RECENT PROGRESS IN PRODUCING LIGNIN-BASED CARBON FIBERS FOR FUNCTIONAL APPLICATIONS

Ryan Paul, Deanna Burwell, Xuliang Dai
GrafTech International Holdings Inc.
982 Keynote Circle
Brooklyn Heights, OH 44131

Amit Naskar, Nidia Gallego, Kokouvi Akato
Oak Ridge National Laboratory
Oak Ridge, TN 37831-6053

ABSTRACT

Lignin, a biopolymer, has been investigated as a renewable and low-cost carbon fiber precursor since the 1960s. Although successful lab-scale production of lignin-based carbon fibers has been reported, there are currently not any commercial producers. This paper will highlight some of the known challenges with converting lignin-based precursors into carbon fiber, and the reported methods for purifying and modifying lignin to improve it as a precursor. Several of the challenges with lignin are related to its diversity in chemical structure and purity, depending on its biomass source (e.g. hardwood, softwood, grasses) and extraction method (e.g. organosolv, kraft). In order to make progress in this field, GrafTech and Oak Ridge National Laboratory are collaborating to develop lignin-based carbon fiber technology and to demonstrate it in functional applications, as part of a cooperative agreement with the DOE Advanced Manufacturing Office. The progress made to date with producing lignin-based carbon fiber for functional applications, as well as developing and qualifying a supply chain and value proposition, are also highlighted.

1. INTRODUCTION

The majority of carbon fiber produced today is used in the manufacture of high-performance composites. However, there are non-composite applications for carbon fiber, such as high-temperature insulation and filtration, which require a carbon fiber that is functional (non-structural) and low-cost. Because carbon fiber precursors represent approximately 50% of production costs [1], the development and commercialization of a low-cost precursor could speed up carbon fiber usage in high-temperature insulation, filtration, energy storage, and other industrial applications. However, currently there is a lack of proven low-cost precursors available, although there are considerable ones under development, including lignin.

Lignin, the biopolymer that is the glue in trees, has potential to be a renewable, abundant, and low-cost precursor. Lignin can be extracted from pulp and paper making and from biorefining, making it potentially available in very large quantities. Lignin-based carbon fibers are expected to have reduced energy demand and lower CO_2 emissions versus fibers from current precursors, since lignin is already polymerized. In addition, under certain conditions lignin can be melt spun, which is a lower cost process as compared with current precursor production methods [2].

In order to realize the potential of lignin, a number of barriers need to be overcome. For one, the diversity of lignin has precluded a single strategy for converting it into carbon fiber without process bottlenecks. Furthermore, the chemical structure of lignin has produced carbon fiber properties that do yet meet structural requirements, although they appear acceptable for functional applications [3]. Qualifying lignin-based carbon fiber for functional applications first should promote further advances in mechanical properties optimization. In addition, there is currently no supply chain for lignin carbon fiber as most research has been at lab scale, with little published work available on scale-up capability. For commercialization, a supply chain requires multiple scalable qualified lignin sources without process bottlenecks.

This paper will first provide a background on carbon fibers and the reason that lignin has been studied as a potential low-cost carbon fiber precursor, in addition to a summary of the challenges with lignin. Next, a literature review will be presented, focusing on the reported methods to improve lignin as a carbon fiber precursor. Finally, there will be a discussion on supply chain development, applications, and the current project between GrafTech and Oak Ridge National Laboratory (ORNL).

2. BACKGROUND

2.1 Carbon Fibers

Over 90% of carbon fibers produced today employ polyacrylonitrile (PAN) as a precursor, using wet or dry spinning to form the fibers [4]. PAN fibers typically have high tensile strength, which makes them suitable for high-performance composites. Mesophase pitch is used to make carbon fibers with high tensile modulus, and as such is also used for high-performance composites. For functional (non-structural) non-composite applications, isotropic pitch or cellulose precursors are often used to make carbon fibers. Isotropic pitch and cellulose carbon fibers have relatively low strength versus PAN or mesophase pitch carbon fibers partly due to their isotropic structure.

One of the current challenges is that PAN is derived from petroleum and is therefore a non-renewable resource that can be subject to petroleum supply and demand price instability. In addition, toxic (cyanide) gases are emitted during PAN processing. Furthermore, there are limited options to improve PAN fiber cost through energy efficiency or higher production volumes. A potentially lower cost route than wet or dry spinning is melt spinning, which requires a precursor that is meltable and possesses well-controlled molecular weight distribution. However, since 50% of the cost is in the precursor, ultimately lower costs precursors than PAN are needed, coupled with efficient conversion processes, to drive costs lower for industrial applications.

2.2 Lignin

Lignin is a heterogeneous biopolymer and is a component of biomass, along with cellulose and hemicellulose. Lignin’s role in biomass is often described as the glue that holds the internal structure of trees together. During pulp and paper making, and in a biorefinery, lignin is separated from cellulose and hemicellulose components by one of several industrial methods in use. Although cellulose has found many applications, to date lignin has not. There is an estimated 40-50 million tons per year of lignin currently produced, although only a fraction of that is separated out from the processing stream as a sellable product, and most of that is burned as fuel [5].

Part of the challenge is due to the diversity of lignin. The first source of diversity comes from the biomass. Lignin is composed of three main phenol monomer units, as shown in Figure 1, which are bonded together in a complex branched structure. Softwoods, e.g. pin and spruce, contain mostly coniferyl alcohol units (guaiacyl lignin). Hardwoods, e.g. oak, beech poplar, and birch, have more sinapyl alcohol units (syringyl lignin). Grasses contain mainly p-coumaryl alcohol units (graminaceous lignin). That is, the main differences among lignin from hardwood, softwood, and grasses are in the ratios of the different units and the branching and inter-unit linkages. However, due to the complexity of lignin chemistry, it is not possible to determine the exact structure of lignin with current methods, and this remains an active area of research.

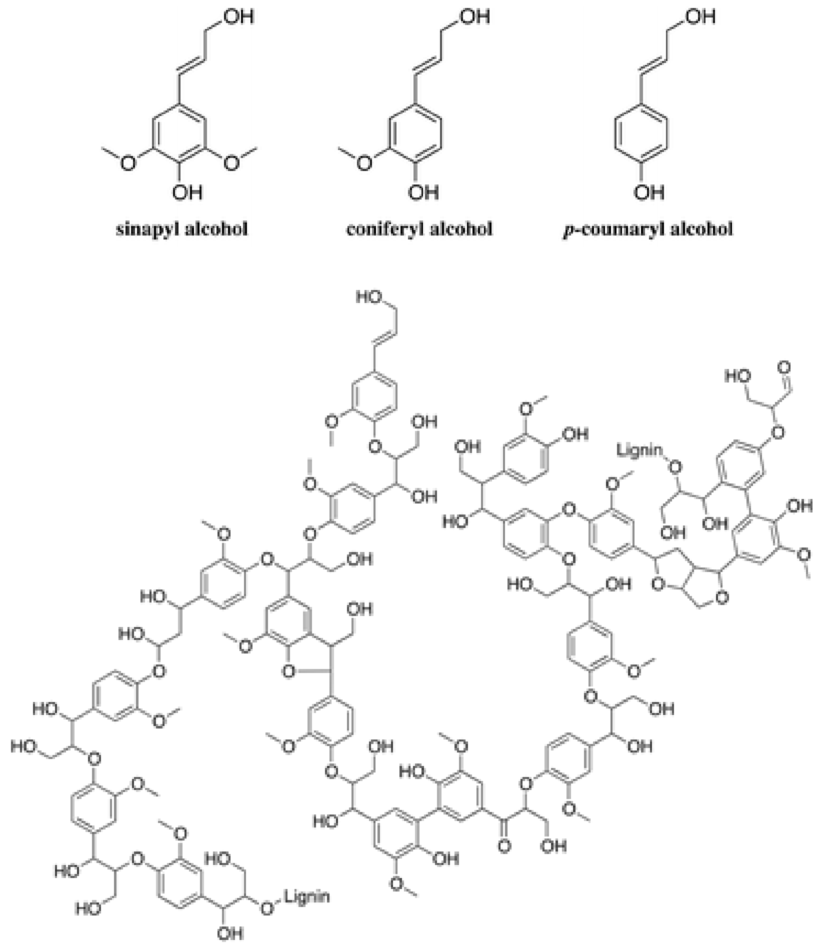

Figure 1. *Top*: The 3 basic phenol monomer units in lignin: sinapyl alcohol or syrin (left); coniferyl alcohol or guaiacyl lignin (middle); p-coumaryl alcohol or graminaceous lignin (right).

Adapted from [41]. *Bottom*: Representative heterogeneity in lignin polymer bonding and branching. Adapted from [42].

The second source of diversity comes from the extraction process. The kraft pulping process is currently the dominant process for extraction of lignin. However, it produces lignin that is relatively high in sulfur, which negatively impacts melt spinning. Lignin from sulfite pulping is called lignosulfonate, and due to the high sulfur content is not readily melt spinnable. Lignin from the organosolv process is high purity, which is desirable for melt spinnability, but organosolv lignin currently has very limited to no availability. Lignin from steam explosion is also high purity, but also has very limited availability.

Following extraction and drying, lignin is a brownish powder. For carbon fiber precursor production, the powder is first pelletized to facilitate the melt spinning process. Examples of lignin powder and pellets are shown in Figure 2.

Figure 2. Lignin powder (left) and lignin pellets (right).

2.3 Converting Lignin to Carbon Fibers

One proposed conversion route for lignin-based carbon fibers is shown in Figure 3; the process includes melt spinning, although there are other conversion routes. Raw lignin is obtained after lignin is extracted from one of the processes reported earlier, and can be from one of several biomass sources. After extracting, raw lignin needs to be treated, which at minimum is pelletization but can include drying, thermal or chemical treatment, and/or the addition of a plasticizer. Lignin is then melt spun into fiber, and for good spinning the lignin must have suitable molecular weight distribution and rheology. After spinning, the fibers are stabilized. The heating rate at which the fibers can be stabilized depends on the molecular weight distribution, and it has been found in general that higher glass transition temperature correlates with faster stabilization heating rates. Following stabilization, the fibers can be carbonized at high temperature. Post-treatment of the carbon fibers could also be performed, such as sizing, which is not shown.

Important lignin parameters include purity, glass transition temperature (Tg), molecular weight (MW), rheology, and carbon yield, which depend on the biomass and extraction process. For example, to-date only organosolv hardwood lignin has shown to be melt spinnable without treatment, but without treatment its stabilization time was too long to be practical [1]. In general, hardwood lignin is more melt spinnable than softwood lignin, but softwood lignin has faster stabilization times than hardwood lignin, due to differences in chemical structure. To have a scalable process, there must be no bottlenecks in melt spinning. The melt spinning process can be impacted by purity and transient rheology, as well as stabilization time, which can further be dependent on purity and molecular weight distribution. In addition, the costs associated with purification and modification must be considered.

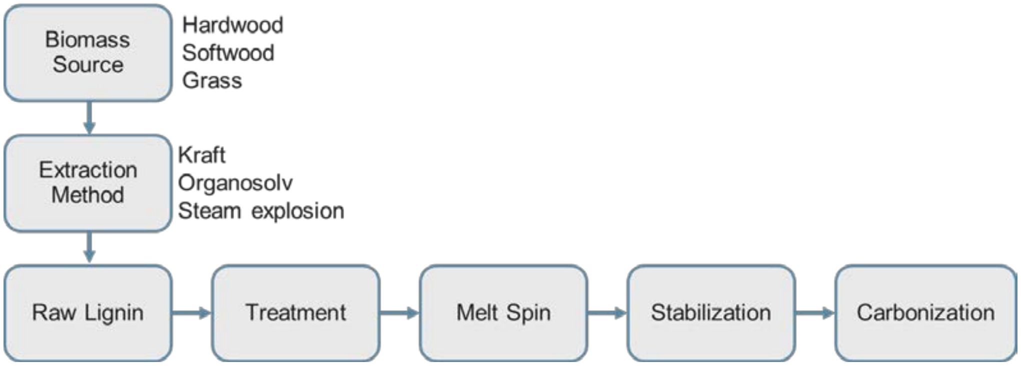

Figure 3. Lignin-based carbon fiber manufacturing process.

2.4 Early Lignin-Based Carbon Fibers

Although there is much recent interest, lignin based carbon fibers have been researched for over fifty years. As one of the first reports, U.S. patent 3,461,082 (1969) assigned to Otani described several lignin-based precursors and methods including melt spinning and dry spinning [6]. This led to the commercialization of Kayacarbon, which was available for a brief time by Nippon Kayaku. The carbon fiber was produced by dry spinning of an alkali lignin solution with polyvinyl alcohol. Although it was shown that lignin-based carbon fibers could be commercially produced, they were outpaced by PAN in the commercial market, and production was eventually ceased.

Later work became more focused on producing lignin fibers through melt spinning. Sudo and Shimizu [7-9] described steam-exploded lignin with solvent or alkali extraction. The hydrogenated lignin was melt spinnable but had low yield. It was reported that phenolation of lignin followed by vacuum thermal treatment almost tripled the yield versus hydrogenated lignin.

Uraki et al. [10] described acetic acid fractionated lignin (organosolv lignin) which showed partial acetylation. They examined both hardwood and softwood lignin sources. They found that both hardwood and softwood lignin from the organosolv process could be melt spun. They found that hardwood lignin from the kraft process could be melt spun but not softwood kraft lignin. In addition, thermal treatment of lignin resulted in overall higher molecular weight and better melt spinning.

The work by Sudo and Uraki et al. showed that melt spinning of kraft lignin was possible with treatments, which was promising, but commercial feasibility was not fully investigated. It was recognized that clear paths needed to be defined for low-cost melt spinning and stabilization of different lignin sources, with the focus on controlling purity and molecular weight distribution in order to achieve scalable throughput, yield, and properties.

3. LITERATURE REVIEW

There are a number of strategies that have been reported for improving lignin as a low cost carbon fiber precursor, which for discussion purposes can be categorized into several areas.

- Purification: to reduce impurity content to improve melt spinnability
- Fractionation: to separate different molecular weight components to improve melt spinnability and stabilization
- Thermal and chemical modification: to modify the molecular weight distribution and chemical structure to improve melt spinnability and stabilization
- Blending: to plasticize lignin to improve melt spinnability, structure, and mechanical properties
- Fillers: to incorporate non-lignin components to improve melt spinnability, structure, and mechanical and thermal properties

3.1 Purification and Fractionation

Given that the kraft process is the dominant process for lignin, purification is a first step that is often needed. For organosolv lignin, purification has not been necessary for melt spinning. Bahl et al. [11] purified hardwood kraft lignin with organic solvents and successfully melt spun it, but they found it required slower stabilization heating rates. Baker [12] purified lignin with organic solvents and found that the purified lignin showed better thermal stability (transient rheology) but like Bahl identified, it required slower stabilization heating rates. Baker and Gallego [13-14] purified and thermally treated lignin to obtain the desired molecular weight distribution for melt spinning, including softwood lignin. Saito et al. [15] fractionated softwood kraft lignin with methanol and showed the higher molecular weight fraction had higher glass transition temperature and char yield.

A different approach than chemical fractionation is physical fractionation using filtration. Nordstrom et al. [16] filtered softwood kraft lignin and hardwood kraft lignin through a ceramic membrane to modify the molecular weight distribution (lignin permeate). As-is, the hardwood kraft lignin was barely spinnable while softwood kraft lignin was not spinnable. A blend of softwood kraft lignin with hardwood kraft lignin permeate had improved spinnability. They showed an inverse correlation of glass transition temperature with increasing hardwood kraft lignin permeate fraction. Norberg et al. [17] in related work filtered softwood kraft lignin and hardwood kraft lignin through a ceramic membrane to modify molecular weight distribution (lignin permeate). The softwood kraft lignin permeate showed the fastest stabilization time, with potential to skip a separate stabilization step. Softwood kraft lignin blended with hardwood kraft lignin permeate had slower stabilization.

The reported purification and fractionation work performed to date has not only shown that lignin can be made melt spinnable but has revealed the importance of molecular weight distribution. The low molecular weight fraction in lignin acts as a plasticizer for melt spinning while the higher molecular weight fraction allows for faster stabilization. Since softwood lignin by itself is not readily melt spinnable due to its generally higher molecular weight distribution, hardwood lignin can be used as a plasticizer. To illustrate the difference, the molecular weight distribution for two softwood (SW) and two hardwood (HW) lignin samples (a total of four) is shown in Figure 4. The spectra were generated by Gel Permeation Gas Chromatography (GPC) and show that the softwoods have a molecular weight distribution that peaks at higher molecular weights, while the hardwoods have a distribution that peaks at lower molecular weights.

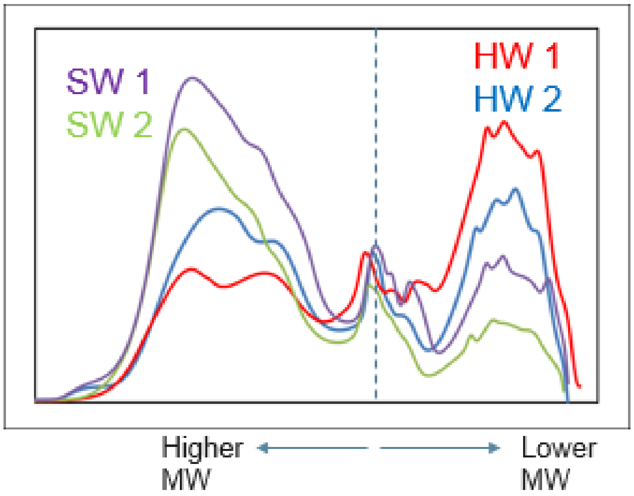

Figure 4. Example spectra from Gel Permeation Gas Chromatography (GPC) for softwood (SW) and hardwood (HW) lignin showing their general differences in molecular weight distribution.

3.2 Thermal and Chemical Modification

Thermal treatment of lignin has been performed by a number of researchers. Kadla et al. performed vacuum thermal treatment at 145 °C for one hour to improve melt spinning of organosolv and kraft lignin [18]. Baker et al. [12-14] performed thermal treatment to increase organosolv glass transition temperature. Qin and Kadla [20] performed thermal treatment of pyrolytic lignin derived from bio-oil and found that increasing treatment temperature increased the molecular weight distribution and Tg, while the polydispersity was similar. On the other hand, increasing heat treatment time increased the molecular weight, Tg, and polydispersity, but these reached a plateau after several hours.

Thermal treatment has been shown to modify certain functional groups in the lignin chemical structure. For example, Figure 5 illustrates spectra from before and after thermal treatment of lignin at 250 °C for one hour in an inert atmosphere. The spectra were obtained from Fourier Transform Infrared Spectroscopy (FTIR). The circled peak intensity differences correspond to hydroxyl groups from the treatment.

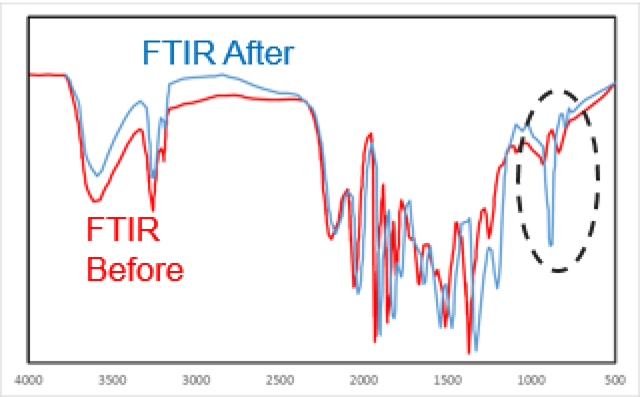

Figure 5. Example spectra from Fourier Transform Infrared Spectroscopy (FTIR) showing the differences in hydroxyl functional groups before and after thermal treatment.

Chemical treatment has also been performed to modify lignin. Eckert [21] described acetylated softwood kraft lignin. Zhang and Ogale [22] described acetylated softwood kraft lignin which was dry spun, stabilized under tension, and carbonized under tension to produce fiber with 1 GPa (150 ksi) tensile strength. Thunga et al. [23] butyrated softwood kraft lignin to improve miscibility for blending with polylactic acid (PLA). Increasing PLA content decreased yield but increased tensile strength and modulus in the carbon fiber. Chatterjee et al. [24-25] reported in two papers on esterification of organosolv hardwood lignin, which had a small effect on melting behavior, but the carbonized fibers showed 3-4X higher BET surface area, which may be useful for filtration applications. In addition, they found that esterification of softwood kraft lignin enabled melt spinning. Maradur et al. [26] reported oligomerized acrylonitrile blended with hardwood lignin. Wohlman [27] reported modification of free hydroxyl groups in lignin to add plasticizing ester, ether, or other groups to promote better melt spinning.

The thermal and chemical treatment work reported in the literature have demonstrated that the lignin structure and molecular weight can be modified to achieve suitable glass transition temperature, molecular weight distribution, spinnability, and to increase the yield. However, the scalability of thermal and chemical treatments needs further investigation.

3.3 Lignin Blends

To facilitate melt spinning, there are a number of reports of blending lignin with plasticizing polymeric agents. Kadla et al. [18] reported hardwood kraft lignin blended with 3-5% polyethylene oxide (PEO). The blends showed improved melt spinnability but required slower stabilization rates. They found that 3% PEO resulted in approximately 10% better tensile strength, which appeared to be an optimum amount. Dallmeyer [28] reported softwood kraft lignin blend with PEO. Kubo and Kadla [29] described polyvinyl alcohol (PVA) blended with lignin as a plasticizer. They found that the lower molecular weight PVA with lignin showed good spinning. Kubo and Kadla [30] reported hardwood kraft lignin blended with 5-25% polyethylene terephthalate (PET) improved stabilization and tensile strength by 10-17%. They also found that polypropylene (PP) was immiscible in lignin and gave poor tensile results. Similar to the previous workers, Compere et al. [31] reported that blending lignin with a PET plasticizer worked well, and found that it facilitated multifilament melt spinning. Baker et al. [32] reported blending lignin with PET and PE plasticizers, but tensile strength was not improved in the resulting carbon fibers over not using a plasticizer. Awal and Sain [33] reported that soda hardwood lignin was able to be melt spun into fine fibers through the addition of PEO as a plasticizer.

In addition to blending lignin with polymer plasticizing agents, lignin has also been blended with lignin. Warren [19] reported hardwood lignin as plasticizer for softwood lignin to enable spinning. Nordstrom et al. [16-17] reported softwood kraft lignin with hardwood kraft lignin plasticizer. Baker et al. [12-14] reported hardwood lignin as plasticizer for spinning and faster conversion.

Other lignin blends have also been reported. Ichikawa et al. [34] described phenylated lignin coextruded with isotropic pitch to improve carbon fiber properties. Kim et al. [35] blended hardwood lignin with pyrolized fuel oil which was then heat treated.

The reports demonstrate that lignin spinnability can be improved through blending with PET or PEO, but tensile strengths were only improved by about 10%, which is in the right direction towards a structural carbon fiber but not a step change.

3.4 Fillers

One method to improve lignin-based carbon fibers has been to add clay to the precursor. Sevastyanova et al. [36] reported organoclay added to organosolv hardwood lignin improved the spinnability, and the resulting carbon fibers had increased tensile strength. It was found that 5 wt% of organoclay addition nearly doubled the tensile strength for two different organoclays tested. Qin and Kadla [37] added organoclay to lignin pyrolized from bio-oil. They reported the tensile strength was improved by 12%, which was not nearly that reported by Sevastyanova for organosolv hardwood lignin. Qin and Kadla found that 1% organoclay was optimal for improvement in tensile modulus.

Carbon nanotubes (CNT) have also been added to lignin. Baker [38] described up to 10 wt% addition of multiwalled carbon nanotubces (MWCNT) to purified hardwood kraft lignin and a blend of softwood kraft lignin and purified hardwood kraft lignin. Baker found that melt spinnability was improved and that tensile strength was improved by 20% with MWCNT incorporation. Teng [39] reported addition of MWCNT to electrospun softwood kraft lignin based fibers. Tensile strength was not improved, but electrical conductivity was improved by 30% with 6% MWCNT. The 6% MWCNT level was the maximum that could be dispersed in the fiber precursor.

Upon review, it is seen that the addition of fillers to lignin improved the melt spinnabiliy and the resulting carbon fiber tensile strength. However, tensile strength improvements were on the order of 10%, which is positive, but not a step change.

4. SUPPLY CHAIN DEVELOPMENT

Fundamental to the realization of lignin-based fiber in insulation and other products is development of a robust supply chain of suitable quality lignin (see Figure 6). Due to the fact lignin carbon fiber is not yet commercialized, there currently exists no supply chain for precursor lignin of appropriate quality. As indicated previously, all lignin carbon fiber work to-date has been either lab or bench scale, with very little information in the public domain regarding scale-up or related raw material requirements. The sheer biochemical diversity of biomass sources, as well as the post-processing and extraction processes necessary to make these biomasses into usable carbon fiber and the fact that these processes themselves in their infancy, make anticipation of the exact supply chain a challenge. It is therefore necessary to map the extraction and post-processing treatment requirements necessary for a broad variety of biomass sources including softwood, hardwoods, and grasses; a major consequence of which will be supply chain development in the most profitable and promising areas and development of a healthy lignin fiber precursor supplier base.

As approximately 50% of the cost of lignin-based carbon fiber is the precursor raw material (biomass source + extraction process), a main impetus of the supply chain development is identifying from a wide variety of biomass sources, any post-treatment steps required for those sources, and the associated costs. The value of a given lignin source will include whether post-processing is required for a specified application, so a knowledge at the bench scale of those requirements informs the supply chain development. The lower cost the lignin carbon fiber (source cost + post-processing costs), the more likely it is to be accepted and adopted into commercial applications.

GrafTech and ORNL are evaluating lignin from a variety (10+) of biomass sources, having various extraction processes. A controlled approach to evaluating the post-processing requirements necessary for making this lignin usable as lignin carbon fiber is being executed. As part of this process, the team is engaging promising suppliers of lignin raw materials. The purpose of this engagement is to establish mutual understanding of development goals and to identify suppliers who display ability and organizational will to scale up to commercial production, with a focus on the needs (quality, cost, etc.) of the lignin carbon fiber customer. Multiple suppliers are being pursued in order to build in diversification and ensure a robust and stable supply chain.

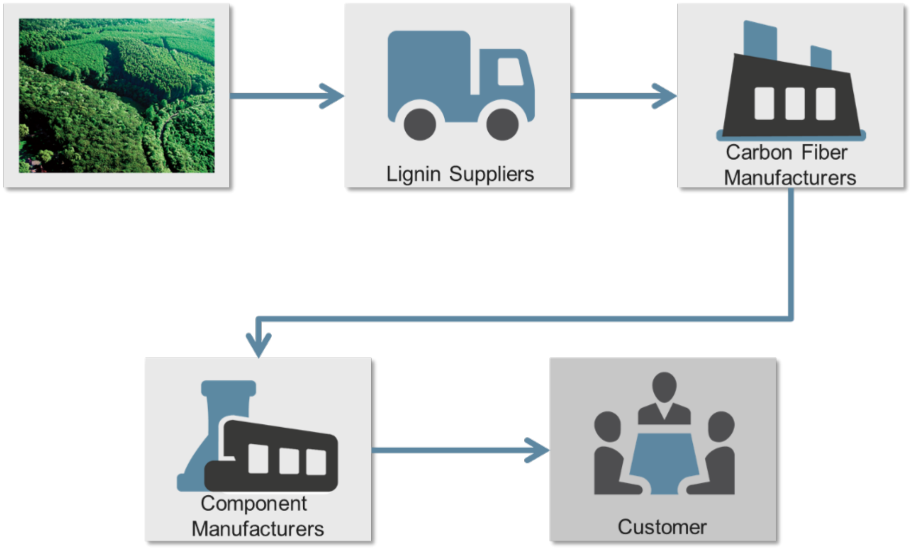

Figure 6. Potential supply chain for lignin-based carbon fibers.

5. FUNCTIONAL APPLICATIONS

As reviewed in Section 3, there are a number of strategies that have been employed to improve lignin as a carbon fiber precursor. In terms of lignin-based carbon fiber properties, the best tensile strength observed to date has been approximately 1 GPa (150 ksi). Although this is not adequate for most structural applications, there are no tensile strength requirements for functional applications, such as insulation and filtration, and hence it is viable for those applications. In fact, lignin tends to form an isotropic fiber, which is better suited for insulation and filtration applications than are the higher strength fibers made from PAN. Therefore, what at first appears to be a disadvantage for lignin can actually be an advantage.

The functional nature of lignin-based carbon fiber is currently being further explored by GrafTech and ORNL [3]. GrafTech and ORNL, working together in 2011-2012, demonstrated that lignin-based carbon fibers from organosolv hardwood lignin were a drop-in replacement for pitch fibers used in GrafTech's GRI^{TM} rigid insulation, which has been a commercial product for many years. GRI^{TM} is a high-temperature insulation used in furnaces, including furnaces for high-purity crystal growing. The lignin powder was pelletized, melt blown into mat form, stabilized, carbonized, milled, and formed into GRI^{TM} rigid insulation prototypes. This work was among the first to show lignin carbon fiber processing above the lab scale. Although this work was very productive only one lignin source was used, and, at approximately one hundred hours the stabilization time was too long. Continuous melt blowing was also a challenge. Therefore, ongoing work through a DOE cooperative agreement is focused on qualifying multiple lignin sources and eliminating bottlenecks in melt spinning and stabilization. This work will also evaluate the lignin in prototypes and commercial products.

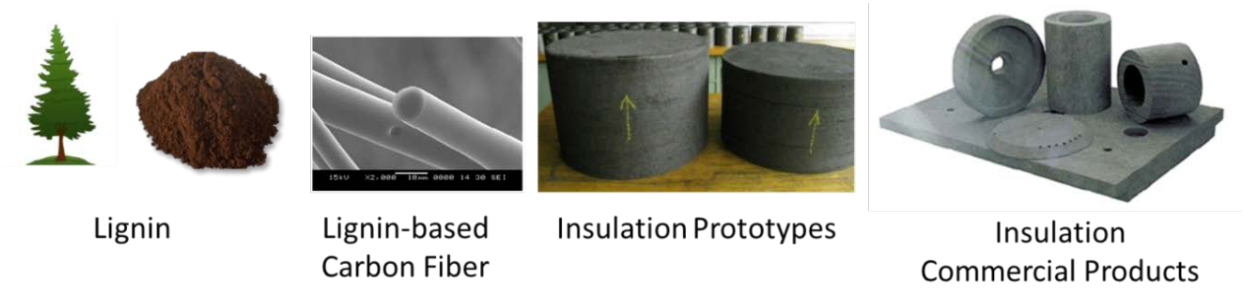

Figure 7. Lignin to insulation.

In addition to the insulation applications, filtration is another application for lignin-based carbon fibers [32,40]. For filtration, a high surface area is required, which can be achieved through an activation step, but as with insulation there is no strength requirement. Several workers have investigated lignin for filtration and have noted that it has several potential advantages over other fiber types. This is an ongoing area of work and, like high-temperature insulation, has commercial potential.

6. CONCLUSIONS

The motivation for low-cost carbon fibers is to increase their adoption rate in industrial applications. However, there are additional benefits if the precursor is not only low-cost but abundant and renewable, as is lignin.

Lignin is a potential low-cost and renewable carbon fiber precursor. Given that it would require a new supply chain, it would be decoupled from non-renewable petroleum-based precursors . As a biopolymer, lignin should require less energy to process, and it would produce fewer CO_2 emissions as well. Carbon fibers would also create an additional outlet for lignin, which should help economics of biorefineries that generate excess lignin.

Lignin is a diverse biopolymer, since different biomass sources and lignin extraction conditions are in use in industry. The diverse structure has prevented a single strategy for low cost processing. However, there are a number of reported strategies for improving lignin as a precursor (purification, fractionation, modification, polymer blending, fillers), each of which has its strengths and weaknesses in terms of throughput, cost, scale-up and commercialization potential. Although some of the best methods have increased the tensile strength of lignin-based carbon fiber to upwards of 1 GPa (150 ksi), a true structural carbon fiber has not yet been produced from lignin. Research continues in this area.

A lignin-based carbon fiber supply chain requires multiple scalable qualified lignin sources, in addition to a fiber production process that does not have bottlenecks. Finally, there must be qualified applications. Currently functional applications such as insulation and filtration appear to offer the most promise for the entry of commercial products into the marketplace.

7. ACKNOWLEDGEMENT AND DISCLAIMER

Acknowledgement: The information, data, or work presented herein was funded in part by the Office of Energy Efficiency and Renewable Energy (EERE), U.S. Department of Energy, under Award Number DE-EE-0005779.

8. REFERENCES

1. Baker, Darren A., and Timothy G. Rials. "Recent advances in low-cost carbon fiber manufacture from lignin." Journal of Applied Polymer Science 130.2 (2013): 713-728.
2. Cliff Eberle, ORNL, Carbon Fiber from Lignin, Carbon Fiber Composites Consortium Panel Discussion, April 12, 2012.
3. Eberle, Cliff, Daniel C. Webb, Tracy Albers, and Chong Chen. Commercialization of New Carbon Fiber Materials Based on Sustainable Resources for Energy Applications. No. ORNL/TM-2013/54. Oak Ridge National Laboratory (ORNL), 2013.
4. Liu, Yaodong, and Satish Kumar. "Recent progress in fabrication, structure, and properties of carbon fibers." *Polymer Reviews* 52, no. 3 (2012): 234-258.
5. The International Lignin Institute, About Lignin, http://www.ili-lignin.com/aboutlignin.php
6. Otani, Sugio, Yoshihiko Fukuoka, Bunjiro Igarashi, and Kesao Sasaki. "Method for producing carbonized lignin fiber." U.S. Patent 3,461,082, issued August 12, 1969.
7. Sudo, K.; Shimizu, K. JP Pat. 62,110,922 (1987).
8. Sudo, K.; Shimizu, K. J. Appl. Polym. Sci. 1992, 44, 127.
9. Sudo, K.; Shimizu, K.; Nakashima, N.; Yokoyama, A. J. Appl. Polym. Sci. 1993, 48, 1485.
10. Uraki, Y.; Hubo, S.; Nigo, N.; Sano, Y.; Sasaya, T. Holzforschung 1995, 49, 343.
11. Bahl O P, Shen Z, Lavin J G and Ross R A. (1998). Manufacture of carbon fibers. In Carbon Fibers Ed(s). Donnet J-B, Wang T K, Peng J C M and Reboulliat S, Marcel Dekker, New York, pp. 1-83.
12. Baker, D. A.; Gallego, N. C.; Baker, F. S. J. Appl. Polym. Sci. 2012, 124, 227

13. Baker, Darren A., Frederick S. Baker, and Nidia C. Gallego. Thermal engineering of lignin for low-cost production of carbon fiber. Oak Ridge National Laboratory (ORNL); Shared Research Equipment Collaborative Research Center, 2009.
14. Baker, F. S. "Low cost carbon fiber from renewable resources." EERE, US Dept of Energy Project ID# lm_03_baker (2010).
15. Saito, Tomonori, Joshua H. Perkins, Frederic Vautard, Harry M. Meyer, Jamie M. Messman, Balazs Tolnai, and Amit K. Naskar. "Methanol fractionation of softwood kraft lignin: impact on the lignin properties." ChemSusChem 7, no. 1 (2014): 221-228.
16. Nordström, Ylva, Ida Norberg, Elisabeth Sjöholm, and Rickard Drougge. "A new softening agent for melt spinning of softwood kraft lignin." Journal of Applied Polymer Science 129, no. 3 (2013): 1274-1279.
17. Norberg, Ida, Ylva Nordström, Rickard Drougge, Göran Gellerstedt, and Elisabeth Sjöholm. "A new method for stabilizing softwood kraft lignin fibers for carbon fiber production." Journal of Applied Polymer Science 128, no. 6 (2013): 3824-3830.
18. Kadla, J. F., S. Kubo, R. A. Venditti, R. D. Gilbert, A. L. Compere, and W. Griffith. "Lignin-based carbon fibers for composite fiber applications." Carbon 40, no. 15 (2002): 2913-2920.
19. Warren, C. D. "Future lower cost carbon fiber for autos: international scale-up & what is needed." In 8th-Annual Automotive Composites Conference and Exhibition (ACCE 2008): The Road to Lightweight Performance, pp. 50-108. 2008.
20. Qin, W., and J. F. Kadla. "Carbon fibers based on pyrolytic lignin." Journal of Applied Polymer Science 126, no. S1 (2012): E204-E213.
21. Eckert, Carbon fibers from kraft softwood lignin, US 7678358 B2, Mar 16, 2010
22. Zhang, Meng, and Amod A. Ogale. "Carbon fibers from dry-spinning of acetylated softwood kraft lignin." Carbon 69 (2014): 626-629.
23. Thunga, Mahendra, Keke Chen, David Grewell, and Michael R. Kessler. "Bio-renewable precursor fibers from lignin/polylactide blends for conversion to carbon fibers." Carbon 68 (2014): 159-166.
24. Chatterjee, Sabornie, Amy Clingenpeel, Amy McKenna, Orlando Rios, and Alexander Johs. "Synthesis and characterization of lignin-based carbon materials with tunable microstructure." RSC Advances 4, no. 9 (2014): 4743-4753.
25. Chatterjee, Sabornie, Eric B. Jones, Amy C. Clingenpeel, Amy M. McKenna, Orlando Rios, Nicholas W. McNutt, David J. Keffer, and Alexander Johs. "Conversion of lignin precursors to carbon fibers with nanoscale graphitic domains." ACS Sustainable Chemistry & Engineering 2, no. 8 (2014): 2002-2010.
26. Maradur, Sanjeev P., Chang Hyo Kim, So Yeun Kim, Bo-Hye Kim, Woo Chul Kim, and Kap Seung Yang. "Preparation of carbon fibers from a lignin copolymer with polyacrylonitrile." Synthetic Metals 162, no. 5 (2012): 453-459.
27. Wohlmann, Bernd, Michael Wolki, Andreas Ebert, Gunnar Engelmann, and Hans-Peter Fink. "Lignin derivative, shaped body comprising the derivative and carbon fibers produced from the shaped body." U.S. Patent Application 13/144,879, filed January 11, 2010.

28. Dallmeyer, Ian, Li Ting Lin, Yingjie Li, Frank Ko, and John F. Kadla. "Preparation and Characterization of Interconnected, Kraft Lignin-Based Carbon Fibrous Materials by Electrospinning." Macromolecular Materials and Engineering 299, no. 5 (2014): 540-551.
29. Kubo, Satoshi, and John F. Kadla. "The formation of strong intermolecular interactions in immiscible blends of poly (vinyl alcohol)(PVA) and lignin." Biomacromolecules 4, no. 3 (2003): 561-567.
30. Kubo, S., and J. F. Kadla. "Lignin-based carbon fibers: Effect of synthetic polymer blending on fiber properties." Journal of Polymers and the Environment 13, no. 2 (2005): 97-105.
31. Compere, A. L., W. L. Griffith, C. F. Leitten Jr, and S. Petrovan. "Improving the fundamental properties of lignin-based carbon fiber for transportation applications." In Proceedings, SAMPE long Beach Symposium, pp. 16-20. 2004.
32. Kubo, Satoshi, Takahiro Yoshida, and John F. Kadla. "Surface porosity of lignin/PP blend carbon fibers." Journal of wood chemistry and technology 27, no. 3-4 (2007): 257-271.
33. Awal, Abdul, and Mohini Sain. "Characterization of soda hardwood lignin and the formation of lignin fibers by melt spinning." Journal of Applied Polymer Science 129, no. 5 (2013): 2765-2771.
34. Ichikawa, H.; Yokoyama, A.; Nankjima, N. JP Pat. 04,194,029 (1992).
35. Kim, Moo Sung, Dong Hun Lee, Chang Hyo Kim, Yang Jin Lee, Jun Yeon Hwang, Cheol-Min Yang, Yoong Ahm Kim, and Kap Seung Yang. "Shell–core structured carbon fibers via melt spinning of petroleum-and wood-processing waste blends." Carbon 85 (2015): 194-200.
36. Sevastyanova, Olena, Wei Qin, and J. F. Kadla. "Effect of nanofillers as reinforcement agents for lignin composite fibers." Journal of applied polymer science 117, no. 5 (2010): 2877-2881.
37. Qin, W., and J. F. Kadla. "Effect of organoclay reinforcement on lignin-based carbon fibers." Industrial & Engineering Chemistry Research 50, no. 22 (2011): 12548-12555.
38. Baker, F. S.; Baker, D. A.; Menchhofer, P. A. Carbon nanotube enhanced precursor for carbon fiber production and method of making a CNT-enhanced continuous lignin fiber. US Patent Application 2011285049, 2011, to be assigned to Oak Ridge National Laboratory.
39. Teng, Nai-Yu, Ian Dallmeyer, and John F. Kadla. "Incorporation of multiwalled carbon nanotubes into electrospun softwood Kraft lignin-based fibers." Journal of Wood Chemistry and Technology 33, no. 4 (2013): 299-316.
40. Rosas, Juana M., Raúl Berenguer, María José Valero-Romero, José Rodríguez-Mirasol, and Tomás Cordero. "Preparation of Different Carbon Materials by Thermochemical Conversion of Lignin." Frontiers in Materials 1 (2014): 29.
41. Strassberger, Zea, Stefania Tanase, and Gadi Rothenberg. "The pros and cons of lignin valorisation in an integrated biorefinery." RSC Advances 4, no. 48 (2014): 25310-25318.
42. National Renewable Energy Laboratory (NREL), Biomass Research page, Gregg Beckham, http://www.nrel.gov/biomass/staff_pages/gregg_beckham.html.