3. LOW-COST CARBON FIBER

A. Low-Cost Carbon Fibers from Renewable Resources

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Objective

- Carbon-fiber resin composites could greatly decrease the weight of passenger vehicles resulting in substantial increases in fuel efficiency. However, carbon fiber is currently too expensive for large-scale use in production vehicles. This project will demonstrate methods for the use of new precursor materials, largely based on renewable resources, which decrease cost and increase availability of carbon fiber that meets the performance and price requirements of the automotive market. The project goal is to identify at least one precursor formulation, comprising both renewable and recycled materials, which could be used to produce industrial-grade carbon fiber at a cost in the range of $3-5 per pound. In addition to precursor, cost savings will also be achieved through improved processing methods and more efficient energy utilization.

Approach

- Provide the data needed to scale up process steps to industrial levels and to consistently achieve desired fiber properties on an industrial scale.
- Develop the technical knowledge base required to support production of lignin-based, carbon-fiber precursor feedstock on an industrial scale, comprising:
  - Lignin isolation to obtain the best molecular weight, low-volatile, and low-salt content material.
  - Spinning technology, including production die structure, plasticizers, and nucleating agents.
  - Oiling and sizing technology.
  - Selection of appropriate polyesters.
  - Plasma treatment and sizing technology to make the fiber compatible with selected resin systems.
  - Properties and economics of carbon-fiber and composite systems.
- Scale and transfer the technology for the production of carbon-fiber precursors from lignin-blend feedstock:
  - Evaluate melt-extrusion properties of lignin-based feedstock at increasing scale using near-industrial equipment that can be readily obtained by fiber manufacturers.
  - Evaluate production of carbon fiber using research and pilot-scale production lines.
  - Evaluate mechanical and composite compatibility properties of graphitized lignin-based fibers.
  - Collaborate with partners to evaluate, define and develop process metrics, economics and standards.
- Transfer technology and intellectual property for the production of lignin-based carbon fibers to industry.

Accomplishments

- Proof-of-concept demonstration of the melt extrusion of 28-filament tow of lignin-based fibers was made. This validated selected compositions, processing methods, and testing technologies. It also provided a basis for understanding the process improvements required for large-scale manufacture of lignin-based, carbon-fiber precursor.
- Significant amounts of 28-filament tow were successfully spun at the University of Tennessee at Knoxville (UTK) using a two-step process. No sticking problems were apparent and fiber diameter was reduced from ~ 45 microns to ~15 microns with an apparent improvement in mechanical properties.
- Preliminary data indicate that carbon-fiber yields of 50% are feasible, consistent with lignin carbon content.
- Preliminary evaluation of a plasma surface treatment (plus silanation) of lignin-based, carbon fibers indicated a significant improvement in fiber-resin bonding compared to conventional carbon fibers.
- Small epoxy-resin composites made using carbon fibers produced from 28-filament lignin-based fiber tow, exhibited target composite mechanical properties.
- Identified sources of volatiles within lignin and developed purification methods which selectively remove residual carbohydrates, one source of volatiles, in a single process step.
- Developed potential process-control technologies for the production of low salt content (low-ash) lignin.
- Developed preliminary specification for lignin precursor and demonstrated bench-scale methods to produce lignin meeting the specification.

Future Direction

- Methods for production of industrial-quality carbon fibers from lignin feedstocks will be developed. Work will include:
  - Optimization of lignin isolation conditions to achieve the target specifications with respect to contaminant content (salts, carbohydrates and particulates) and provide the best molecular weight.
  - Identification of conditioning and spinning processes which remove volatiles both prior to and during precursor fiber production.
  - Selection of plasticizers and nucleating agents for melt-spinning of lignin-based precursor materials.
  - Design of spinning dies to provide the best internal structure of the fiber.
  - Development of techniques for spooling and oiling lignin-based precursor fibers at each step.
  - Identification of methods for surface treating and sizing the surface of carbon fibers to improve compatibility with proposed resin systems. This is particularly critical for chopped- fiber composites.
- Collaborate with industrial, government and academic partners to:
  - Address raw fiber production issues (lignin, preconsumer recycled polyesters, plasticizers, spinning and winding technologies, process scale-up).
  - Demonstrate carbon-fiber production from lignin-based, multifilament tow using a pilot-scale industrial process line.
- Transfer the low-cost carbon-fiber production technology to industry.

Introduction

The use of carbon-fiber resin composites would greatly reduce the weight of passenger vehicles, resulting in substantial increases in fuel efficiency. However, carbon fiber is presently too expensive and too limited in production capacity to support large-scale use in production vehicles. To address these impediments to the commercial use of carbon-fiber in the automotive industry, this project is directed to the development of methods for the production of carbon-fiber feedstock from high-volume, low-cost materials based on renewable resources and recycled materials. The goal is the development of technologies which will reduce precursor and processing costs, and which could be implemented to produce low-cost carbon fiber on a scale sufficient to support its large-scale use in passenger vehicles. Use of renewable and recycled materials also decreases sensitivity of carbon-fiber cost to changes in petroleum production and energy costs.

Proof-of-concept production of single fibers from a variety of natural, renewable and recycled materials available in high volume was demonstrated. Single-fiber, melt-spun from blends of Kraft hardwood lignin (an inexpensive, high-volume, wood-pulping byproduct) and small amounts of routinely recycled polyolefins and polyesters, could be processed using conventional stabilization (oxidizing atmosphere), carbonization, and graphitization (inert atmosphere) furnace technologies to yield carbon fibers. Carbon-fiber mechanical properties improved when the fibers were stretched during thermal treatment. Graphite content, as measured by x-ray diffraction, increased with increasing temperature of treatment. Carbon-fiber yield from the lignin-based feedstocks was ~ 50%. Physically, the fibers were dense, smooth-surfaced, and uniformly round.

Larger quantities of a lignin-polyester (recycled) feedstock were melt-spun as a multifilament tow (4-28 fibers) using a 27-mm-diameter twin-screw Leistritz extruder at the University of Tennessee at Knoxville (UTK) to meet a September, 2003 composite preparation and testing milestone. This Leistritz machine is the smallest member of a line of commercial melt extruders, and can be used to obtain data to design larger-scale, melt-spinning equipment. Meeting the milestone showed that:
1) lignin-polyester blend can be melt-extruded as a small tow using near-commercial-scale melt-spinning equipment; 2) resin-fiber composites made using the graphitized lignin-polyester-based carbon fibers exhibited normal fracture patterns; and
3) although very smooth surfaced, lignin-polyester-based carbon fibers can be plasma treated and silanated to provide good fiber/resin adhesion.

Analysis of the samples obtained indicated that bubbles and inclusions were the major flaws in the lignin-polyester-based carbon fibers. Flaws are known to decrease the strength of carbon fibers and are typically the initiation point for fiber breakage. Inclusions were typically natural particulates associated with wood and the pulping process, namely, sand, cellulose, and water. Bubbles were caused by water trapped in carbohydrates co-precipitated with lignin during conventional processing of lignin for commercial products. Methods were developed to mitigate these problems. Additionally, methods for controlling salt content in the fibers and for pre-filtering black liquor prior to lignin isolation were developed.

Project Deliverables

Goal: By the end of this multi-year program, production of one or more environmentally-friendly, economically-feasible, carbon-fiber precursors will be demonstrated and transfer of production technologies and related intellectual property to industry initiated.

In FY 2004, major milestones, including the initial tests of the effect of lignin molecular weight on fiber properties were completed on time.

FY 2005, milestones included development of a lignin feedstock specification that will facilitate industrial production of carbon fibers meeting program goals (5/2005) and establishment of basic rheology for extruding and winding lignin-fiber bundles with improved handling characteristics (9/2005).

FY 2006 milestones comprise production of significantly larger quantities of lignin-based carbon fiber, with near-target mechanical properties, needed to demonstrate use in automotive composites. Also, demonstration by a pulping company of the ability to produce, in a cost-effective manner, purified lignin material meeting the specifications for ash, particulate, and volatile contents.

Planned Approach

Production of industrial-grade carbon fibers from a radically new type of feedstock requires the simultaneous development of methods for feedstock recovery, characterization, preparation, blending, spinning, handling, and spooling in addition to the thermal processing, stretching/orientation, oiling, and sizing technologies required for conventional fibers. These are combined with evaluations of fiber quality and suitability for use in composites.

First priority was placed on developing cost-effective, environmentally-friendly, precursor-fiber preparation and thermal processing conditions. Carbonization of lignins, which typically do not contain aromatic nitrogen, does not result in the cyanide emissions typical in the processing of acrylic fibers. Lignins can also be melt-spun or dry-spun, which eliminates the petrochemical solvents used in producing raw acrylic fiber.

Use of modern thermal processing techniques, such as hot-stretching and controlled-atmosphere treatment, will be evaluated to improve the properties and yield of carbon fiber from the lignin feedstock.

Industrial partners have worked with project staff on the selection of polymers to blend with lignin, strategies for production of cleaner (purer) lignin, and spinning of fiber. In the later stages of the project, quantities of lignin-based, carbon-fiber tow sufficient for composite fabrication will be produced using a pilot-scale fiber production line.

Transfer of project technology, including intellectual property, is planned.

Lignin Feedstock Quality

Lignins are inexpensive, high-volume forest- and biomass- industry byproducts. A number of different commercial processes produce lignin streams from which carbon fibers could be manufactured, including: 1) alkaline pulping processes (Kraft and soda); 2) ethanol production from wood and other biomass; and 3) organosolv pulping. The ORNL research work has been focused on alkaline pulping liquors because these represent about 80% of the total domestic pulping industry. In both processes, liquid streams containing lignin are concentrated and burned to provide both process energy and pulping chemicals recycle.

Historically, only two Kraft mills worldwide have isolated dry lignin for commercial sale as chemicals, but all Kraft pulp mills could, in principle, isolate lignin as a potential precursor material for carbon-fiber production. This is accomplished by acidification of black liquor to form a loose gel which is recovered as a precipitate, washed, dried, and marketed for use in many high volume applications, including dyestuff dispersants, asphalt emulsifiers, concrete additives, lead-acid battery plate extenders, soil micronutrients, and metallurgical mold releases. These applications are, however, relatively insensitive to the presence of contaminants such as particulates, cellulose fibers, water, volatiles, and inorganic pulping chemicals entrained during lignin precipitation.

Production of a cost-effective, industrially-feasible, lignin-based, carbon-fiber feedstock will require the development of methods to effectively remove salts, particulates, and volatiles from the crude lignin isolated from conventional pulping operations. The methods developed at ORNL, which typically involve purification of the liquid streams from which lignin is recovered, are discussed below. Using these methods, it was possible to produce very high-quality lignins from alkaline pulping liquors.

It is also possible to extract low-salt-content, low-volatile-content lignins using novel pulping technologies that are emerging on a commercial scale. Novel biomass-derived lignins produced by project partners were evaluated for potential use as carbon-fiber precursor materials.

Evaluation of Purified Lignins from Conventional Alkaline Pulping

Alkaline pulping technologies, which include Kraft pulping ($NaOH + Na_2S$) and soda pulping ($NaOH$), dominate domestic production of pulp for use in paper products. In alkaline pulping, wood chips are contacted with the alkaline solution and cooked at high temperature and pressure. At the end of the cooking cycle, a lignin-rich stream, “black liquor,” is separated from the wood pulp. Black liquor is concentrated by evaporation and burned to recover the pulping chemicals (>99% recovery) and to provide energy for the pulping and paper production operations (some mills include power co-generation, providing a net energy gain).

Because the process uses wood chips, alkaline pulping is a year-round industry, with the potential of providing a large volume of lignin for use as carbon-fiber feedstock. To put this into perspective, approximately 10% of the lignin passing through alkaline pulping operations, could, if used for carbon-fiber production, supply enough carbon fiber to replace approximately half of the ferrous metals used in passenger transport vehicles.

It is important to keep in mind, however, that pulp and paper mills operate under demanding economic and environmental standards. For example, mills must meet Environmental Protection Agency Cluster Rule emission and effluent standards. To apply the technology developed in this project to the production of enough purified lignin to support widespread automotive use of carbon fiber, the lignin isolation/purification process technology must be tailored to mill needs.

Commercial lignin products isolated from black liquor typically contain a variety of solid materials (sand, diatoms, cellulose fibers) and chemicals (salts, carbohydrates, wood extractives). In order for this lignin to be used as a feedstock for production of carbon fibers, which are typically <10 micron in diameter, solids >1 micron in diameter must be removed. This can be accomplished by micron-scale filtration of the black liquor prior to lignin isolation. Additionally, carbohydrates, which sorb water, can be precipitated and removed by filtration prior to precipitation of the lignin itself. Using commercial filter media, selectively precipitated and coagulated carbohydrates can be removed from alkaline pulping liquors in a single step.

Thermogravimetric analysis (TGA) curves for desalted, carbohydrate-stripped Kraft and low-sulfur soda hardwood lignins are shown in Figure 1, revealing that these lignins exhibited low volatiles content (<5% weight loss at 250°C). Furthermore, as shown by the solution nuclear magnetic resonance (nmr) spectroscopy data in Figure 2, the carbohydrate-stripped Kraft and soda hardwood lignins contained only very small amounts of residual carbohydrate material.

Biomass Lignins from Ethanol Production

One of the emerging leading processes for production of ethanol from biomass involves: 1) pretreating the biomass by alkaline or organosolv pulping; 2) hydrolyzing the cellulose fibers to sugars; and 3) fermenting the sugars to ethanol. The mills are being deployed to meet Kyoto-treaty requirements for production of fuels and chemicals

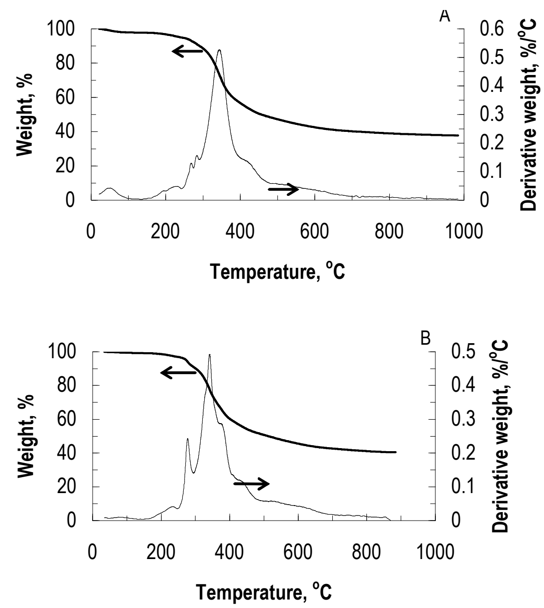

Figure 1. Thermogravimetric analyses of desalted, carbohydrate-stripped, soda-anthraquinone (A) and Kraft (B) hardwood lignins.

from biomass. Operators of these mills are interested in developing markets for the significant quantities of lignin byproduct which they currently produce. Although this process is not being tested in domestic bioethanol plants, increasingly high petroleum prices could make these biomass ethanol processes attractive in the U.S. Woody biomass wastes have good year-round availability. A fraction of the ethanol produced from the cellulose pulp is used in the pulping process, and the overall process energy is supplied by burning part of the lignin precipitated during ethanol recovery and recycle.

Granit, a project partner, started pulping-based ethanol production mills this year, and is already able to supply about 10,000 tons/year of lignin, i.e., enough precursor material to support the equivalent of 20% of the worldwide production capacity of carbon fiber. Similarly, Lignol Innovations has started construction of an ethanol-organosolv pulping test facility in which conversion of wood residues, such as sawdust and insect-damaged trees, to alcohol is being evaluated. Deployment of this biomass technology is accelerating because the ethanol fuel produced from the process plays a key part in Kyoto-treaty compliance strategies for many countries. In the U.S., it would provide an attractive opportunity for reuse of smaller or older non-profitable pulp mills.

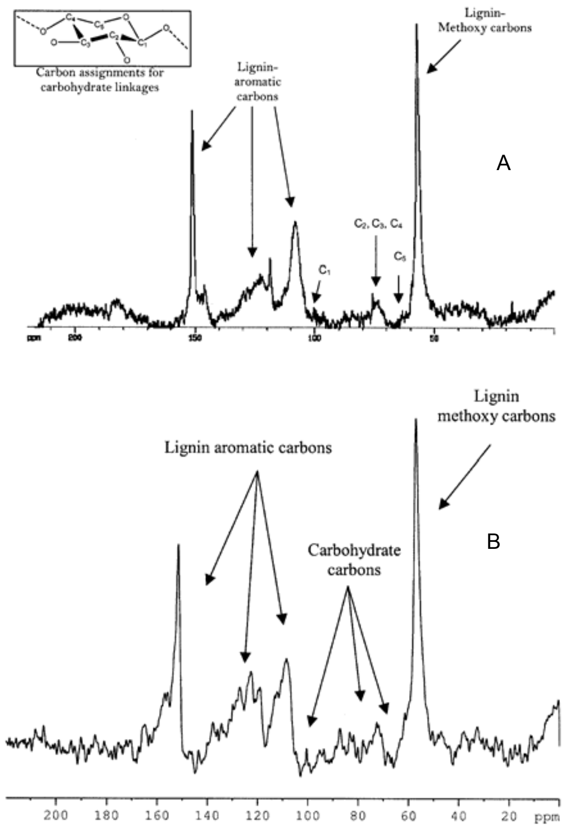

Figure 2. Nuclear magnetic resonance spectra of desalted, carbohydrate- stripped, Kraft (A) and soda-anthraquinone (B) lignins.

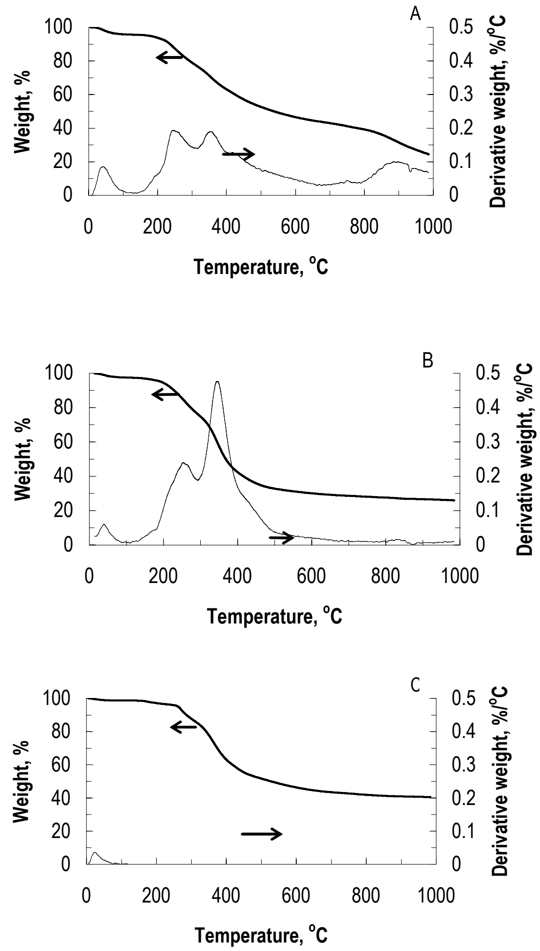

Figure 3. Thermogravimetric analyses for Sarkanda grass (A), flax (B), and Lignol Innovations (C) lignins (derived from biomass ethanol production).

Because the lignins in biomass feedstocks, such as grass or flax, are different in composition and chain length from those typical of wood-derived lignins, their basic properties have been evaluated in this project.

In Figure 3, TGA curves are shown for three lignins derived from biomass ethanol production: Sarkanda grass (“Ecobind 100SA140”); flax (“Ecobind100FA”); and a Lignol Innovations experimental lignin produced from softwood sawdust. From the TGA curves and data in Table I, it is apparent that the Lignol softwood lignin showed potential as carbon-fiber feedstock, at least on the basis of its low volatile content (3%) and low ash content (0.2%), which almost met the target specification (0.1%). The grass and flax lignins exhibited higher volatile contents of 8 and 10%, respectively, about twice the target specification of <5%. Both also exhibited lower residual carbon contents (< 30% at 1000°C) compared to commercial Kraft hardwood lignin (40%). In keeping with commercial, alkaline-pulped, softwood-lignin products, the Lignol softwood lignin exhibited a carbon content of ~40%. Furthermore, as shown by the nmr spectroscopy data in Figure 4, the Lignol experimental softwood lignin contained very low levels of residual carbohydrate.

Table 1. Ash and volatiles in biomass lignins

Lignin	Ash, %	Volatiles, %
Lignol Innovations	0.2	3
Flax	0.6	10
Sarkanda grass	3	8

A major difficulty associated with biomass lignins would be variability in lignin properties due to changes in either the type or condition of biomass feedstock to the pulp mill. Additionally, some

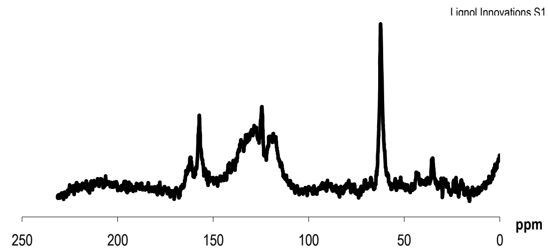

Figure 4. Nuclear magnetic resonance spectra of Lignol Innovations ethanol organosolv lignin.

biomass feedstocks, such as rice straw, contain significant concentrations of insoluble inorganic materials, such as silicates.

The ash content of the Sarkanda grass lignin was 3%, comparable to that of commercial Kraft hardwood-lignin products. Almost all of this ash material could be removed as base-insoluble, filterable particulates. The flax lignin exhibited a lower ash content of 0.6% and, as already noted, the Lignol experimental softwood lignin exhibited a notably low ash content of 0.2%, which would facilitate its purification for use as a carbon-fiber feedstock. Microscopic examination revealed that the particulates in all three of the biomass-ethanol lignins predominantly comprised cellulosic residues from the pulped biomass.

Biomass-lignin production technology is, for the most part, being developed outside of the US as part of the effort to meet Kyoto-treaty compliance goals. However, the low cost and potentially high volume of ethanol production from pulped wood wastes and annual biomass could drive the use of these two technologies into the U.S. market. Additionally, both the Granit and Lignol processes could be adopted by Mexican or Canadian companies with near-border plants. Furthermore, the technologies could be retrofitted into older or smaller pulp mills, which would significantly increase the availability of domestic commodity lignin.

Solvent Extraction Lignins

Although fractions of commercial lignins are soluble in some solvents, carbohydrates and salts are relatively insoluble in both alcohols and ketones. Therefore, MeadWestvaco, a project partner, felt that it should be possible to produce low-salt, low-carbohydrate lignins by solvent extraction of commercial dry lignin. Several such lignin samples were produced for evaluation.

The ash and volatiles contents of these materials are shown in Table 2. As shown by the TGA data in Figure 5, there was considerable variation in the thermogravimetric behavior of the different solvent-extracted lignins evaluated. Although most of the samples showed relatively high volatile contents at temperatures well below probable melt-spinning temperatures, the LPX-83777-OID sample exhibited low volatile content (4% at 250ºC) and a high carbon content (40% residue at 1000ºC). Nuclear magnetic resonance spectra of the samples also showed considerable variation in carbohydrate content, with the LPX-8377-OIA sample exhibiting particularly low carbohydrate content.

Ash and particulate levels in the solvent-extracted samples were also variable. As expected for this lignin source, most of the samples had ash levels around or below 1%. However, the LPX-377-61-M sample exhibited a high ash content of 2.6%, but nevertheless still comparable to that of commercial lignin products.

With optimization, solvent-extracted lignins could potentially be useful carbon-fiber feedstocks or feedstock constituents.

Table 2. Solvent extracted lignin ash and volatiles content

Lignin	Ash, %	Volatiles, %
LPX-8377-OID	0.3	11.2
LPX-8377-61-M	2.6	14.5
LPX-8377-OIA	0.2	8.5
LPX-8393-48	0.6	9.2
LPX-8393-49	0.2	8.6
LPX-8393-50	0.1	2.5
LPX-8393-49	0.1	4.6

Lignin Specification

Industrial partners requested that ORNL develop an initial specification for lignin to be used as a precursor material for the production of carbon fibers. The preliminary specifications established are based on data for commercial pitch-based carbon fiber and on the requirements for the twin-screw extrusion of textile fibers, such as polyesters, at 250°C. The lignin specifications comprise:
< 1000 ppm ash, < 500 ppm non-melting

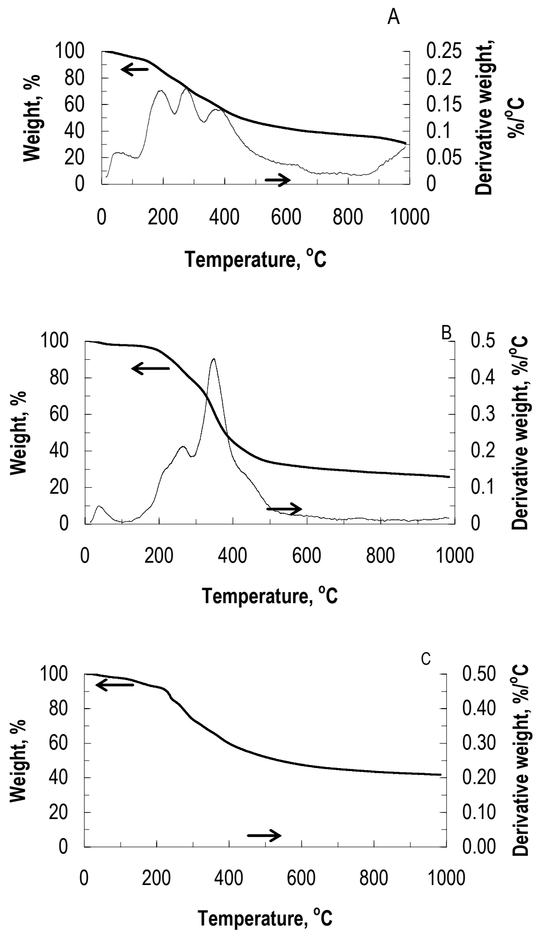

Figure 5. Thermogravimetric analyses of solvent extraction lignins LPX-8377-61-M (A), LPX-8393-48 (B), and LPX-8377-OID (C).

particulates (e.g., cellulosic fibers), <5% volatiles by 250°C, and the removal of all particulates >1 micron in size.

The volatiles and non-melting particulate-content requirements were developed to match the standard requirements for high-temperature textile melt-spinning. The specifications for ash and particulates contents were set on the basis of early pitch fiber data, with the objective of minimizing inclusions and defects which weaken carbon fibers. These specifications have been met with lignins purified at ORNL using a bench-scale process.

With increasing experience and better understanding of the factors that influence lignin melt-spinning, the specifications will be extended to include relevant physical and chemical properties of lignins deemed suitable for carbon fiber feedstocks.

Future Directions

Production of lignin-based multifilament tow (28 filaments) and successful use of this material in small resin-fiber composites was demonstrated in FY 2003. The project was re-proposed and extended to permit evaluation of methods for producing high-quality, lignin-based feedstocks for low-cost production of automotive carbon-fiber resin composites.

Having established proof-of-concept, the project staff is systematically addressing the technical issues required to produce industrial-grade, lignin-based carbon fiber at prices and properties meeting automotive need. Because domestic lignins evaluated by this process are derived from alkaline (Kraft and soda) pulping, a major concern has been the need to develop an understanding of the levels and types of contaminants in the lignins which are detrimental to multifilament spinning. This work has been paired with efforts to develop cost-effective, scaleable process technology for selective removal of carbohydrates, non-melting particulates, and ash from lignin.

Using project-developed technologies, it has been possible to consistently produce bench-scale quantities of purified lignin material which meets the preliminary specifications. The specifications will be upgraded and broadened as requirements for a satisfactory precursor material are better defined, e.g., to include physical and chemical properties relevant to blending and melt-spinning.

The techniques for precipitation and purification of lignin are expected to evolve and improve. The goal is an industrially-practicable method which permits one-step removal of better than 90% of the hemicellulose carbohydrate in black liquor prior to lignin precipitation. The carbohydrate material isolated by this means could potentially be reused in paper manufacture if only small amounts of flocculants are used and if the carbohydrate structure is preserved. Incorporating the recovered carbohydrate material (hemicellulose) into paper would enhance the mechanical properties of the paper, as well as offset lignin cost. Alternatively, the hemicellulose carbohydrate could be returned to the black-liquor recovery boiler for energy and chemical recycle.

Efforts in FY 2006 will be focused on the development and demonstration of a commercially viable process for the production of lignin-based precursor material meeting the specifications established for carbon-fiber production. Working in partnership with Pacific Northwest National Laboratory (PNNL) and MeadWestvaco (MWV), a combinatorial chemistry approach will be used to screen a large permutation of process conditions to establish the most cost-effective means of producing purified, melt-spinnable lignin on a commercial scale. Economic analyses will be an integral part of the effort to ensure that the lignin could be produced at a cost consistent with the target for finished carbon fiber. In addition to establishing commercially-viable lignin processing technology, the deliverable from the proposed PNNL/ORNL/MWV program of work is several hundred pounds of on-spec lignin precursor material that can be used to produce carbon-fiber tow for composite testing (in mid-FY 2007).

Studies on biomass-derived lignins will continue, but with reduced emphasis. Biomass utilization is an emerging business, and it is still too early to gauge its potential for commercial success. Nevertheless, if the Granit and Lignol processes for ethanol production from biomass materials are commercially successful, worldwide production of dried biomass lignin could increase by more than 50,000 tons per year, each year. On the downside, shipping costs could be too high for its cost-effective use as a carbon-fiber precursor material. In this context, the major question is whether and to what extent pulp-based biomass ethanol production will become commercially feasible in the U.S., as well as near-border areas of Mexico and Canada.

Die designs for spinning of lignin-based fibers will be further evaluated. Initial test data indicated that the high-shear dies similar to those used for spinning pitch-based feedstocks create a more uniform internal structure in the raw fiber. Spinning parameters, including rheology of the blend, will be optimized for multifilament production.

Production techniques that provide high-quality, handleable, spoolable, raw lignin-based fiber are required, and will be evaluated. The techniques include selection and evaluation of plasticizers and nucleating agents, raw fiber coatings and oils, and spooling.

Following carbonization/graphitization of the lignin-based fiber, the carbon fiber must be surface treated and sized to increase its compatibility with a given resin system. Fiber-resin compatibility is particularly critical in automotive applications, because the current program plan calls for use of chopped, rather than woven or wound fiber.

As the project work progresses and challenges are resolved, project partners expect to become increasingly involved in scaling up the processes with respect to lignin production and purification, and to melt-spinning and thermal processing of the fibers.

Partnerships

A number of partners have been instrumental in helping to develop the lignin-based, carbon-fiber technology. During the early part of the project, North Carolina State University spun a variety of lignin-polymer blends into single fibers, which were used for the initial feasibility evaluations. Similarly, the University of Tennessee (Knoxville) produced significant quantities of multifilament tow for project use.

The participation of several wood-pulping and biomass companies has greatly improved project access to a variety of different lignin materials. Since its inception, the project has benefited from the participation of MeadWestvaco Corporation, which provided hundreds of pounds of softwood and hardwood lignin products for project use, including a wide variety of research lignins. MeadWestvaco is currently the only producer of lignin products derived from alkaline pulping (specifically the Kraft process).

Later, in FY 2004, the project attracted interest and participation from three other pulp and paper companies: Weyerhaeuser, Granit, S.A.; and Lignol Innovations. The participation of these companies has broadened the variety of lignins available to the project, including biomass-derived lignins which exhibit lower volatile contents.

Conclusions

The project was re-proposed in FY 2003 and, in FY 2004, re-tasked to focus on larger-scale production of carbon-fiber feedstock. Relationships with MeadWestvaco Corporation, Eastman Chemical Company, and Granit, S.A., were formalized. A third paper company, Weyerhaeuser, informally furnished samples of black liquors from which lignins were isolated for melt-spinning evaluation.

Initial evaluations of the melt-spinning of small lignin fiber tow demonstrated the feasibility of producing precursor fibers by melt-spinning and that carbon fibers could be produced from the lignin fiber, successfully surface treated, and used to prepare small resin composites. However, it was clear from an examination of the carbon fibers that the contaminants inherently present in commercial Kraft lignin products had to be reduced. This was necessary to both improve melt- spinnability of the lignin precursor fiber and to decrease the subsequent contaminant levels (particulates and volatile materials) in the carbon fibers themselves, which caused small defects that adversely impacted mechanical properties.

During this period, purification technologies were demonstrated on a lab-scale. Carbohydrate, in the form of cellulosic polysaccharides coprecipitated with lignin, was found to contribute significantly to evolution of gas during lignin fiber spinning and also to production of char if held for long periods above 200°C. Carbohydrate-stripped lignins showed significantly reduced volatile evolution between 150 and 250°C.

Initial technical evaluations indicate that the carbohydrates recovered prior to lignin separation and purification could be simply incorporated into cellulose pulp with significant increases in tensile and burst indices of the paper (+15%). Recovery of this carbohydrate, primarily hemicellulose, could provide a significant revenue stream to offset the cost of lignin production.

Additionally, preliminary specifications were established for lignin precursor suitable for melt-spinning into fiber. The specifications, which define acceptable levels of ash, particulates, and volatiles, were based on a combination of the specific requirements for spinning lignin fiber tow and the specifications used for commercial production of pitch-based carbon fibers. Small amounts of lignin purified on a bench scale consistently met the specifications.

Overall, using a combination of desalting and carbohydrate-stripping techniques, it has been possible to significantly improve, by >75%, the strength and stiffness of lignin-based carbon fibers produced as single filaments. A 7 kg batch of purified Kraft hardwood lignin material was produced to support further efforts to demonstrate multifilament spinning and rewinding.

Presentations/Publications/Patents

W. L. Griffith; A. L. Compere; and C. F. Leitten, Jr., 2004. “Lignin-Based Carbon Fiber for Transportation Applications”. In *Proceedings of the 36th International SAMPE Technical Conference*, San Diego, CA, 15-18 November, 2004. Covina, CA: Society for the Advancement of Material and Process Engineering. (CD, no paper or page number.)

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Invention Disclosure: “Method for Improving Separation of Carbohydrates from Wood Pulping and Wood or Biomass Hydrolysis Liquors”; William L. Griffith, Alicia Compere, and Carl F. Leitten, Jr. Submitted on July 19, 2005; elected for patent application on August 16, 2005. Lab Docket No. 1300001598. DOE No. S-105, 200.