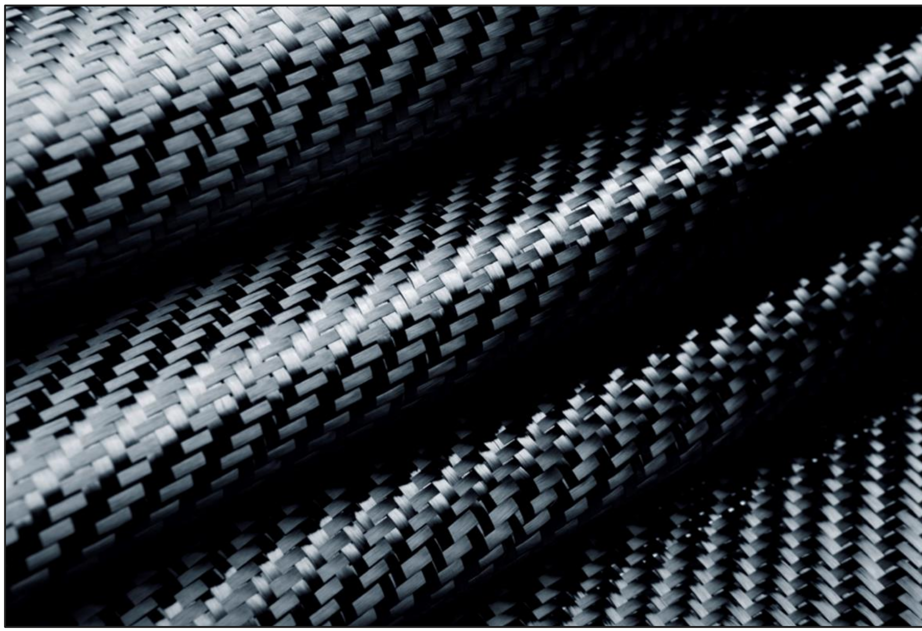
Treatment of Lignin Precursors to Improve their Suitability for Carbon Fibers: A Literature Review



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GrafTech International | Redefining limits

GrafTech Graphite Solutions

Leader in Graphite Materials	Value-Added Proposition	Diverse End Markets
• NYSE: GTI • Founded 1886 • Unique technologies & expertise • ~715 patents & pending applications	• Innovative solutions for wide range of applications including: – Energy management – Thermal management – High temperature processing	• EAF steel production • Advanced electronics • Alternative energy • Aerospace
		

Two Business Segments

- **Industrial Materials (IM)**
  - Graphite electrodes
  - Refractory materials
  - Needle coke
- **Engineered Solutions (ES)**
  - Flexible graphite
  - Additive materials
  - Carbon composites
  - Advanced graphite materials

Flexible Graphite (Thermal Management)

Advanced Graphite (Energy Management)

Carbon Composites (High Performance Lightweighting)

Advanced Materials (Multifunctional)

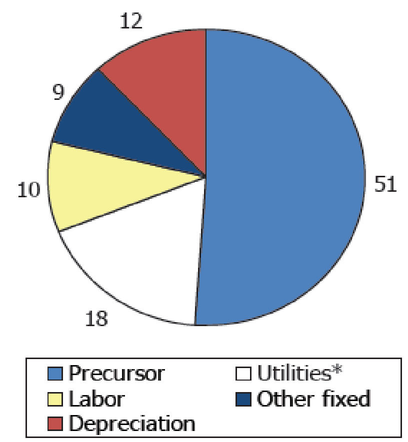
Agenda

- Motivation for low-cost carbon fibers
- Lignin as a low-cost and renewable carbon fiber precursor
- Unique challenges with lignin as a carbon fiber precursor
- Reported strategies for improving lignin as a precursor
- Overview of GrafTech-ORNL collaboration focused on lignin-based carbon fiber for insulation applications
- Acknowledgement

Motivation for Lignin-Based Carbon Fibers

Problem Statement

- Carbon fiber is expensive, which limits industrial uses
- Precursor is 50% of production costs. Lack of proven alternatives



Kline & Company

Potential Solution

- Lignin has potential to be low-cost renewable precursor
- Higher carbon yields. Reduced energy demand and CO_2 emissions

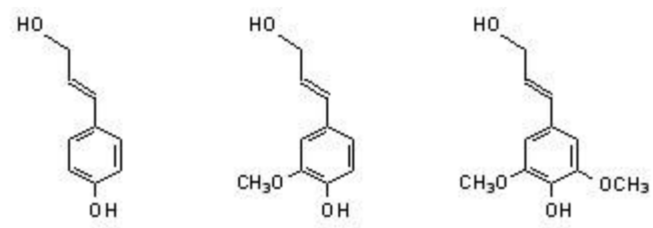
Current Barriers

- No current supply chain
- Most work at lab or bench scale with little scale-up
- Lignin diversity complicates low-cost melt spinning and stabilization
- Only organosolv hardwood lignin has shown melt spinning without any modification
- Supply chain requires multiple qualified lignin sources without process bottlenecks

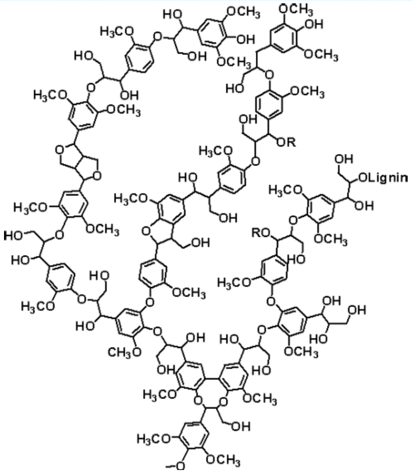
This review will highlight reported methods to improve lignin as a carbon fiber precursor.

Lignin is Diverse

- Lignin is a heterogeneous biopolymer
- Glue that holds trees together
- 40-50 million tons per year
- Most abundant after cellulose
- Three main units
- Complex structure
- Not linear like PAN



p-Coumaryl alcohol Coniferyl alcohol Sinapyl alcohol



Biomass sources are diverse

- Softwoods (SW): e.g. pin and spruce. Mostly coniferyl alcohol (guaiacyl lignin)
- Hardwoods (HW): e.g. oak, beech poplar, birch. More syringyl alcohol (syringyl lignin)
- Grasses: Mainly p-coumaryl alcohol units (graminaceous lignin)

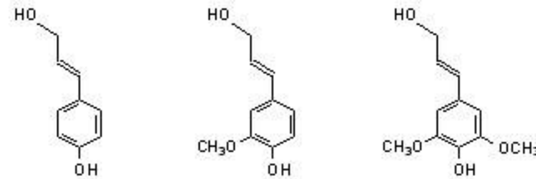
Extraction processes are diverse

- Kraft pulping: Dominant process. Potentially high impurities
- Sulfite pulping: Lignosulfonates are produced
- Organosolv: High purity lignin is produced. Limited availability
- Steam explosion: High purity lignin is produced. Limited availability
- Extraction process large effect on lignin structure

Lignin purity, Tg, molecular weight (MW), rheology depend on biomass and extraction process. Supply chain requires multiple qualified lignin sources without manufacturing bottlenecks.

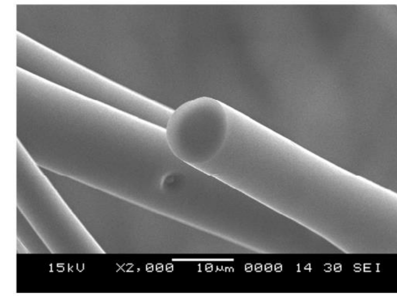
From Biomass to Carbon Fibers

Biomass Source
- Hardwood (HW)
- Softwood (SW)
- Grass (GR)



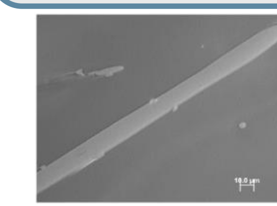
p-Coumaryl alcohol | Coniferyl alcohol | Sinapyl alcohol

Naturally polymerized



Extraction Method
- Kraft
- Organosolv
- Steam explosion

Raw Lignin → Treatment* → Melt Spin → Stabilization → Carbonization



- Only organosolv HW lignin was melt spun without treatment but stabilization time too long
- HW easier to melt spin while SW easier to stabilize due to chemical structure differences
- High purity needed to melt spin while control of MW / Tg needed for stabilization and high yield
- Supply chain requires multiple qualified lignin sources and no manufacturing bottlenecks

Early Lignin-Based Carbon Fibers

- **Otani** U.S. patent 3,461,082 (1969) described several lignin-based precursors and methods (melt spinning and dry spinning)

- **Kayacarbon** lignin carbon fiber was commercially available for brief time. Dry spinning of alkali lignin solution with poly (vinyl alcohol)

NIPPON KAYAKU

- **Sudo & Shimizu** (1987-1993 patents and papers) described steam-exploded lignin with solvent or alkali extraction. Hydrogenated lignin spinnable but had low yield. Phenolation followed by vacuum thermal treatment almost tripled yield

- **Uraki et al** (1995-2001 papers) described acetic acid fractionated lignin (organosolv) which showed partial acetylation. HW and SW lignin melt spun, but SWKL lignin did not. Thermal treatment of lignin gave higher MW and better melt spinning

Early Kayacarbon was promising but trumped by other methods.
Melt spinning shown possible with treatments but commercial feasibility not known.
Need clear paths for melt spinning and stabilization of different lignin (control of Tg and MW).

Strategies for Improving Lignin as a Precursor

Purification

- Reduction of ash content to improve spinnability

Fractionation

- Separation of MW components to improve spinnability and stabilization

Thermal and chemical modification

- Elimination of lower MW or derivitization to improve spinnability and stabilization

Polymer blending

- Incorporation of plasticizing components to improve spinnability

Fillers

- Incorporation of fillers to improve spinnability and tensile strength/modulus

LBCF seen to date show isotropic structure and low to mid tensile strength (25-150 ksi).
Applications such as insulation and filtration are suitable initial commercialization markets.

Lignin Purification and Fractionation

Organic solvent purification and fractionation	• **Bahl et al** (1998) purified HWKL with organic solvents for melt spinning and found it required lower stabilization heating rates. • **Baker** (2008-2012) purified lignin with organic solvents and found the purified lignin showed better thermal stability (transient rheology) but required lower stabilization heating rates. • **Baker and Gallego** (2010) purified and thermally treated lignin to obtain desired molecular weight distribution for melt spinning. • **Baker et al** (2012) purified and thermally treated SWKL for melt spinning. • **Saito et al** (2014) fractionated SWKL with methanol and showed the higher MW fraction had higher Tg and char yield.
Filtration and fractionation	• **Nordstrom et al** (2012) filtered SWKL and HWKL through ceramic membrane to modifiy molecular weight distribution (permeate). As-is HWKL barely spinnable while SWKL was not spinnable. Blend of SWKL with HWKL permeate had improved spinnability. Showed inverse correlation of Tg and increasing HWKL permeate fraction. • **Norberg et al** (2013) in related work filtered SWKL and HWKL through ceramic membrane to modify molecular weight distribution (permeate). SWKL permeate showed fastest stabilization with potential to skip separate stabilizatoion. SWKL blended with HWKL permeate had slower stabilization.

Low MW fraction acts as plasticizer for melt spinning while higher MW fraction gives necessary Tg for stabilization.   HW can act as plasticizer for SW for melt spinning.

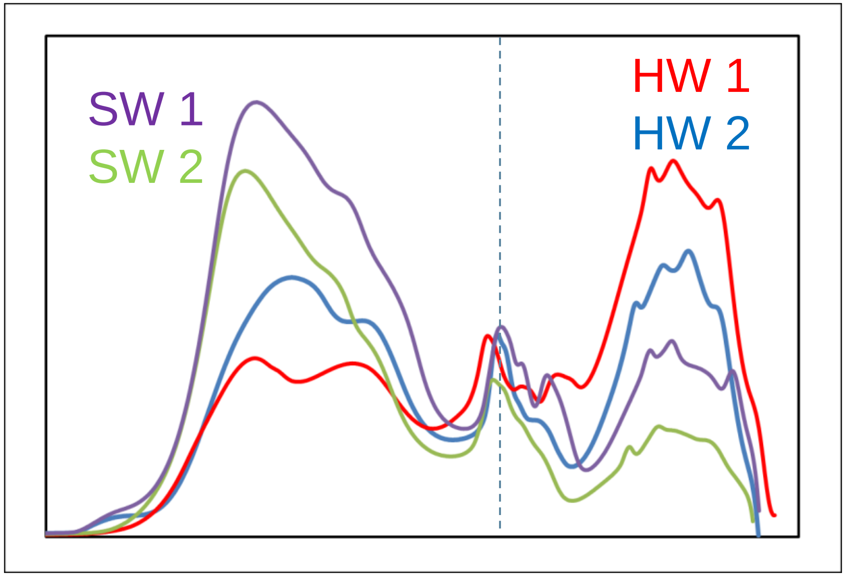
Lignin Modification

Thermal Treatment	• **Kadla et al** (2002) performed vacuum thermal treatment at 145 °C for 1 hour to improve melt spinning of organosolv and kraft lignin. • **Baker et al** (2008, 2009) performed thermal treatment to increase organosolv Tg. • **Qin and Kadla** (2012) performed thermal treatment of pyrolytic lignin of bio-oil. Increasing treatment temperature increased MW and Tg while PDI similar, while increasing treatment time increased MW, Tg, and PDI but plateaus after hours. • **Wells** (2013) performed ultrasonication polymerization of kraft lignin.
Acetylation	• **Eckert** (2007 patent app) described acetylated SWKL. • **Zhang and Ogale** (2014) described acetylated SWKL which was dry spun & stabilized & carbonized under tension to produce fiber with 150 ksi TS.
Butryation	• **Thunga et al** (2014) butyrated SWKL to improve miscibility for blending with PLA. Increasing PLA decreased yield but increased tensile strength/modulus.
Esterification	• **Chatterjee et al** (2014) reported in two papers esterification of organosolv HW, which had small effect on melting behavior, but carbonized fibers showed 3-4X higher BET. Esterification of SWKL enabled melt spinning.
Other Chemical Modification	• **Maradur et al** (2012) reported oligomerized AN blend with HW. • **Saito et al** (2012-2013) described formaldehyde cross-linked lignin. • **Wohlman** (2010) reported modification of free hydroxyl groups in lignin to add plasticizing ester, ether, or other groups.

Thermal and chemical modifications to lignin can improve Tg, rheology, spinnability, and yield.

Examples

Molecular Weight Distribution by Gel Permeation Chromatography (GPC)

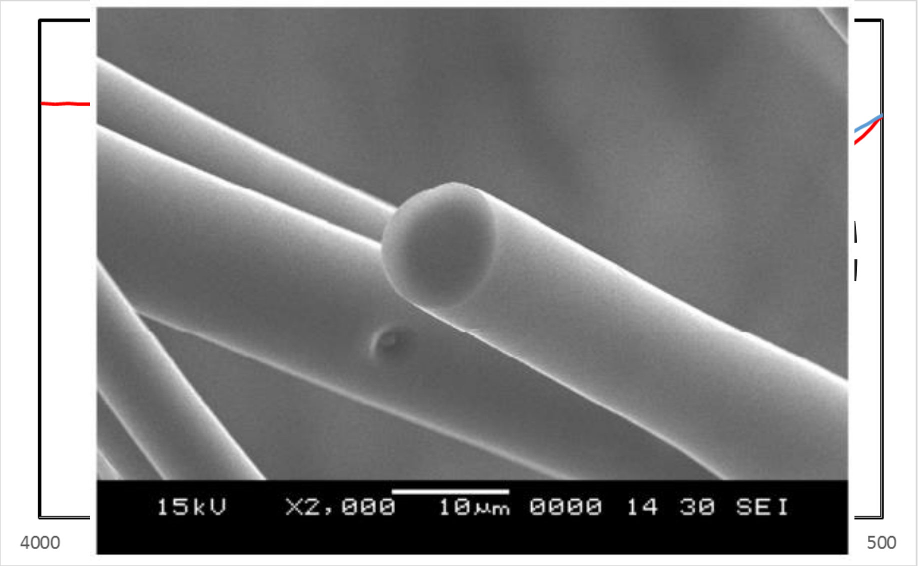


Higher MW ← → Lower MW

Comparison of HW vs SW

- GPC shows HW has more lower MW fractions while SW has higher MW fractions
- Corresponded to HW being easier to melt spin while SW is easier to stabilize

Functional Groups Analysis by Fourier Transform Infrared Spectroscopy (FTIR)



Thermal Treatment of Lignin in Inert Atmosphere 250 °C for 2 hours

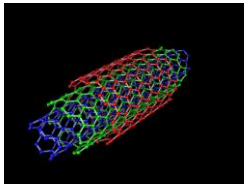
- FTIR shows changes (increased ether bonding) which correspond to increase in Tg by 30 °C
- Corresponded to reduction in stabilization time by 10X without negative effect on spinning

Lignin Blends

Blend with polymers	• **Kadla et al** (2002) reported HWKL blended with 3-5% PEO showed improved melt spinnability but stabilization slower. 3% PEO showed ~10% better TS. • **Kubo and Kadla** (2003) described PVA blended with lignin as a plasticizer. Lower MW PVA showed good spinning. • **Kubo & Kadla** (2005) reported HWKL blended with 5-25% PET showed improved stabilization and tensile strength by 10-17%. Found PP was immiscible in lignin and gave poor tensile results. • **Compere et al** (2005) reported lignin-PET blends with good tensile strength. • **Baker et al** (2011) reported PET, PE MPP but tensile strength not improved. • **Awal & Sain** (2012) reported soda HW and PEO blends for melt spinning. • **Dallmeyer** (2014) reported SWKL blend with PEO.
Blend with lignin	• **Nordstrom et al** (2011-2013) reported SWKL with HWKL plasticizer • **Warren** (2008) reported HW as plasticizer for SW to enable spinning. • **Baker et al** (2011) reported HW as plasticizer for spinning and faster conversion.
Blend with other	• **Ichikawa et al** (1992 JP patent) described phenylated lignin coextruded with isotropic pitch to improve carbon fiber properties. • **Kim et al** (2015) blended HW with pyrolized fuel oil then heat treated 230 °C/4h.

HWKL blended with PET or PEO improved spinnability but TS only improved by ~10%.
SWKL blended with purified HWKL showed good spinnability.

Lignin Fillers

Organoclay	• **Sevastyanova et al** (2010) reported organoclay added to organosolv HW lignin improved spinnability (increased Tg) and tensile strength. 5 wt% of organoclay nearly doubled tensile strength for two different organoclays tested. • **Qin and Kadla** (2012) added organoclay to pyrolytic lignin from bio-oil. Tensile strength was improved by 12%, which was not nearly that reported above for organosolv HW lignin. Found that 1% organoclay was optimum for improvement in tensile modulus.
Carbon nanotubes (CNT) 	• **Baker 2010** (2011 patent application) described up to 10 wt% addition of multiwalled carbon nanotubces (MWCNT) to purified HWKL and blend of SWKL and purified HWKL. Found that melt spinnability was improved. Reported that tensile strength was improved by 20% with MWCNT incorporation. • **Teng** (2013) reported addition of MWCNT to electrospun SWKL based fibes. Tensile strength not improved. But electrical conductivity improved by 30% with 6% MWCNT (6% was max could be dispersed in fiber).

Addition of fillers improved melt spinnability and improved strength but not step change.

GrafTech-ORNL Collaboration

US DOE Cooperative Agreement DE-EE0005779 (project period 2015-2017)

Objectives

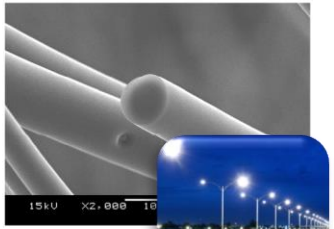
- Develop and demonstrate scalable lignin-based carbon fiber (LBCF) technology
- Demonstrate LBCF in high-temp products and applications, including **insulation**
- Show progress towards LBCF supply chain

Approach

- Take a fresh look at lignin sources, purification, modification, and stabilization
- Focus on scalable technologies for producing LBCF in **ORNL CFTF**
- Make 500 pounds of LBCF in year 2 and 5000 pounds in year 3 for **insulation**

High potential for LBCF to be 50% lower in cost and more insulating than current fibers.

Insulation made with Lignin



Summary

Motivation for low-cost carbon fibers

- Increase adoption rate in industrial applications

Lignin as an potential low-cost and renewable carbon fiber precursor

- Renewable resource decoupled from petroleum based precursors
- Lower cost, energy, and CO_2 emissions than petroleum based precursors

Unique challenges with lignin as a carbon fiber precursor

- Diverse structure has prevented single strategy for low cost processing

Reported strategies for improving lignin as a precursor

- Purification, fractionation, modification, polymer blending, fillers

Objectives of GrafTech-ORNL collaboration

- Develop LBCF and demonstrate in high-temperature products and applications
- Show progress towards LBCF supply chain

Acknowledgement

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