# Low Cost Carbon Fiber from Renewable Resources

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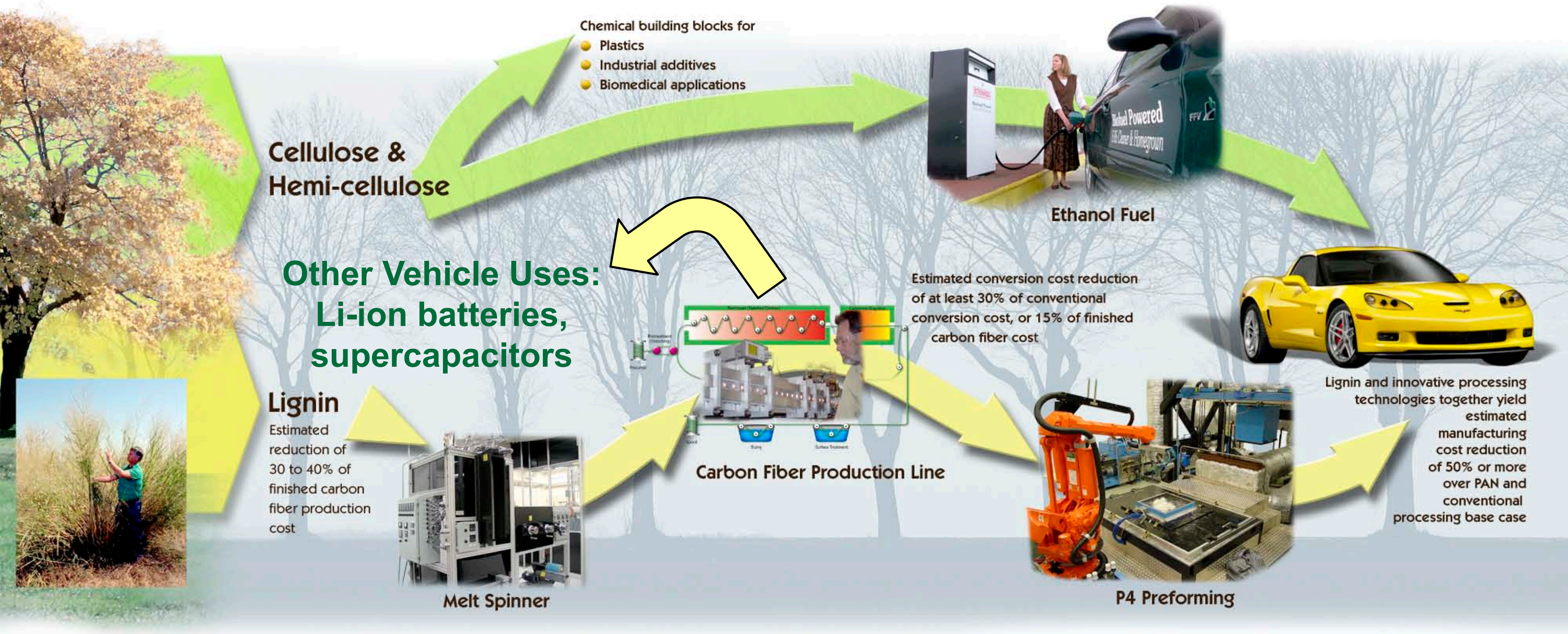
LM005

# ORNL Research Directed Towards Production of Multiple Value-added Streams from Biomass Feedstock




## DOE Office of Vehicle Technologies Lightweight Materials Program

# Overview

## Timeline

Project start date: FY'01
Project end date: FY'12
65% Complete

## Budget

Total project funding thru' FY'08:
- DOE, $6,173
- MeadWestvaco, ~ $500 K (in-kind)

FY'09 Funding - $900 K
FY'10 Funding - $975 K

## Barriers

Barriers:
- Vehicle weight reduction (60-70% potential)
- Affordability (target $5-7/lb price)
- Recyclable/renewable materials

Targets (strength):
- Tensile - 250 Ksi (1.72 GPA)
- Modulus - 25 Msi (172 Gpa)
- Strain - ≥ 1%

## Industrial Partners

MeadWestvaco Corporation, USA (2000 through Aug. 2007)
Kruger Wayagamack, Canada (from Sept. 2007)
Lignol Innovations, Canada (from Mar. 2008)
Innventia (former STFI-Packforsk), Sweden (from Mar. 2009)

# Focus Research Areas in FY'09

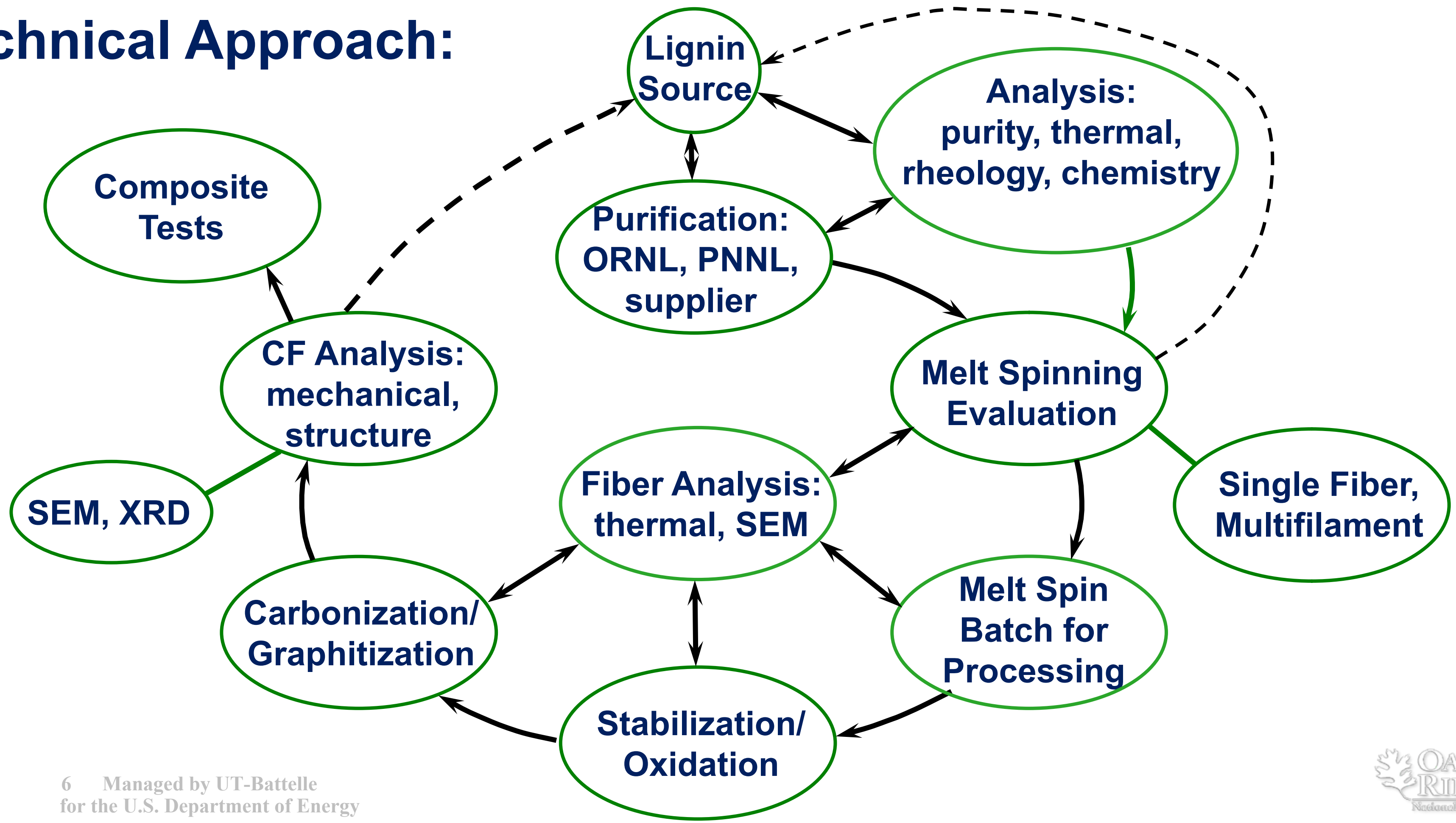
- Establishment of Melt Spinning Conditions for Organosolv™ Lignin
- Enhancement of Lignin Properties to Facilitate Fiber Stabilization
- Establishment of Maximum Spinning Speed of Lignin Fibers
- Correlation of Fundamental Properties of Lignin Materials with Melt Spinnability and Conversion to Carbon Fiber (CF)
- Conversion of Lignin Precursor Fiber into Carbon Fiber
- High Temperature Treatment of Lignin-based Carbon Fiber
- Correlation of CF Mechanical Properties with Processing Conditions

# Industrial Partners:

- **Lignol Innovations**, Vancouver, Canada (from March'08)
  - Organosolv™-pulped Lignins from Cellulosic Ethanol Fuel Production
- **Kruger Wayagamack**, Quebec, Canada (from Sepember'07)
  - Kraft-pulped Softwood Lignin
- **Innventia (former STFI-Packforsk)**, Stockholm, Sweden (from March'09)
  - Kraft-pulped Softwood and Hardwood Lignins (high purity)

# Low-cost, Lignin-based Carbon Fiber

## Technical Approach:



# Low Cost Carbon Fiber from Renewable Resources

## Animation of Process of Lignin Isolation from Biomass and Melt Spinning into Precursor Fiber for Carbon Fiber Production

# Lignin as a Precursor Material for Carbon Fiber Production

## Advantages:

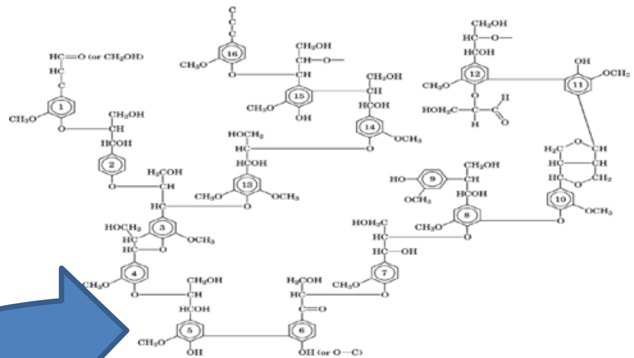
- Sustainable, renewable resource material
- Second most abundant organic substance (polymer) on earth after cellulose
- Accounts for 70% of $CO_2$ sequestered by plants
- “Readily available”: Co-product of pulping processes; about 200 million metric tons annually pass through pulp and paper mills worldwide (2005 data)
- Increasingly available 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

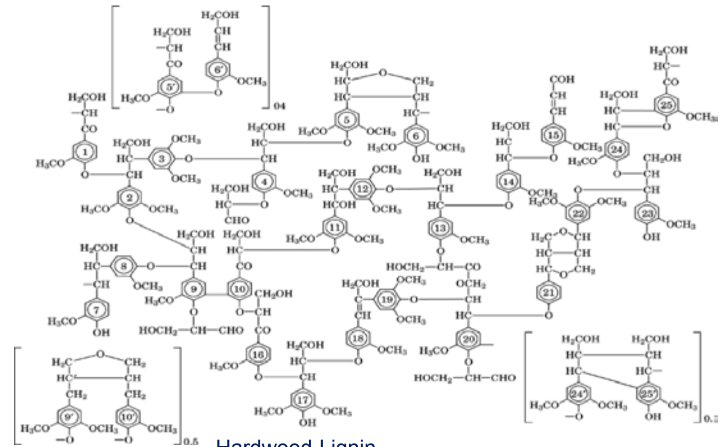
## Technical Challenges:

- 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
- Attainment of target engineering properties

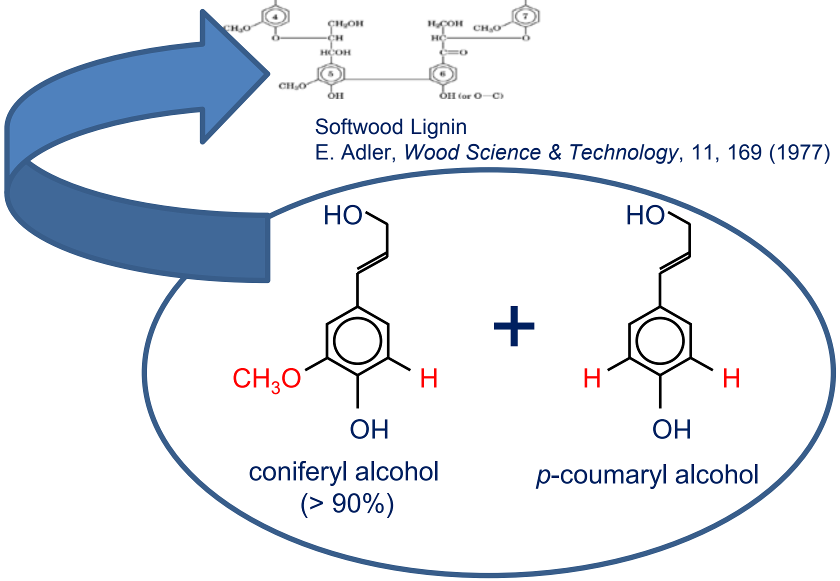
# Influence of Lignin Chemistry – Broad Conclusion

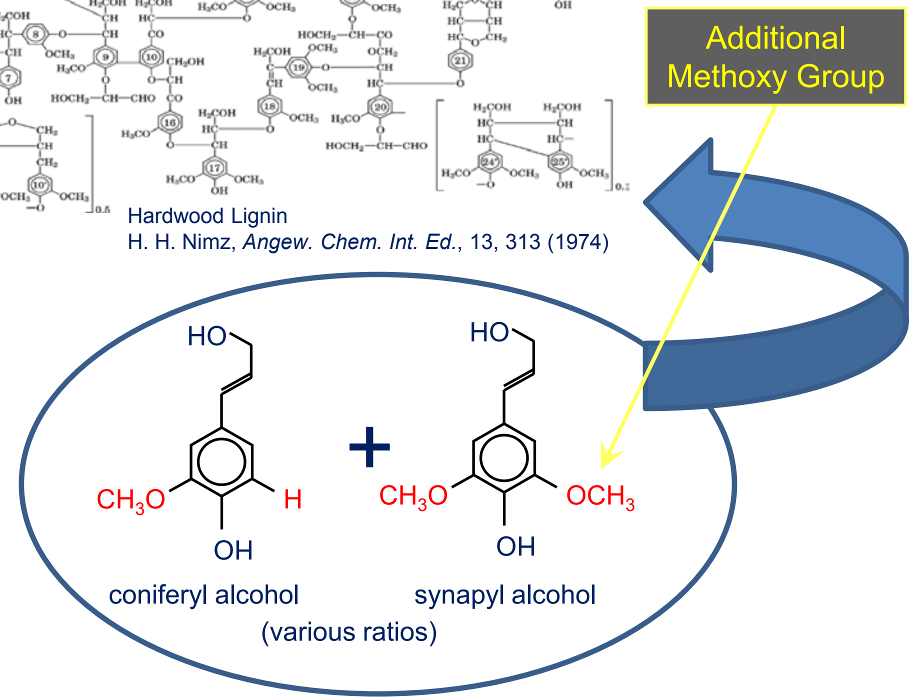


Softwood Lignin
E. Adler, *Wood Science & Technology*, 11, 169 (1977)



Hardwood Lignin
H. H. Nimz, *Angew. Chem. Int. Ed.*, 13, 313 (1974)



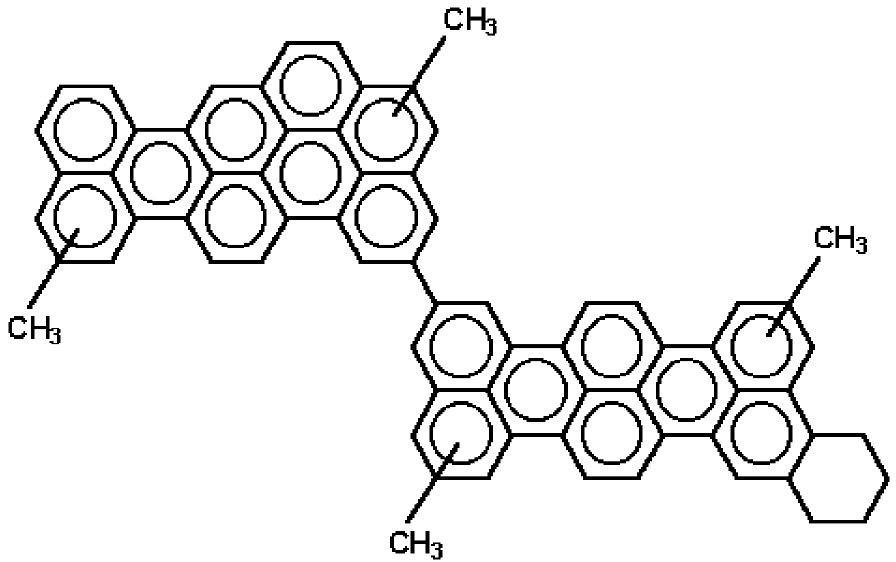




More difficult to melt spin
More amenable to X-linking

More amenable to melt spinning
More difficult to X-link

Conversely

# 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**

# Lignin Materials - Summary

| Feature/Property | Kraft-Pulped | Organosolv-pulped |
|---|---|---|
| Current Availability<br>Future Availability | Commercial (1 supplier, MWV)<br>P&P mills moving to lignin isolation | Semi-commercial<br>Biorefineries on horizon |
| Price, as isolated<br>Price, purified | 20¢/lb<br>Aqueous purified: ≤ 50¢/lb<br>Organic purified: near target 50¢/lb | ≤ 50¢/lb<br>Purification not necessary |
| Purity (as isolated from black liquor) | MeadWestvaco – Poor<br>Kruger – Progressing to Good | Excellent<br>(Lignol Innovations) |
| Melt Spinnable, as isolated | Hardwood – Yes*<br>Softwood – No, as is;<br>Yes*, with plasticizer | Hardwood – Yes<br>Softwood - ? |
| Melt Spinnable, purified | Aqueous purified hardwood – No, but Yes with plasticizer<br>Organic purified hardwood - Highly | Purification not necessary |
| Control Pulping Conditions (to tailor lignin properties) | No<br>Lignin isolation and any necessary purification is tied to pulping process (modern Kraft mills are highly integrated, closed loop operations) | Yes<br>Organosolv process conditions highly adaptable to enhance lignin properties |



*** Impurities not withstanding**

# Lignin Materials – Summary (cont.)

| Feature/Property | Kraft-Pulped | Organosolv-pulped |
| --- | --- | --- |
| Molecular Weight | Hardwood: 2000-3000<br>Softwood: 1000-2000 | > 2000<br>Process controllable |
| Glass Transition ($T_g$) | Hardwood: "low" **<br>Softwood: "high" ** | Process controllable |
| Melting Point ($T_m$) | Hardwood: "low" **<br>Softwood: typically decomposes | Process controllable |
| Reactivity to Oxygen | Hardwood: "low" **<br>Softwood: "high" ** | "low" ** |
| Cross-linking Rate | Hardwood: "low" **<br>Softwood: "high" ** | "moderate" ** |
| Carbon Content (wt% C) | Hardwood: 55-60<br>Softwood: 60-65 | 55-65 |

** Relative, not absolute terms

# Melt Spinning Facilities Installed at ORNL

# Technical Accomplishments

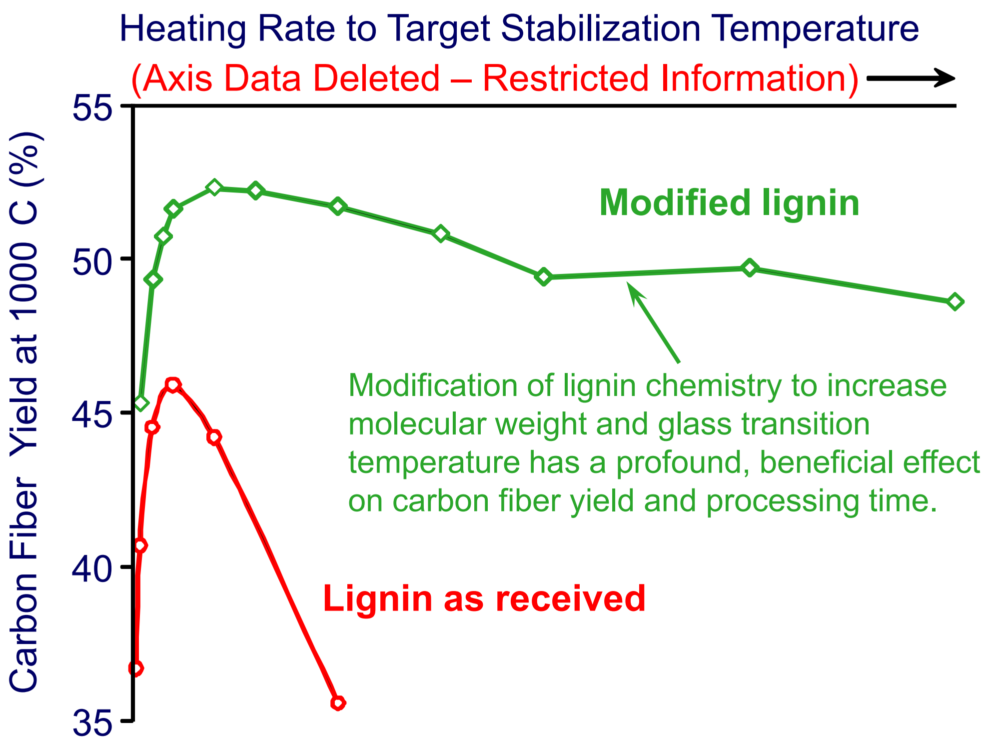
## High Melt Spinning Speeds Consistently Demonstrated

12-filament fiber spun from Kraft hardwood lignin

- **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**

# Technical Accomplishments

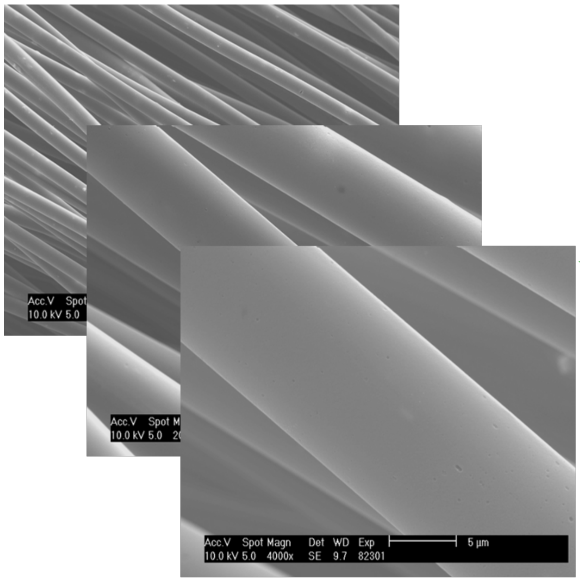
## Rapid Stabilization of Lignin Fiber Demonstrated

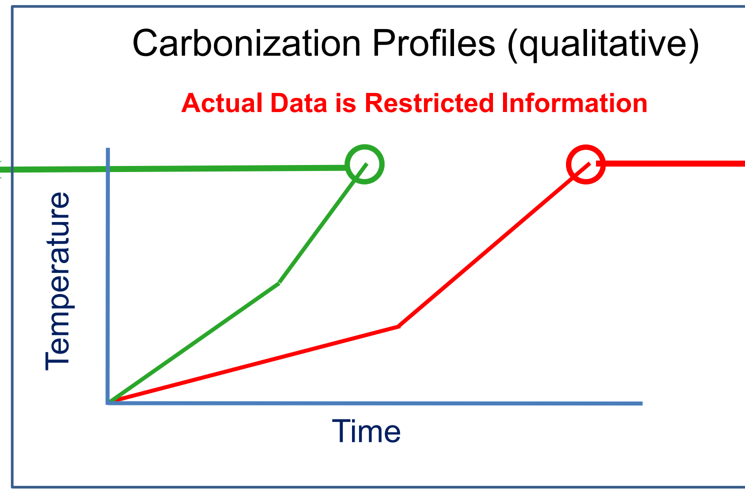


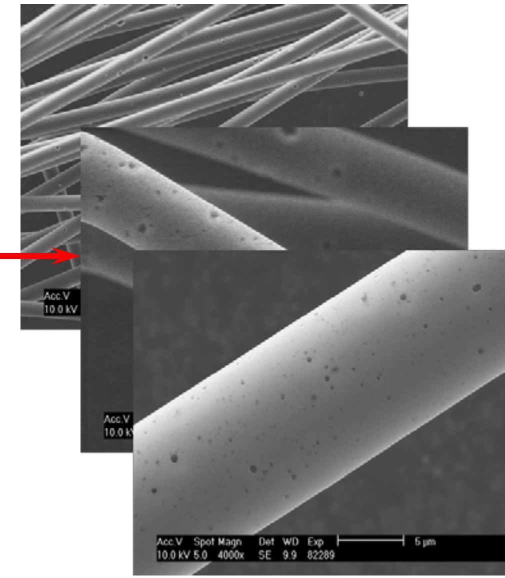

- Time for satisfactory stabilization of lignin fiber reduced from several days to minutes
- May be possible to stabilize fiber "on-the-fly"; i.e., immediately after spinneret
- All reported work on lignin-based carbon fiber involved very long stabilization times
- Cost of lignin modification << 1¢/lb
- 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!

# Technical Accomplishments

## Identified Mechanism of Defect Development During Carbonization of Lignin Fiber





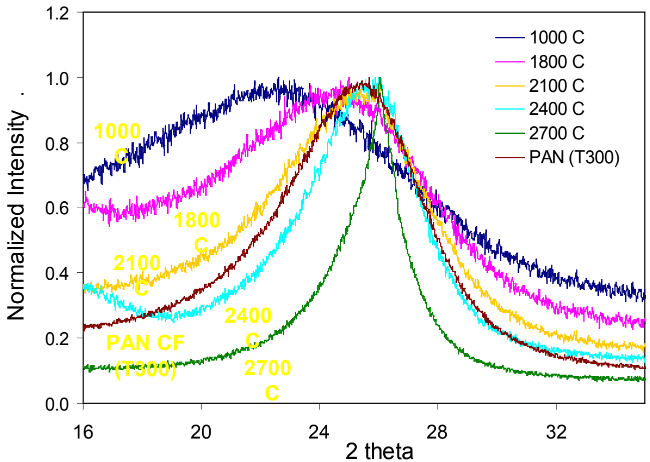
Good Fiber Structure

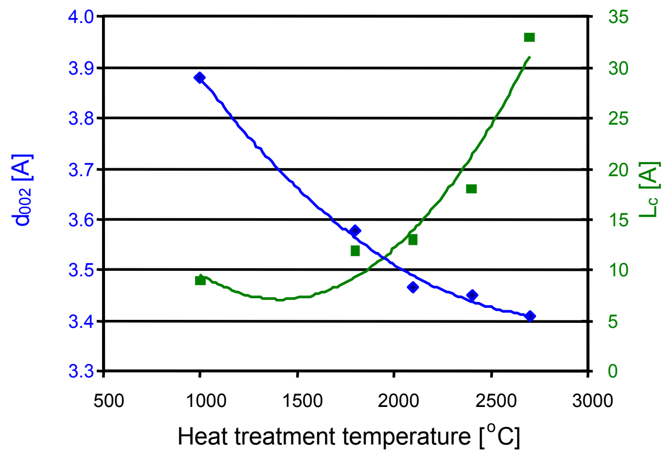
Poor Fiber Structure

- Relatively slow rates of carbonization expose carbon to gasification conditions ($H_2O$, $CO_2$ 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

# Technical Accomplishments

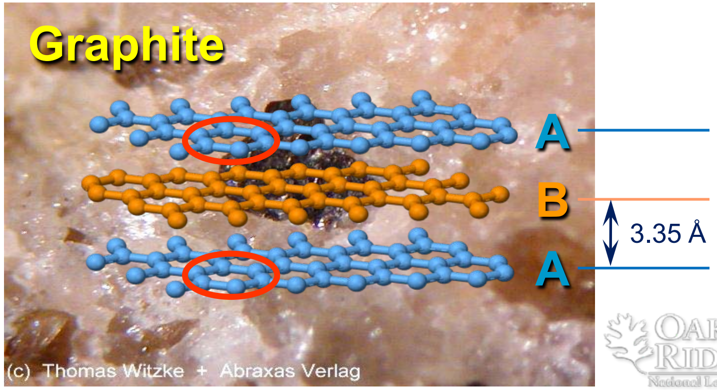
## “Graphitization” of Lignin-based Carbon Fiber – XRD data



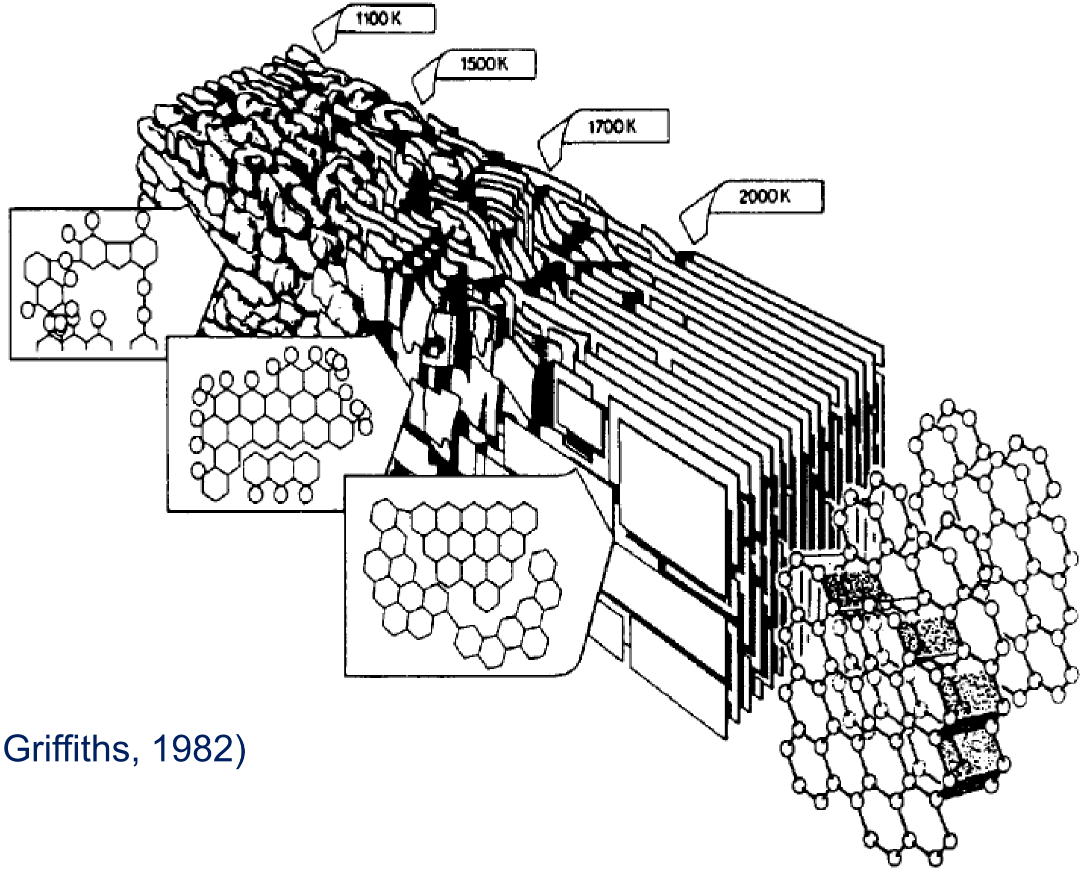

| HTT<br>[ C] | $d_{002}$<br>[Å] | $L_c$<br>[Å] |
|---|---|---|
| 1000 | 3.878 | 9 |
| 1800 | 3.576 | 12 |
| 2100 | 3.468 | 13 |
| 2400 | 3.450 | 18 |
| 2700 | 3.408 | 33 |
| PAN (T300) | 3.464 | 14 |

- 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!



# Possible Cause: Inhomogeneous Structure of Fiber

## Model of Carbonization/Graphitization Process




(from Marsh and Griffiths, 1982)

# Technical Accomplishments

## Highlights of Progress on the Lignin-based Carbon Fiber Project, FY'09/10

- Consistently demonstrated sustainable melt spinning of multifilament tow from both Kraft-pulped and Organosolv-pulped hardwood lignins, as received, at 1500 m/minute
- Through a very low cost modification of lignin properties, accelerated the rate of stabilization of lignin fiber by three orders of magnitude; viable process achieved
- Indications obtained that it may be possible to eliminate conventional stabilization step
- Increased understanding of lignin-chemistry and how to manipulate it to enhance processing of lignin into carbon fiber
- Yield of carbon fiber from lignin feedstock material increased to near 55%; i.e., about 85-90% of average theoretical carbon content of lignin
- Demonstrated high degree of "graphitizability" of lignin-based carbon fiber
- Tensile strength of lignin-based carbon fiber increased to near 70% of target 250 Ksi
- On downside, modulus of fiber hovering around 50% of target 25 Msi

# Low Cost Carbon Fiber from Renewable Resources

## Challenges and Path Forward – FY'10/11

- Continue efforts to refine lignin chemistry to facilitate conversion to carbon fiber
- Continue to optimize fiber conversion conditions to enhance mechanical properties
- Increase work on addition of polymers (PEO, PET) to enhance mechanical properties
- Firmly establish cause of fiber modulus not tracking degree of graphitic structure
- Increase work on continuous conversion of lignin fiber into carbon fiber
- Establish whether lignin precursor fiber can be stabilized "on-the-fly" to eliminate conventional stabilization step

# Estimated Production Cost of Lignin-based Carbon Fiber (Kline Economic Model – $ per lb)

Lignin → Precursor Spinning → Oxidation 2-4 Stages $0.75

$0.50

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

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

Carbonization 1-2 Stages $0.65 → Graphitization 1-2 Stages $0.70 → Surface Treatment $0.10 → Spooling $0.15

Total $2.85/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.

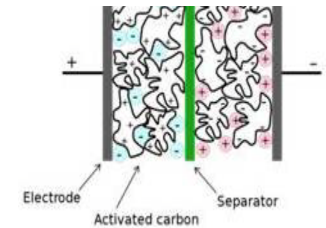
# Leveraging of Knowledge Base Developed on Low Cost Carbon Fiber Through the EERE/Vehicle Technologies Lightweight Materials Program

# Cross-cutting Applications of Lignin-based Carbon Fibers

# ORNL Projects Underway

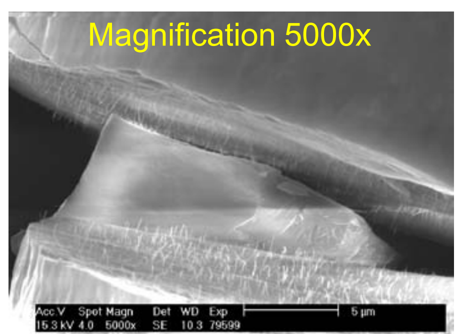
# Electrical Energy Storage for Plug-in Hybrid & All-electric Vehicles (etc.)

Supercapacitor (EDLC)



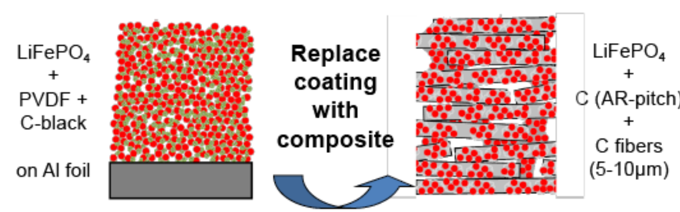

- Supercapacitors: High surface area, nanoporous (activated) carbon fibers for electrostatic energy storage in electrodes
- Lithium-ion Batteries
  - ✓ Structural reinforcement and active energy storage in anode
  - ✓ Structural reinforcement of cathode
  - ✓ Enhanced electrical and thermal conductivities of both electrodes

*In situ* incorporation of carbon nanotubes during melt spinning of lignin fiber (to enhance electrical and thermal conductivity properties)




**Approach - *graphite current collector***

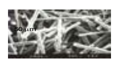
- A conductive carbon skeleton will improve uniformity of current and temperature in cathode - extending lifetimes and safety.



# Energy Efficient HVAC Systems with $CO_2$ and VOC Capture

- Regenerable $CO_2$/VOC adsorption system with very low parasitical energy consumption (< 0.5%)
  - ✓ HVAC energy use in Buildings Sector = 14% of nation's total primary energy consumption in 2006 (99.5 Quads ≈ 17.1 billion barrels of oil)
  - ✓ 30% of energy squandered to simply heat/cool air drawn into HVAC to dilute respiratory $CO_2$ to ASHRAE 62 Standard (≈ 16% of U.S. oil imports!)

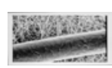
**Solution:** → **Electrical Swing Adsorption (ESA) Systems**


CFCMS Material

Regeneration Cycle $CO_2$ Out

Adsorption Cycle Clean Air Return

Adsorption Cycle Air ($CO_2$) In


Polymer nanofiber for particulate capture

Regeneration by resistive heating (2-24 VDC)

Desorption Zone (30°)

$CO_2$/VOCs

Clean Air

Adsorption Zone (330°)

Air

Air with $CO_2$ and VOCs

Basic Principle of ESA

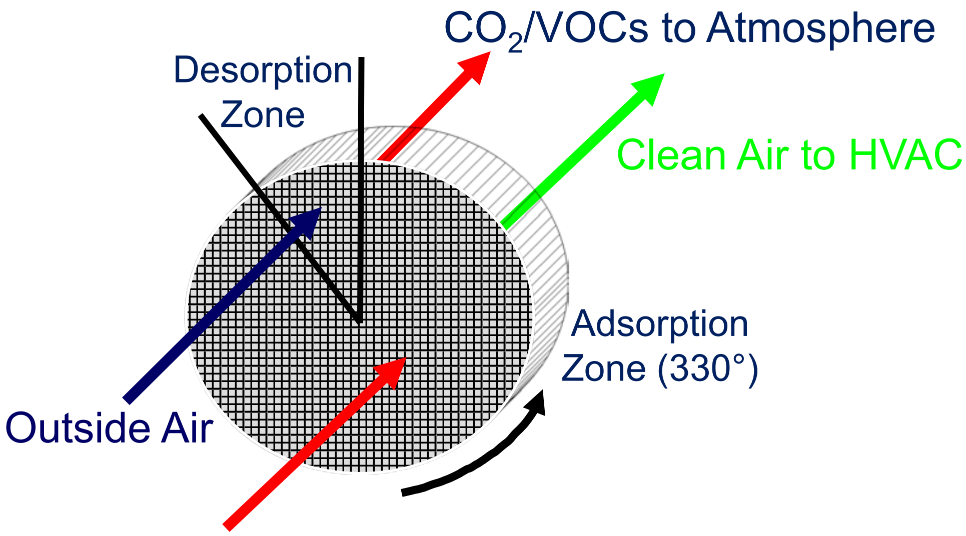
Continuous ESA System

Patent Application: US-2008-0047436-A1; Frederick S. Baker: "Rotary Adsorbers for Continuous Bulk Separations," Published 2/28/08

- Disposable high efficiency filters for VOC Capture

# Continuous Scrubbing of $CO_2$/VOCs in HVAC Systems

A rotary adsorption system can remove $CO_2$ and VOC contaminants in air at large volumetric flow rates and with high energy efficiency




- The $CO_2$/VOC-laden air from HVAC passes through the rotary adsorption unit where the $CO_2$ and VOCs are captured on nanoporous (activated) carbon fiber material in a honeycomb form
- The clean air is re-circulated back into the HVAC system
- The captured $CO_2$ and VOCs are continuously desorbed from the adsorption media as the revolving wheel passes through the desorption (regeneration) zone
- The regeneration air flow with $CO_2$ and VOCs is rejected to outside atmosphere

**UT-B Patent Application: US-2008-0047436-A1; Frederick S. Baker**
**"Rotary Adsorbers for Continuous Bulk Separations," Published 2/28/08**

# Large Industrial Application – Proprietary Research Project

- Structural reinforcement
- Initial test data very positive
- Relevant properties of lignin-based carbon fiber comparable to much more expensive commercial carbon fiber
- Opportunity for near-term commercialization of lignin-based carbon fiber; e.g., 1-2 years

# Acknowledgements

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Industrial Partners

Lignol Innovations (Canada)

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