Low Cost Carbon Fiber from Renewable Resources

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Overview

Timeline

Project start date: FY'01
Project end date: FY'12
60% Complete

Budget

Total project funding thru' FY'07:
- DOE, $5,648
- MeadWestvaco, ~ $500 K (in-kind)

FY'08 Funding - $525 K
FY'09 Funding - $900 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 (2000 through Aug. 2007)
Kruger Wayagamack (from Sept. 2007)
Lignol Innovations (from Mar. 2008)
STFI-Packforsk/Swedish Research Institute (from Mar. 2009)

Focus Research Areas in FY'08

- Replacement of MeadWestvaco Hardwood Lignin
- Establishment of Melt Spinning Conditions for New Lignin Materials, Notably Kraft-pulped Softwood Lignin
- Demonstrate High Spinning Speeds of Lignin Precursor Fiber
- Correlation of Fundamental Properties of Lignin Materials with Melt Spinnability and Conversion to Carbon Fiber
- Conversion of Lignin Precursor Fiber into Carbon Fiber
- Mechanical Property Testing of Carbon Fiber

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
- **STFI-Packforsk/Swedish Research Institute (from Mar. 2009)**
  - Kraft-pulped Softwood and Hardwood Lignins

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

Insert Video Clip Here

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 20¢/lb (45¢/kg)**

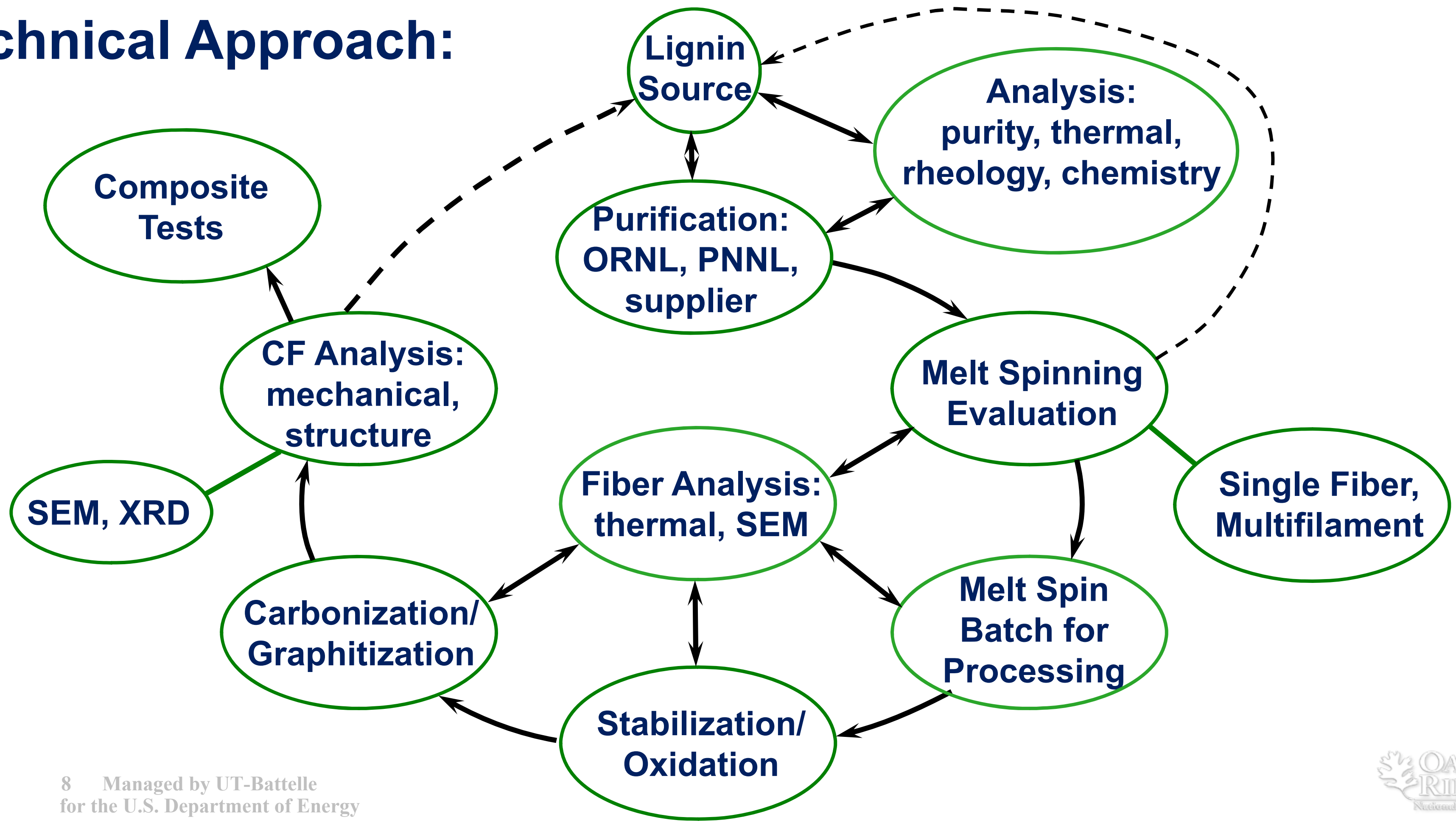
Lignin as a Precursor Material for Carbon Fiber Production

Technical Challenges:

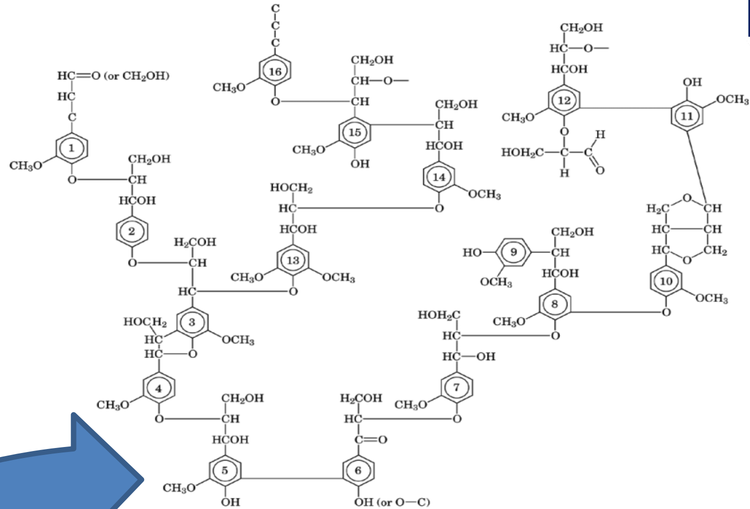
- Complex chemical structure; dependent on biomass species and pulping process and conditions (predominantly Kraft process today)
  - What is the best lignin chemistry?
  - Inhomogeneity and polydispersity (molecular weight, etc.)
- High level of impurities, at least in Kraft-pulped lignins
  - How to obtain desired level of purity?
  - Cost of purification? ……..**rapidly being 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

Low-cost, Lignin-based Carbon Fiber

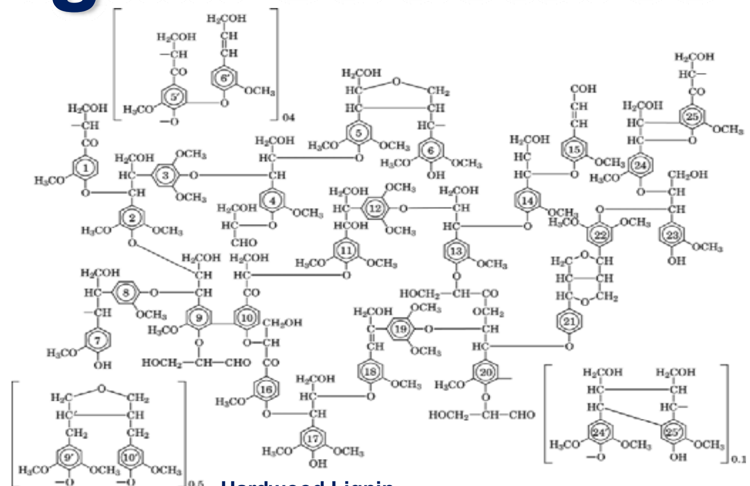
Technical Approach:



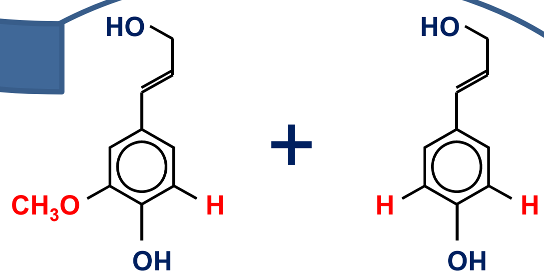
Lignin Structures



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

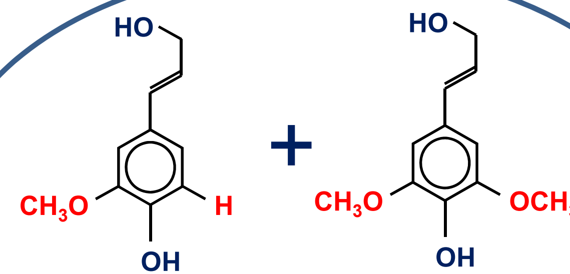


Hardwood Lignin
H. H. Nimz, *Angew. Chem. Int. Ed.*, 13, 313 (1974)



coniferyl alcohol
(> 90%)

p-coumaryl alcohol

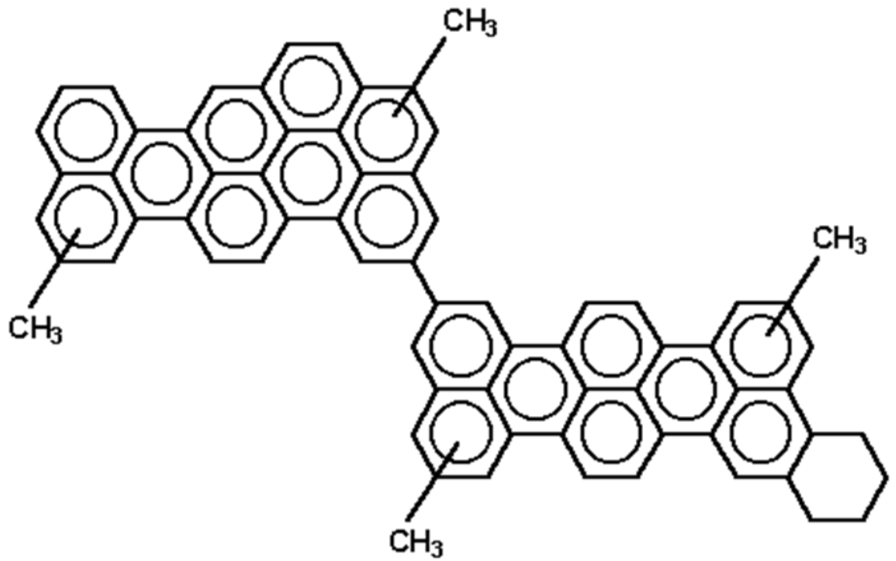


coniferyl alcohol

synapyl alcohol

(various ratios)

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

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

Preliminary lignin “specifications”:

- < 5 wt% volatiles measured at 250ºC (achieved* < 5 wt%)
- < 1000 ppm ash (achieved* 250 ppm)
- < 500 ppm non-melting particulates > 1µm (achieved* 100 ppm)

* achieved in ORNL lignin purification work

Target Price: ≤ 20¢/lb (45¢/kg) ready for melt spinning

Analysis of Lignins – Key Elements

Lignin Material	C (%)	S (%)	Na (ppm)	K (ppm)	Ca (ppm)	Ash (%)
HWL	59	2.45	19,000	1770	650	2.8
HWL-Aq	65	1.48	73	70	255	0.025
HWL-SE	65	1.40	1,160	104	76	0.01
SWL-K2	67	1.18	2,390	100	78	0.2
Alcell	66	0.05	17	44	163	0.001
Target	>60	Low	Low	Low	Low	< 0.1

"HWL" = MeadWestvaco (MWV) hardwood lignin as received

"HWL–Aq" = Hardwood lignin aqueous purified by ORNL

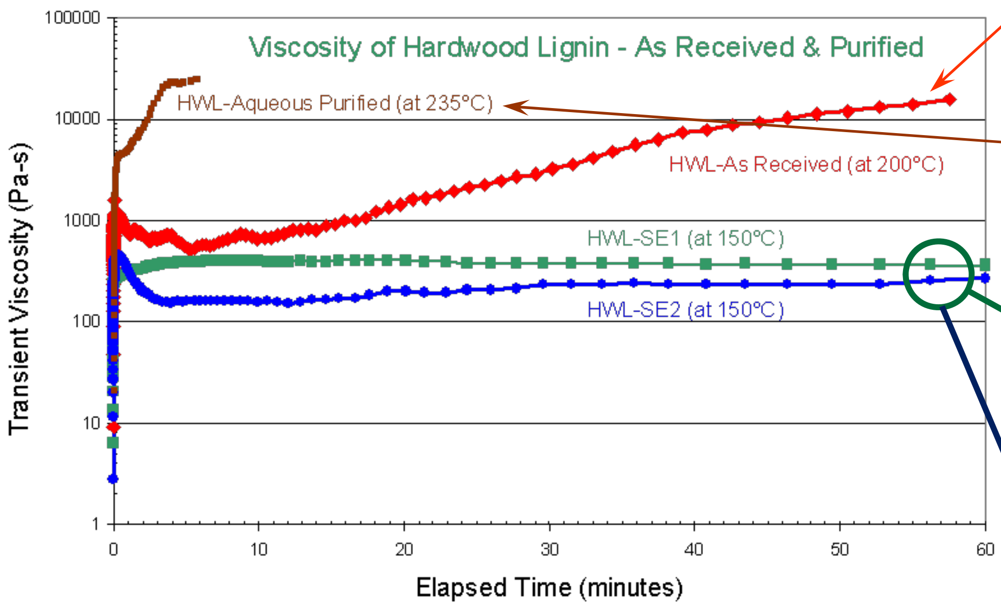
"HWL–SE" = Hardwood lignin solvent extracted by MWV

"SWL-K2" = Kruger softwood lignin as received (2nd sample)

"Alcell" = Lignol Innovations (Organosolv™) lignin as received

Technical Accomplishments

Established Methodology for Characterization of the Rheology of Lignin Materials and Correlation with Melt Spinnability



Kraft hardwood lignin (MeadWestvaco) as received exhibits unstable viscosity characteristics which hinder melt spinnability.

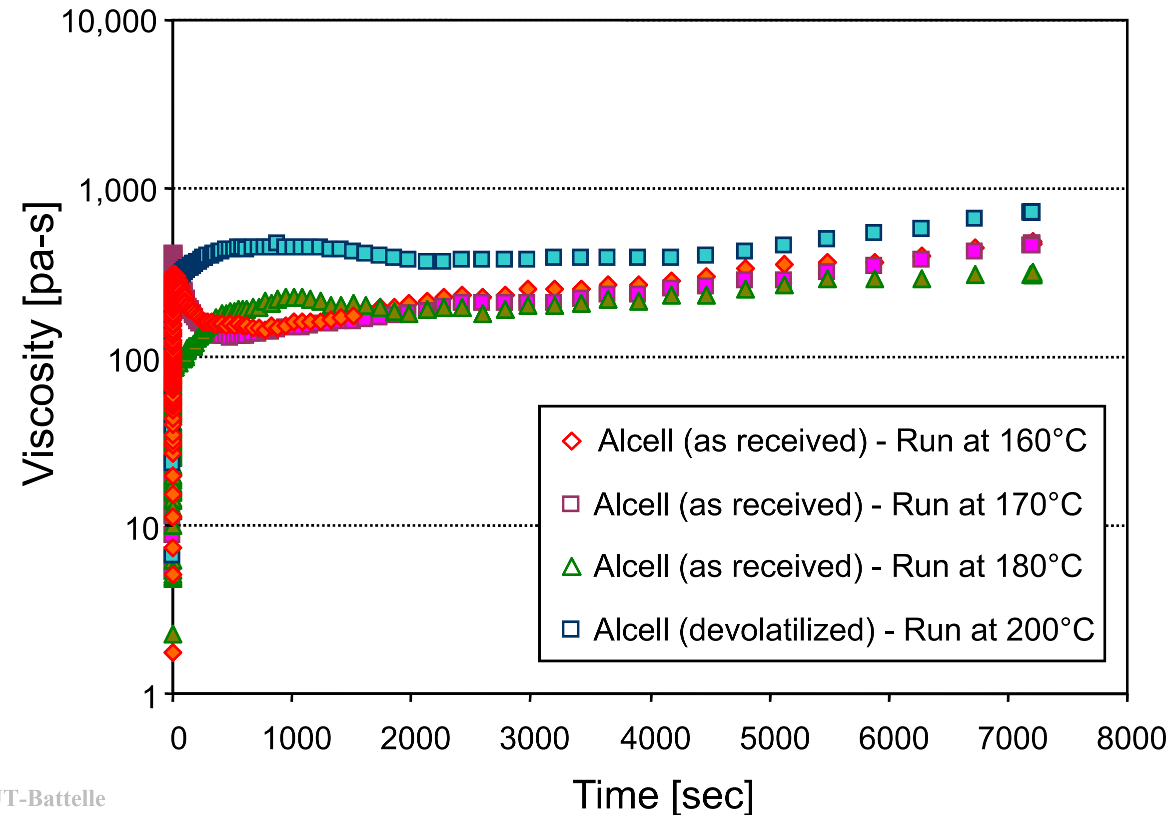
Purification of the lignin using an aqueous procedure further degrades viscosity characteristics and melt spinnability of the lignin.

Purification of the lignin using a solvent extraction procedure greatly enhances viscosity characteristics and melt spinnability.

Hardwood lignin solvent-extracted by MeadWestvaco (HWL-SE1) and PNNL (HWL-SE2), respectively, exhibit similar viscosity characteristics, but the former exhibits a higher degree of stability.

Technical Accomplishments

Established Melt Spinning Conditions for Alcell™ Lignin Through Characterization of its Rheology

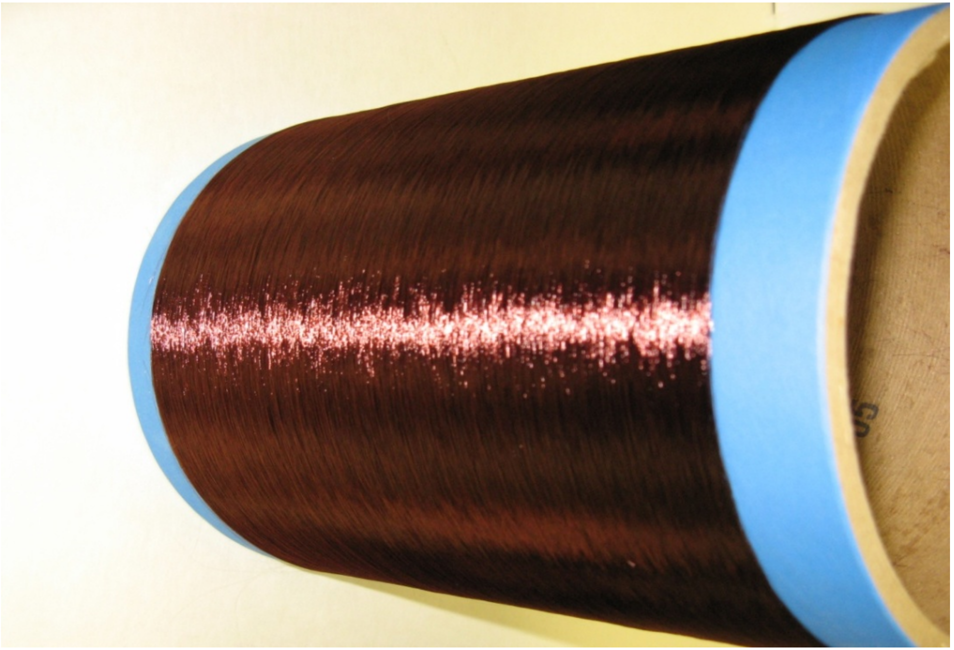


Melt Spinning Facilities Installed at ORNL

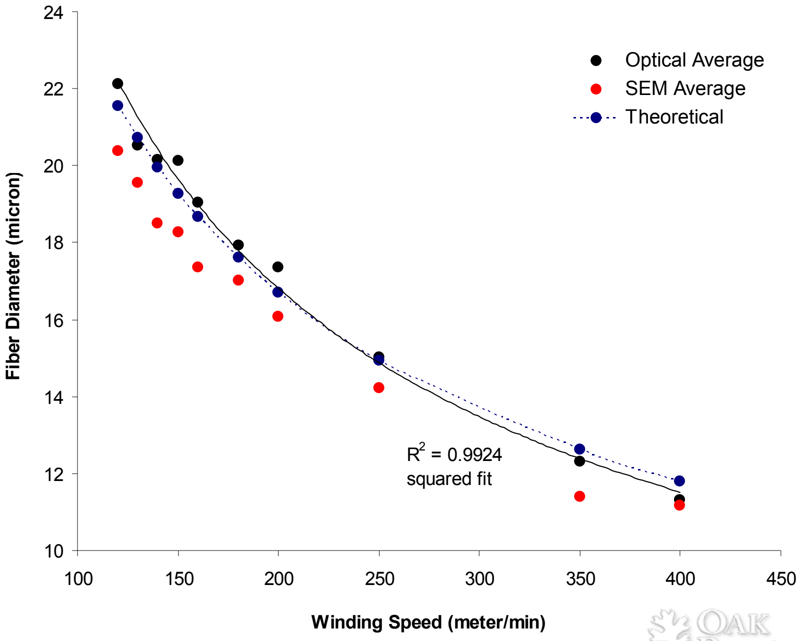
Technical Accomplishments

Relationship Between Winding Speed and Fiber Diameter

Kraft Hardwood Lignin (solvent-extracted) with 150 micron Spinneret

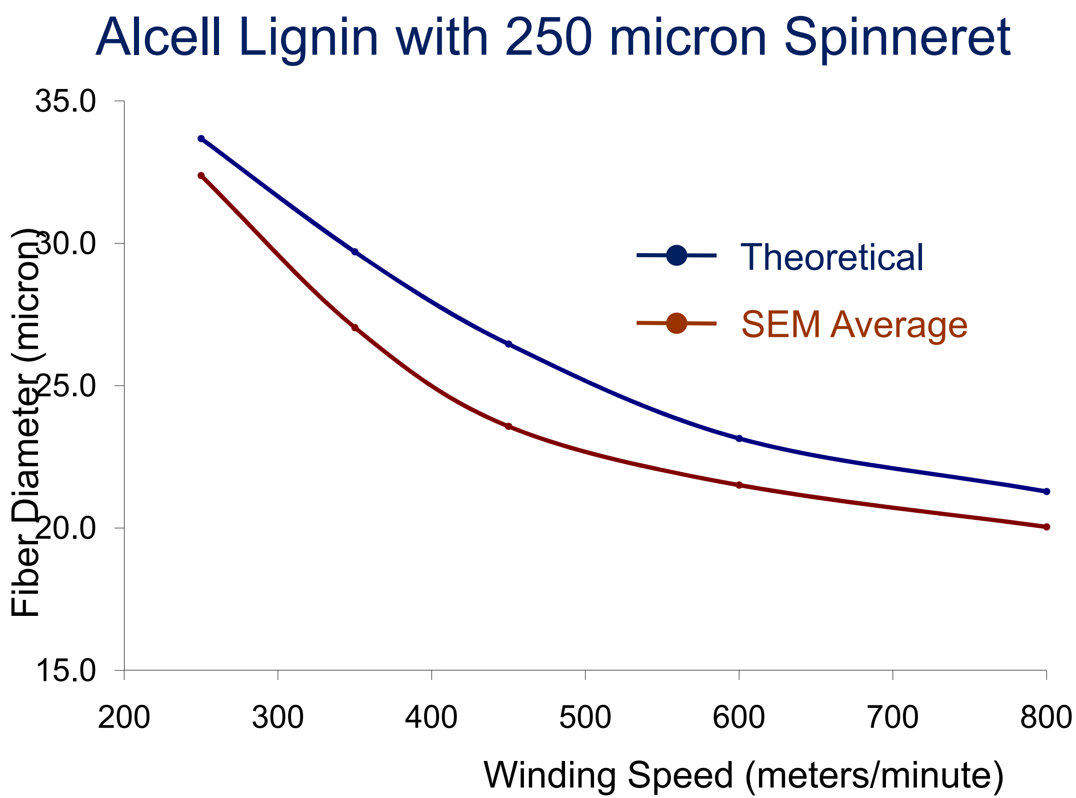


12-filament fiber spun from solvent-extracted hardwood lignin (HWL-SE1)



Technical Accomplishments

Relationship Between Winding Speed and Fiber Diameter



Technical Accomplishments

Established Methodology for Melt Spinning Softwood Lignin Using a Purified Hardwood Lignin as the Plasticizing Agent

Lignin Composition (wt%)		Melting Point (Fisher-John) (°C)	Spinnable (Yes/No)	Melt Description (°C)		
Softwood (K2)[1]	Hardwood (HWL-SE)[2]			*Initial Softening*	*Localized melting*	*Appreciable melting*
100	0	**190**	No	170	178	187
80	20	**179**	Yes	159	166	174
50	50	**140**	Yes	117	123	130
0	100	**128**	Yes	108	112	120

[1] Kraft softwood lignin furnished by Kruger Wayagamack
[2] Kraft hardwood lignin (solvent-extracted) furnished by MeadWestvaco

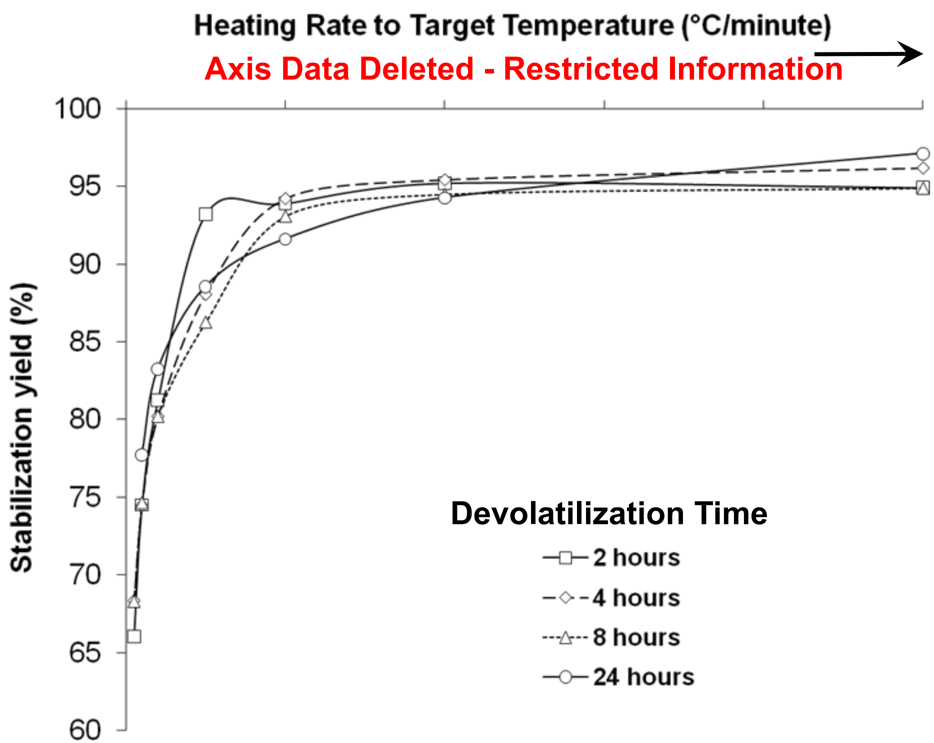
Technical Accomplishments

Establishment of Thermal Processing Conditions for Conversion of Lignin Precursor Fiber into Carbon Fiber

(examples of process factors)

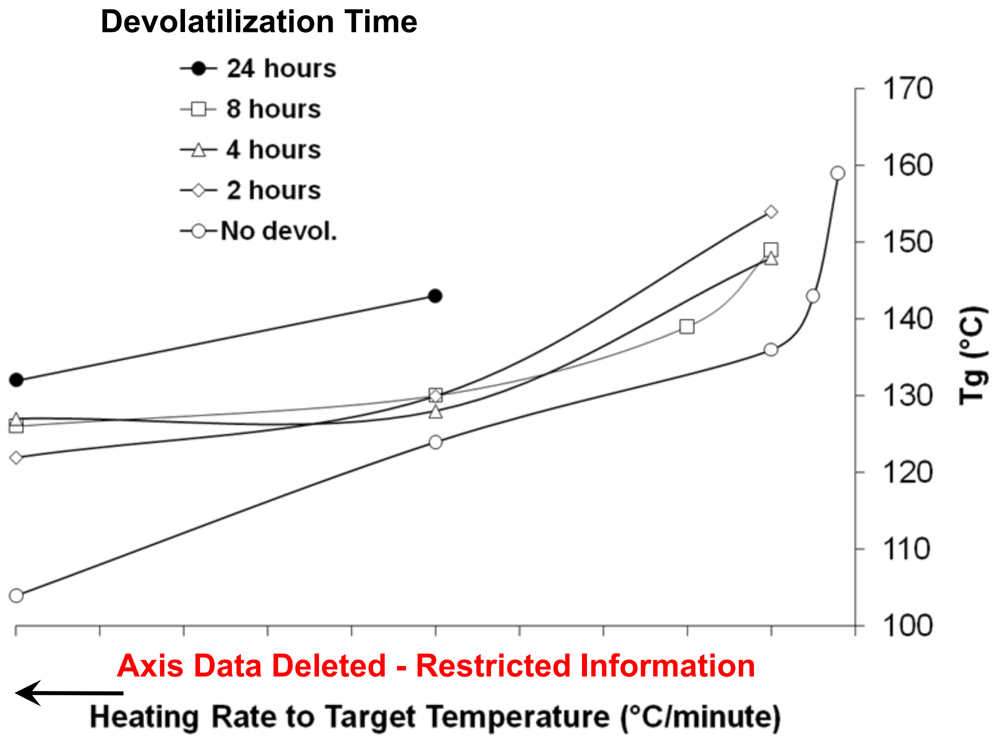
Technical Accomplishments

Relationship Between Rate of Heating and Yield of Stabilized Alcell Lignin Fiber (10 μm diameter)



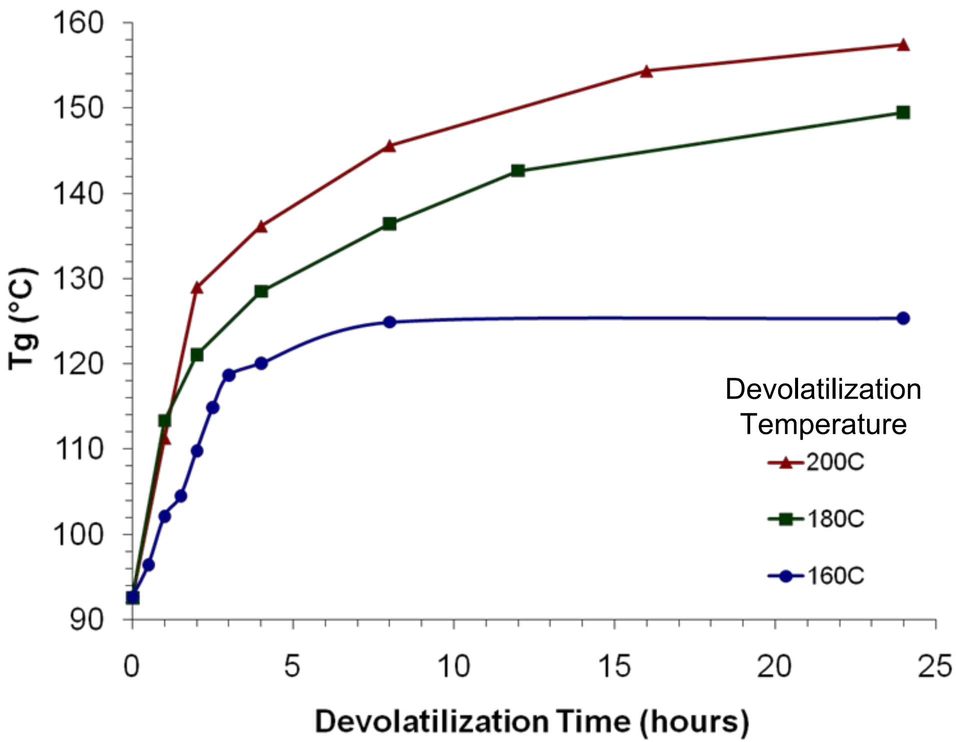
Technical Accomplishments

Relationship Between Rate of Heating and Glass Transition Temperature (T_g) of Stabilized Alcell Lignin Fiber (10 μm diameter)



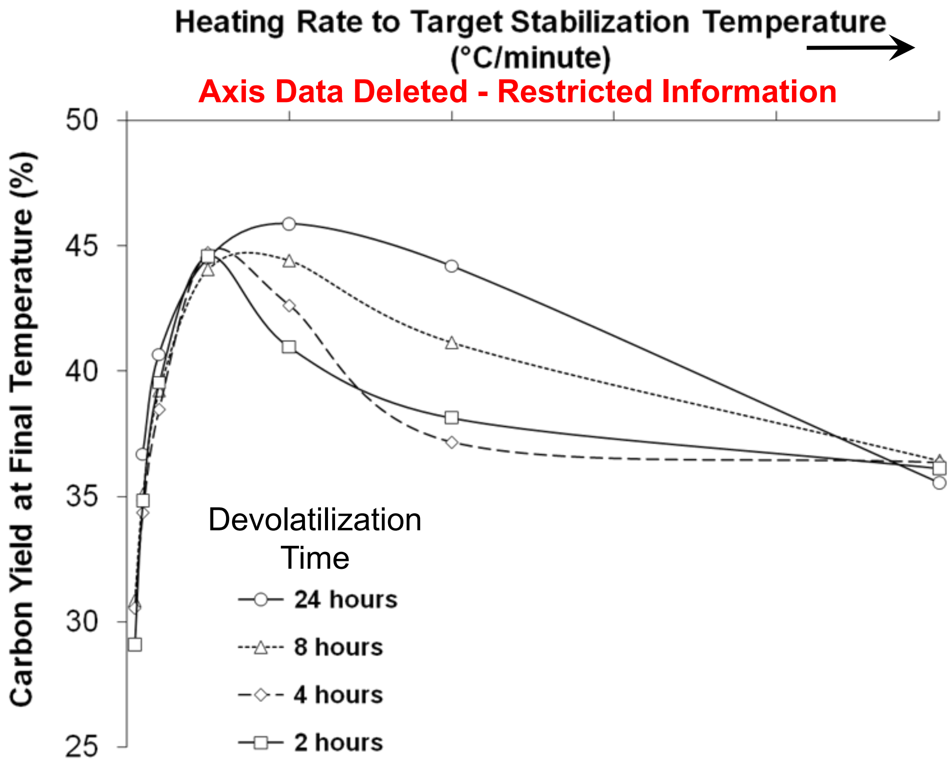
Technical Accomplishments

Relationship Between Devolatilization Time and Glass Transition Temperature (T_g) of Alcell Lignin Fiber (10 μm diameter)



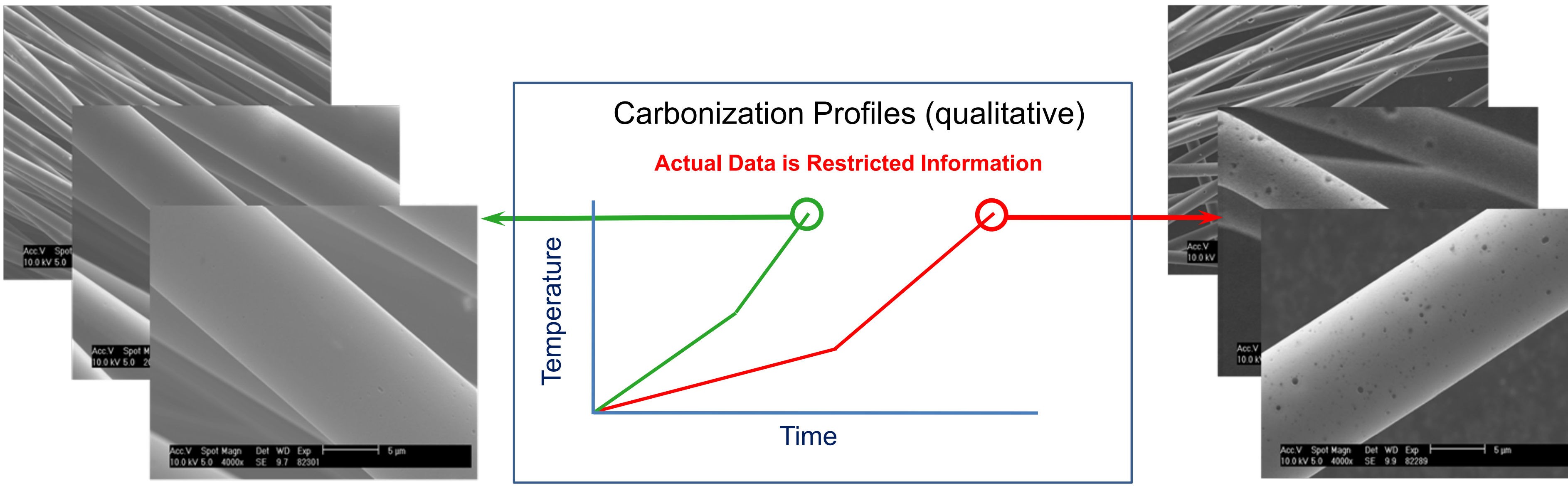
Technical Accomplishments

Relationship Between Stabilization Conditions and Yield of Alcell Lignin-Based Carbon Fiber



Technical Accomplishments

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



Technical Accomplishments

Progress on the Lignin-based Carbon Fiber Project During FY'08

- Consistently demonstrated continuous melt spinning of multifilament tow (12 and 24 filaments, resp.) from a bio-refinery-derived lignin (Alcell™) without purification or addition of a plasticizing agent
- Similarly demonstrated continuous melt spinning of multifilament tow from a Kraft-pulped softwood lignin, without purification, using a hardwood lignin as the plasticizing agent. This is a notable first, with significant economic benefit
- Demonstrated continuous melt spinning of multifilament tow from both lignin materials at 1,200 meters/minute, the maximum speed of the winder; i.e., twice the baseline speed of 600 m/min assumed in the Kline economic model. Faster speeds possible
- Established relationships between fiber winding speed and filament diameter for both lignins and at different mass throughputs. Consistently achieved target fiber diameter

Technical Accomplishments

Progress on the Lignin-based Carbon Fiber Project During FY'08 (cont.)

- Established relationships between residual solvent level of an Organosolv™-pulped lignin (Alcell) and its glass transition temperature (T_g) and influence on melt spinnability
- Similarly established relationships between the Tg and rate of stabilization of Alcell lignin fibers and mass yield upon stabilization
- Established relationships between the rate of stabilization of Alcell lignin fibers and carbon fiber yield (upon carbonization)
- Characterized influence of carbonization thermal profile on the structural integrity of Alcell lignin-based carbon fibers
- Developed a much sounder understanding of the fundamental properties of lignin materials and how they influence their melt spinnability into the target diameter precursor fiber and subsequent conversion to carbon fiber

Low-cost, Lignin-based Carbon Fiber

Challenges and Path Forward - FY'09/10

- Mechanical properties of lignin-based carbon fiber (CF) are currently 50-60% of target
  - Continue to refine fiber conversion conditions to enhance mechanical properties
  - Evaluate addition of polymers (polyolefins, PEO, PET) to enhance CF properties

- Lignin precursor fiber quickly oxidizes, rendering it difficult to unwind for subsequent continuous conversion into carbon fiber
  - Explore options used for commercial production of pitch-based carbon fibers, including melt spinning of the fiber as a web
  - Evaluate heat treatment of the fiber immediately upon exit from the spinneret. Continue to refine fiber conversion conditions to enhance mechanical properties

- Organosolv-pulped lignins readily meet purity specifications for melt spinning (etc.), but Kraft-pulped lignins are still falling short in this respect (but improved over commercial Kraft lignin)
  - Continue to work with Kruger Wayagamack to refine black liquor isolation conditions
  - Collaborate with STFI-Packforsk (Swedish Research Institute) to enhance Kraft lignin properties, including purity
  - Leverage the resources of other potential industrial partners to enhance lignin properties

Low-cost, Lignin-based Carbon Fiber

Challenges and Path Forward - FY'09/10 (cont.)

- Conversion of lignin precursor fiber into carbon fiber currently confined to batch scale processing
  - Work with colleagues on the textile PAN project to build upon the batch processing knowledge and establish conditions for continuous conversion of lignin precursor fiber into carbon fiber

- Actual price of lignin (ready for melt spinning) and precursor fiber spinning cost are projected to be lower than currently assumed in the Kline economic model, but more definite figures required for updating of the economic model
  - Interact with lignin suppliers to define more reliable estimates of the price of lignin materials, notably Kraft-pulped and Organosolv-pulped lignins
  - Upgrade winder on fiber spinning equipment to determine limit for melt spinning speed; i.e., above 1,200 meters/minute.
  - Provide data as required for updating of Kline economic model for low cost carbon fiber production

Estimated Production Cost of Lignin-based Carbon Fiber (Kline Economic Model)