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# Evaluation of Lignin from Alkaline-Pulped Hardwood Black Liquor

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## EVALUATION OF LIGNIN FROM ALKALINE-PULPED HARDWOOD BLACK LIQUOR

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Weyerhaeuser supplied a small amount low-sulfur black liquor from a soda mill pulping hardwood. This has permitted evaluation of lignin from sulfur-free cooks. Robert Eckert kindly shared with us information from analysis of lignins from our research pulp cooks. This analysis was performed at Georgia Institute of Technology under the direction of A. J. Ragauskas.

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## ABSTRACT

This report summarizes the research background developed a project tasked to evaluate methods for the production of carbon fibers from renewable-source and routinely recycled polymers. The Department of Energy Automotive Lightweighting Materials Program has shown that the use of carbon fiber composites to lower vehicle weight could dramatically decrease domestic vehicle fuel consumption. For the automotive industry to benefit from carbon fiber technology, fiber production will need to be substantially increased and fiber price decreased to \$3 - \$5/lb. Additionally, carbon fiber precursor production will need to be increased at least forty-fold. To achieve these objectives, alternate precursors to pitch and polyacrylonitrile (PAN) are being investigated as possible carbon fiber feedstocks.

Wood and biomass-derived renewable materials, including cellulose and lignins, as well as high-volume, routinely recycled polymers, including polyethylene and polypropylene, were initially evaluated for volume and reported carbon yield. Kraft lignin feedstocks were selected for detailed investigation based on low cost, high production volume, and the ability to permit fibers to be drawn from a liquid melt. Initial investigations of spinning indicated that a number of single-phase melts of Kraft lignin and routinely recycled polymers, most notably poly(ethylene terephthalate) could be spun.

Initial evaluations of melt-spinning and fiber stabilization were performed using fibers extruded as single-filaments. The fibers were extruded at North Carolina State University from lignins desalted at Oak Ridge National Laboratory (ORNL). Techniques for preparing carbon fiber and for evaluating structural, chemical, and mechanical properties were developed at ORNL.

Initial evaluations indicated that lignin-based fibers have attractive yields and can be readily stabilized, carbonized, and graphitized. Carbon fiber chemical and physical structure, together with mechanical properties, indicated the feasibility of use in transportation composite applications.

Multifilament extrusion, a step toward industrial use of this technology, was achieved using the University of Tennessee Leistritz twin extruder. Initial evaluations produced coarse fibers, and later experiments demonstrated the feasibility of melt-extruding 28 filament tow.

However, some production problems, most notably the presence of contaminants in commercially-produced lignins, remains. This has required the development of technology to remove contaminants, such as sand, process chemicals, water, and entrained carbohydrates, from Kraft lignin. A combination of filtration, precipitation, and drying can be used to remove process chemicals, water, and entrained carbohydrates. New processing methods and refinements of old techniques have also been required to accommodate the changes in lignin chemical and physical properties. These include the use of a two-step process for extrusion of lignin-blend feedstocks to decrease offgassing of volatile constituents during extrusion. High-shear spinning dies have been used to improve fiber structure. Methods for surface treatment of carbon fiber to increase compatibility with the resin have also been developed.

It was thought that lignins from low and very low sulfur alkaline pulping processes (soda pulping) might have some potential as carbon feedstocks. These processes have many similarities to Kraft pulping but produce a lignin in which sulfurous volatiles are minimized. As a part of these studies, lignin from a black liquor derived by soda pulping of Eastern hardwoods was prepared and evaluated. The results indicate that the lignin meets basic process goals, such as melting temperature and can be processed to remove salts and carbohydrates. However, blends which permit fibers to be drawn from a single phase melt have not been found for the purified lignin.

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## 1. INTRODUCTION

This report describes studies performed on a small amount of black liquor provided by Weyerhaeuser from a hardwood-only soda (caustic) pulp mill. The preparation of lignin from this material was evaluated with respect to lignin preparation and lignin properties. A description of the technical background and ultimate goal of the evaluation as a means to toward development of a melt-spinnable feedstock from which industrial grade carbon fiber could be produced. This work was performed with support from the Department of Energy Automotive Lightweighting Materials (ALM) Program which is interested in the development of carbon fiber-resin composite technology for use in passenger transport.

### 1.1 WHY AUTOMOTIVE CARBON FIBER?

For decades, the Department of Energy has supported research directed toward improvements in energy efficiency of passenger transportation as a means of stimulating increases in efficiency of use for petroleum-based fuels. Supported research has historically included evaluation, development, and deployment of more efficient engine technologies, lighter weight vehicle body materials, and more energy efficient designs. Weight reduction technologies have included a variety of materials substitutions which decrease weight while improving functionality, durability, reliability, cost, or safety (Automotive Lightweighting Materials Program 2005). Examples include: replacement of iron parts with light metals (magnesium transmission cases, cast aluminum parts), use of stronger or stiffer metals (high strength steel substitution for nodular iron), and replacement of metals with composites (glass fiber composite door panels). To decrease barriers to use of new materials, the program focuses on cost reduction, recycling (Jody and coworkers 2003), manufacturing technologies, development of design data, modelling, and development of supporting production technologies (joining, recycling, repair, and non-destructive evaluation technologies).

As technologies are adopted by the industry, the ALM Program shifts emphasis to different classes of lightweight materials. Focus has shifted from glass fiber composites and aluminum to stronger, stiffer lightweight materials, such as titanium, magnesium, and carbon fiber resin composites.

The rising cost of petroleum, which at this writing fluctuates around \$50 per barrel, provides a unique near term opportunity to increase vehicle energy efficiency. Petroleum consumption is presently estimated (Energy Information Administration 2004) at around 39 Quadrillion Btu (Quads). Approximately 27 Quads of petroleum, an amount slightly larger than the total U.S. petroleum imports (26 Quads), were used in transportation. Annually, the daily import of 9.7 million barrels of crude oil at \$50 per barrel amounts to \$175 billion and plays a major role in energy security, balance of trade, and foreign policy. As was the case in the late 1970s to mid-1980s, increased fuel price could increase consumer purchase of lighter weight, more fuel-efficient vehicles.

The availability of cost-effective lightweight materials technologies also encourages development of fuel cells and other efficient new technologies for which vehicle range is limited by vehicle weight.

#### 1.1.1 Low-Cost Carbon Fiber Program

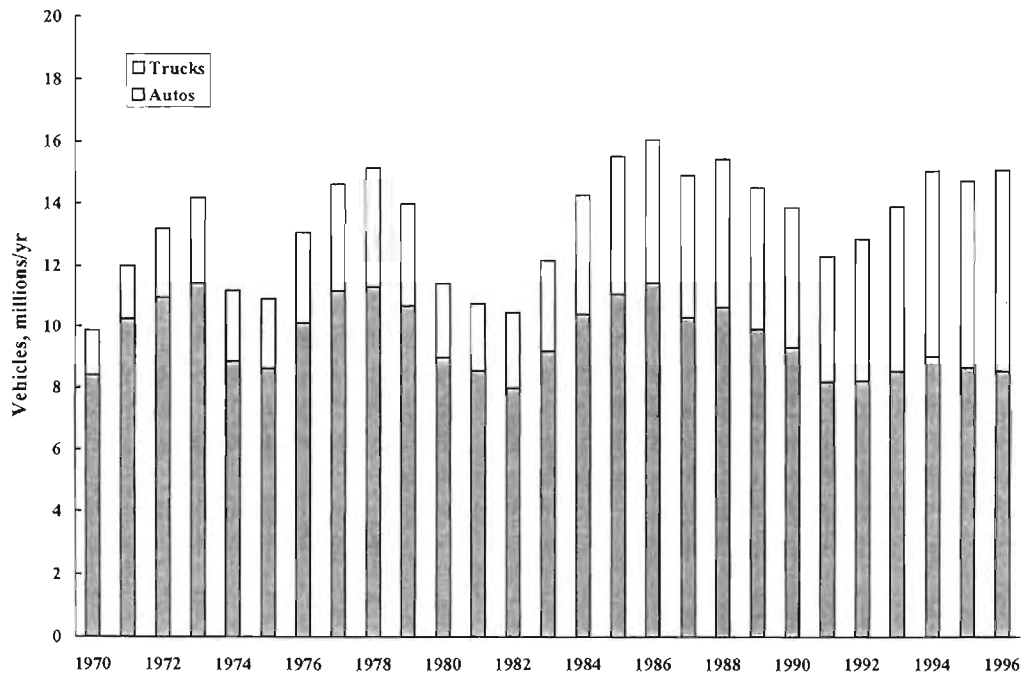
Cost, availability, and manufacturability remain major barriers to use of carbon fiber resin composites in transportation applications. The ALM Program, working with the U.S. Council for Automotive Research (USCAR), the U.S. Automotive Materials Partnership (USAMP), and the Automotive Composites Consortium (ACC), has systematically developed a technical base for use of cost-effective composites in production vehicles. This is likely to be very different from aerospace and sports production because the scale, automation, and product safety requirements are significantly higher. Portions of the technical base which have been completed or are nearing completion include: engineering support, including development of a design database, test and analysis methods, and analysis

of durability and safety issues (Boeman and Johnson 2002; Corum and coworkers 2002; Lee and coworkers 2003; Starbuck and coworkers 2000, 2001); development of a process for microwave-plasma graphitization of partially-oxidized polyacrylonitrile fiber (Paulauskas and coworkers 2002a,b, 2003). A technology, Programmable Powdered Preform Process (P-4), originally developed for high-speed molding of large glass fiber resin composite parts, is being adapted at Oak Ridge National Laboratory (ORNL) for the high-speed production of parts made from chopped carbon-fiber and resin. Also, a project to evaluate the conversion of large-tow textile polyacrylonitrile fiber into a less-expensive carbon fiber has shown good success (Hexcel reference).

Development of high-volume, low cost sources of carbon fiber feedstocks has continued. At present, two approaches to carbon fiber feedstock production are being evaluated: use of chemically-treated split large textile tows and melt spinning of Kraft lignin blend fibers.

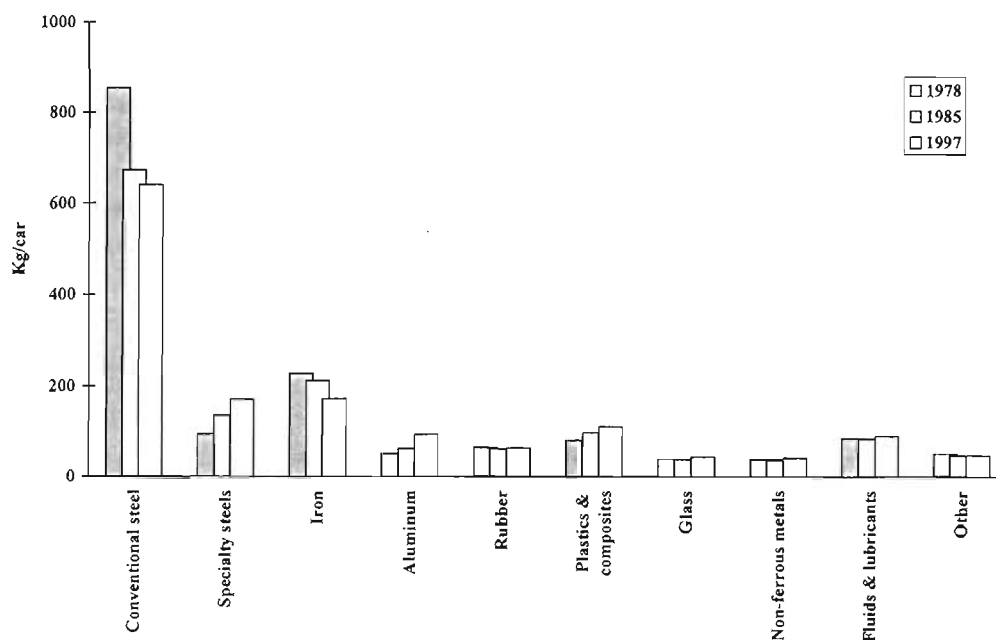
### 1.1.2 Magnitude of Potential Automotive Market

Production of domestic passenger vehicles is shown in Figure 1.1. The relative numbers of cars and trucks have significant annual variation, while the total number of passenger vehicles produced annually in the U.S. has remained relatively constant at 15 - 18 million passenger vehicles. Although there was a 5% decline in total vehicle weight between 1978 and 1997, each car or light truck still averages slightly more than a ton of ferrous metals as iron or steel (Figure 1.2).



**Figure 1.1. Production of automobiles and light trucks between 1970 and 1996.**  
Adapted from American Automobile Manufacturers Association, 1997.





**Figure 1.2. Materials used in an automobile.** Adapted from data developed by Ward's Automotive Yearbook, 1997.

Carbon fiber-resin composite materials weighing approximately 50% as much as ferrous metals could, conservatively, provide equivalent strength and stiffness while providing significant reductions in vehicular weight. Replacement of all of the steel in 15 million vehicles would consume more than 4 million tons of carbon fiber and more than 3 million tons of resin annually. Assuming that the prices of carbon fiber and resin are, respectively, \$5 per lb and \$1 per lb, this represents a considerable market at its very early stages.

As the current global carbon fiber production, which has remained less than 30,000 tons/year, is roughly a hundred times smaller than the capacity which could be used in U.S. passenger vehicles, new carbon fiber production capacity will need to be developed to support the automotive market. Cocurrent development of capacity for production of raw carbon fiber feedstock, any blending polymers or plasticizers, and resins for composites would also be required.

The current strategy by automotive companies is selective use of carbon fiber composites in areas where significant design or marketing advantages can be realized (for example, door support panels or dashboards). In some of these cases, weight reductions well in excess of 1:4 have been demonstrated.

Production of automobiles and light trucks is a very high volume, very highly automated process in which cost is a major factor in materials selection. Cost goals for grades of carbon fiber which could be used in automobiles have ranged from \$7 to \$3 per lb during this project. Industrial carbon fiber meeting these goals will require significant reductions in the current production cost. These will likely be achieved through a combination of increases in scale, vertical integration of processing operations, and development of new feedstocks and new production technologies.

### 1.1.3 Energy Value in Reducing the Weight of Vehicles

Although it could take a number of years for carbon-fiber resin composites to effect significant replacement of the ton of steel used in each new passenger vehicle, the energy and cost impacts are

potentially very large. The ALM Program periodically sponsors studies evaluating the maximum impact of all technologies on production vehicles. These studies generally show decreases in fuel consumption on the order of 50% or more. Weight reduction technologies are also applicable, with roughly comparable effects, to heavy transport. Assuming that a smaller decrease in fuel consumption, on the order of 25%, could be effected in all categories of vehicles by carbon fiber-resin composite technology replacement of steel, a reduction of approximately 70% in imported petroleum (7 Quads, \$125 billion annually in decreased imports of \$50 per barrel crude oil) might be expected. In addition to significant decreases in energy usage, reductions in vehicle weight are typically correlated with matching decreases in greenhouse gas emissions.

For heavy transport (trucks and trains), use of lightweight materials has the additional advantage of increasing the amount of material which can hauled. This is particularly significant in rural areas where weight limitations on bridges or roads, rather than vehicle capacity, limit the amount of material, such as coal or green logs, which can be hauled by a single truck.

In addition to direct, weight-related reductions in petroleum consumption, carbon fiber composites facilitate the use of highly energy efficient vehicle power systems, such as fuel cells or hybrid engine-electric systems.

## 1.2 WHY RENEWABLES?

Production yields of carbon fiber from polyacrylonitrile, the highest volume current feedstock, is roughly 40%. Lower yields, typically 20-25%, are expected for rayon feedstocks. As illustrated by theoretical and experimental yields in Table 1.1, raw feedstock production will likely be in the range of 2 to 5 times ultimate carbon fiber production.

**Table 1.1. Carbon Yield from Various Precursors**

Precursor	Fraction carbon	Expected yield	Reference
Rayon	0.44	0.10-0.30	Bahl, <i>et al</i> , 1998
Pitch	0.92-0.96	0.80-0.90	Bahl, <i>et al</i> , 1998
PAN	0.68	0.33-0.50	Watt 1985
Lignin	0.68	0.45-0.55	
Poly(ethylene terephthalate)	0.58		
Polyethylene	0.85	0.09-0.40 <sup>a</sup>	Leon y Leon, <i>et al</i> , 2001
Polypropylene	0.88	0.05-0.54 <sup>a</sup>	Leon y Leon, <i>et al</i> , 2001

<sup>a</sup> Higher yields require complete sulfonation of fiber

Industrial chemicals and textiles are typically produced from petroleum in relatively small amounts, typically 1 to 20 lb per capita per year. Although the cost of some post-consumer recycled polymers, such as polystyrene, are low, these materials are not produced in volumes needed by the automotive industry. Some could, however, serve as blending agents to improve mechanical properties or handlability of raw fiber. Assuming complete replacement of steel and a yield of 33% carbon fiber relative to feedstock, roughly 12 million tons of raw feedstock would be needed annually. This would make carbon fiber feedstock a high-volume industrial chemical.

The only materials available at in sufficient quantities to support significant automotive use of carbon fibers are either very high volume petrochemicals, such as gasoline, or renewable materials, such as wood, biomass, crop residues, natural fibers, or black liquor.

Renewable sources of feedstocks for carbon fibers were evaluated because they are typically produced in large quantities, often have low costs, and meet automotive manufacturers' goals for renewable or recycled content. The major problems with renewable materials are associated with intermittent production (annual grasses), wide dissemination of low densities of material (stover and other crop residues), drying (woody brush), hauling, and storage. High volumes of some recycled materials are also a potential source of blending polymers for carbon fiber feedstocks.

### **1.2.1 Reasons for Selecting Renewable Feedstocks**

The high volumes and low cost of biomass-derived feedstocks, such as cellulose and lignin, were attractive. Also, rayon and lignosulfonate, derivatives of biomass components, have been reported as raw feedstocks for the production of carbon fiber. Rayon, a derivatized cellulosic, is still used as a feedstock for the production of aerospace composites. Although the yield, shown in Table 1.1, is low, rayon remains in commercial use as a carbon fiber feedstock.

Production of carbon fibers from lignin and lignin derivatives has not been commercialized, although a number of publications report studies on carbon fiber production from this class of materials. Carbon fiber from dry spun acid sulfite or alkaline pulping liquors, which contain lignin or lignin derivatives, were reported by Otani (1969) and Mannsmann (1973). A Japanese firm, Nippon Kayaku Company, was able to wet spin concentrated lignosulfonate pulping liquors to dry spin pilot-scale amounts of industrial carbon fiber feedstocks in the 1970s (Johnson 1975). The Nippon Kayaku Company fibers were reported to have short stabilization times and low firing temperatures, but fiber strength was lowered by voids created by crystallization and volatilization of salts.

A number of studies of carbon fibers production from chemically-modified lignins have also been reported: demethylated lignins (Yang 1981), hydrogenated lignins (Sudo 1992), and lignins produced by phenolysis (Sudo 1993, 1994). All of these methods either require significant downstream chemical processing of the lignin or a fundamental change in the pulping process itself, factors which were thought likely to limit use. Lignin from the Kraft pulping process, which comprises the bulk of U.S. chemical pulping (Lemire 1999) has received limited attention as a carbon fiber feedstock. Although there is one domestic Kraft lignin supplier, MeadWestvaco, most Kraft mills burn black liquors rich in lignin to provide mill steam, mill electric power, and inorganic chemical recycle.

### **1.2.2 Downselection of Renewable Feedstocks: Alkaline-Pulped Lignin Blend Fibers**

A variety of different cellulosic and lignin-based materials were considered as feedstocks for carbon fiber production. Prioritization of the materials for evaluation was performed. Most cellulose received low priority for two reasons: 1) environmental hazard and restrictions and 2) low yield. Classic rayon production technology, which is still practiced in developing countries, uses significant quantities of carbon disulfide. Carbon disulfide is highly flammable, produces toxic vapor, and is a recognized ozone depletion agent whose use is embargoed or controlled in most developed countries. Additionally, rayon fiber is wet spun, which creates gaseous emissions.

Lyocell, a carbon disulfide-free cellulosic has also been evaluated at significant scale. However, unlike rayon, there is little reported experience in the production of carbon fiber from this material. In lyocell, a solvent, most typically N,N-methylmorpholine, is used to extract cellulose from plant fibers. The cellulose is then wet spun. Solvent recycle and flammability have remained major difficulties with the Lyocell fiber production system. However, like rayon, Lyocell would be expected produce a low yield of carbon fiber because of the low carbon content and chemical structure of the starting material.

Wet-spun lignosulfonates from concentrated acid sulfite liquors were evaluated as carbon fiber feedstocks by Nippon Kayaku Company in the 1970s. This material was given a modest priority for several reasons: 1) limited availability due to low production of acid sulfite pulp, 2) difficulties in

desalting lignosulfonates, 3) difficulty in desalting the fiber feedstock, and 4) the likelihood of low carbon fiber yields due to the high oxygen content of lignosulfonate.

Lignins appeared to offer a combination of high volumes, a high carbon content, continuous production, and the likelihood, based on reported melting points and limited academic evaluation, of melt-extrudability. Based on a combination of likely carbon yield, initial bench evaluations, cost, and availability, organosolv and Kraft lignins appeared to offer the highest probability of success as carbon fiber feedstocks.

Organosolv lignins, which are produced by solvent extraction to remove lignin from wood, were also evaluated as carbon fiber feedstocks. The highest-volume organosolv lignin produced in North America was AlCell, an ethanol-extracted lignin produced by Repap. This material is attractive from the viewpoints of high purity and melt extrudability. However, organosolv pulping is not used at industrial-scale in North America and, additionally, the AlCell lignin which was evaluated at ORNL had a low melting point.

The largest amount of domestic wood pulp is produced by the Kraft process. Dried commercial Kraft lignins, produced by acid precipitation, are produced and marketed by MeadWestvaco. Historically, several other companies have produced commercial dried lignins and because the technology is straightforward and broadly applicable, it may be possible to produce very large quantities of Kraft lignin. Based on initial evaluations and on consideration of commercial materials, Kraft lignins were judged to have a high probability of success as a renewable feedstock for industrial grade carbon fiber. The amounts of potentially available lignin were very high because of the large number of Kraft pulp mills; the cost of technical grade lignin reported in earlier decades was very low; and the carbon content of lignin was high. However, literature reports describing the preparation of carbon fiber from Kraft lignin were limited and dried commercial Kraft lignin contained significant amounts of salts and extractives, as well as some sulfur. One dissertation reported studies of the rheology and spinnability of lignin blends (Schmidl 1992). However, the lignins in these studies used less environmentally friendly wet or dry spinning, as opposed to melt spinning.

Based on this reasoning, a variety of lignin samples were obtained and evaluated to determine the feasibility of spinning. Routinely recycled polymers were obtained and evaluated as blending or plasticizing agents for lignin. Evaluations of cellulose received lower priority.

### 1.3 EARLIER RESULTS

Evaluation of Kraft lignin as a material from which carbon fiber feedstocks could be produced was initiated. The first priority was to establish proof-of-concept for melt extrusion of lignin to produce carbon fiber feedstock. In order to do this, a low-ash spinnable lignin had to be produced. Desalting of Indulin AT showed that it was possible to "wash" salts from lignin powders with slightly acidified distilled water. The water was decanted from the settled lignin particles and the process was repeated until the desired level of ash was reached. The lignin was then dried or freeze-dried. Desalted lignin samples were used in all single and multiple fiber spinning runs.

Melt-block evaluations of blends containing a wide variety of desalted lignins and textile polymers were conducted. These evaluations showed that 1) fibers could be pulled up from both neat lignin melts and those containing polyesters, polyolefins, and polyoxyalkanes and that 2) it was likely that lignin would require the addition of a plasticizer or an alloying polymer in order to form moderately strong raw fiber.

At this time, it was decided to subcontract fiber spinning in order to avoid the lengthy process of establishing a spinning line at ORNL. Lignin preparation, fiber furnacing, and fiber evaluation were performed at ORNL. North Carolina State University was selected as the fiber extrusion subcontractor.

### 1.3.1 Single Fiber Extrusion

North Carolina State University houses a 300,000 ft<sup>2</sup> Textile Center which offers a variety of blending, rheometric, and spinning equipment. Professor Richard Gilbert, who was assigned to both the North Carolina State University Wood and Paper Science Department and the Textile Center, was funded to evaluate single fiber lignin extrusion. Results in late 1999 provided coarse, fragile fiber which showed poor blending with alloying polymers. The fibers were not well suited to transport between the two facilities.

Eventually, continuing ORNL melting block studies showed that blends of Indulin 1369 hardwood lignin and poly(ethylene terephthalate) or poly(ethylene oxide) could be melt extruded to form thick stable “shoelace” using an Atlas Laboratory Mixer. Although the North Carolina State University intent was preparation of samples for evaluation of phase separation by transmission electron microscopy, ORNL staff members asked the NCSU post doctoral fellow to chop and spin the extruded “shoelace.” This was later adapted to involve production of polymer-blend pellets followed by melt extrusion.

The need to spin “pellets” prior to fiber production was a continuing problem for the NCSU staff because the Textile Center had only one small Atlas Laboratory Mixer/Extruder for pellet preparation. The ORNL project staff purchased a small mixer extruder which was lent to NCSU. The extruder was deliberately ordered with small diameter spinnerettes to permit production of 1 to 5 gram batches of melt extruded fiber.

Using this equipment, the NCSU staff prepared small amounts of a number of fiber blends from both hardwood and softwood Kraft lignin and AlCell organosolv lignin. Alloying polymers included poly(ethylene terephthalate), polypropylene, poly(ethylene oxide), polystyrene, and poly(vinyl alcohol). In general, Kraft lignins formed single phase blends with long-chain polymers which were oxygenated, such as polyolefins or poly(ethylene oxide). These could be extruded and wound. AlCell lignin formed fibers with less oxygenated materials, such as polypropylene. It was also possible to form two-phase blends in which volatilization of a low-firing phase gave rise to a porous structure (Kadla and coworkers 2004). Results were published in the open literature as developed (Compere and coworkers, 2001, 2004; Griffith and coworkers, 2000, 2002-2004; Kadla and coworkers, 2002; Leitten and coworkers, 2002).

During this period, a technology base for carbon fiber production from Kraft lignin was developed at ORNL. This included techniques for stabilizing, hot stretching, carbonizing, and graphitizing small amounts of single filament fibers. Results from these studies were promising. Stabilization parameters remained within thermal and time ranges conducive to commercialization. Scanning electron micrographs showed that melt extruded lignin blend feedstocks formed smooth, dense raw, stabilized, and carbonized fibers (Figures 1.3-1.5, respectively) which did not stick to each other. No onionskin structure or pie wedge split was apparent in the large numbers of fiber blends evaluated.

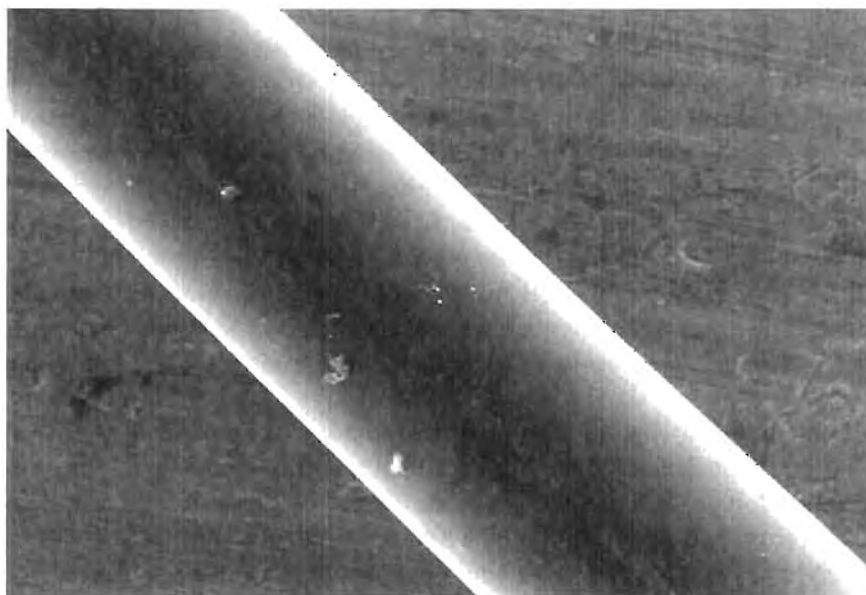
As with carbon fibers derived from pitch and polyacrylonitrile, formation of a graphitic carbon structure was evident in x-ray diffraction studies of powdered carbon fibers (Figure 1.6). The graphitic peak, which is a measure of fiber graphitization, was demonstrated to rise with increasing graphitization temperature.

Initial evaluations of fiber physical properties showed, although the diameter was significantly higher than desired due to the spinning method, the fibers were comparable in strength and stiffness to early, high diameter, polyacrylonitrile fibers.

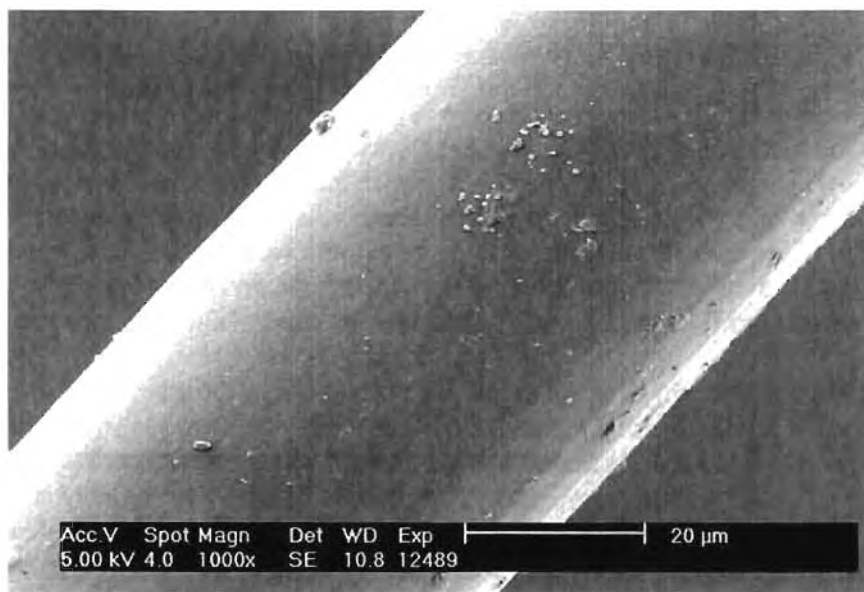
In 2001, a decision was made to terminate the subcontract lignin blend spinning with North Carolina State University Wood and Paper Science Department. The North Carolina State University Textile Center had single-screw extruders, rather than twin screw extruders. This forced a two-step lignin blend

extrusion. The University of Tennessee (UT) had obtained a Leistritz twin-screw extruder which had the potential to provide one-step polymer blending, more precise control of extrusion conditions, and the ability to spin 20-100 filament tow from 3-4 kg. batches of lignin blend feedstock.

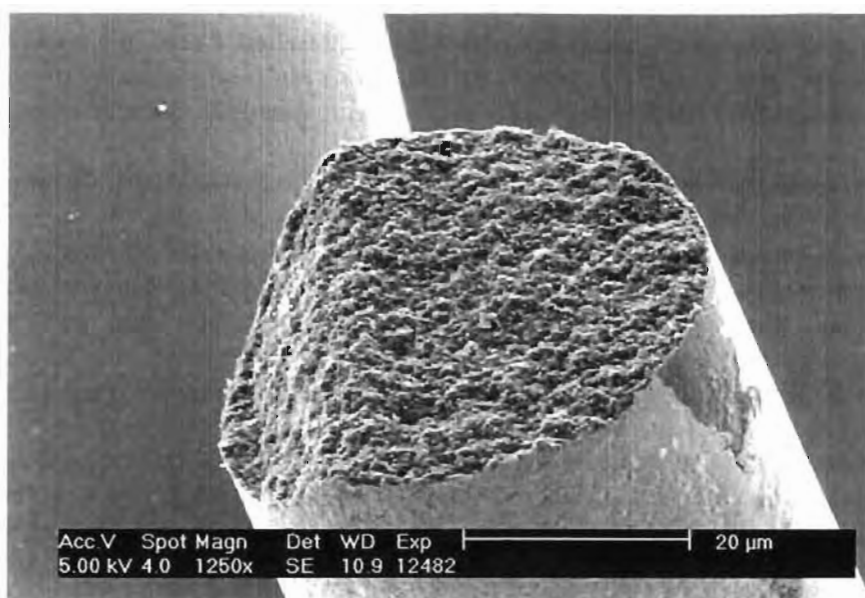
From the standpoint of technology transfer, the use of a domestically-produced twin screw extruder which could be scaled-up from UT data was also attractive.



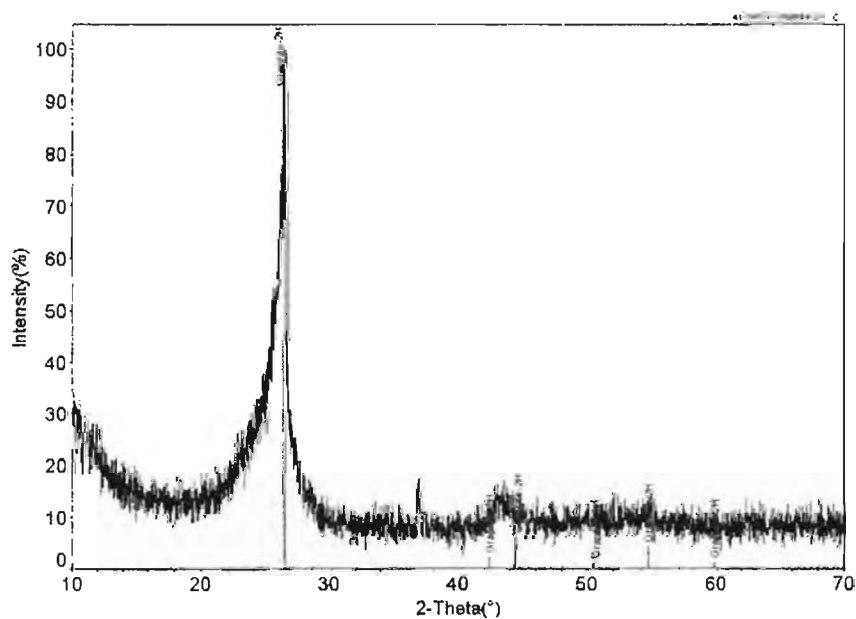
**Figure 1.3. Raw lignin blend fiber from single-filament extruder.**



**Figure 1.4. Carbonized lignin blend fiber from single-filament extruder.**



**Figure 1.5.** Graphitized lignin blend fiber from single filament extruder.



**Figure 1.6.** Powder x-ray diffraction shows a graphitic peak in 1600 °C lignin blend fiber.

### 1.3.2 Multifilament Extrusion

Significant quantities of Indulin 1369 hardwood lignin were desalted, freeze-dried, and provided to staff of the UT Chemical Engineering Department. Melting block tests and evaluation of single filament lignin blend fibers were used to illustrate the spinnability of lignin blend fibers and to estimate spinning temperature ranges.

Initial experiments evaluated the production of a small tow of 4 relatively coarse filaments from a 15% PET - 85% desalted Indulin 1369 blend. The die used in these studies, which had ~ 400 micron diameter spinnerettes, became blocked during spinning and volatiles offgassing occurred. Additionally, UT did not have standard winding equipment for carbon fibers and wound the filaments onto sections of file folders taped to form near cylinders. Additionally, it was difficult to form blends of PET pellets and fluffy lignin powder.

As more lignin was being desalted and dried, remedies for these problems were sought by both ORNL and UT staff.

Dry lignin was examined to determine the cause of particles large enough to block die spinnerettes. It was thought that this was correlated to a hundred pound lot of hardwood lignin provided by Westvaco, but ashed lignin did not have significant quantities of debris large enough (> 50 micron) to block spinnerettes. Conventional 3-dimensional sieving did not show significant quantities of particulate materials even at small sieve sizes.

A combination of 2 dimensional sieving and microscopic examination of raw lignin was effective in separating significant quantities of non-melting contaminants from lignin. Microscopic examination, coupled with EDX, showed these materials to be a combination of cellulosic fibers, sand, clay, large diatoms, and wood pulp (Figures 1.7 and 1.8).



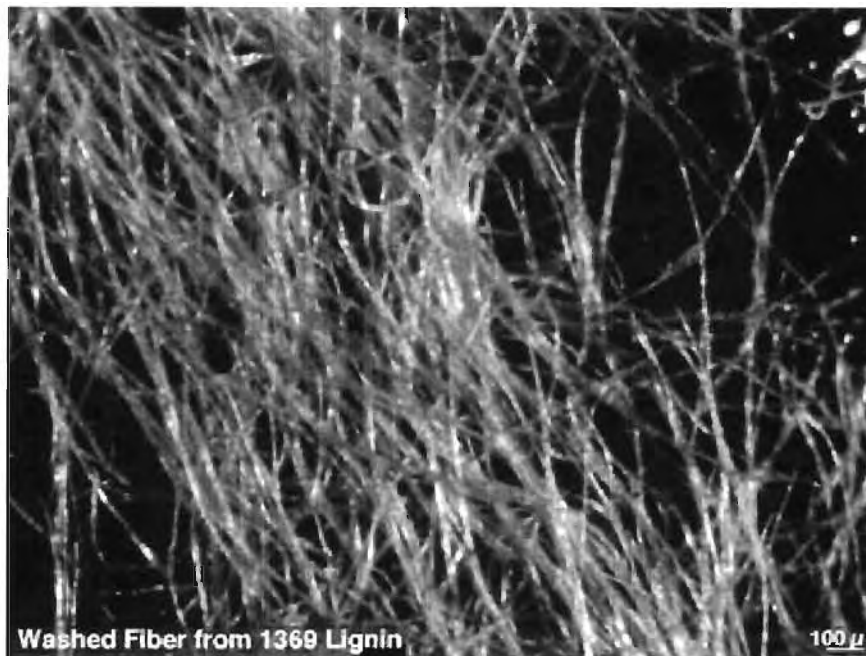
**Figure 1.7. Mat of wood pulp and fibers isolated from desalted commercial Kraft lignin.**

Freeze-dried, desalted lignin was 2 dimensionally sieved and sent to UT for melt spinning.

A series of experiments indicated that pelletized poly(ethylene terephthalate) could not be readily reduced in size to facilitate preparation of lignin blend feedstock. Eastman, a project participant which has supplied both materials and expertise, provided powdered pre-consumer recycle poly(ethylene



terephthalate). This material was sieved to provide a controlled particle size. It readily mixed with powdered lignin and was extruded to form pellets.



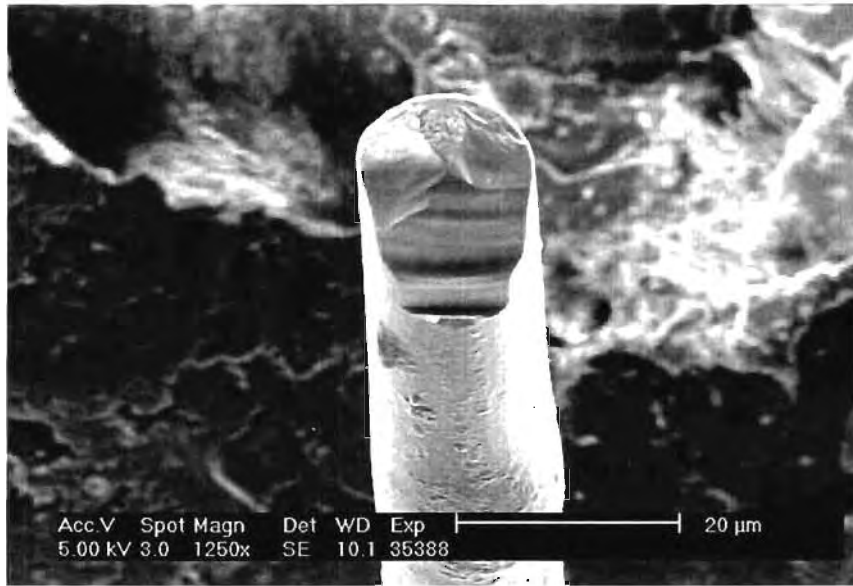
**Figure 1.8. Cellulose ester fibers isolated from desalted commercial Kraft lignin.**

At the same time, the UT staff modified the spinning head of the Leistritz by adding an extra pump, screens, and a sand pack filter ahead of the spinning die. It was decided to first extrude pellets of the PET-lignin blend and then to re-spin the pellets. This provided “double filtration.”

A spinning die, which had 28 filament tapered spinnerettes, was modified by the UT shop as a shear die. This improved the strength and stiffness of lignin blend fibers carbonized at 1200 °C as shown in Table 1.2. Strength and stiffness are expected to increase as firing temperature is raised to 1600 °C. Surface fracture patterns of lignin-based fibers spun through a shear die were similar to those of carbonized or graphitized pitch fiber as shown in Figure 1.9.

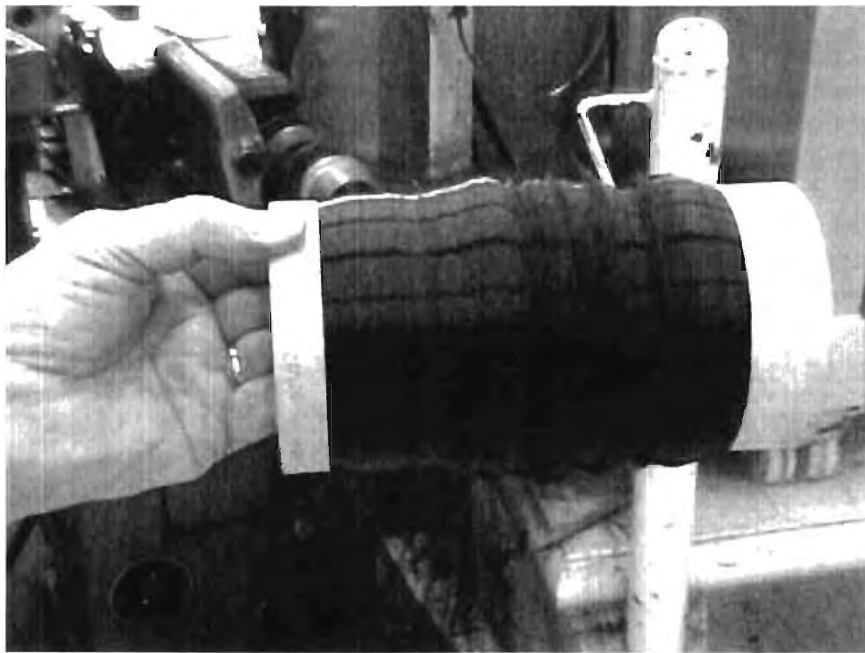
**Table 1.2. 1200 °C Carbonized Lignin Blend Single Fiber Tensile Data**

Specimen ID	Diameter, (microns)	Peak Stress, (ksi)	Modulus, (Msi)	% Strain at Peak Stress
Tapered Die Used for Extrusion				
B1-Sp2-S4	13.0	125.2	7.9	1.63
B1-Sp2-S5	12.3	110.4	10.3	1.14
B1-Sp2-S7	13.4	149.5	9.2	1.69
B1-Sp2-S9	10.8	141.8	10.1	1.49
Shear Die Used for Extrusion				
B2-Sp5-S2	11.8	149.5	15.8	1.07



**Figure 1.9. Effect of shear die on internal structure of carbonized lignin blend fiber.**

To meet a project milestone, significant amounts of lignin blend fiber were produced. Due to the inability to wind standard 30 degree crosshatch tow, UT provided lignin blend fiber back as standard textile spools, as shown in Figure 1.10. For evaluation in a small composite, this winding method forced hand preparation of individual fibers during stabilization, carbonization, and graphitization processing.



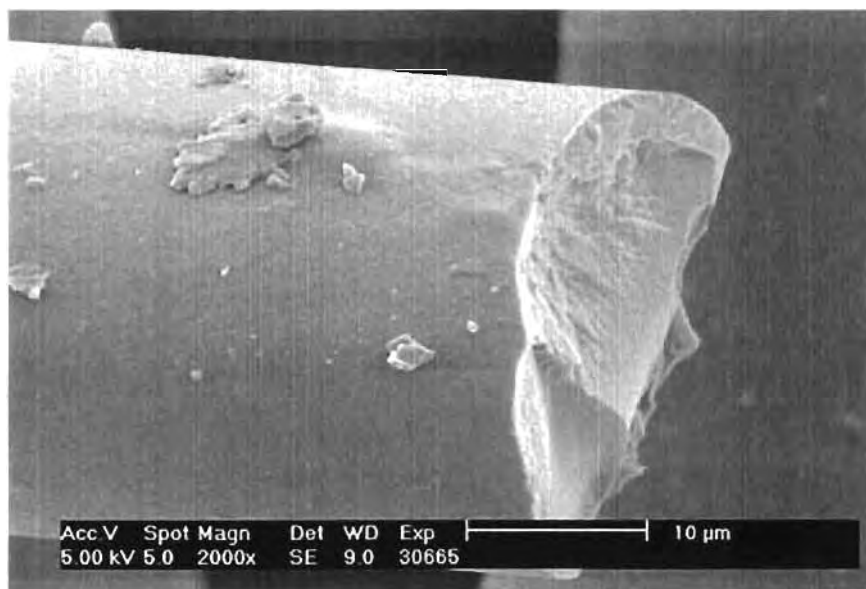
**Figure 1.10. Spool of raw lignin blend fibers from multifilament spinning.**

Raw multifilament fibers are shown in Figure 1.11, and carbonized, in Figure 1.12. These fibers are smaller in diameter and more uniform in size than those from single filament extrusion, although they are still somewhat larger in diameter than current commercial polyacrylonitrile or pitch fibers.

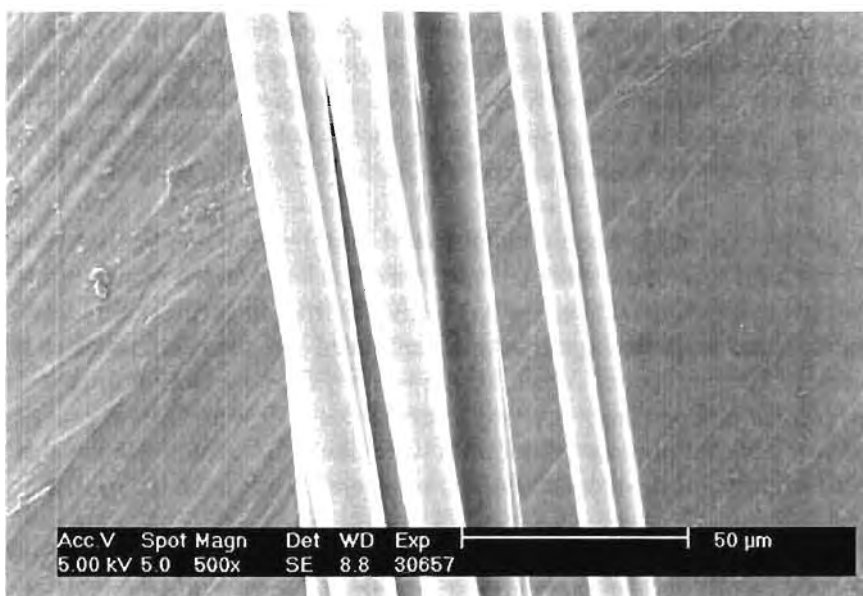
After processing, the fibers were sized and small epoxy composites prepared and evaluated. Photomicrographs showed that the lignin-based fibers could be effectively sized and were retained in the composite to a much greater extent ( $> 95\%$  in counted sections of photomicrographs) than were commercial sized PANAX polyacrylonitrile-based carbon fibers ( $<< 50\%$  in counted sections of photomicrographs).

These results showed that carbon fiber could be produced from lignin blend feedstock using conventional multifilament melt spinning methods in equipment. The twin-screw melt spinning equipment can be scaled to meet industrial needs and is available from a domestic producer. The carbon fiber produced from lignin blend feedstock could be surface treated and silanated, much as glass fiber is, and used in conventional epoxy composites. The diameter of multifilament fiber is approaching the values needed for conventional carbon fiber. A process economics review and report produced by Kline and Associates (2003) indicated that process economics were likely to be favorable for lignin blend feedstocks and for other technologies developed with the sponsorship of the Low Cost Carbon Fiber Program.

The “Low-Cost Carbon Fiber from Renewables” project was extended and selected to move toward larger scale production. As a part of this process, industrial partners for the project were sought. Staff of several large chemical and paper producers, as well as staff from smaller or more regional companies, were contacted. Eastman and MeadWestvaco, which have partnered the project since its inception, were joined by Granit, a producer of pulps from annual crops (grasses and flax) and woody biomass materials.



**Figure 1.11. Raw lignin blend fibers from multifilament spinning.**



**Figure 1.12. Carbonized lignin blend fibers from multifilament spinning.**

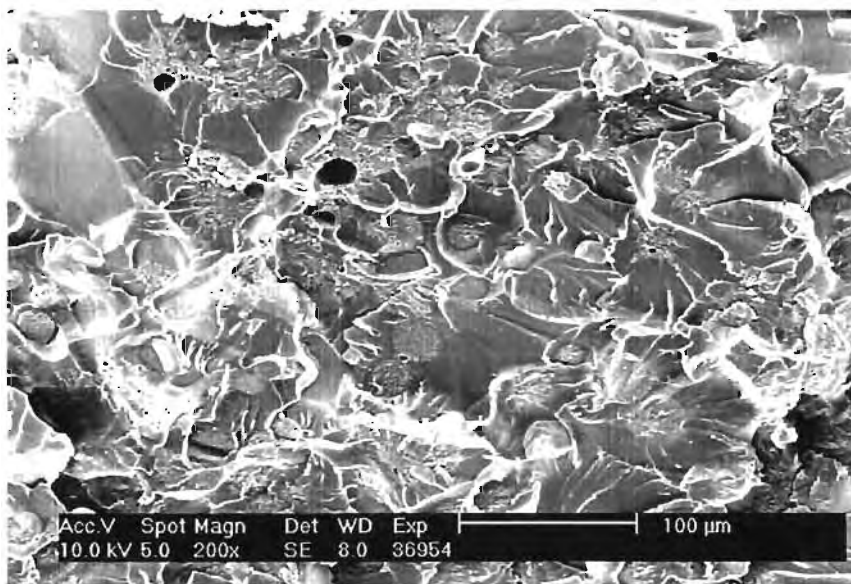
## 2. RESOLUTION OF MULTIFILAMENT SPINNING DIFFICULTIES

With the establishment of proofs of principle (graphitic carbon fibers from lignin blends) and concept (multifilament extrusion of lignin-based feedstock for carbon fiber), the focus of the Low Cost Carbon Fibers from Renewables project shifted toward development of technologies required to support larger scale production of carbon fiber from conventional lignins. The focus was development of lignins in which materials which interfered with melt spinning were minimized. This would later be followed by development of methods for handling the lignin-based fiber at industrial scale and transfer of the knowledge required to support this technology from ORNL to interested industrial partners.

### 2.1 PROBLEMS ENCOUNTERED IN PREPARING LIGNIN-BASED CARBON FIBER

As described earlier, a number of contaminants were found in lignins prepared for melt spinning small tow. The time required to prepare significant quantities of desalted, dried Kraft lignin using bench scale equipment available to the project limited the methods which could be used to prepare the lignin. It was, however, clear from visual examination of lignin fibers and from microscopic evaluation of the broken edge of small composites, shown in Figure 2.1, that significant improvements in commercial lignin were needed to improve spinnability.

Visual examination showed a significant variation in the diameter and color of lignin fibers during the spinning process. The longer that the lignin blend melt was held in the extruder, the darker the fiber color became. Additionally, UT staff reported that carbon deposits were found in parts of the extruder. This indicated that processing time of lignin blends in the extruder needed to be minimized and, if possible, an inert gas blanket provided.



**Figure 2.1. Scanning electron micrograph showing lignin fibers at composite break.**

Additionally, voids were found on the broken surface of many fibers. The voids were often more than a micron in diameter and a fiber might have several voids. Voids, or bubbles, are a defect which weakens fibers by creating a breakpoint. A number of different potential causes for voids were evaluated: overpressurization at the sand pack filter which could cause dissolution of normally-insoluble gases, such as nitrogen, in the melt; presence of small volatiles, such as water or alcohols, in the lignin and poly(ethylene terephthalate); and volatilization of a component of lignin structure during melting.

A literature evaluation, combined with practical analysis of lignin on hand, was performed. Additionally, it was requested that black liquor samples from a wood pulping technology development project supported by the DOE Industrial Technology Program be collected and sent back to ORNL with return sample drums. This provided small amounts of sample materials for initial evaluation of lignin purification technologies.

## **2.2 MITIGATING SPINNING DIFFICULTIES**

Initial considerations of methods for improving lignin started with evaluation of modifications to lignin production methods which would provide a higher quality starting material. Commercial lignins are precipitated as a loose gel from black liquor by acidification and then washed and dried. The gelatinous lignin precipitate tends to sweep a variety of undesirable materials from solution. These are discussed in detail below.

### **2.2.1 Particulate Removal**

Particulate contaminants in lignin-blend fibers can include inclusions (dried salts, sand, clays, and larger bodies). Such materials can cause defects, variation in fiber size, or voids in fibers in a number of different ways. All of these defects weaken carbon fibers.

Removal of particulate contamination was discussed with both industrial partners and the University of Tennessee staff. Lignin producers indicated that it would be difficult to filter black liquor prior to precipitation of lignin because existing production facilities would be difficult to modify. They also indicated that black liquor was difficult to filter.

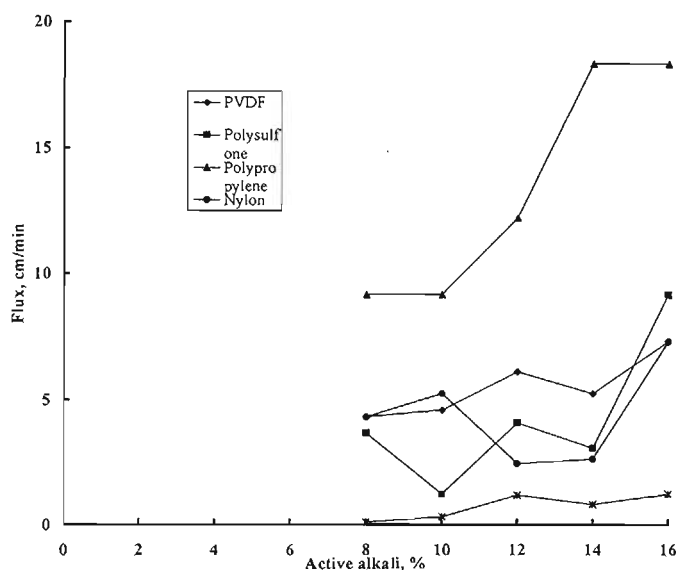
In a ten micron diameter fiber, even one micron inclusions and defects can cause significant weakening. This argues the need for submicron filtration prior to lignin precipitation. The last few years have seen considerable improvements in filtration materials. New materials for filters are becoming common and existing materials are becoming available in grades which can remove micron-scale particles.

Using small black liquor samples from the wood pulping technology project, small filtration tests to provide an initial estimate of filterability of room temperature black liquor samples were conducted. As shown in Figure 2.2, submicron black liquor filtration appears feasible. Since viscosity decreases as the cube of absolute temperature, filtration of warm or hot black liquor immediately after the digester appeared to be feasible even with membrane filters. Since filtration rate typically increases as medium surface area increases, filtration of black liquors with felts, such as polypropylene felts, which can be mounted on belt or plate and frame filters, would likely provide industrially acceptable fluxes.

### **2.2.2 Water Content of Lignins and Blending Polymers**

Commercial lignin powders typically contain around 10% water on a weight basis. Mass spectrometry in conjunction with thermogravimetric analysis indicated that water vapor was the major volatile from commercial lignins heated to the ~ 250 °C typically used for melt spinning. Minimizing water content of lignin and of any blending polymers, such as poly(ethylene terephthalate) was judged to be a critical factor in minimizing voids from volatiles produced during melt spinning. Although the size

(approximately one micron), high surface area, and salt content of dry lignin particles are factors in water sorption, it was felt that other factors might play critical roles.



**Figure 2.2. Filtration of black liquors through 0.45 micron membranes.**

Desalted, freeze dried lignin has the same rapid water uptake from humid air found in dried commercial lignins. This indicated that salt-associated water was likely not a major contributor to lignin water sorption.

Eastman staff indicated that poly(ethylene terephthalate), which was blended with lignin to produce multifilament tow, does sorb significant quantities of water. As with lignin blend fibers, this results in formation of bubbles and voids during extrusion and can also affect the intrinsic viscosity of the polymer during spinning. However, the amount of poly(ethylene terephthalate) was around 15% in the lignin blends being extruded for this project. This would correspond to a weight loss of 0.1% to 1.5%, a value much smaller than observed for lignin blends. The Eastman staff indicated that poly(ethylene terephthalate) used as feedstock for fiber extrusion is typically dried prior to extrusion. They provided the details of a the standard technology used for drying that poly(ethylene terephthalate) and indicated that some industrial scale extruders could be configured to minimize void formation in polyolefin fibers extruded at temperatures near those used for lignin blends.

This was verified with Leistritz and the extruder setup required to minimize voids was communicated to the UT staff.

### 2.2.3 Carbohydrate Removal

Because hemicellulose and other gel-like carbohydrates play a major role in water chemisorption in whole wood, it was thought that these might play a major role in water retention in lignin. The question was whether commercial lignins contained significant quantities of carbohydrates. Discussions with paper company staffs indicated that this was either poorly understood or unlikely.

However, ORNL does have good nuclear magnetic resonance (NMR) capabilities. To be sure that samples were not chemically modified, the initial analysis were made using a nuclear magnetic resonance instrument in which solid samples are rotated at high speed. This indicated that commercial lignins contained at least 10% carbohydrate.

The next question was finding a method for separating the carbohydrate. Several literature methods for separating or removing any retained carbohydrates from lignin were evaluated conceptually. These included standard industrial technologies, such as simulated moving bed chromatography and enzyme hydrolysis of carbohydrate, as well as more esoteric techniques, such as formation of two pseudophases by addition of a long chain surfactant to black liquor. Although simulated moving bed chromatography is used to recover prepare almost all high fructose corn syrup, the high initial inorganic concentrations in black liquor seemed likely to preclude use of the strong acid resins typically used for sugar separation. Pseudophase formation was ruled out because of the high associated chemical losses and the lack of an effective recycle system.

A suite of commercial mixed beta glucosidase enzymes, which could be purchased in high volumes with consistent quality and a reasonable cost, were obtained from Novozyme and incubated with lignin for several days at pH values suitable for each enzyme. Dried lignins analyzed by NMR did not show perceptible decreases in carbohydrate content after enzyme hydrolysis, although it is important to remember that solid state NMR does not provide precise resolution of high-volume contaminants.

A method for separating carbohydrate from lignin was sought. In discussions, Arthur Fricke, who serves as a consultant on wood pulping projects, indicated that one of his students had been able to get some separation of carbohydrate from lignin by using a combination of a fractional precipitation technique and centrifugation of the carbohydrate-enriched solids.

This method was evaluated originally using black liquors from an Industrial Technology Program pulping project. A series of precipitates were made at various pH levels and the pellets washed and freeze dried. Nuclear magnetic resonance analysis indicated that the lignin samples showed significant reductions in carbohydrate concentration and that the carbohydrate samples had reasonably low lignin levels. However, because the method required successive iteration between carbohydrate and lignin precipitations to get good separation, the technology was modified to permit replacement of centrifugation by filtration. This minimized the number of iteration steps required to achieve a given purity level.

In addition to decreasing moisture content of lignins, removal of carbohydrate is also expected to minimize formation of carbon char within the extruder during melt extrusion.

#### **2.2.4 Desalting**

Commercial lignins contain significant quantities of salts. Dried lignins can be desalted by mixing the powder into acidified distilled water, letting the lignin settle, and decanting the water. This can be repeated until an acceptably low salt content is reached. The problem lies in determining the final salt content of the lignin prior to drying.

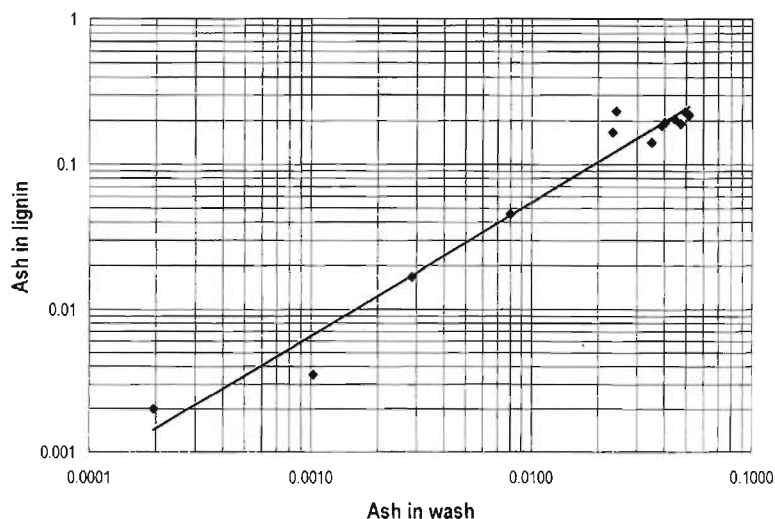
Using lignin samples from a variety of different sources, the ash contents of the distilled water washed and dried lignin samples were determined. As shown in Figure 2.3, there is a reasonable correlation between the salt content of wash waters and the final ash content of dried lignin. This correlation can be used to design process control systems to provide acceptably low ash content in lignins.

#### **2.2.5 Minimizing Water Uptake after Drying**

After freeze drying, lignins have a low moisture content. To prevent water uptake, lignin samples have generally been stored in closed bottles or in a desiccating cabinet. This reduces moisture content from around 10% when stored open to room air down to 1 to 2%.



On an industrial scale, this could be accomplished by spinning raw lignin fiber at the production site to minimize exposure to air. Alternatively, the manufacturer could replace current Kraft paper bags with moisture resistant packaging, such as plastic coated or plastic lined multilayer bags. Developing a method for producing lignin or lignin blend feedstocks as pellets, rather than powder, would also minimize moisture content by minimizing surface area.



**Figure 2.3. Correlation between wash water and dried lignin ash contents.**

## 2.3 STRATEGIES FOR IMPROVING LIGNIN SPINNABILITY

For both lignins from research Kraft black liquors (8 to 16 active alkali range) and commercial hardwood lignins, it appeared feasibly to mitigate most of the processing difficulties encountered with earlier samples. These included removal of particulates and fibers, minimization of water and other volatiles, and minimization of ash. The technical solutions proposed are shown in Table 2.1.

**Table 2.1. Solutions to Lignin Spinning Problems**

Problem	Solution
Particulates and fiber block spinnerettes	Prefilter black liquor prior to lignin preparation.
Voids formed by water vapor	Minimize water uptake by prompt processing or proper packaging. Remove hemicellulose carbohydrate which chemically binds water.
High ash content of commercial lignins and pulping liquors.	Desalt by washing lignin powder or gel with distilled or deionized water.
Produce consistently low ash lignins.	Measure dissolved solids (ash) content of wash water, control based on correlation.

The technical solutions selected were likely to be feasible at pilot or industrial scale. Simple and inexpensive solutions were preferentially selected. For example, it would be feasible to filter black liquor prior to downstream processing and to pack dried lignin powder in plastic coated or plastic lined paper bags rather than in two layer paper bags. These solutions were evaluated later in preparation of lignins from black liquor samples and commercial lignins.

Some consequences of lignin modification were also anticipated. For example, desalting was expected to remove low molecular weight lignin-like materials, such as monomeric or dimeric subunits. This was expected to increase the molecular weight and melting point of desalted samples. This is useful because it would increase the rate at which fibers could be stabilized. However, changes in lignin average molecular weight and in the structure of the lignin-carbohydrate complex were thought likely to change the materials which formed single phase blends with lignin. The most likely effects are expected to be a decrease in the surfactancy of lignin (decreased range of compatible materials) and decreased hydrophile-lipophile balance (HLB) of the lignin.

### **3. LIGNIN FROM WEYERHAEUSER ALKALINE-PULPED HARDWOOD BLACK LIQUOR**

Low sulfur content was desirable in the selection of pitches for melt spinning. Because lignin structure is like pitch, aromatic in structure, it was thought that a low-sulfur lignin might be desirable as a carbon fiber feedstock. Although not a project partner, Weyerhaeuser offered to provide samples of hardwood black liquor pulped without added sodium sulfide from a regional mill. Weyerhaeuser also offered to support a limited number of analytical studies of both lignins and carbohydrates derived from research black liquors as well as those from the black liquor which it supplied.

#### **3.1 PHYSICAL PROPERTIES OF BLACK LIQUOR**

As-received soda-pulped hardwood black liquor was a dark brown solution with a density of 1.10 at 25 °C. The 105 °C solids (volatile + fixed) content was 19.6% w/w and the ash (fixed solids) content, 11.1%. These values indicate that it will be difficult to remove fine solids from this black liquor by centrifugation.

#### **3.2 PREPARATION OF HEMICELLULOSE AND LIGNIN**

Commercially, lignin is prepared by the precipitation of hot, partially-evaporated Kraft black liquors using a combination of stack gas (or carbon dioxide) and, at appropriate pH levels, dilute acid. Similar methods are used in lignin analysis.

For initial studies, it was decided to simply use sulfuric acid to precipitate as-received, unconcentrated, room-temperature black liquors. This was tractable at bench scale, although it is likely that larger scale pilot and industrial applications will use stack gas or carbon dioxide to precipitate hot black liquors. Depending on the final use, various concentrations of liquor can be processed.

##### **3.2.1 Initial Filtration to Remove Particulates**

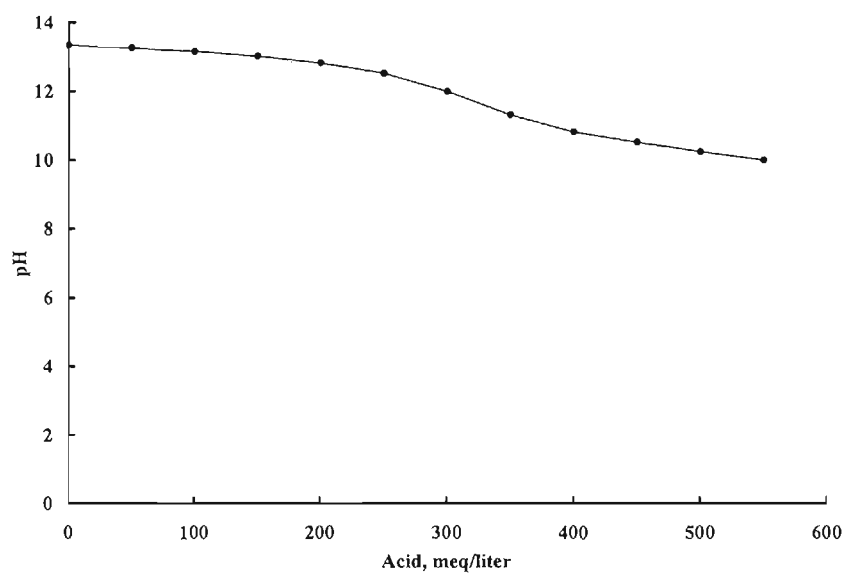
Visual and microscopic observation of as-received black liquor indicated the presence of solids in sizes large enough to serve as a barrier to lignin-blend fiber spinning or to create defects in melt-spun fibers. These were removed by filtration.

The media used for initial filtration of as-received black liquor depended on the scale of the work. For 1 to 5 liter samples, rough filtration was through 1 micron polypropylene felt supported in a Buchner filter or multilayer bag filters. At a 2.5 to 5 gallon batch scale, multilayer bag filtration was followed by a combination of 3 micron and 0.45 micron polypropylene cartridge filters. Filtered black liquor was batched to facilitate hemicellulose precipitation.

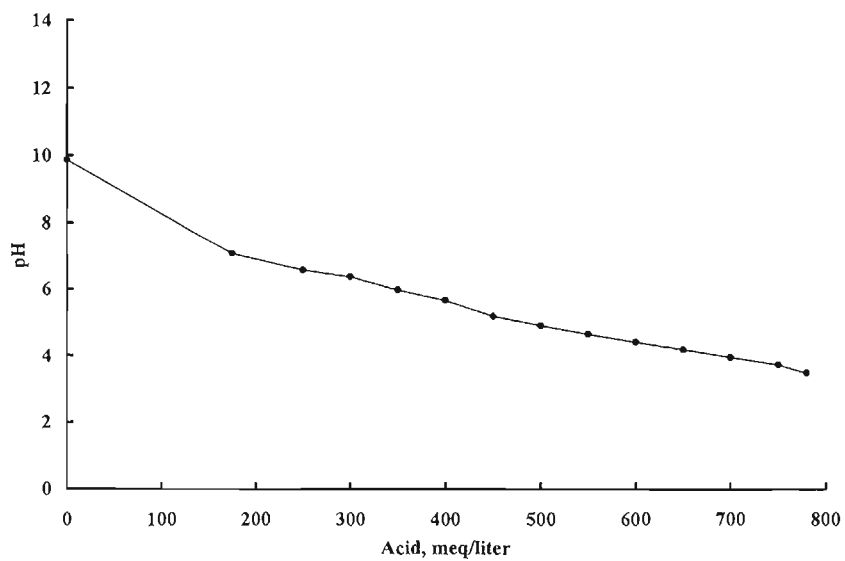
##### **3.2.2 Fractional Precipitation with Sulfuric Acid**

Hemicellulose and lignin were removed from black liquor by fractional precipitation. Figures 3.1 and 3.2 illustrate the reduction in pH of the Weyerhaeuser black liquor between pH 13.4 and a final pH of 10, and between pH 10 and pH 3.5, respectively. During the titration, care was taken to ensure that the samples approached equilibrium as this is typically a slow process in carbonate systems. The higher pH range spans hemicellulose precipitation; the lower range, lignin precipitation from a filtered, hemicellulose-stripped liquor.

Discussions with mill person indicated that considerable variation with processing batch is expected for these systems.



**Figure 3.1. Titration of as-received, filtered weak hardwood soda liquor from pH 13.4 to pH 10.**



**Figure 3.2. Titration of filtered hemicellulose-stripped hardwood soda liquor from pH 10 to pH 3.5.**

### 3.2.3 Hemicellulose Separation

Hemicellulose was prepared from prefiltered weak black liquor by direct precipitation with diluted sulfuric acid at room-temperature. Depending on the scale of the preparation, black liquor was stirred in a large beaker or in a polyethylene bottle and sulfuric acid was added dropwise. Trace amounts, typically 10-30 ppm, of antifoam was added to improve stirring by minimizing formation of a solid floating layer. At larger scale, 10-30 ppm of flocculating agent could be added to improve the consistency of solids during stirring. After pH was reduced to 9.8 to 10.0, stirring was stopped and the precipitate allowed to settle. The hemicellulose was then removed by filtration. If appropriate, the hemicellulose could also be resuspended and washed. When filtration was finished, the hemicellulose paste was refrigerated. Lignin was then prepared from the filtrate.

### 3.2.4 Lignin Precipitation

Lignin was prepared from filtered weak black liquor (or hemicellulose stripped black liquor) by direct precipitation with diluted sulfuric acid. Filtered weak black liquor or filtered hemicellulose-stripped black liquor was stirred in a beaker or polyethylene bottle at room temperature depending on the scale of the preparation and diluted sulfuric acid was added dropwise. At 2.5 to 5 gallon scale, trace amounts, typically 10-30 ppm, of antifoam, commercial beta glucosidases, and food-grade flocculants were added to control foam and improve solid stability. When pH was reduced from 10 units to 3.5 to 4 units, the stirring was stopped and the precipitate was allowed to settle. The lignin gel was then washed or filtered and washed.

### 3.2.5 Desalting

After lignin precipitate settled, the supernatant was decanted and replaced with acidified distilled water several times. The lignin precipitate could also be filtered and resuspended in acidified distilled water. After desalting was completed, lignin gel was filtered to minimize water content. This was typically performed using a Buchner funnel with layered media which provided good separation and retention of the thixotropic gel.

### 3.2.6 Lyophilization, Sieving, and Storage

The lignin filter cake was divided into portions suitable for lyophilization or air drying. Portions were individually frozen and lyophilized in a Refrigeration for Science #5006 lyophilizer until dry. After drying, lignin powder was sieved to pass 30 mesh using a 2-dimensional stroke to remove any minor contaminants, such as polypropylene filter felt, and stored in sealed bottles.

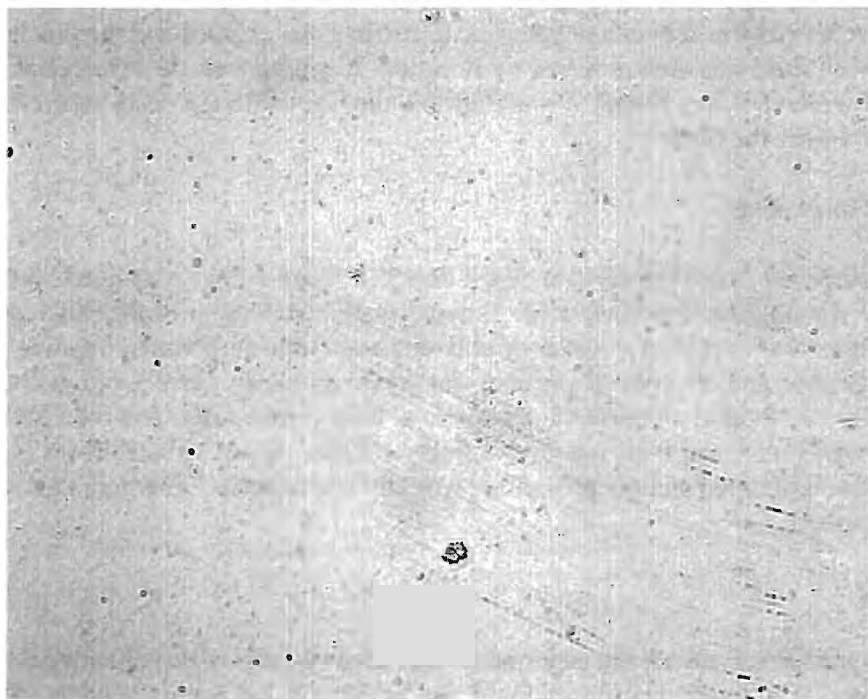
## 3.3 HEMICELLULOSE

Hemicellulose was recovered as a dark brown, gelatinous paste. Three gallons of this material was sent to Weyerhaeuser, while the remaining 2 gallons was stored at ORNL. Microscopic examination of this material, provided in Figure 3.3 shows it to be in the form of relatively uniform globular particles with diameters on the order of a micron.

The consistency of a stirred hemicellulose sample was 19.3% w/w and the ash, 11.6%. These values were as expected from ash content of the black liquor from which the hemicellulose was recovered. It may be possible to facilitate mill chemical recycle by increasing inorganic content of hemicellulose recycled to increase pulp yield.

The methods used for conditioning the solution prior to filtration, as well as the trace additives and conditions used for filtration, significantly impact the downstream recovery of the gelatinous

hemicellulose precipitate. Because the precipitate is very soft, it was best filtered at low pressure through 1 micron (or finer) media which are graded or structured to build and hold a wet filter cake. Because the ash content, and thereby likely density of the hemicellulose particles, is similar to those of the black liquor itself, and because the particles are small, hemicellulose will likely be difficult to remove or recover by centrifugation.



**Figure 3.3 Transmitted light micrograph of hemicellulose particles at 400X.**

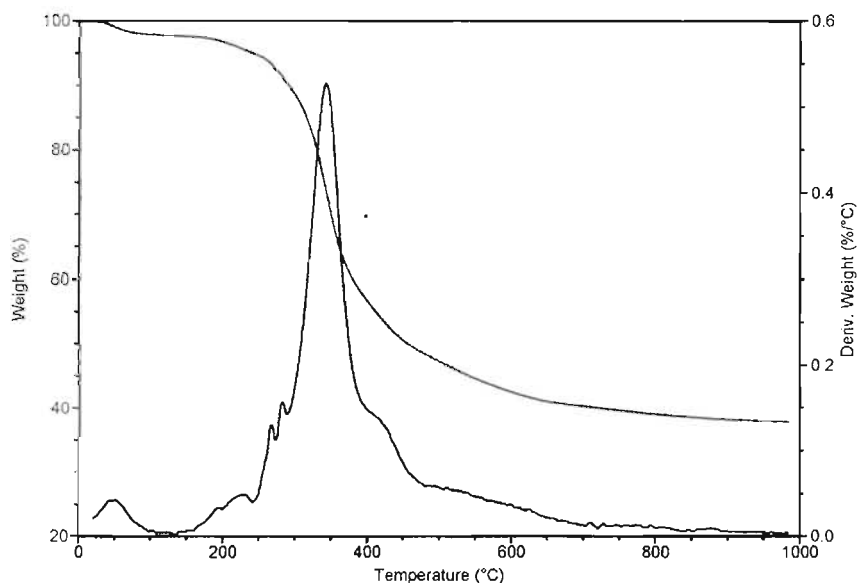
### **3.4 ASSESSMENT OF SODA LIGNIN AND RELATED MATERIALS**

Hemicellulose-stripped soda lignin was evaluated to determine whether it had a reasonable likelihood of utility as a feedstock for carbon fiber. From preparation of lignin, it is clear that initial preparation goals can be met: 1) the black liquor can be filtered to decrease particulates, 2) hemicellulose can be removed from the lignin by filtration, and 3) the lignin can be filtered, desalted, and lyophilized.

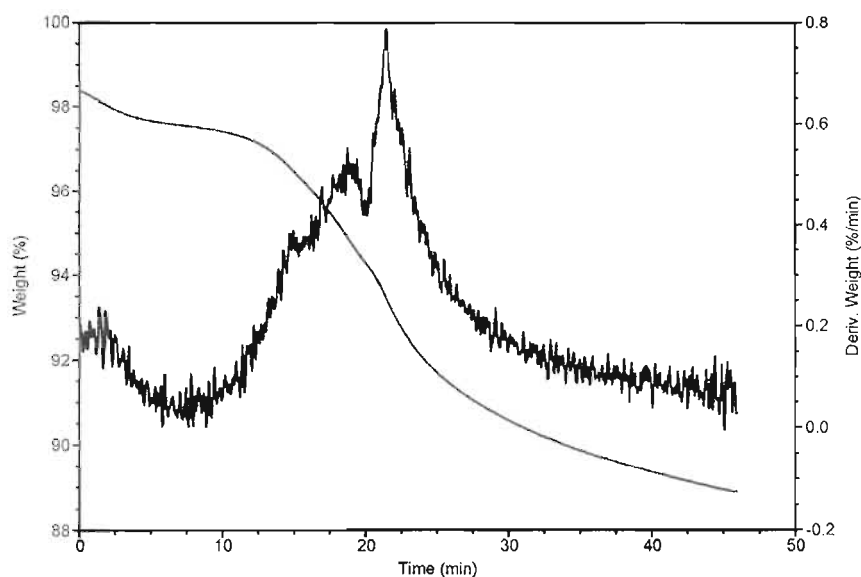
However, the ultimate use of lignin as a carbon fiber feedstock requires that it be extrudable and processable as a carbon fiber. Although bench scale thermogravimetric, nuclear magnetic resonance, or differential scanning calorimetry measurements do not provide proof that a starting material will ultimately be processable as carbon fiber feedstock, they do provide a good indication of characteristics, such as volatiles evolution or failure to melt at acceptable processing temperatures, which could preclude development of a useful fiber. Although it is possible that additional research or different production conditions can overcome fundamental problems with the starting lignin, failure to draw a plastic fiber from a melt or the failure to find alloying polymer or plasticizers which form single phases with lignin indicates a particular lignin is not likely to serve as a satisfactory base for production of carbon fiber feedstock by melt extrusion.

### 3.4.1 Thermogravimetric Analysis

Thermogravimetric analyses (TGA) of hemicellulose-stripped soda lignin using both a standard resolution TGA 2050 and a high resolution TGA 2950 are shown in Figures 3.4 and 3.5, respectively. These analyses indicate that weight loss is less than 10% up to the melting temperatures expected for soda lignin blends with plasticizers (~250-270 °C).



**Figure 3.4. Thermogravimetric analysis of hemicellulose-stripped hardwood soda lignin.**



**Figure 3.5. High resolution thermogravimetric analysis of hemicellulose-stripped hardwood soda lignin.**

The limited weight loss from these materials indicates that volatiles offgassing, and thereby bubble, formation in fibers, could potentially be controlled by a pellet and fiber two-step extrusion. These levels of volatiles, primarily water, are comparable to those of poly(ethylene terephthalate) pellets used in commercial melt-spinning of textile fibers and should be amenable to similar processing technologies.

The other feature of note is that, even without surface-protective air stabilization, 38% of powdered lignin remains as a carbon material at 1000 °C in a significant purge gas stream. This indicates that, like Kraft lignins, low sulfur lignins are good potential carbon formers.

### 3.4.2 Initial Fiber Extrusion Screening

Initial fiber extrusion screening was evaluated using small samples, typically 0.1-0.5 g, of dried, hemicellulose stripped hardwood soda lignin weighed into 10-12 mm diameter precleaned test tubes. Small amounts of alloying polymers or plasticizers could be added and mixed into the lignin if desired. The tubes were initially blanketed with an inert gas and were placed in a preheated aluminum block on an electronically-controlled hot plate and the temperature was gradually increased to permit evaluation of temperatures between 225 to 275 °C. A stainless steel cylinder around the aluminum block was used to maintain the inert gas blanket. The samples were periodically evaluated and stirred. If melting occurred, fibers were drawn up on a wooden applicator stick. Neat lignin samples were also evaluated.

Table 3.1 lists the plasticizer materials which were initially evaluated at ~10% w/w. Fibers could not be pulled from melts of these materials.

**Table 3.1. Polymers and Plasticizers Evaluated at ~10% in Initial Screenings of Hemicellulose Stripped Hardwood Soda Lignin**

Material	Supplier
Pitch, mesophase	AR
Pitch, A240	Ashland
Poly(butylene terephthalate) 545A	Intercontinental
Poly(butylene terephthalate) 550	Intercontinental
Poly(ethylene terephthalate) F80CS	Eastman
Poly(ethylene terephthalate) F65HC	Eastman
Poly(ethylene terephthalate), recycled	Eastman
Cinnamyl acetate	Sigma-Aldrich

A number of additional blends of plasticizers and polymers were evaluated. These included the groupings of materials shown in Table 3.2. Eastman staff recommended evaluation of a high-melting cellulose ester, Tenite, as well as cellusolves and phthalates, as plasticizers. These materials are conventionally used in fiber production as either plasticizers or the feedstock blend. Materials with boiling points high enough to minimize volatiles during fiber melt extrusion were evaluated.

So far, it has not been possible to find plasticizers for hemicellulose-stripped hardwood soda lignin. It may be necessary to spin this material, as Conoco pitch has been spun, at lower temperature with a significant addition of a low-boiling solvent.



**Table 3.2. Some of the Polymer and Plasticizer Blends Evaluated at 5-20% in Initial Screenings of Hemicellulose Stripped Hardwood Soda Lignin**

Materials
A240 pitch + cinnamyl acetate
A240 pitch + cinnamyl acetate + F61HC poly(ethylene terephthalate)
A240 pitch + cinnamyl acetate + 550 poly(butylene terephthalate)
A240 pitch + cinnamyl acetate + polyvinyl alcohol
F61HC poly(ethylene terephthalate) + Tenite cellulose acetate propionate
F61HC poly(ethylene terephthalate) + Tenite cellulose acetate propionate + A240 pitch
A240 pitch + recycled poly(ethylene terephthalate)
A240 pitch + Tenite cellulose acetate propionate + cinnamyl acetate
A240 pitch + Tenite cellulose acetate propionate + recycled poly(ethylene terephthalate)
Tenite cellulose acetate propionate + recycled poly(ethylene terephthalate) + butoxyethoxyethyl cellusolve
Tenite cellulose acetate propionate + recycled poly(ethylene terephthalate) + butyl cellusolve
Tenite cellulose acetate propionate + recycled poly(ethylene terephthalate) + cinnamyl acetate
Tenite cellulose acetate propionate + recycled poly(ethylene terephthalate) + dimethyl phthalate

### 3.4.3 Nuclear Magnetic Resonance Spectra

Carbohydrate content, typically hemicellulose content, of lignins was determined using nuclear magnetic resonance (NMR). Original studies were performed using a solid state NMR instrument. In this analysis, solid lignin was rotated at high speed through the instrument field. Results indicated that concentration of carbohydrate in dried lignin was above 10%.

Solution nuclear magnetic resonance was preferred for evaluation of the low concentrations of carbohydrate expected in hemicellulose-stripped lignin. To perform this evaluation, small samples (~100 mg) were dissolved in 0.5 ml DMSO- $d_6$  or D $_2$ O/NaOD mixtures. Solution phase  $^{13}\text{C}$  and  $^1\text{H}$  NMR were performed using a Bruker MSL-400 wide-bore multinuclear nuclear magnetic resonance instrument at 60 °C.

Figure 3.6 shows the spectrum for a hemicellulose-stripped hardwood soda lignin. The spectrum indicates that single-step hemicellulose stripping is very effective in reducing carbohydrates in lignin and that the lignin was relatively pure.

### 3.4.4 Differential Scanning Calorimetry

Differential scanning calorimetry was performed using a TA Instruments model TA DSC 2010. Samples of ~ 10 mg were weighed into hermetically sealed aluminum pans with a pin-hole at the top. Most samples were heated at 10 °C per minute to 210 °C. Samples were run several times the data averaged.

As shown in Figure 3.7, hardwood soda lignin has a glassy transition temperature around 195 °C. No actual melting point for carbohydrate-stripped desalted soda lignin was found between ambient and 400 °C. Commercial hardwood Kraft lignin has a well defined melting point around 165 °C.

In spite of the very high melting temperature, it may be possible to spin hardwood soda lignin by use of some of the commercial methods used to spin mesophase pitch. These methods vary with

manufacturer but typically include formation of a solution or emulsion which can be spun and rapidly dried.

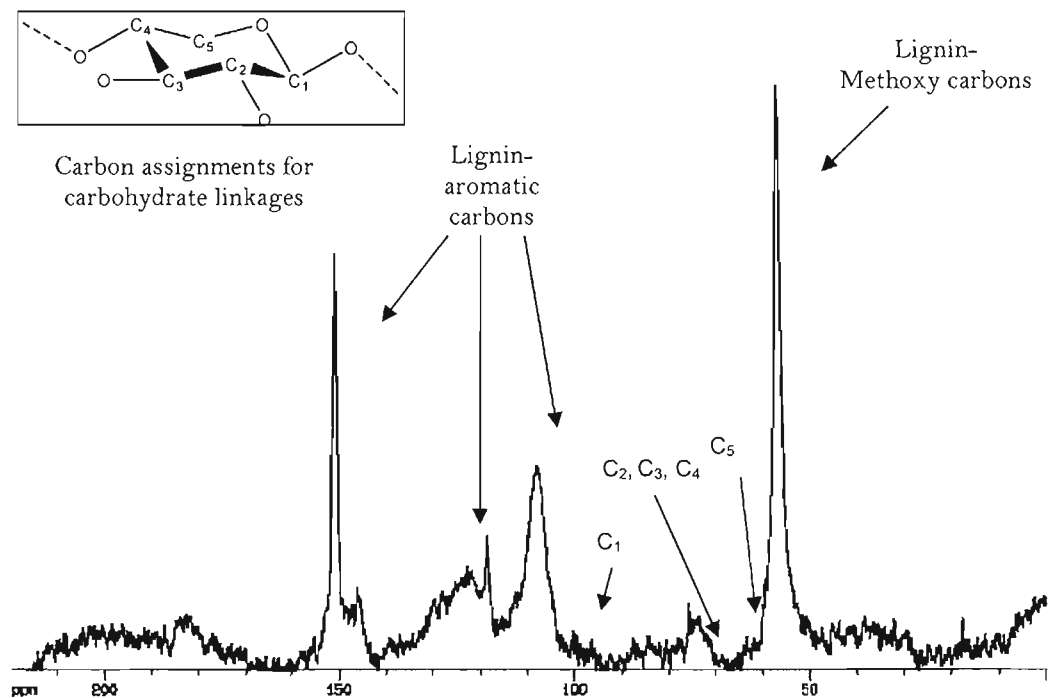


Figure 3.6. Solution nuclear magnetic resonance spectrum of hemicellulose-stripped hardwood soda lignin.

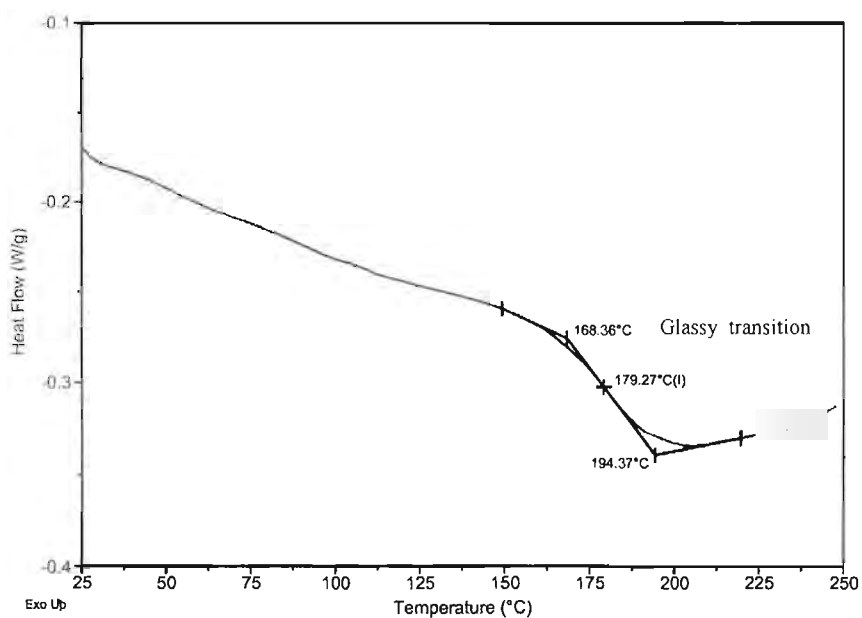


Figure 3.7. Melting behavior of hemicellulose-stripped hardwood soda lignin using differential scanning calorimetry.

## 4. DISCUSSION

In order to prepare clean hardwood soda lignin as a potential feedstock for carbon fiber production, several goals had to be met. These included proof-of-principle demonstration of contaminant removal, ability to melt the lignin in the thermal range needed, the ability of hardwood soda lignin to form carbon, and lignin blendability with plasticizers and alloying polymers. These are summarized below.

### 4.1 CONTAMINANT REMOVAL FROM SODA HARDWOOD LIGNIN

As discussed in Chapter 2, proof-of-principle demonstration of the removal of several contaminants: 1) micron (and, if possible, submicron) particulates, 2) inorganic chemicals (ash or fixed solids), and 3) hemicellulose is needed in a lignin used for carbon fiber feedstock. As shown in Table 4.1, proof-of-principle has been shown for these goals for lignins from soda-pulped hardwoods using the limited black liquor sample provided.

**Table 4.1. Proof-of-Principle Removal of Hardwood Soda Lignin Contaminants**

Problem	Solution	Proof-of-principle?
Particulates and fiber block spinnerettes	Prefilter black liquor prior to lignin preparation	Micron prefiltration with polypropylene felts, submicron with cartridges.
Voids formed by water vapor	Minimize water uptake by prompt storage in proper packaging.	Closed bottles keep lignin moisture content < 2%.
	Remove hemicellulose carbohydrate which chemically binds water	Introduction of a single filtration step at a pH slightly below that of hemicellulose precipitation but above that of lignin precipitation.  Hemicellulose can be recycled to increase yield and strength of paper.
High ash content of commercial lignins and pulping liquors.	Desalt by washing lignin powder or gel with acidified distilled or deionized water.	Ash content < 0.1%.
Produce consistently low ash lignins.	Measure dissolved solids (ash) content of wash water, control based on correlation.	Established for soda lignin.

### 4.2 MELTING AND BLENDING OF SODA HARDWOOD LIGNIN

Proof-of-principle demonstration of melting parameters in an acceptable range for extrusion with likely blending polymers is needed. Because neat lignin forms brittle, friable fibers, it will likely be blended with a plasticizer prior to extrusion. High molecular weight blending, or alloying, polymers can also provide a “structure” around which lignin organizes.

Although soda hardwood lignin meets the melting point requirements and is likely to form carbon at levels which encourage its use as a carbon fiber precursor, plasticizers for this material have not been found.

**Table 4.2. Proof-of-Principle Evaluation of Hardwood Soda Lignin as a Fiber Feedstock**

Characteristic	Proof-of-principle?
Forms liquid melts at 250-275 °C	Forms liquid melts in desired thermal range.
Forms solid carbon at acceptable levels	Demonstrates a residue of ~38% as an unstabilized powder during thermogravimetric analysis to 1000 °C.
Plasticizers demonstrated in small tests?	No. Have not found an acceptable plasticizer for low-hemicellulose hardwood soda lignin.
Blending polymers demonstrated in small tests?	No. Have not found an acceptable alloying, or blending, polymer for low-hemicellulose hardwood soda lignin.

### 4.3 ADDITIONAL STUDIES NEEDED TO ESTABLISH PROOF-OF-PRINCIPLE

In order to establish proof-of-principle for production of carbon fiber feedstock from hardwood soda lignin, small amounts of feedstock fiber which can be evaluated at bench scale is needed. Typically, this will require the production of several kg of clean, desalted lignin together with establishment of compositions (stable single phase melts) and conditions (temperature, etc.) whereby the lignin may be extruded to produce small amounts of handleable fiber.

After fiber is available, bench scale trials of stabilization and carbonization will provide information needed to determine whether the lignin blends selected will form dense, solid fibers and the likely yield of carbon fiber. Evaluations of the mechanical properties of single fibers and small composites (called broomstraw composites) will provide information which, by comparison with other fibers, indicates whether the lignin blends being evaluated have significant potential for use as carbon fiber feedstocks.

If proof-of-principle is established, larger scale evaluations could be warranted.

## 5. MATERIALS AND METHODS

The materials and methods described below were used in the preparation and analysis of lignin from Weyerhaeuser soda-pulped hardwood liquor. Materials and methods, such as x-ray diffraction or scanning electron micrography, used to analyze other liquors or lignins are as described in the papers or reports detailing that research.

### 5.1 ASHING

The ash content of lignin wash water solutions and of dried lignin were determined by drying at 105-110 °C for at least one hour followed by ashing at 600 °C for at least an hour. A small aluminum weighing pan was used to hold the samples.

### 5.2. DENSITY

Density was measured at ~25 °C using a standard hydrometer. The black liquor was decanted carefully to minimize particulates and the hydrometer was rotated after immersion to dislodge bubbles. The reading was then taken. Alternatively a one-liter volume of black liquor in a volumetric flask was weighed at ~25 °C.

### 5.3 DESALTING

After lignin precipitate settled, the supernatant was decanted and replaced with acidified distilled water several times. The lignin precipitate was also filtered several times. When an acceptable lignin ash content, as judged by the inorganic solids content of lignin wash water, was reached, the lignin precipitate was vacuum filtered, divided into smaller aliquots, and frozen until dried.

### 5.4 DIFFERENTIAL SCANNING CALORIMETRY

Differential scanning calorimetry was performed using a TA Instruments model TA DSC 2010. Samples of ~ 10 mg were weighed into hermetically sealed aluminum pans with a pin-hole at the top. Most samples were heated at 10 °C per minute to 210 °C. Samples were run several times the data averaged.

### 5.5 FIBER FURNACING

Computer control using the LabVIEW system in conjunction with mass flow controllers was used to provide precise control of furnacing atmospheres and furnace section time/temperature profiles. Furnaces were controlled by a Eurotherm 2416 setpoint controller using Eurotherm ITOOLS computer software. Single fibers were stretched on quartz sheets during stabilization in an air or oxygen-enriched atmosphere within a 130 mm diameter quartz tube in a 3-zone Lindberg / Blue M furnace. In a typical experiment, temperature in the 50 cm. long furnace was stabilized at 60 °C, gradually increased to 200 °C, and held for 1 hr. During carbonization in a 3-zone Lindberg / Blue M furnace equipped with a 77 mm diameter tube, inlet N<sub>2</sub> was maintained < 0.5 ppm O<sub>2</sub> by passage through a heated zirconium sponge. Exit O<sub>2</sub> was < 3 ppm oxygen. The temperature was gradually increased to 1200 °C. In some experiments, batches of single fibers were also heated to 1600 °C in a graphite resistance furnace under a nitrogen / argon atmosphere.

## 5.6 FILTRATION

The equipment used for sample filtration was varied to suit the volume of sample filtered. Smaller samples were typically filtered in a large Buchner filter. To provide removal of micron-size particles, a graded series of media were used. Typically, this would include a lower layer of Whatman 5 or 6 paper, a polypropylene non-woven tissue layer, and an upper layer of 1 micron retention polypropylene felt. The graded media were prevented from floating with a stainless steel edge-ring.

Black liquor samples were initially filtered through a bag filter and subsequently through 3 micron and 0.45 micron polypropylene pleated cartridge filters. in a standard bottom-load polypropylene single filter housing. The cartridge filters were set up as a single assembly and fed from a stainless steel blowcase.

Larger samples which contained significant amounts of cake were filtered by gravity flow through a 1 micron polypropylene multilayer industrial bag filter, such as a Filtration Group P-1-MBP-12-US filter, supported above a stainless steel drum.

## 5.7 HEMICELLULOSE SEPARATION

Hemicellulose was prepared from filtered weak black liquor by direct precipitation with diluted sulfuric acid. In a typical preparation, ~ 10 L of black liquor was placed in a 14-18 L wide mouth polyethylene bottle and stirred using a Lightnin LabMaster mixer. A 1:4 dilution of concentrated sulfuric acid was added dropwise. The pH was monitored using an Orion model 710 pH meter with a combination electrode. Trace amounts, typically 10-30 ppm of antifoam and food-grade flocculants were added during and after precipitation. At pH 9.8-10.0, the stirring was stopped and the precipitate was allowed to settle. After settling, the hemicellulose precipitate was filtered and refrigerated. Lignin was precipitated from the filtrate.

## 5.8 LIGNIN PRECIPITATION

Lignin was prepared from filtered weak black liquor (or hemicellulose stripped black liquor) by direct precipitation with diluted sulfuric acid. In a typical preparation, ~ 10 L of black liquor was placed in a 14-18 liter wide mouth polyethylene bottle and stirred using a Lightnin LabMaster mixer. A 1:4 dilution of concentrated sulfuric acid was added dropwise. The pH was monitored using an Orion model 710 pH meter with a combination electrode. Trace amounts, typically 10-30 ppm of antifoam, commercial beta glucosidases, and/or food-grade flocculants were added during and after precipitation. At pH 3.5, the stirring was stopped and the precipitate was allowed to settle. Lignin gel was then desalted or filtered and desalted.

## 5.9 LYOPHILIZATION

Individual frozen aliquots were lyophilized in a Refrigeration for Science #5006 lyophilizer until dry. They were removed from the lyophilizer and promptly sieved to pass 30 mesh using a 2-dimensional stroke to remove any minor contaminants. Static was minimized during sieving to prevent clumping. The lignin was then stored in sealed bottles.

## 5.10 MELT-BLOCK EVALUATIONS OF FIBER EXTRUDABILITY

Fiber formation in lignin and lignin-blend samples was used as a screening technique to determine initial spinning conditions and spinnability. Small samples, typically 0.1 to 0.5 g, were weighed into 10 - 12 mm diameter 75 to 100 mm glass test tubes and mixed. The tubes were placed in a pre-heated aluminum block and the temperature was gradually raised until melting occurred or until the sample

visibly decomposed or charred. If the sample melted, a wood applicator stick was used to stir the mixture and draw up fibers.

At temperatures  $< 165\text{ }^{\circ}\text{C}$ , a conventional heating block assembly, with shield, was used to contain the aluminum block. At temperatures  $> 165\text{ }^{\circ}\text{C}$ , the block was placed on a heated stirrer, surrounded with a stainless steel cylinder, and the temperature controlled by a Dynasense MK II controller with a thermal probe.

As needed, an inert gas blanket was maintained within the stainless steel cylinder.

## 5.11 PH

Sample pH values were determined using an Orion Model 710 pH meter with a standard combination electrode. Prior to use, the pH meter was calibrated following the manufacturer's procedure. During use, readings were taken only after the pH reading became steady as indicated by the meter.

## 5.12 POWDER X-RAY DIFFRACTION

Graphitized fiber specimens were prepared by making a slurry mixture of sample powder and methanol and spreading the slurry on a zero background plate. Room temperature x-ray powder diffraction measurements were conducted using a Scintag PAD V vertical  $q/2q$  goniometer with CuK $\alpha$  radiation (45 kV and 40 mA) and a Si(Li) Peltier-cooled solid state detector. The data were collected as step scans, with a step size of  $0.02^{\circ} 2q$  at a count time of 1 second/step between  $10$  and  $70^{\circ} 2q$ . The ambient temperature during data collection was  $298 \pm 1\text{ }^{\circ}\text{K}$ .

## 5.13 SIEVING

Sieving was performed using a full-height VWR Scientific stainless steel 30 mesh screen with stainless top and pan. The sieve was shaken using a 2-dimensional motion to ensure that any fibrous contaminants were removed. If it appeared necessary, lyophilized lignin lumps were reduced in size using a glass mortar and pestle.

## 5.14 SOLID STATE NUCLEAR MAGNETIC RESONANCE

Solid-state NMR spectra were recorded on a Bruker MSL 100 Spectrometer operating at 2.35 T. Conventional  $^1\text{H}$ - $^{13}\text{C}$  cross polarization, magic angle spinning (CP/MAS) experiments were used with a proton rf field of 50 kHz for  $^1\text{H}$  excitation, spin lock and dipolar decoupling. The CP contact time was 2.5 ms for all materials. FIDs (1K data points, 15 kHz spectral width) were acquired with quadrature detection, zero filled to 8K, and smoothed (25 Hz, 1 ppm line broadening). The 600 ppm frequency domain spectra have 3.7 Hz/point. Carbon chemical shifts are expressed on the TMS scale:  $\delta$  (TMS) (0 ppm). The methyl resonance of hexamethylbenzene ( $\delta$ ) 17.3 ppm) was used as secondary chemical shift reference. Dipolar dephasing experiments were performed by inserting a 40  $\mu\text{s}$  delay after the contact time and before the acquisition time in the standard CP/MAS experiment (Alla and Lippmaa, 1976)

## 5.15 SOLUTION NUCLEAR MAGNETIC RESONANCE

Samples ( $\sim 100\text{ mg}$ ) were dissolved in 0.5 ml DMSO- $d_6$  or  $\text{D}_2\text{O}/\text{NaOD}$  mixtures. Solution phase  $^{13}\text{C}$  and  $^1\text{H}$  NMR were performed using a Bruker MSL-400 wide-bore multinuclear nuclear magnetic resonance instrument at  $60\text{ }^{\circ}\text{C}$ .

## 5.16 THERMOGRAVIMETRIC ANALYSIS

Thermogravimetric analysis was performed using either a TGA 2050 or 2950 (high resolution). A 20 mg sample was weighed into an open platinum pan. The samples were heated in an inert gas (helium or argon) purge. Weight loss was analyzed at 10 degrees per minute up to 250 °C and held at 250 °C for 25 minutes. In some cases, high resolution dynamic mode analysis was used to measure weight loss up to 900 °C.

Where mass spectrographic analysis was performed during thermogravimetric analysis, a Balzers Thermostar™ was used to analyze evolved gases for species between 1 and 100 amu.



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