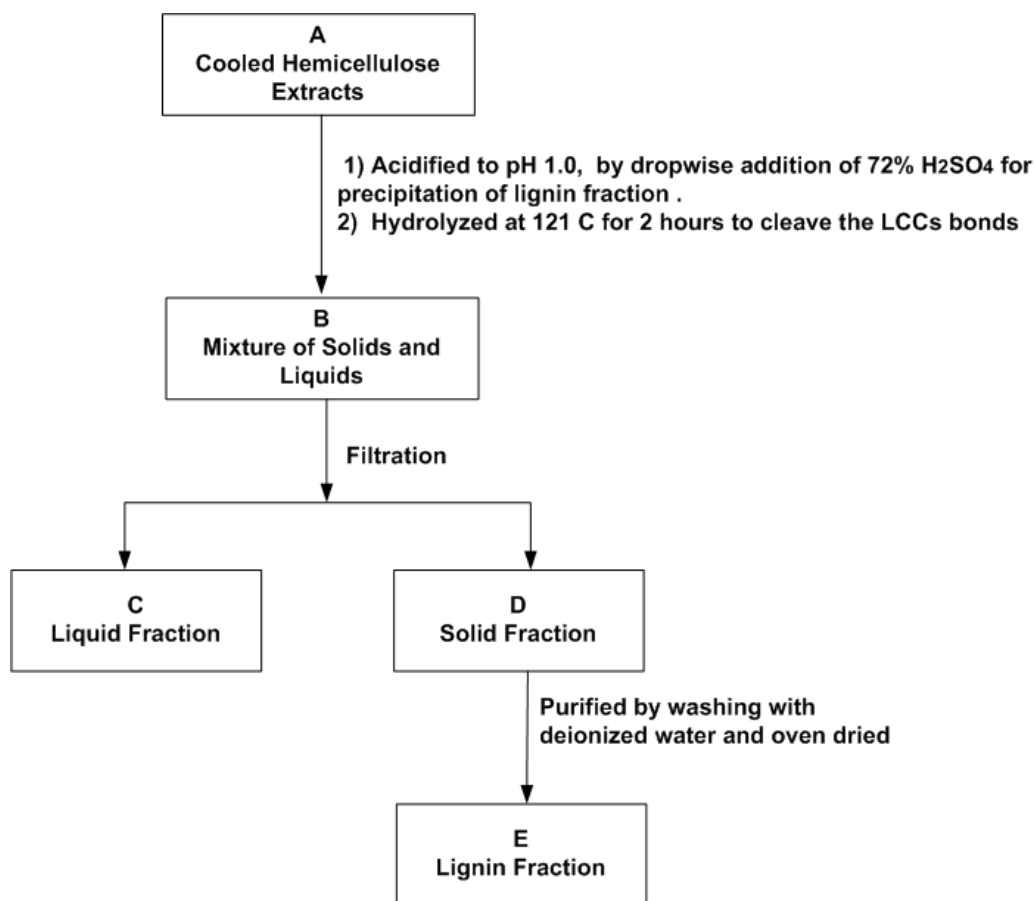

Fig. 2. Protocol for the lignin isolation method by hydrolysis with strong acid

Analytical Methods

Samples of lignin isolated by the two methods were then characterized for lignin content, ash content, volatile material content, particulate matter content, carbon content, glass transition temperature, molecular weight, and surface structure.

Lignin content

The insoluble or Klason lignin content in the isolated samples was estimated by following TAPPI Useful Method T-249. The soluble lignin was estimated by following the method of Effland (1977).

Ash content

The ash content was determined by following TAPPI Test Method T-413. In this method a moisture-free sample of the recovered lignin was ignited in a muffle furnace at 900°C. The weight fraction of residual ash was measured relative to the weight of the original sample.

Volatile material content

The volatile material content of the recovered lignin samples was measured in accordance with the ORNL standard (Table 1). This was done by heating the lignin sample in a muffle furnace for six (6) hours at 250°C. The volatile material was estimated from the loss of mass of the sample and reported as a percentage weight loss.

Particulate matter content

The content of particulate matter was estimated by following the Mead-Westvaco Standard Method 017.04. In this method, a moisture-free sample of recovered lignin was completely dissolved in 5% NaOH solution. The liquid sample was then filtered through Whatman No. 41 filter paper to remove any insoluble particulate matter. The percentage of insoluble matter was estimated from the mass of solids filtered and the mass of the original sample.

Carbon content

The carbon content of the recovered lignin samples was determined by combustion of the sample in an induction furnace operated at approximately $1,200^{o}C$ in an oxygen atmosphere. The carbon dioxide (CO_2) released in the combustion process was carried by helium gas through a packed bed of steel wool to remove residual oxygen. An aliquot of the CO_2 helium mixture was then sent to an infra-red detector where the concentration of CO_2 was determined.

Glass transition temperature

The recovered lignin samples were characterized for glass transition temperature (T_g) with a DSC 2000 Q Series differential scanning calorimeter (DSC). The analyses for the glass transition temperatures were carried out over the temperature range 30°C to 200°C for the lignin samples. The sample was submerged in a nitrogen environment (50 mL/min) and heated at a rate of 3°C/min. Polystyrene was used as a standard for calibration of the DSC instrument.

Molecular weight

The isolated lignin samples were characterized for weight-average molecular weight (M_w) by using Gel Permeation Chromatography (GPC). The recovered lignin

sample was completely dissolved in 0.8 gm/L of lithium chloride/dimethylacetamide (LiCl/DMAc) solution, and the GPC column was operated at 80°C. Pullulan was selected as the molecular weight standard to permit comparison with data obtained from Mead-Westvaco Corporation for the molecular weight of Indulin AT.

Surface microstructure

A scanning electron microscope (SEM) was used to observe the surface microstructure of the carbon fiber.

x-Ray Diffraction Measurement

The structure of the recovered lignin samples was investigated using a PANalytical X'PertPro X-ray diffractometer.

Carbon Fiber Production

The process used to produce carbon fiber consisted of three steps; 1) lignin fiber spinning, 2) thermal-stabilization, and 3) carbonization as suggested by Sudo (1992).

Lignin fiber spinning

Lignin is a thermoplastic polymer; it melts and flows upon heating. Therefore, the melt spinning technique is applicable to forming lignin fiber. An Atlas Laboratory Mixing Extruder (LME) was used to form lignin fiber by melt spinning. In the apparatus a heated rotor is used to melt the polymer, which is then pumped to a spin pack. The molten polymer samples exits the spin pack through a spinneret nozzle. The cylindrical fiber that is formed in the extrusion process is wound onto a spinning spool in a take-up system. A nozzle diameter of 0.8 mm was used to spin lignin fibers of approximately 80 μm diameter, under the assumptions of a flow velocity out the nozzle of 3 m/s and a draw ratio of 100 to 1.

Lignin fiber thermal-stabilization and carbonization

In order to convert lignin fiber into carbon fiber, a thermo-stabilization stage is necessary. This step prevents the lignin fiber from softening, which would result in fiber deformation. Thermo-stabilization involves oxidation of the lignin. The resulting reactions raise the lignin softening temperature (Chung 1994). The thermoplastic character of lignin is changed during the thermosetting process, enabling the lignin fiber to maintain a fiber form during the subsequent carbonization. Heating during thermo-stabilization was performed in air at 200°C by using a Lindberg/Blue M Tube Furnace. The thermo-stabilization process was carried out in two heating stages. First, the lignin fiber was heated from room temperature to 105°C at a rate of 1°C/min. The lignin fiber was then held at 105°C for 1 hour to remove moisture in the sample. Second, the lignin fiber was then heated from 105°C to 200°C at a rate of 0.25°C/min. In the last step the lignin fiber sample was held at 200°C for 24 hours to oxidize the lignin and raise the glass transition temperature (T_g) value, thus reducing vaporization of low molecular weight material during carbonization (Sudo 1992).

Lignin fiber carbonization

After the thermo-stabilization process, the lignin fiber was carbonized by heating the samples to 1,000°C by following the method suggested by Sudo (1992). The purpose of carbonization is to eliminate all elements except carbon. To accomplish this goal, oxygen must be excluded during the carbonization process to prevent combustion of the lignin during the carbonization process. Consequently, the carbonization process was performed using argon at 1,000°C at a rate of 5°C/min in the Lindberg/Blue M Tube Furnace. Once the sample reached the maximum temperature of 1,000°C, the sample was maintained at temperature for 20 minutes. No attempt was made to graphitize the carbon fibers.

RESULTS AND DISCUSSION

Lignin Yield

Depending upon the green liquor application rate, the total lignin extracted from the raw wood varied between 2.36% for extraction with 2% green liquor to about 2.94% in the experiment conducted using 4% and 6% green liquor (Fig. 3). As the green liquor application rate increased, the Klason lignin from the raw wood in the extraction liquor increased to about 1.39% at a green liquor application rate of approximately 6%. This is considerably greater than that obtained with water, which was approximately 0.87%. Acid-soluble lignin was approximately constant with increasing GL application rate and exceeded the Klason lignin content.
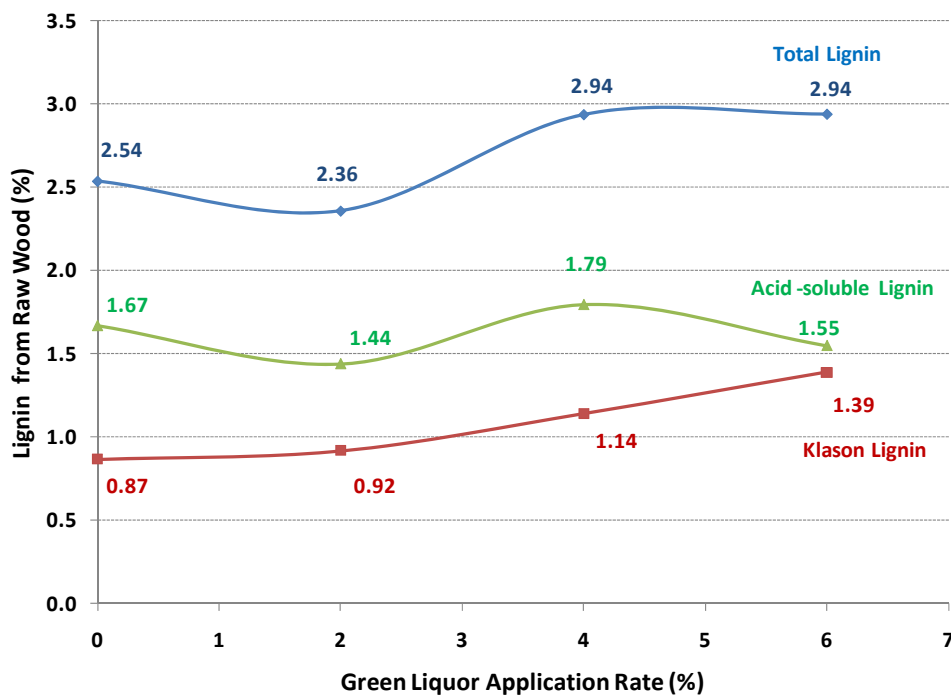

Fig. 3. Lignin yield resulting from green liquor extraction of mixed NE hardwood chips

Evaluation of Isolation Methods

The experimental data obtained using the two isolation techniques were compared by performing a two-sample t-test. The objective of the statistical analysis was to determine which of the two lignin isolation procedures was more appropriate given the ORNL criteria (Table 1). In this method, six extraction experiments were carried out using 6% GL. The six samples were split into two sub-sets of 3-samples each, that is three extractions for each method. The lignin in each of the 3-sample sub-sets was then isolated by the ethanol and hydrolysis methods. Samples of the lignin recovered by the two isolation techniques were then analyzed in duplicate for lignin purity, ash content, volatile material content, particulate matter, and carbon content. For each property the mean values ($\overline{X}_A$ and $\overline{X}_B$) and standard deviations (s_A and s_B) were determined from the experimental measurements. The two-sample t-test was then performed for each property to determine if there were differences in the mean values between the two methods (Luo 2010).

The results for the property evaluation by the ethanol and hydrolysis methods are shown in Table 3. Statistical differences at the 95% confidence level were found to exist between the ethanol method and the hydrolysis method for the Klason lignin, acid soluble lignin, total lignin, and volatile matter between the two methods. No difference was observed in the ash content, particular matter, and carbon content. Based on this analysis the hydrolysis method was thought to be more effective than the ethanol method for meeting the criteria given in Table 1, and it was simpler to use. Consequently, the hydrolysis method was selected for isolating lignin samples for the production of lignin fibers.

Lignin Properties from Different Sources

Crude extract was obtained for the wood extracts using 0% (pure water), 2%, 4%, and 6% green liquor. Lignin was then isolated by using the hydrolysis method on each crude extract and the properties determined. For comparison purposes, two samples of commercial lignin, Alcell and Indulin AT lignin, were also obtained and their properties determined. Alcell lignin is manufactured by Repap Technologies Limited (RTL). The sample of Alcell lignin was obtained by ethanol pulping of northeastern hardwood in a pilot facility and the lignin isolated by precipitation. The sample of Indulin AT was supplied by Mead-Westvaco Corporation and is a commercial lignin product isolated from kraft black liquor following pulping of southern softwoods. The results for the properties of the lignin samples are presented in Table 4. The first row in the table contains the lignin specifications defined by ORNL (Baker et al. 2005) as a precursor material.

Ash content

The samples generated by the hydrolysis method had an ash content less than 0.1% and met the lignin specification given by ORNL (Baker 2005). The ash values were very low in the recovered lignin samples from the experiments in which pure water (0% green liquor) and 2% green liquor were used to extract lignin and carbohydrates. These low values for the inorganic matter in the recovered lignin are thought to result because

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Table 3. Summary of the t-test Applied to the Properties of Lignin Isolated by the Two Methods

Method	Sample ID	Ash (%)	Klason Lignin (%)	Acid-soluble Lignin (%)	Total Lignin (%)	Volatile Matter (%)	Particulate Matter (%)	Carbon (%)
Sun Method (A)	1A	0.018	76.48	13.53	90.01	21.24	0.04	61.2
	2A	0.065	78.93	12.11	91.01	17.95	0.03	59.2
	3A	0.056	77.85	14.29	92.14	21.63	0.03	62.2
	$\overline{X}_A \pm$Error	0.05 ±0.05	77.75 ±3.04	13.31 ±2.75	91.05 ±2.64	20.27 ±5.01	0.03 ±0.01	60.9 ±3.8
Hydrolysis Method (B)	1B	0.04	89.31	9.27	98.59	9.26	0.03	63.4
	2B	0.05	93.43	4.71	98.14	12.13	0.01	58.7
	3B	0.05	88.71	9.95	98.65	10.17	0.01	62.6
	$\overline{X}_B \pm$Error	0.04 ±0.02	90.48 ±6.38	7.97 ±7.08	98.46 ±0.70	10.52 ±3.64	0.02 ±0.02	61.6 ±6.2
t-Statistic	$t_{0.025}(4)=2.776$	0.39	7.75	3.03	11.69	6.76	1.90	0.41
Significance (Yes or No)		No	Yes	Yes	Yes	Yes	No	No

the initial amounts of sodium carbonate and other sodium salts were very low. The Indulin AT sample had the highest ash (900 °C) content at 1.59% ± 0.12% and was thought to be related to sodium and sulfur salts from the kraft process.

Lignin content

The total lignin content is thought to be the most important parameter given by ORNL in their specification sheet and was required to be greater than 99% (Table 1). The range on the lignin content varied between 89.69% ± 0.92% and 99.48% ± 0.41%. The lignin content in all of the samples obtained using green liquor extraction and isolated using the hydrolysis method exceeded 98%. The lignin extracted using water (0% green liquor) had the highest total lignin content of any of the samples (99.48% ± 0.41%). The lignin content in the Alcell sample was 94.22% ± 0.86% and was lower than lignin isolated from samples obtained by green liquor extraction. The lowest lignin content (89.69% ± 0.92 %) was obtained for Indulin AT.

Volatile material content

The ORNL specification for loss of volatile matter upon heating is less than 5% (Table 4). The volatile material content varied between 8.77% ± 0.96% for the lignin sample recovered from the 4% green liquor extraction experiment and 15.42% ± 3.45% for the Alcell sample. The highly volatile material content present in the Alcell lignin was thought to be caused by the conditions used in the ethanol pulping process for hardwood, which lead to low molecular weight lignin being removed in the ethanol pulping process. It is clear from the volatile material data shown in Table 4 that none of the lignin samples investigated met the ORNL specification. The highly volatile material content for the lignin samples is thought to result from lignin decomposition at 250°C rather than low molecular weight lignin in the sample being vaporized.

Particulate matter content

The ORNL specification for lignin in Table 1 requires 100% removal of particulate matter greater than 1 micron in the sample. All of the samples evaluated had particulate matter that is less than about 0.05%, which is thought to be low, but the variability in the measurement was high. The high variability in the results was thought to be due to the method of analysis and the fact that the particulate matter in the samples was low. The Whatman filter paper used in the analysis had a distribution of pore sizes thought to be greater than 1 micron. The Indulin AT sample had the highest particulate matter content at 0.05% ± 0.01%, which was measured by the author.

Carbon content

Coniferyl alcohol, which is a common precursor of lignin found in softwood, has a carbon content of about 72%. By contrast, sinapyl alcohol, a common lignin monomer found in hardwood, has 63% carbon, while PAN, which is the premiere precursor material used in the manufacture of commercial carbon fiber, has a carbon content of 68%, respectively. ORNL does not give a specification for the carbon content for lignin samples in Table 1.

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Table 4. Properties of Isolated Lignin Samples

Lignin Source	900 ºC Ash (%)	Klason Lignin (%)	Acid-soluble Lignin (%)	Total Lignin (%)	Volatiles Matter (%)	Particulate Matter (%)	Carbon (%)
ORNL Lignin Specification (Baker 2005)	<0.1	Not Given	Not Given	≥99	<5	100 removal[a]	/
0% GL (Water)	0.00 ±0.00	95.71 ±0.66	3.78 ±0.25	99.48 ±0.41	11.38 ±0.13	0.01 ±0.01	64.7
2% GL	0.00 ±0.00	90.78 ±1.40	7.19 ±0.97	97.97 ±0.43	10.50 ±0.92	0.01 ±0.00	64.6
4% GL	0.03 ±0.01	90.26 ±0.47	8.54 ±0.48	98.80 ±0.95	8.77 ±0.96	0.01 ±0.01	64.3
6% GL	0.04 ±0.02	90.48 ±6.38	7.97 ±7.08	98.46 ±0.70	10.52 ±3.64	0.02 ±0.02	61.6 ±6.2
Alcell (Organosol Process)	0.08 ±0.01	90.76 ±0.41	3.46 ±0.60	94.22 ±0.86	15.42 ±3.45	0.01 ±0.01	64.4
Indulin AT from Softwood Using Kraft Process [a]	1.61 ±0.07	86.8 ±0.42	3.10 ±0.17	89.69 ±0.55	9.83 ±0.99	0.05 ±0.01	66.0
(a) Particulate matter greater than 1 micron.							

The carbon content of lignin isolated from green liquor extraction varied between 61.6% and 64.7%, which is close to the theoretical value for sinapyl alcohol (63%). The carbon content of Alcell lignin was 64.4%. The carbon content of Indulin AT had the highest carbon content and was estimated to be 66%. However, this value is lower than the theoretical value for coniferyl alcohol (72%). The lignin content of Indulin AT was only 89.69% (Table 4). Thus the low carbon content in the Indulin AT samples results from the presence of impurities, which are thought most likely to be primarily carbo-hydrates.

Lignin Molecular Weight and Glass Transition Temperature

Table 5 lists glass transition temperature, molecular weight, and polydispersity (M_w/M_n) values for a series of lignin samples reported by Schmidl (1992). Indulin AT had the highest glass transition temperature (171 ^{o}C) and weight average molecular weight (6,060 g/mole). By contrast, the organosolv lignin recovered from aspen had the lowest T_g (97 ^{o}C) and lowest M_w (2,400). The Indulin AT lignin also had the highest polydispersity (3.83); while the organosolv lignin had a low polydispersity. The lignin samples obtained from southern and northern hardwoods by the kraft process had intermediate T_g values (132 and 161 ^{o}C) when compared to those of Indulin AT obtained from southern pine (171 ^{o}C) and organosolv aspen (97 ^{o}C). Similar intermediate values have been obtained for the molecular weight for the lignin obtained by hardwood kraft pulping. Factors such as the degree of cross-linking, chain flexibility, molecular structure, and branching are known to affect the glass transition temperature (T_g) in addition to molecular weight (Cowie and Arrighi 2007).

Table 5. Lignin Molecular Weight Measurements Reported by Schmidl (1992)

Lignin	T_g (°C)	M_n (Daltons)	M_w (Daltons)	M_w/M_n
Indulin AT Pine Kraft Pulping (Mead-Westvaco)	171	1,580	6,060	3.83
Mixed Southern Hardwood Kraft Pulping (Charleston ,S. C)	161	997	3,360	3.36
Birch (Northeastern Hardwood) Kraft Pulping (Maine Paper Mill)	132	1,150	3,130	2.72
Organosolv Aspen	97	809	2,400	2.97

Measured glass transition temperature

Table 6 summaries the measured values for the glass transition temperature (T_g) of the lignin samples used in the present investigation. In general, the values were similar to data reported by Schmidl (1992). The values for the glass transition tempera-ture for the recovered lignin samples ranged between 86.4 ^{o}C and 147.5 ^{o}C. The lignin isolated from the 0% GL extraction experiment had the highest measured T_g value and was about 167°C, while the lignin isolated from the 6% GL extraction experiment had the lowest T_g value (102.5 ^{o}C). Both the lignin isolated from the 0% GL extraction

experiment and the Alcell lignin had two T_g values. The measured T_g value of Indulin AT was 146.8°C, which compares well with that reported by Schmidl (171°C). The T_g value of the polystyrene sample was used as a standard for calibration of the instrument. The measured T_g value of the polystyrene was 90.5°C, which compares well with that reported by Okubo (82.4°C) (1995). The DSC results are shown in Figs. 4 through 8.
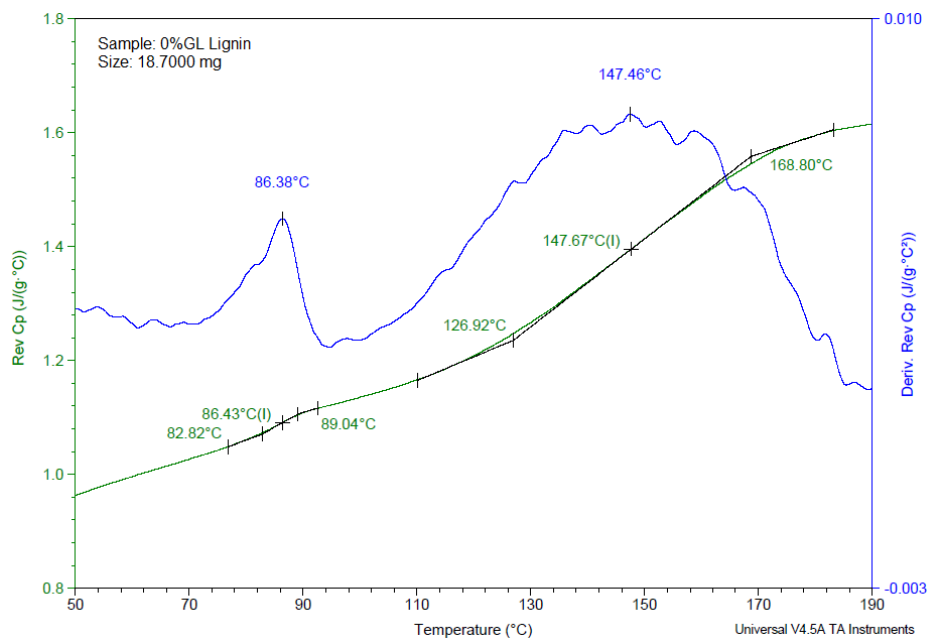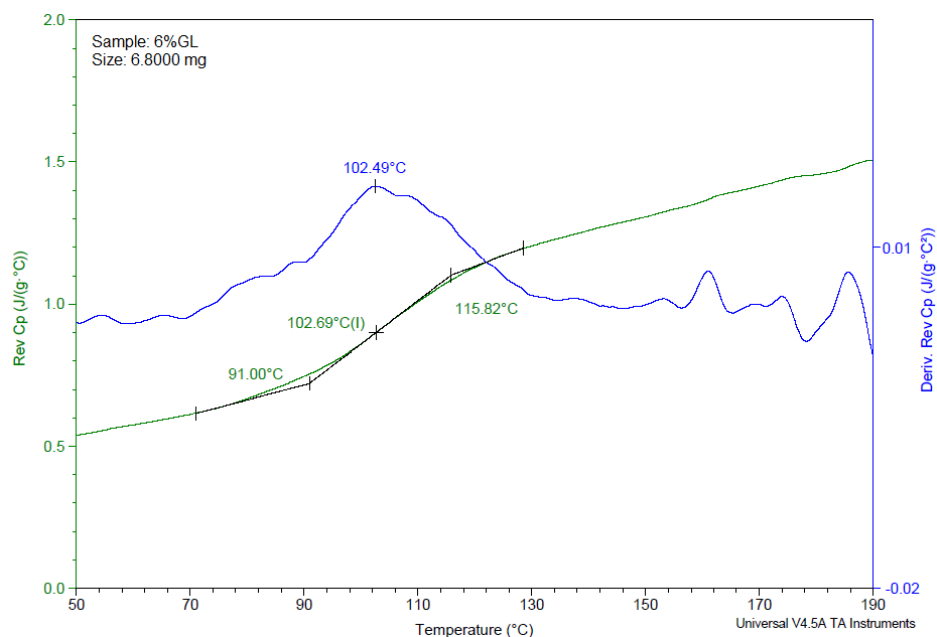

Fig. 4. Thermogram of lignin sample from 0% GL

Fig. 5. Thermogram of lignin sample from 6% GL
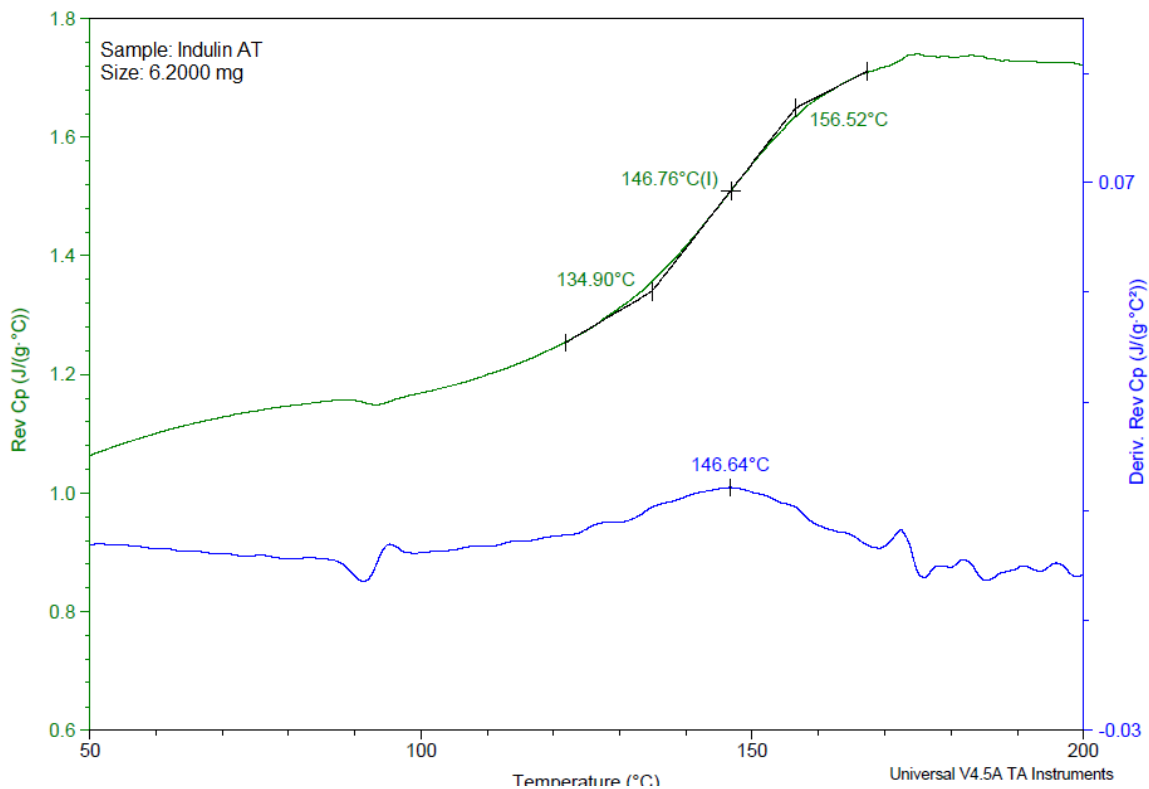
Fig. 6. Thermogram of Indulin AT
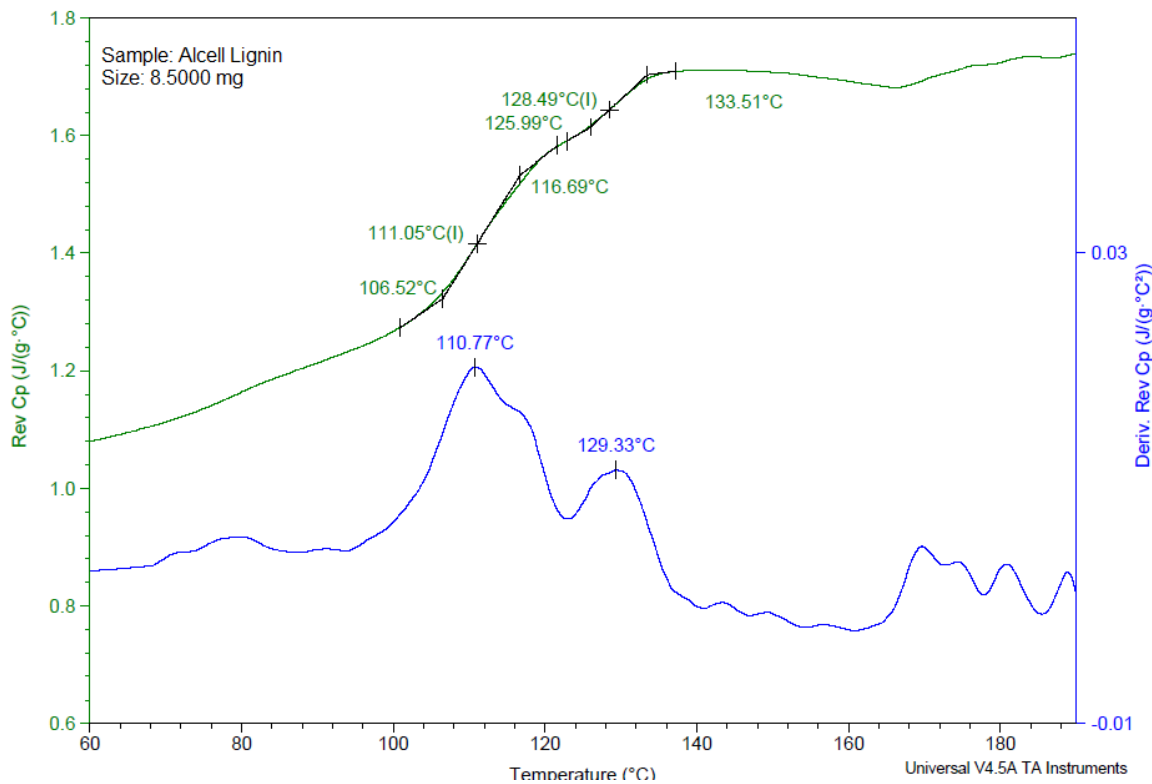
Fig. 7. Thermogram of Alcell
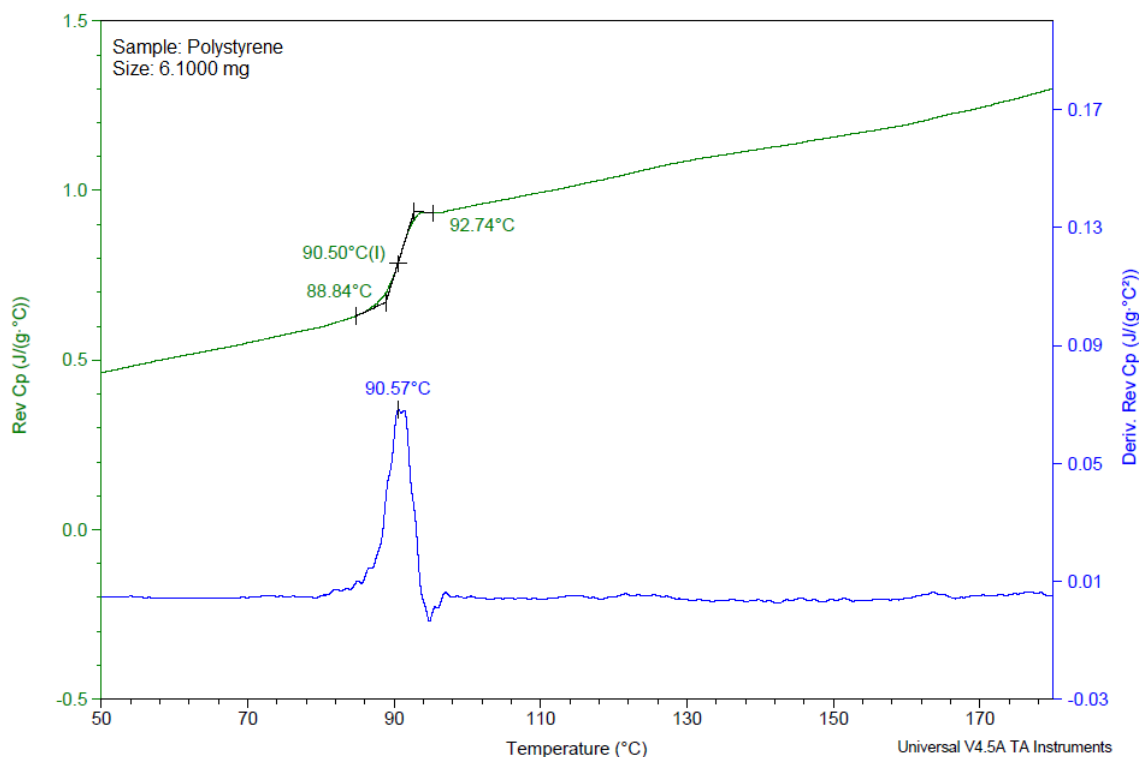
Fig. 8. Thermogram of polystyrene

Measured molecular weight

Table 6 summaries the measured values for the weight-average molecular weight (M_w) in grams per mole (Daltons). The weight-average molecular weight (M_w) of the isolated lignin decreased with increasing green liquor application rate. The lowest weight-average molecular weights occurred in the lignin samples recovered from the 4% and 6% green liquor extraction experiments. This was thought to result from the higher pH values that occurred during these experiments. Increasing the GL application rate exposes the wood to a higher alkali concentration for a longer period of time before neutralization occurs. Thus, it was thought that greater lignin and carbohydrate degradation and dissolution occurred under the higher pH conditions.

The weight-average molecular weight of Alcell lignin was approximately 4,600 Daltons and was close to the value of 3,900 Daltons reported by Baumberger et al. (2007). A small difference was observed between the weight-average molecular weight (M_w) for the Alcell lignin (4,600 Daltons) and lignin recovered from the pure water (0% GL) extraction experiment (5,200 Daltons). By contrast, there was a significant difference in the measured values for the glass transition temperature (T_g) between the Alcell lignin sample (108.6°C) and the lignin recovered in the pure water (0% GL) extraction experiment (167°C). The weight-average molecular weight of Indulin AT was approximately 4,600 Daltons, which was close to the results of 4,800-5,800 Daltons reported by Mead-Westvaco (2009).

Table 6. Measured Glass Transition Temperatures (T_g) and Molecular Weight (M_W) for Different Lignin Samples

Lignin Type	Recovered Lignin T_g (°C)	M_w (Daltons)	Extraction Final pH
0% GL (Water) (HW Hemicellulose Extraction)	86.4, 147.5	5,200	3.34
2% GL (HW Hemicellulose Extraction)	129	4,000	4.77
4% GL (HW Hemicellulose Extraction)	125	3,200	5.64
6% GL (HW Hemicellulose Extraction)	102.5	3,400	8.91
Indulin AT[a] (Pine Kraft Pulping)	146.8	4,600	NA
HW Alcell[b] (Ethanol Pulping)	111.1, 128.5	4,600	NA
Polystyrene	90.5	5,610[c]	NA
Polystyrene[d]	82.4	5,480	NA
(a) Sample obtained from Mead-Westvaco Corp. (b) Sample obtained from Repap Technologies Limited (RTL). (c) Certification of Analysis of PSS-ps5.6k. (d) Okubo, N.1995.			

Lignin X-ray diffraction (XRD) results

XRD is the most common technique used to characterize the crystalline content in a polymer structure. Figure 9 shows XRD results for three lignin samples; lignin from 6% GL extraction and isolated by hydrolysis method (A), Alcell lignin (B), and lignin from 6% GL extraction and isolated by Sun's method (C). The measurements reveal one very weak and broad peak at 2.5 deg, indicating that the samples were essentially amorphous. These results are similar to those of Sevastyanova (2010) who also performed XRD analysis on lignin samples which showed no pattern, hence it was concluded that the lignin was amorphous. The lignin is glassy and has little if any crystal structure. This we feel is one cause of the brittleness in the lignin fibers and subsequently in the carbon

fiber. To utilize lignin as a precursor for carbon fiber, we feel that methods must be found for improving the crystallinity of lignin.
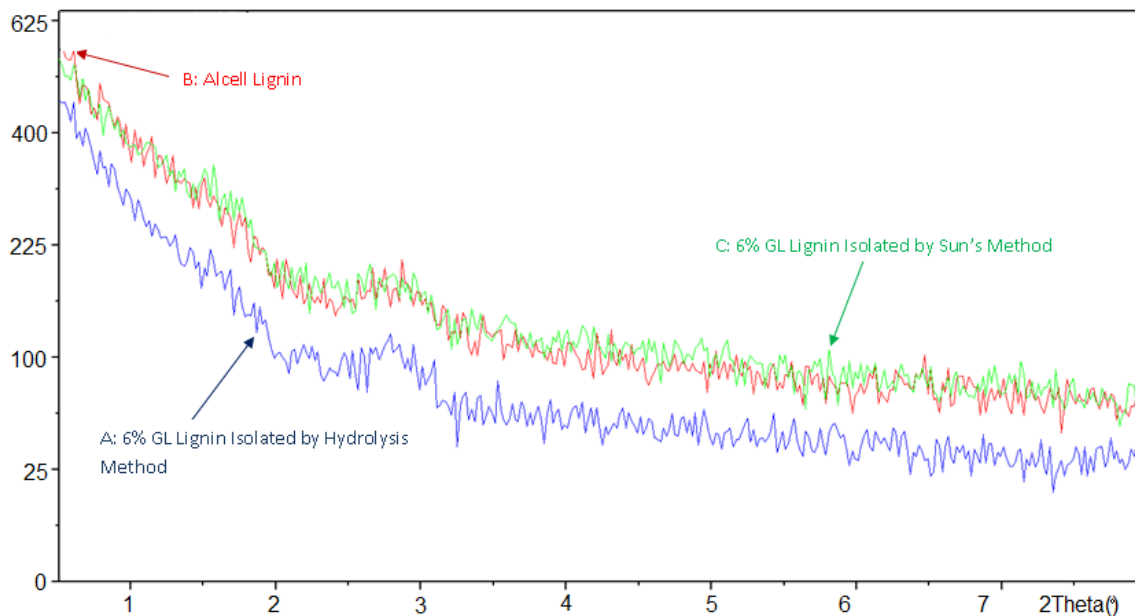

Fig. 9. XRD patterns of three lignin samples

Lignin Fiber Spinning

Fiber spinning experiments were conducted in the Atlas Laboratory Mixing Extruder using linear low-density polyethylene (LLDPE) as a standard and various recovered lignin samples. A summary of the spinning experiments including the thermal conditions in the extruder and the appearance of the fiber are summarized in Table 7. Initially, linear low-density polyethylene (LLDPE) samples were tested in the Atlas Laboratory Mixing Extruder and were easily processed into flexible-uniform-fine fiber. The spinning temperatures required in these experiments varied between 140°C and 180°C.

Spinning experiments were performed using commercial Indulin AT lignin at spinning temperatures between 140°C and 250°C. However, the Indulin AT could not be spun into acceptable lignin fiber. Extrusion experiments performed at the lower temperatures did not soften the lignin sufficiently to form a solid fiber. Experiments performed at high temperature lead to charring of the Indulin AT before melting occurred.

Lignin spinning experiments were conducted using samples recovered from the hydrolysis method applied to the 0% GL and 6% GL extraction experiments. Continuous spinning was readily achieved with the lignin with all of the green liquor samples. The lignin fiber, although readily spun, was extremely brittle and could not be wound on the drum in the take-up system. The spinning temperature required for lignin recovered from the 6% GL experiment varied between 185°Cand 208°C. By contrast, the spinning temperature required for lignin that was recovered from the water (0% GL) extraction experiment varied between 165°Cand 190°C; and was approximately 20°C lower than the temperatures required for spinning the 6% GL lignin.

Table 7. Summary of Fiber Spinning Experiment

Sample		Spinning Temperature (°C)		Fiber Appearance
		Rotor	Nozzle	
LLDPE	Linear Low-density Polyethylene	140-160	150-180	Fine Fiber
Indulin AT	Kraft Pine Lignin (MeadWestvaco)	140-240	240-250	Charring
0% GL Lignin	Mixed Hardwood Lignin from 0% GL	165-170	180-190	Fine Fiber
6% GL Lignin	Mixed Hardwood Lignin from 6% GL (Luo, Jie 6/05/09) Extracts	185-190	202-208	Fine Fiber
Alcell	Repap Tech. Inc. Organosolv Lignin	145-150	160-170	Fine Fiber

The Alcell lignin could be readily spun into lignin fiber. Indeed, fiber spun from the Alcell lignin was considerably more flexible than fiber spun from lignin isolated from green liquor extraction. Even with this improvement, however, the Alcell lignin fiber was still brittle. The spinning temperature required in the Alcell lignin spinning experiments ranged between 145°C and 170°C and was considerably lower than the spinning temperature required for the GL lignin (Table 7). The lower spinning temperature was thought to result from molecular differences in the Alcell lignin, which was thought to be less cross-linked due to its method of manufacture.

Surface Microstructure of Carbon Fiber

SEM micrographs for the carbon fibers produced in the current study are represented in Figs. 10 through 14. Carbon fibers produced from commercial PAN (PANEX35) and commercial pitch are shown in Figs. 10 and 11 respectively. The fiber diameter for the PAN carbon fiber is 8.4 μm (Fig. 10). There are no holes on the surface of PAN-based carbon fiber, but some lines. The lines on the surface were thought to be caused by ridges in the orifice used to extrude the PAN fiber. Also, some flaws are contained on the fiber. The cross-section displayed in Fig. 10 suggests that the PAN based carbon fiber is a solid fiber with little porosity. Fig. 11 shows the surface structure of carbon fiber from pitch (P25). The fiber diameter for the carbon fiber produced from pitch was approximately 11.6 μm. The cross-section displayed in Fig. 11 suggests that the carbon fiber produced from pitch is considerably more porous than carbon fiber produced from PAN (see Fig. 10). This higher level of porosity most likely results in the lower physical properties of the pitch-based carbon fiber (Baker 2011).
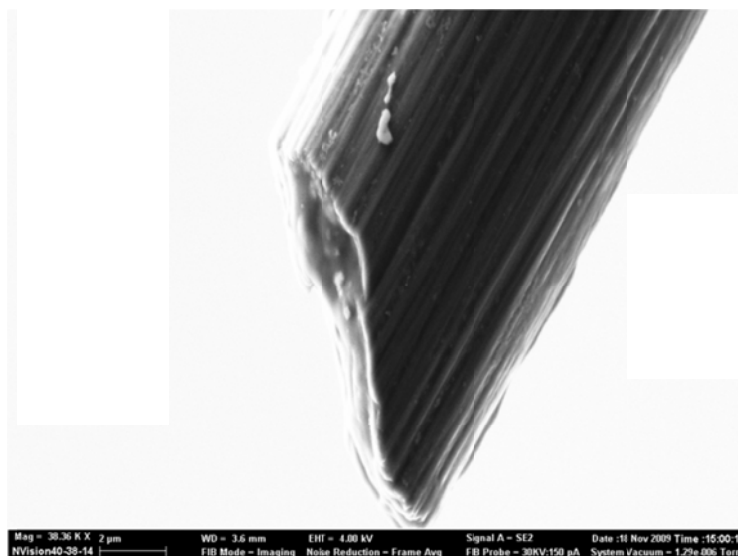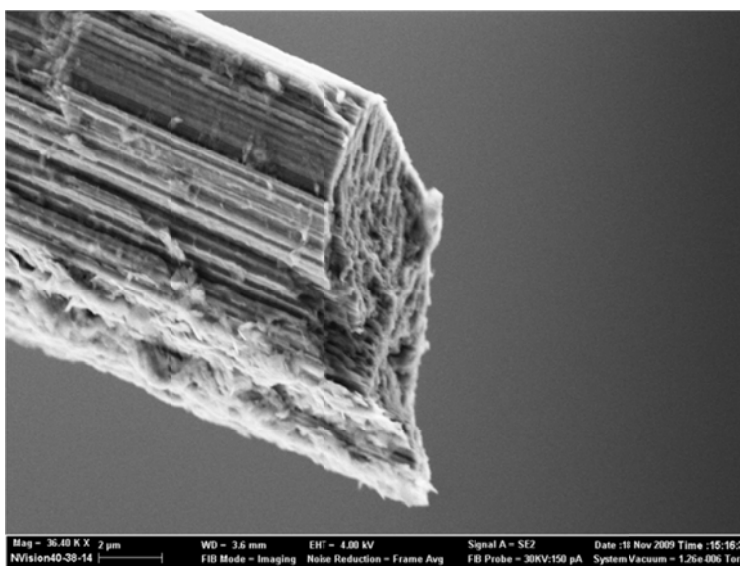
Fig. 10. Carbon fiber from PAN (D=8.4 µm)

Fig. 11. Cross section of carbon fiber from P25 Pitch (D=11.6 µm)

Micrographs are presented for the carbon fiber samples prepared from lignin obtained for the 0% GL (Fig. 12) and 6% GL (Fig. 13) extraction experiments as well as the Alcell lignin (Fig. 14). These micrographs indicate that the laboratory carbonization process significantly alters the surface of the carbon fiber and its porosity. The surface features of the carbonized fiber samples prepared in the laboratory display numerous imperfections and flaws. Figure 12 shows carbon fiber produced using lignin isolated from the 0% GL (water) and represents a cross section of the fiber. Figure 12 shows imperfections deep within the structure of the fiber and gives credence to the hypothesis that the major cause of the imperfections consists of the release of volatile material (see

Table 4).   The micrographs of carbon fiber produced from the Alcell lignin and that from lignin obtained by extraction using 6% GL show considerably less surface imperfections.
         The major cause of these flaws is thought to be the release of volatile materials (Fig. 12) during the carbonization process.
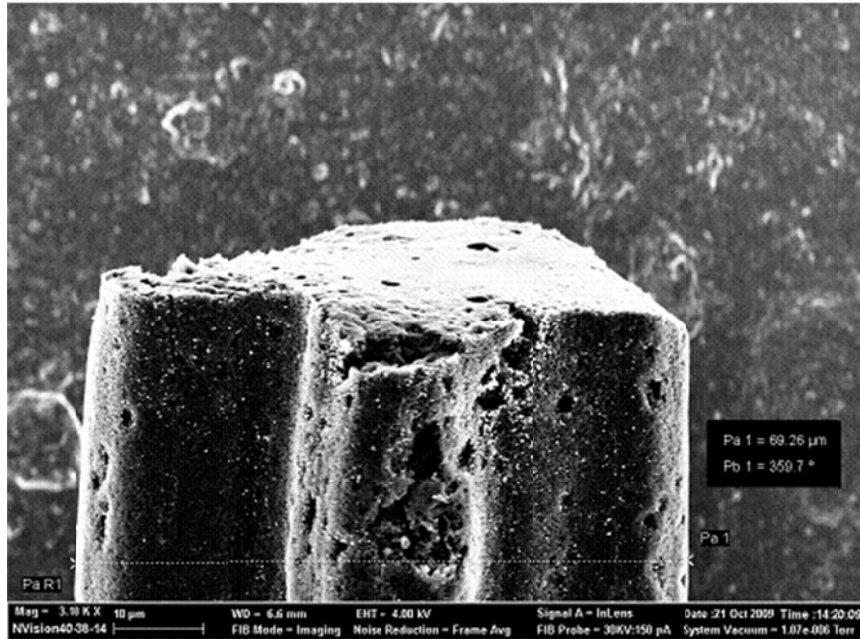

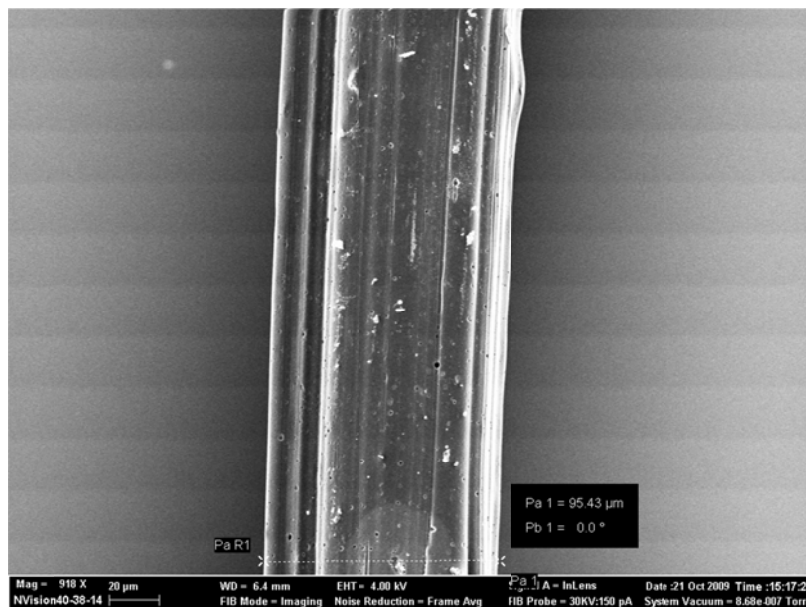**Fig. 12.** Carbon fiber from 0% GL lignin fiber (D=69.3 µm)

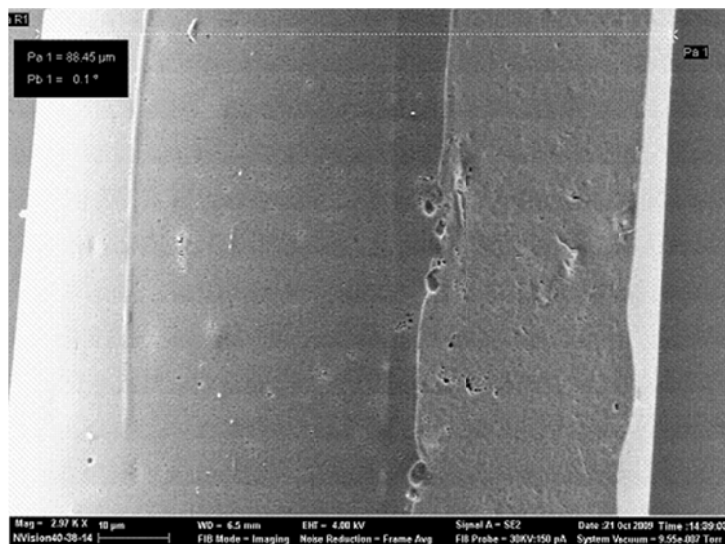**Fig. 13.** Carbon fiber from 6% GL lignin fiber (D=95.4 µm)

Fig. 14. Carbon fiber from Alcell lignin fiber (D=88.4 μm)

Kubo and Kadla (2005B) suggest that the "noted brittleness of lignin is caused by the globular structure of lignin fragments and could be abolished by the incorporation of a variety of polyether components into the network structure". Baker (2011) on the other hand presents data that show that the carbonization heating rates have a major effect on the structure of lignin-based carbon. Slow heating rates give rise to poor fiber structure, while rapid heating give rise to carbon fiber with good fiber structure and few imperfecttions. Relatively slow rates during carbonization expose the carbon structure to evolution of gases such as H_2O and CO_2, which lead to poor fiber structure. Porosity is introduced into the carbon fiber, including pores with dimensions down to < 1 nm (10 Å) in width. Pore development is adverse with respect to achieving high mechanical properties.

CONCLUSIONS

The hydrolysis method was found to be simpler to use and more effective than the ethanol precipitation method developed by Sun (1999). An advantage of the hydrolysis method is that it produces high-purity lignin. However, a disadvantage of the acid hydroylsis method is the resultant lignin is highly condensed because of the severe acid hydrolysis treatment (Fengel and Wegener 1984; Lawoko 2005).

Lignin obtained by the hemicellulose pre-extraction process and isolated by the hydrolysis method met all of the specification stipulated by ORNL (Baker 2005) except for the specification related to the volatile material content at 250˚C. The ORNL standard requires that the volatile matter in the lignin precursor be less than 5% of the mass of the precursor when heated to 250°C. The Indulin AT (softwood lignin) could not be processed into lignin fiber because of lignin charring before melting. The hardwood lignin recovered by extraction with GL and lignin extracted using ethanol in the Alcell process could readily be formed into continuous fibers with diameter values of approximately 35 to 40 μm using the Atlas Laboratory Mixing Extruder.

The lignin fibers produced were brittle with low tensile strength. Several investigators also have reported brittle carbon fiber from recovered lignin (Schmidl 1992; Sudo 1992; Kadla 2002). Brittleness is thought to be caused by low-molecular masses and the glassy nature of lignin, as demonstrated in the x-ray diffraction patterns shown in Fig. 9. A contributing factor to the brittleness might be related to the sulfur content in the lignin samples, since the Indulin AT as well as the green liquor extraction samples would be expected to contain sulfur, which could give rise to crosslinking similar to what happens during the vulcanization process. The lignin fiber produced from Alcell lignin was found to be the least brittle of all of the lignin samples evaluated and was not produced using sulfur. SEM micrographs were taken of the lignin-based fiber obtained from the green liquor and Alcell processes and compared to micrographs taken of commercial materials. Flaws existed both in the interior structure and also at the surface of the laboratory-prepared carbon fiber. The imperfections in the laboratory samples of carbon fiber were thought to be caused by the high volatile material content of the lignin precursor. The slow heating rate during carbonization may contribute to high porosity and the brittleness problem, as postulated by Baker (2011).

ACKNOWLEDGMENTS

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