Utilization of Sustainable Resources for Production of Carbon Fiber Materials for Structural and Energy Efficiency Applications

Frederick S. Baker
Oak Ridge National Laboratory, Tennessee

Frontiers in Biorefining: Biobased Products from Renewable Carbon
St. Simons Island, Georgia
October 19-22, 2010
ORNL Research Directed Towards Production of Multiple Value-added Streams from Biomass Feedstock

Positive findings from “Billion Ton” biomass study Economics of cellulosic ethanol fuel production would be enhanced by value-added lignin utilization

Cellulose & Hemi-cellulose Nano-porous & non-porous carbon fibers

Lignin Estimated reduction of 30 to 40% of finished carbon fiber production cost

Hybrid Vehicle Uses (e.g., supercapacitors, Li-ion batteries)

Chemical building blocks for
- Plastics
- Industrial additives
- Biomedical applications

Ethanol Fuel

Carbon Fiber Production Line

Melt Spinner

P4 Preforming

Lignin and innovative processing technologies together yield estimated manufacturing cost reduction of 50% or more over PAN and conventional processing base case

DOE Office of Vehicle Technologies
Lightweight Materials Program
Transportation Uses of Petroleum in USA

• **Reason for Project:** Transportation fuels account for 70% of the oil used in the USA, of which 60% is imported and is increasing substantially while domestic oil production is declining.

Weight reduction is one of the most practical ways to increase the fuel economy of vehicles.

- 10% Vehicle Weight = + 6-8% Vehicle Mileage/gallon

An important additional benefit of increasing fuel economy is a reduction in greenhouse gas emissions, notably CO$_2$.

1.85 billion metric tons (1,850,000,000 tons) of CO$_2$ emitted by vehicles on U.S. roads in 2002.
Carbon Fiber is in Some US Cars Today

**Ford GT**
- Carbon fiber composite rear deck lid and seat (4500 units total)
- Carbon fiber fenders, wheel house, and floorpan (7000 units/year)

**2006 Z06 Corvette**

**2006 Dodge Viper**
- Carbon fiber LH/RH fender/sill supports, LH/RH door inner reinforcements, windshield surround reinforcement (2000 units/year)

But not yet **Affordable for high volume production vehicles!**
Lamborghini Sesto Elemento

“Sixth Element”

Curb weight of 2202 pounds
Powered by 5.2-liter, 570-horsepower V-10 engine
Estimated 0-62 mph time of 2.5 seconds
Ultimate Example of “Vehicle” Lightweighting

The Boeing 787 Dreamliner comprises 50% by weight carbon fiber composite materials.

- Five (5) tons of weight saved on the wings alone
- Ultimate-load tests completed April 7, 2010: wings were flexed upward by 25 feet (7.6 meters) during tests!

First flight: December 15, 2009
Manufacture of Carbon Fiber – Key Stages

**Oil-Based**

1. "Drill Baby, Drill"
2. Refine Oil
   - Produce PAN
3. Solvent Spin Fiber
4. Stabilize Fiber
5. Carbonize Fiber
6. "Graphitize" Fiber

**Lignin-Based**

1. Harvest Biomass
2. Isolate Lignin
3. Melt Spin Fiber
4. Stabilize Fiber
5. Carbonize Fiber
6. "Graphitize" Fiber
Carbon Fiber Production

Conversion of Precursor Fiber into Carbon Fiber (Conventional Process)
Structural Applications of Carbon Fibers

Fiber Tensile Strength, GPa

Fiber Modulus, GPa

Automotive Target
Strength: 1.72 GPa
Modulus: 172 GPa

Target
Strength: 1.72 GPa
Modulus: 172 GPa

Managed by UT-Battelle
for the U.S. Department of Energy
Carbon Fiber Costs (Baseline)

With conventional processing using a carbon fiber-grade PAN, precursor is over 50% of the carbon fiber cost

Four Elements of Cost Reduction:
1. Scale of Operations
2. Precursors
3. Conversion
4. Manufacturing of Composite
#1 Priority: Reduce CF Cost to $5 - $7 per lb

Mechanical Property Targets:
- Strength \( \geq 1.72 \text{ Gpa} \) (250 Ksi)
- Modulus \( \geq 172 \text{ Gpa} \) (25 Msi)
- Strain: \( \geq 1\% \)

13 Kg of CF on each North American vehicle would consume world CF supply!

London, June 11, 2009: Boeing projects market for 29,000 new commercial airplanes valued at $3.2 trillion over next 20 years
Projected Carbon Fiber Market Demand

Source: Zoltek Annual Report, February 2007

100 MM lbs Carbon Fiber Produced in 2008

The Growth and Challenges are Multi-Industry, not just Automotive

700% Growth in Next 10 Years
Longer blade designs would benefit from the incorporation of CF:
- Energy captured is greater with longer blades (square of radius)
- Blades must be both stiff and light.

- Insufficient supply of CF at any price
- Lower price needed for more efficient designs
- Greatly increased supply of CF at lower price needed now for rapid deployment of CF-composites in wind turbine blades (a fatigue-critical component of wind energy farms)
Low Cost Production of Carbon Fiber from Lignin

Specifications for Lignin Material Suitable for Melt Spinning and Carbon Fiber Production

Preliminary lignin “specifications”:

• > 99% lignin

• < 5 wt% volatiles measured at 250ºC (achieved* < 2 wt%)

• < 1000 ppm ash (achieved* 250 ppm)

• < 500 ppm non-melting particulates > 1μm (achieved* 100 ppm)

* achieved in ORNL lignin purification work

Target Price: ≤ 50¢/lb ($1.10/kg) ready for melt spinning
Low Cost Production of Carbon Fiber from Lignin

The Rocky Road to Process Development:

**Myth:** “Lignin is Readily Available”........It is NOT!
- Kraft Lignin: Only one commercial source worldwide (60,000 tpy)
- Sulfite Lignin: Not suitable for CF; declining production
- Soda Lignin: Difficult to process into CF; declining production
- Organosolv Lignin: No current commercial source
- Biorefinery Lignin: Not yet available

**Fact:** “Kraft Process is Designed to Destroy Lignin”!
Robin Rogers, in *Frontiers in Biorefining Conference*, 10/20/2010

**Fact:** “We Want Less Lignin in Plants, Not More”!

**Fact:** “In the Bioenergy World, Lignin is the Enemy”!
## Analysis of Lignins – Key Elements

<table>
<thead>
<tr>
<th>Material</th>
<th>C (%)</th>
<th>S (%)</th>
<th>Na (ppm)</th>
<th>K (ppm)</th>
<th>Ca (ppm)</th>
<th>Ash (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HWL</td>
<td>59</td>
<td>2.45</td>
<td>19,000</td>
<td>1770</td>
<td>650</td>
<td>2.8</td>
</tr>
<tr>
<td>HWL-A</td>
<td>65</td>
<td>1.48</td>
<td>73</td>
<td>70</td>
<td>255</td>
<td>0.03</td>
</tr>
<tr>
<td>HWL-O</td>
<td>65</td>
<td>1.40</td>
<td>1,160</td>
<td>104</td>
<td>76</td>
<td>0.01</td>
</tr>
<tr>
<td>SWL-K2</td>
<td>67</td>
<td>1.18</td>
<td>2,390</td>
<td>100</td>
<td>78</td>
<td>0.2</td>
</tr>
<tr>
<td>Alcell</td>
<td>66</td>
<td>0.05</td>
<td>17</td>
<td>44</td>
<td>163</td>
<td>0.001</td>
</tr>
</tbody>
</table>

“HWL” = MeadWestvaco Kraft hardwood lignin as received  
“HWL–A” = “HWL” hardwood lignin aqueous purified by ORNL  
“HWL–O” = “HWL” hardwood lignin organic purified by MeadWestvaco  
“SWL-K2” = Kruger Kraft softwood lignin as received (2nd sample)  
“Alcell” = Lignol Innovations (Organosolv) lignin as received

**Preliminary Target Specification:**

- Volatiles (%) < 5 wt%  
- Ash (ppm) < 1000 (< 0.1 wt%)  
- > 1 µm Particulates (ppm) < 500 (< 0.05 wt%)
Low Cost Production of Carbon Fiber from Lignin

Animation of Process of Lignin Isolation from Biomass and Melt Spinning into Precursor Fiber for Carbon Fiber Production
ORNL Research Directed Towards Production of Multiple Value-added Streams from Biomass Feedstock

Lignin as a Precursor Material for Carbon Fiber Production

Advantages:

• Sustainable, renewable resource material

• Third most abundant organic substance (polymer) on earth after cellulose and chitin

• Accounts for 70% of CO₂ sequestered by plants

• “Readily available”: Co-product of pulping processes; about 200 million metric tons annually pass through pulp and paper mills worldwide (2005 data)

• Future availability from bio-refineries; by-product of cellulosic ethanol production

• Low cost; target of ≤ 50¢/lb ($1.10/kg) ready for melt spinning
Lignin as a Precursor Material for Carbon Fiber Production

Technical Challenges:

• Complex chemical structure; dependent on biomass species and pulping process and conditions (predominantly Kraft process today)
  - What is the best lignin chemistry?
  - Inhomogeneity and polydispersity (molecular weight, etc.)

• High level of impurities, at least in Kraft-pulped lignins
  - How to obtain desired level of purity?
  - Cost of purification? ........eliminated as an issue!

• Rendering the lignin melt spinnable, if not spinnable alone; e.g., softwood

• Stabilizing the lignin precursor fiber at an acceptable rate.......Achieved.

• Attainment of target engineering properties
Influence of Lignin Chemistry – Broad Conclusion

Coniferyl alcohol (90%)

More difficult to melt spin
More amenable to X-linking

Conversely

More amenable to melt spinning
More difficult to X-link

Hardwood Lignin

Softwood Lignin
E. Adler, Wood Science & Technology, 11, 169 (1977)
The poly(phenolic) molecular structure of lignin is very different from that of the poly(aromatic) hydrocarbon structure of petroleum pitches used to make commercial carbon fibers.

Typical pitch molecule

Amenable to melt spinning
Amenable to X-linking (very reactive)
Low Cost Production of Carbon Fiber from Lignin

Melt Spinning and Thermal Processing of Lignin into Carbon Fiber
Melt Spinning Facilities Installed at ORNL
Compounding/Pelletization Line and Multifilament Melt Spinning Line
Melt Spinning of Lignin Fibers

High Melt Spinning Speeds Consistently Demonstrated

- Sustained melt spinning of lignin fiber of target diameter (10 µm) consistently demonstrated at 1500 meters/minute, the maximum speed of the winder on the lab scale equipment.
- Both Kraft and Organosolv-pulped lignins (hardwood).
- Almost 3-times speed of commercial mesophase pitch-based fibers; almost 4-times commercial wet spinning speed of PAN-based fibers.
- Much higher melt spinning speeds appear within reach; e.g., 5000 meters/minute with appropriate winding equipment.
Alcell Lignin Fibers – Melt Spun Fibers

SEM at 2,000 X
Lignin-CNT Fibers – Melt Spun Fibers
SEM at 5000 X
Kraft hardwood lignin (HWL) as received exhibited unstable viscosity characteristics, which hindered melt spinnability.

Aqueous purification of the HWL lignin further degraded viscosity characteristics and melt spinnability of the lignin.

Organic purification of the HWL lignin greatly enhanced viscosity characteristics and melt spinnability of the lignin.

Kraft hardwood lignin (HWL) as received exhibited unstable viscosity characteristics, which hindered melt spinnability.
Influence of Atmosphere During Melt Spinning of Lignin

Complex Viscosity of Organosolv (Alcell) Lignin in Air

Complex viscosity, Pa s

Angular velocity, s$^{-1}$

$T = 210 \text{ C in air}$

managed by UT-Battelle
for the U.S. Department of Energy
Influence of Atmosphere During Melt Spinning of Lignin

Complex Viscosity of Organosolv (Alcell) Lignin in Nitrogen

\[ \text{Complex Viscosity, } \text{Pa s} \]

\[ T = 210 \, ^\circ \text{C in N}_2 \]

Angular velocity, \( s^{-1} \)

Managed by UT-Battelle
for the U.S. Department of Energy
Low Cost Production of Carbon Fiber from Lignin

Relationship Between Devolatilization Time and Glass Transition Temperature ($T_g$) of Organosolv (Alcell) Lignin
Low Cost Production of Carbon Fiber from Lignin

Rapid Stabilization of Lignin Fiber Demonstrated

- Time for satisfactory stabilization of lignin fiber reduced from several days to minutes
- May be possible to stabilize fiber “on-the-fly”; i.e., immediately after spinneret
- All reported work on lignin-based carbon fiber involved very long stabilization times
- Cost of lignin modification << 1¢/lb
- Stabilized fiber yield increased from 95% to > 100% - confirms oxidative cross-linking
- Carbon fiber yield (at 1000°C) from lignin feedstock increased from 46% to 53%
- Overall, lignin chemistry very important!

Modification of lignin chemistry to increase molecular weight and glass transition temperature has a profound, beneficial effect on carbon fiber yield and processing time.

Carbon Fiber Yield at 1000°C (%) vs. Heating Rate to Target Stabilization Temperature

Modified lignin

Lignin as received

Managed by UT-Battelle for the U.S. Department of Energy
Good Inventions are often a Result of Serendipity!

Relationship Between Carbonization Heating Rate(s) and Structure of Lignin-Based Carbon Fiber

- Relatively slow rates of carbonization expose carbon to gasification conditions (H₂O, CO₂ evolution)
- Porosity is introduced into the carbon fiber, including pores with dimensions down to < 1 nm (10 Å) in width
- Pore development is adverse with respect to mechanical properties, but..............................

Can be exploited in other applications where nanoporosity and low cost are pre-requisites; e.g., supercapacitors; CO₂ and VOC capture
High Temperature Heat Treatment of Lignin-based Carbon Fiber

“Graphitization” of Lignin-based Carbon Fiber – XRD Data

- A high degree of graphitic structure can be created in lignin-based carbon fiber through high temperature treatment
- “Graphicity” of lignin-based carbon fiber heat-treated to 2100°C comparable to that of a “T-300” Grade PAN-based carbon fiber
- But, modulus of lignin-based carbon fiber not “tracking” degree of graphitic structure!

Graphite

(c) Thomas Wülke & Abraxas Verlag

3.35 Å
High Temperature Heat Treatment of Lignin-based Carbon Fiber

Model of Carbonization/Graphitization Process

(from Marsh and Griffiths, 1982)
X-Ray Diffraction Data (July’10)

Fiber Rotated to Scan Orientations

Radial scattering

Axial scattering
Lignin-based Carbon Fiber
Heat Treated to 2700°C

Diffraction Patterns are Qualitatively Similar for Radial and Axial Scans

Peak intensities do **not** depend strongly on angle of tilt indicating **absence** of preferred orientation along the fiber axis.
PAN-based Fiber (T300)
Graphene layers (002) aligned in radial direction

![Graph](image_url)

- **(002)**
- **(100)**
- **(004)**
- **(110)**

Counts / second

2-theta (deg)

- Red: Radial
- Black: Axial
Conclusions from X-Ray Diffraction Data

High degree of graphitic structure (crystallites) obtained, but, low degree of preferential orientation of the crystallites.

---

40 Managed by UT-Battelle for the U.S. Department of Energy
Melt Spinning and Thermal Processing of Lignin into Carbon Fibers

Mechanical Properties (to date):

Tensile Strength: 155 Ksi (62% of Target 250 Ksi)

Modulus: 10-12 Msi (40-48% of Target 25 Msi)

- Properties as measured. No adjustment for porosity (density) of fiber; e.g., adjusted for 20% porosity, highest mechanical properties “increase” to:
  - Tensile strength of 194 Ksi (78% of target)
  - Modulus of 15 Msi (60% of target)

- Highest values obtained with softwood lignin
Melt Spinning and Thermal Processing of Lignin into Carbon Fibers

Does this mean that the targeted carbon fiber properties cannot be obtained with a lignin-based system?? **NO!!**

It means that although we have come a long way in developing an understanding of lignin chemistry as it relates to carbon fiber production, we still have more to learn about what is a complex system, and especially the role of lignin chemistry

**Note**: During the development of PAN-based carbon fibers, it took roughly ten years to reach the engineering properties achieved to date for lignin-based carbon fiber!
Estimated Production Cost of Lignin-based Carbon Fiber
(Kline Economic Model – $ per lb)

Lignin

Precursor Spinning

Oxidation 2-4 Stages $0.99

Note: The Kline economic model currently does not take into account:
- Purification of lignin has been eliminated (potential for lignin cost < 50¢/lb)
- Each 1¢ reduction in lignin price reduces carbon fiber cost by 2¢/lb
- Precursor fiber spinning speed currently almost 3-times Kline baseline

Graphitization 1-2 Stages $0.77

Carbonization 1-2 Stages $0.71

Surface Treatment $0.33

Spooling $0.41

Note: The Kline economic model currently assumes stabilization of lignin fiber will be comparable to conventional stabilization of PAN fiber:
- Stabilization time reduced to minutes
- May be possible to eliminate conventional stabilization step entirely

Total $3.71/lb

Note: The Kline economic model currently assumes a carbon fiber yield of 35%. In fact, carbon fiber yield has been increased to almost 55% using more appropriate lignin chemistry and processing conditions.
Estimated Production Cost of Lignin-Based Nanoporous Carbon Fiber for Electrical Energy Storage and Applications as an Adsorbent

Total
$2.85/lb

Current commercial selling price is $30-40/lb
Low Cost, Lignin-based Carbon Fiber – Path Forward

To reach target mechanical properties for automotive application, emphasis in the continuing work is being placed on:

- Developing a much higher degree of molecular alignment in the precursor fiber:
  - Spinneret design; increasing fiber quench time (draw time); hot drawing of the fiber
  - Substantial increase in lignin molecular weight (3-5-fold) and narrower distribution

- Greater attention to lignin/polymer blends; addition of x-linking agents and catalysts

- A “surge” in the work on the continuous processing of fiber (precursor evaluation line); reduced “handling” of fiber

- Revisiting the fundamentals of lignin chemistry as they apply to carbon fiber production; closer interactions with ORNL-BESC, University of Tennessee (Knoxville), Innventia (Sweden), and IPST at GaTech (Art Ragauskas)
Ultimately, we must get Nature to do the heavy lifting by:

“Plants Designed for Processing”

“Redesign the Lignin Polymer for Specific Applications”

John Ralph, in *Frontiers in Biorefining Conference, 10/20/2010*
Low Cost Production of Carbon Fiber from Lignin (and other suitable precursor materials)

Next Major Step at ORNL

Construction of a Carbon Fiber Technology Center with a Semi-production Scale Carbon Fiber Line
Carbon Fiber Technology Center (≈ $50 million)

- North America’s most comprehensive carbon fiber material and process development capabilities
- Development and demonstration of carbon fiber technology for energy and national security applications
- Low-cost and high-performance fibers
- Fast, energy efficient processing
- Capability to produce up to 25 tons/year of carbon fibers
- Produce fibers for large-scale material and process evaluations by composite manufacturers
- Train and educate workers
- Grow partnerships with US industry

Managed by UT-Battelle for the U.S. Department of Energy
Sponsored by DOE Industrial Technologies Program
Contacts: Ryan Dehoff, 865-574-1094, dehoffrr@ornl.gov
Potential Facility Locations

Horizon Center
East Tennessee Technology Park
Possible Locations
Oak Ridge National Laboratory
Precursor Fiber Melt Spinning Line

- 120 tpa rated capacity for 1 denier per filament (dpf) polyethylene
- Capability to produce lignin, polyolefin, and pitch precursor filaments; potentially upgradeable for production of melt-spun PAN filaments
- Twin screw extruder with precursor compounding and pelletization capabilities
- Operation temperatures from 150 to 350°C; upgradable to 450°C
- Process-dependent ability to produce fibers of 1 to 1.5 dpf
- Ability to produce designed filaments with varied filament morphology, including bi- and tri-component capability
- Tow production up to 6,000 ft/min
- Spun-bond nonwoven web production up to 1,200 ft²/min
- Three induction-heated Godet drawing units with controlled heating to 200 °C and denier control stand
- Metered finish application
Carbon Fiber Conversion Line

- 25 tpa rated capacity for 24k PAN tows
- Exceptionally wide temperature ranges in all ovens and furnaces
- Ability to feed precursor fibers from a creel, from boxes/bales, or in bulk product form
- Material transport in tow or bulk form
- Tow sizes from 3K to 80K
- Enhanced stretching and tensioning capabilities, with significant differential stretching capability in the oxidation module
- Ovens, furnaces, and exhaust systems designed to handle effluent by-products and rates from PAN, lignin, polyolefin, pitch, and rayon precursors
- Low-temperature carbonization furnace designed to accommodate an oxidizing atmosphere
- Expansion slot to enable the addition of an ultra-high-temperature graphitization furnace for specialized carbon fibers
- Expansion slot for an additional surface treatment module
- Finished fibers spooled or packaged in mat or bulk form
- Fully integrated control system with data logging, web interface, and custom access to control room and all data displays
Carbon Fiber Technology Center (≈ $50 million)

**Unique Features:**
- Multiple precursor materials, including lignin, PAN, polyethylene, and pitches
- Tow line for continuous fiber and belt transport for fiber mats and discontinuous fibers
- Advanced technologies for carbon fiber processing
- Facility readily accessible for trial work by industry, academia, and government entities (off-campus)

**Status:**
- Contract awarded for construction of building
- Bid process for selection of vendor for carbon fiber conversion line equipment completed. Contract award imminent
- Bids for melt spinning line equipment under evaluation; contract award by year end
- Start-up date: Late 2012/early 2013
Acknowledgements

US DOE/EERE Vehicle Technologies Office
US DOE/EERE Industrial Technologies Program

Lignin Team Members
Darren Baker
Ashli Clark
Nidia Gallego
Amit Naskar
Grady “Lex” Nunnery
Simioan Petrovan (University of Tennessee)
Daniel Webb
Acknowledgements

Industrial Partners:

• **MeadWestvaco Corporation**, Charleston, SC (2000 through Aug. 2007)
  - Kraft-pulped Hardwood Lignin

• **Kruger Wayagamack**, Quebec, Canada (from Sept. 2007)
  - Kraft-pulped Softwood Lignin

• **Lignol Innovations**, Vancouver, Canada (from Mar. 2008)
  - Organosolv™-pulped lignins from Cellulosic Ethanol Fuel Production

• **Innventia (former STFI-Packforsk)**, Stockholm, Sweden (from Mar. 2009)
  - High Purity, Kraft-pulped Softwood and Hardwood Lignins
Thank You!

Questions?