Development and Commercialization of a Novel Low-Cost Carbon Fiber

George Husman

Zoltek Companies, Inc.

May 15, 2013

Project ID #
LM048

Overview
(Status Dec 2012)

Timeline

- Start Date – Oct 2011
- End Date – Dec 2014
- ~ 40% Complete

Budget

- Total project funding
  - DOE - $3,748,865
  - Contractor - $5,221,798
- Budget Period 1 Funding (10/1/11 – 4/30/13)
  - $2,309,930 DOE / $2,452,291 Z/W
- Budget Period 2 Funding (CY 2013)
  - $1,182,553 DOE / $1,895,703 Z/W
- Budget Period 3 Funding (CY 2014)
  - $256,382 DOE / $873,804 Z/W

Barriers

- Barriers addressed
  - Low cost carbon fiber
  - Inadequate supply base
  - High performance materials
- Targets
  - Cost = $5.00 / pound
  - Commercial product validation using existing manufacturing assets
  - Defined structural properties

Partner

- Weyerhaeuser Company
  - Provides low cost, high quality lignin polymer technology & supply source
  - Provides lab scale spinning technology and analytical testing

Objectives - Relevance

The objectives of this project are to develop and commercially validate a low cost carbon fiber based on renewable precursor raw materials and meeting DOE defined performance & cost targets.

Project defined targets:

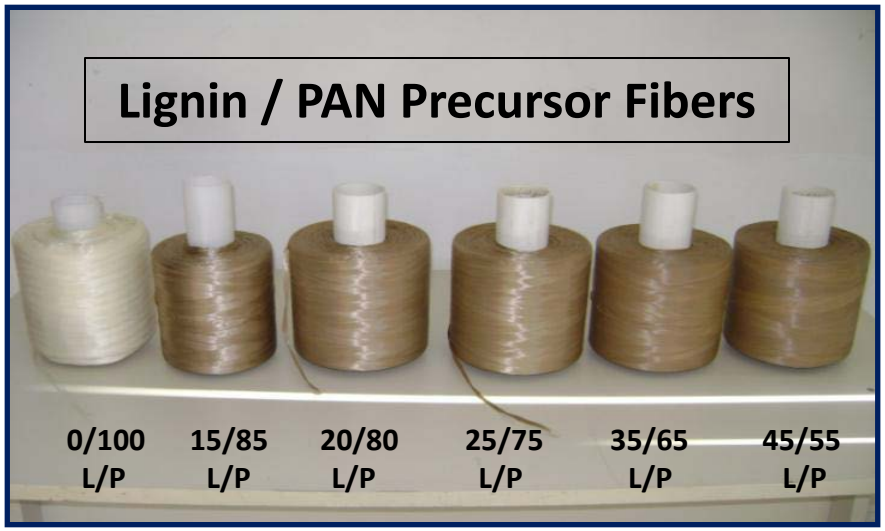
- carbon fiber cost = $5.00 / lb ($11.00 / kg)
- strength > 250,000 psi (1724 MPa)
- modulus of elasticity >25,000,000 psi (172 GPa)
- strain-to-failure > 1%

The specific cost and performance targets clearly address the Cost and Performance Barriers identified in the Vehicle Technologies Multi-Year Plan.

The commercial validation objective of this project will address the Inadequate Supply Base Barrier by demonstrating commercial scale production using existing manufacturing assets and approaches that have proven rapid capacity expansion capabilities.

Approach

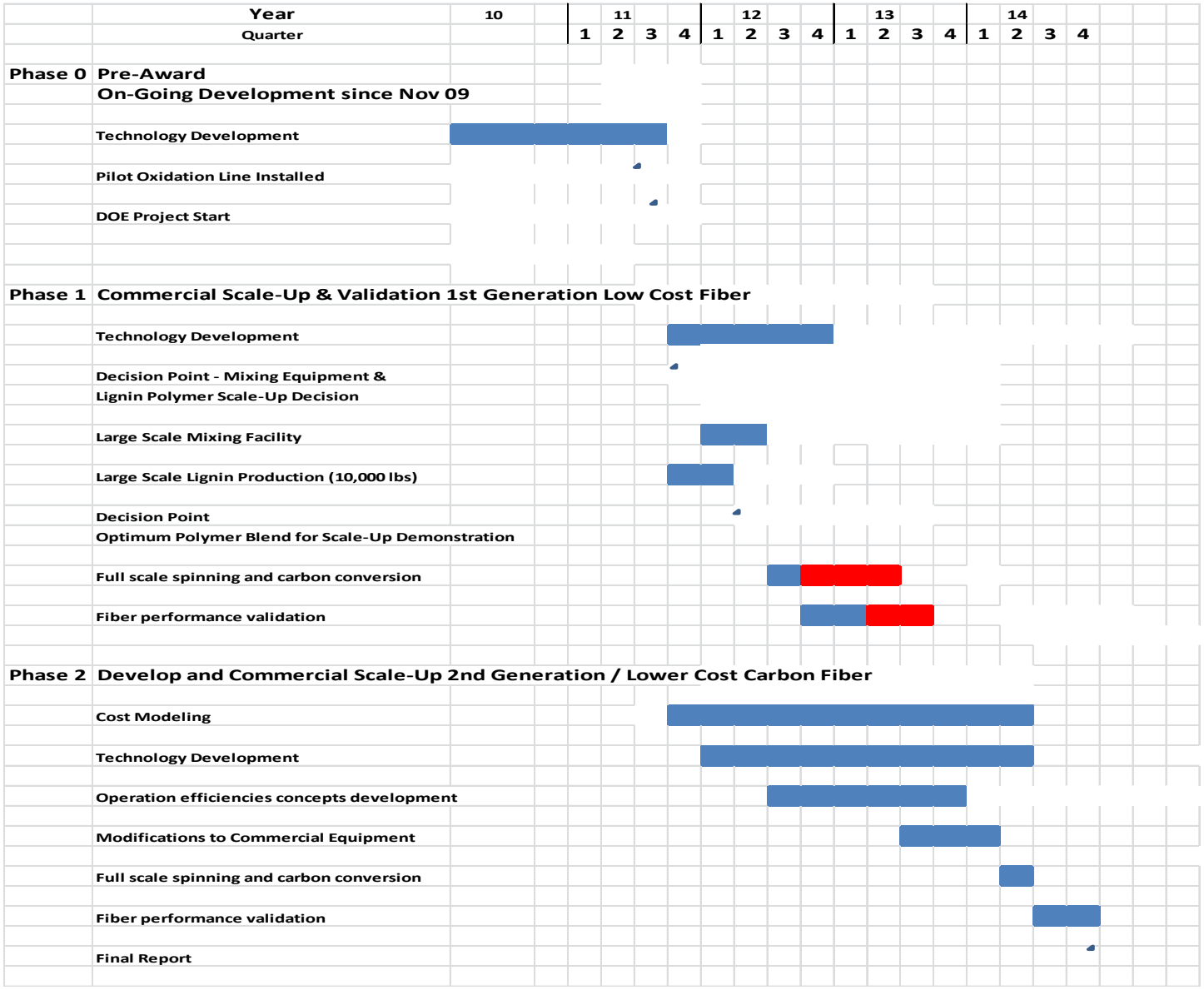
Primary Technical Approach:
Development of Lignin / PAN polymer blend precursor for carbon fiber using solution spinning process



Strategy:

- Different from prior developments with lignin; solution vs. hot melt spinning
- Allows use of existing production equipment ➡ immediate commercialization
- Reduced reliance on PAN (petroleum based)
- Limitation 45% Lignin but still provides substantial cost reduction
- Additional cost reductions possible due to:
  - higher rate stabilization
  - higher carbon yield
- Further cost reductions achieved through operational efficiencies & energy efficiencies in carbon fiber manufacturing

Schedule / Milestones

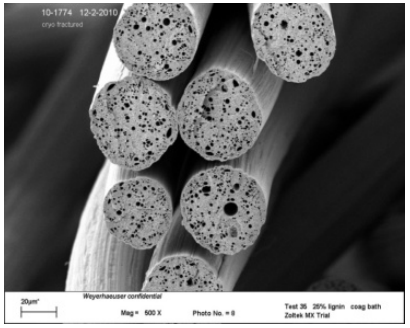
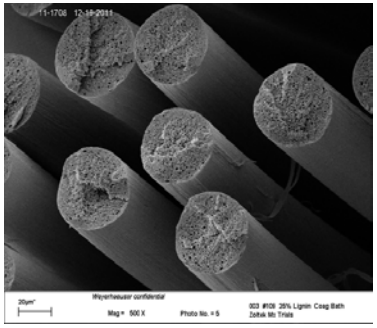
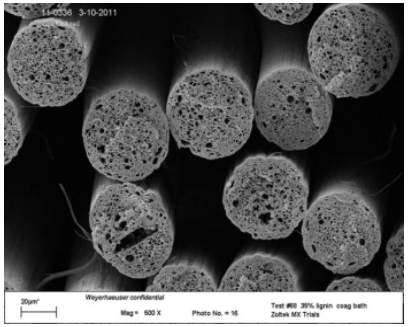
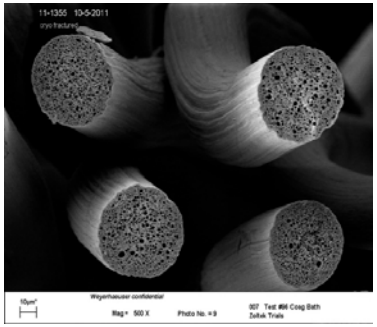
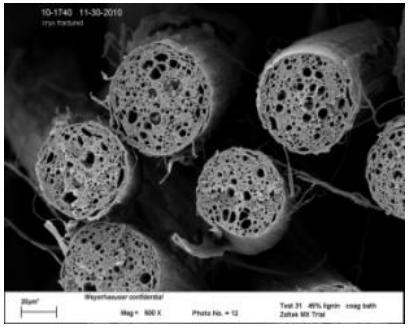
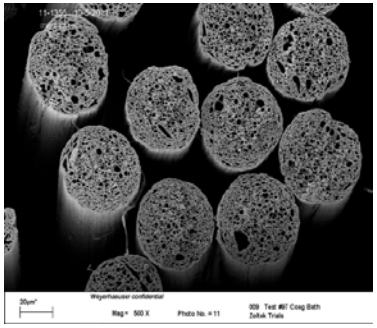


Schedule / Milestones

Month / Year	Milestone or Go / No-Go Decision	Status
• Dec 2011	Large scale lignin / PAN polymer mixing facility $75,000 investment	**Complete**
• May 2012	Go / No-Go Decision to define polymer blends and processing conditions for scale up validation 1	**Delayed Jan 2013**
• Jul 2012	Milestone – first commercial scale demonstration	**Delayed Mar 2013**
• Jul 2013	Go / No-Go Decision for modifications to commercial processes and equipment	**On-going**
• Feb 2014	Go / No-Go Decision to define polymer blends and processing conditions for scale up validation 2	**On-going**
• May 2014	Milestone – commercial process validation	**On-going**

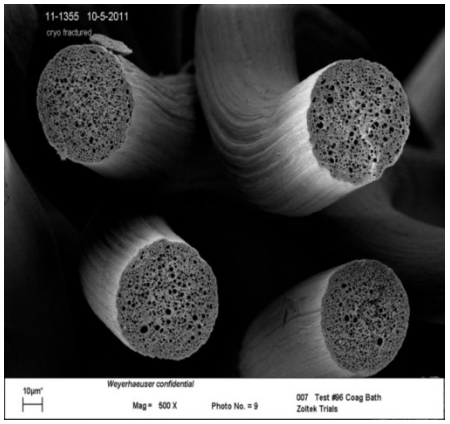
Accomplishments & Progress
Polymer & Fiber Spinning

- Early pilot scale spinning results with lignin and standard MW PAN resulted in morphologies with macro-voids; these were not successful for converting to carbon fiber.
- PAN polymers were developed with higher molecular weights to achieve higher solution solids and viscosities for L/P spinning solutions
- SEM analyses showed much better morphologies with the high MW PAN, however some macro-voids still present in 45% lignin fibers, indicating need for further optimization for maximum lignin content
- During 1st quarter 2012, 35% L/P pilot scale precursor fiber using high MW PAN was successfully converted to carbon fiber

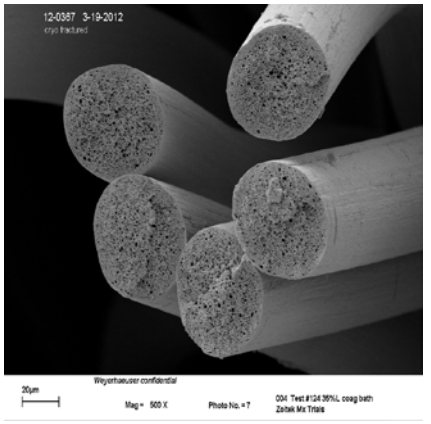
Early Results Precursor Fibers with Standard MW PAN		Results 4th quarter 2011 with High MW PAN
	25% L/P	
	35% L/P	
	45% L/P	

Accomplishments & Progress

- During 1st half 2012 a large number of pilot precursor fiber , oxidation, and carbonization trials were performed to optimize process parameters and validate reproducibility
- Decision was made to proceed with Phase 1 commercial scale validation using 35% lignin and high molecular weight PAN



Precursor Spool # 96



Precursor Spool # 124

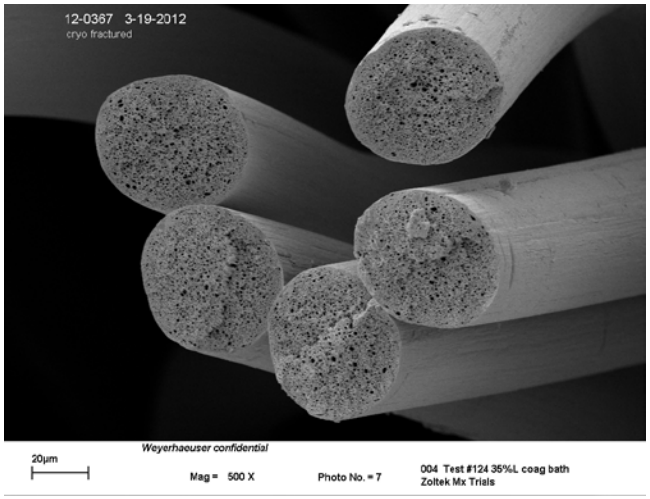
POL	Precursor		Polymer	Density	CF Mechanical Properties		
ID	Spool ID	Lignin (%)	Trial ID	gr/CC	TS (ksi)	TM (Mpsi)	Elongation (%)
POL-7	96	35	Std (+9% MW)	1.770	244	29.2	0.76
POL-22	123	35	44 (+34% MW)	1.770	280	28.81	0.848
POL-25	124	35	46 (+30% MW)	1.770	253	31.65	0.718
POL-27	125	35	44 (+34% MW)	1.700	234	31.92	0.644

Repeated Validation of Carbon Fiber from 35% Lignin / HMW PAN (pilot reactor)

Note: pilot scale process results in lower modulus (~90%) and lower strength (~67%) than commercial process

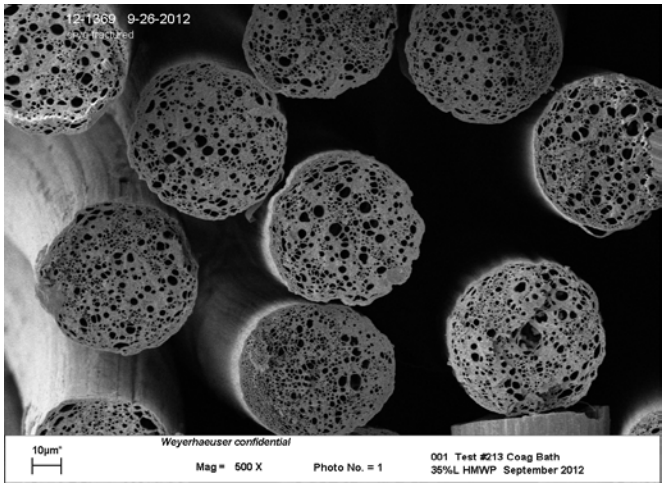
Accomplishments & Progress

- Decision based on 2nd quarter results to **proceed** with commercial scale validation using 35% lignin / HMW PAN
- Produced 10 metric tons of HMW PAN polymer in industrial reactor; excellent polymer with well controlled molecular weight
- Began a series of pilot spinning and oxidation studies to set final parameters for commercial scale validation planned for August, 2012
- Could not achieve precursor fiber morphology without macro-voids; none of the precursor fibers produced with the HMW PAN polymer produced in the industrial reactor could be successfully converted to carbon fiber



Precursor Spool # 124
HMWP Pilot Reactor

??????

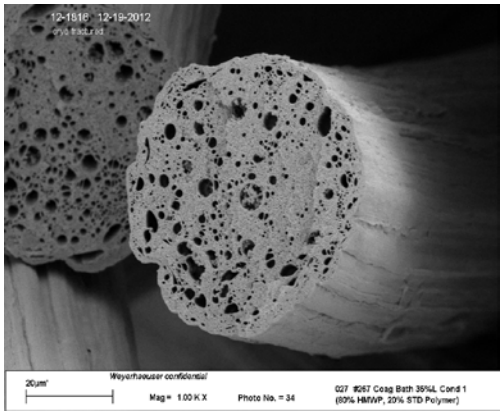


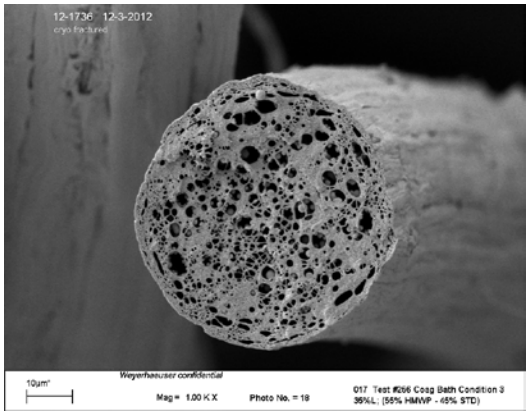
Precursor Spool # 213
HMWP Industrial Reactor

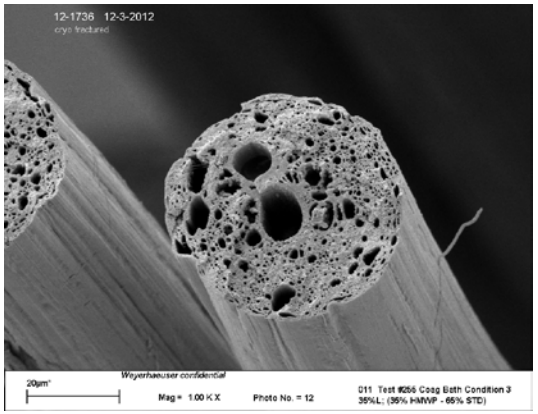
Accomplishments & Progress

- Evaluated a variety of spinning conditions, tried lower % lignin contents, and tried blending HMW PAN polymer with standard MW PAN polymer to increase polydispersity, but no successful solutions defined

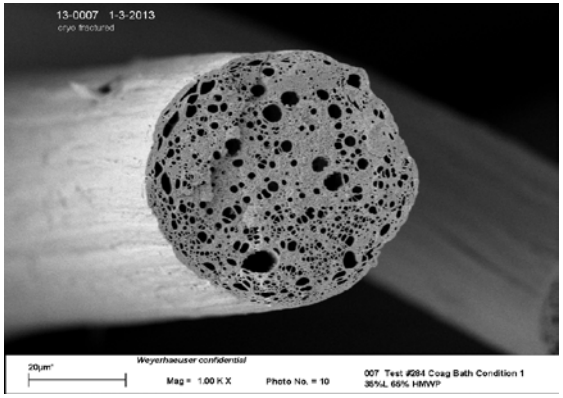
35% Lignin with varying ratios of HMWP & standard MWP

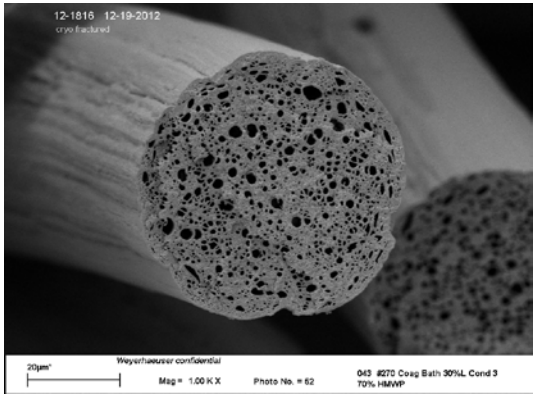


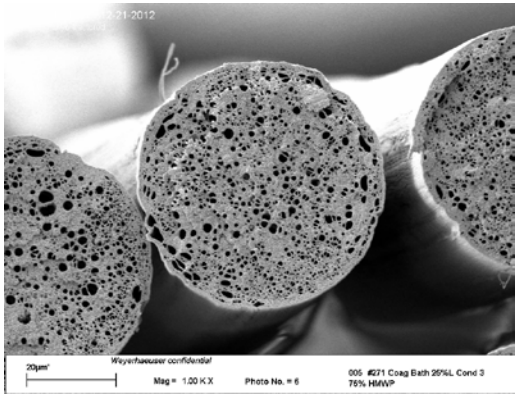




35%, 30%, 25% Lignin with HMWP



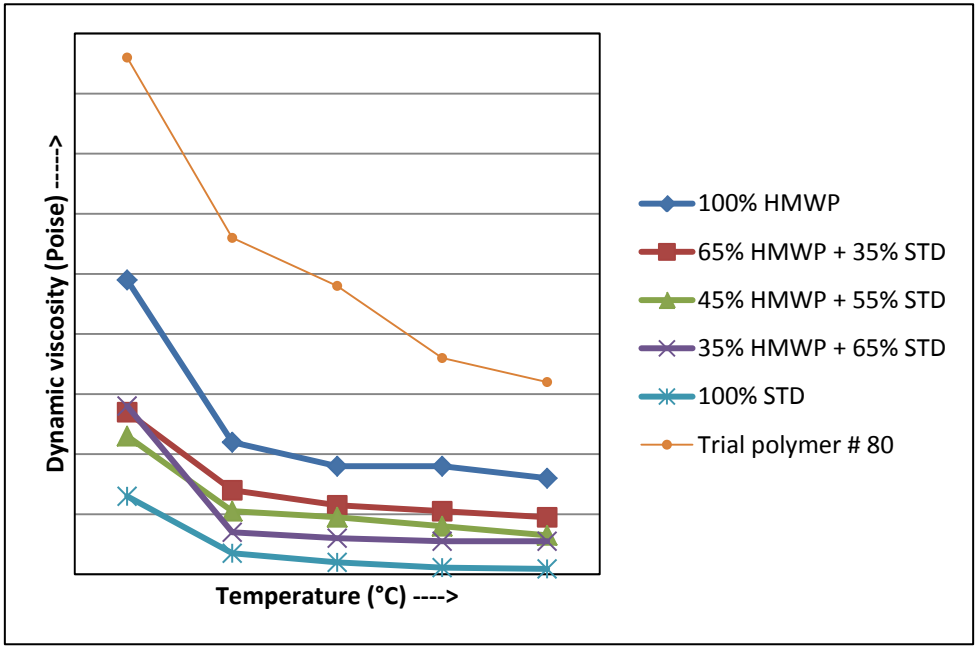




Accomplishments & Progress

Determined that likely cause of precursor morphology problem is tied to molecular weight distribution (polydispersity) difference between the pilot scale and industrial scale HMW Pan polymer, causing different behaviors in solution spinning rheology and fiber coagulation

Polymer	Polydispersity
HMWP industrial	2.91
HMWP Pilot reactor	3.60
STD PAN	3.52



35% lignin / PAN dope viscosities at same solids content

ZOLTEK

Accomplishments & Progress

Weyerhaeuser

- Lack of technical understanding of molecular weight distribution of high molecular weight PAN on the spinning behavior of lignin / PAN precursor fibers has delayed progress by several months
- Over 280 pilot spinning trials and 80 pilot oxidation trials have been accomplished resulting in substantial knowledge and understanding in behavior of lignin / PAN precursor fiber processing
- Because of technical delays , a 4 month no cost time extension to contract Funding Period 1 (Phase1) has been requested and approved.
- Two options being evaluated for commercial scale-up validation:
  - continuing studies on HMW PAN and developing knowledge to produce industrial scale HMWP with required polydispersity
  - developing improved spinning technologies to allow the use of standard molecular weight PAN
- Commercial scale-up demonstration of L/P precursor spinning has been rescheduled for March 2013; carbon fiber commercial scale demonstration scheduled for June 2013; this will complete major milestone for Funding Period 1(Phase 1); composite testing will continue through September 2013

Collaborations

- Within the framework of this project, Zoltek is the prime contractor and Weyerhaeuser is the only subcontractor. In this regard, Zoltek has the administrative lead responsibilities for this project management, but technical and business decisions related to this development are shared jointly.
- Technical and business responsibilities are divided as follows:

Zoltek	Weyerhaeuser
PAN Polymer	Lignin Polymer
Pilot & Commercial Wet Spinning	Lab Scale Wet Spinning
Carbon Conversion	Lignin Polymer Commercialization
Carbon Fiber Commercialization	

- During the commercial scale validation portions of this project, several OEM and Tier 1 manufacturers have expressed interest in participating in product evaluations. These relationships will be defined at appropriate time.

Future Work

- Commercial scale validation milestone for Phase 1 has been rescheduled for March – June 2013; this plan will include coordination with OEM, Tier 1, and other manufacturers to define product validation materials and processes (for example, need to define sizing to put on fibers for various manufacturing processes and intermediate products; thermoplastic, epoxy, vinyl ester compatible sizings); this completes the major milestone for Phase 1
- Composite molding and testing with automotive manufacturers will continue through September 2013; this is the completion of Phase 1
- A Request for Continuation Proposal containing a revised plan and budget for completion of Phase 1 and for Phase 2, “Commercialization”, will be submitted in April to define schedule and milestones for Funding Period 2. Phase 2 objectives and scope will remain the same as originally proposed.
- Phase 2:
  - continue technology development to achieve maximum lignin content precursor (45%)
  - optimize conversion process and equipment for lowest cost
  - develop design and plan for lignin polymer commercial production
  - develop and implement plan for commercial lignin / PAN based carbon fiber

Summary

Objectives of this project are focused on very specific product and commercialization targets directly addressing Barriers defined in the Vehicle Technologies Multi-Year Plan:

Low Cost Carbon Fiber = $5.00 / pound
Tensile Strength > 250,000 psi
Tensile Modulus > 25,000,000 psi
Elongation > 1%
Commercialization and Demonstration of Capacity Growth Potential

During 2012 unforeseen technical problems were encountered, delaying the major Phase 1 commercial scale validation by several months. The technical problem was caused by scale-up of high molecular weight PAN and unknown consequences of molecular weight distribution (polydispersity) on spinning behavior of lignin / PAN precursor fibers.

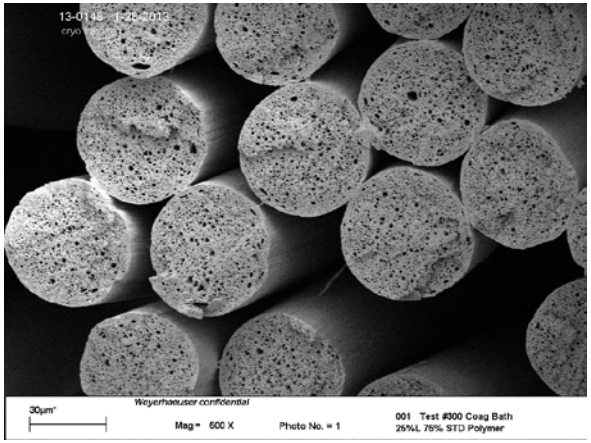
Problem now understood and two options being developed to achieve commercial scale validation milestone in March - June 2013. This has caused a no-cost time extension to Phase 1 (Funding Period 1 extended from December 31, 2012 to April 30, 2013 and may require further extension).

Phase 2 of the project will return to originally proposed schedule

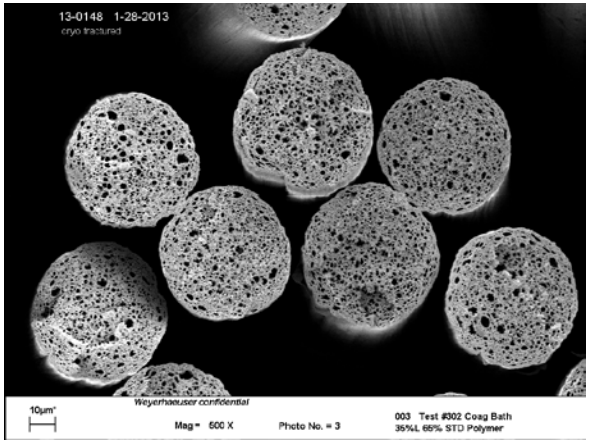
Technical Back-Up Slides

Recent Results

25% Lignin / Standard MW PAN

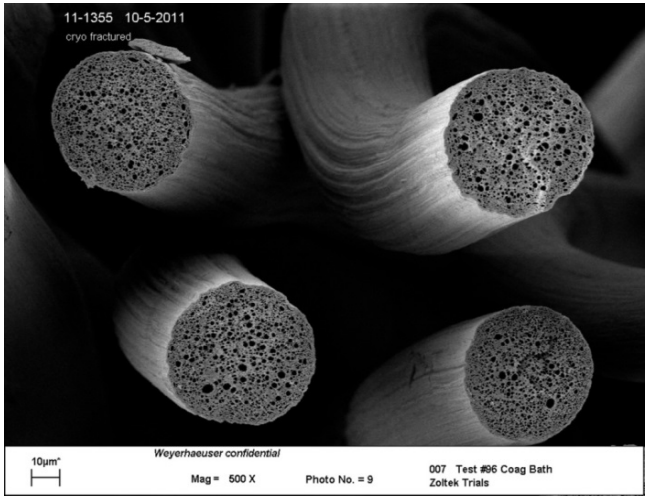


35% Lignin / Standard MW PAN

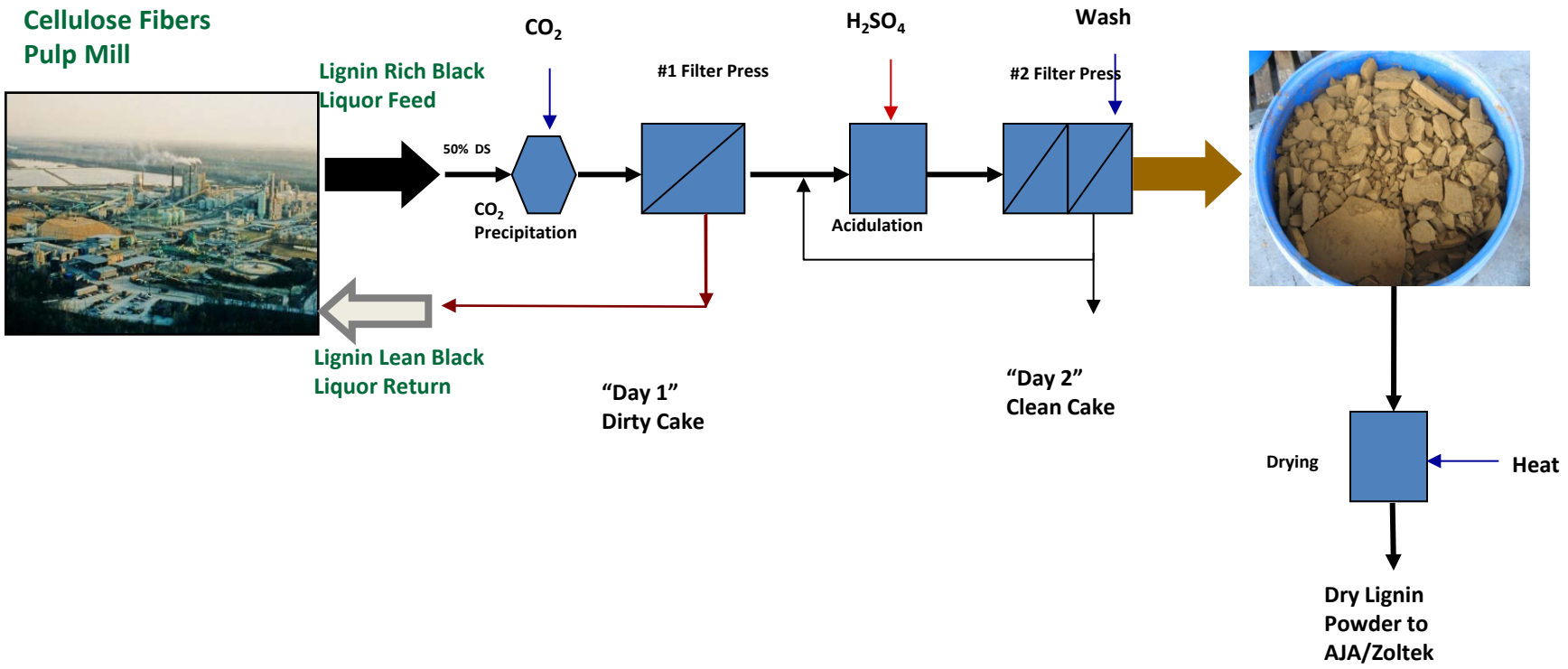


POL and Carbon conversion studies ongoing to prepare for commercial scale demonstration

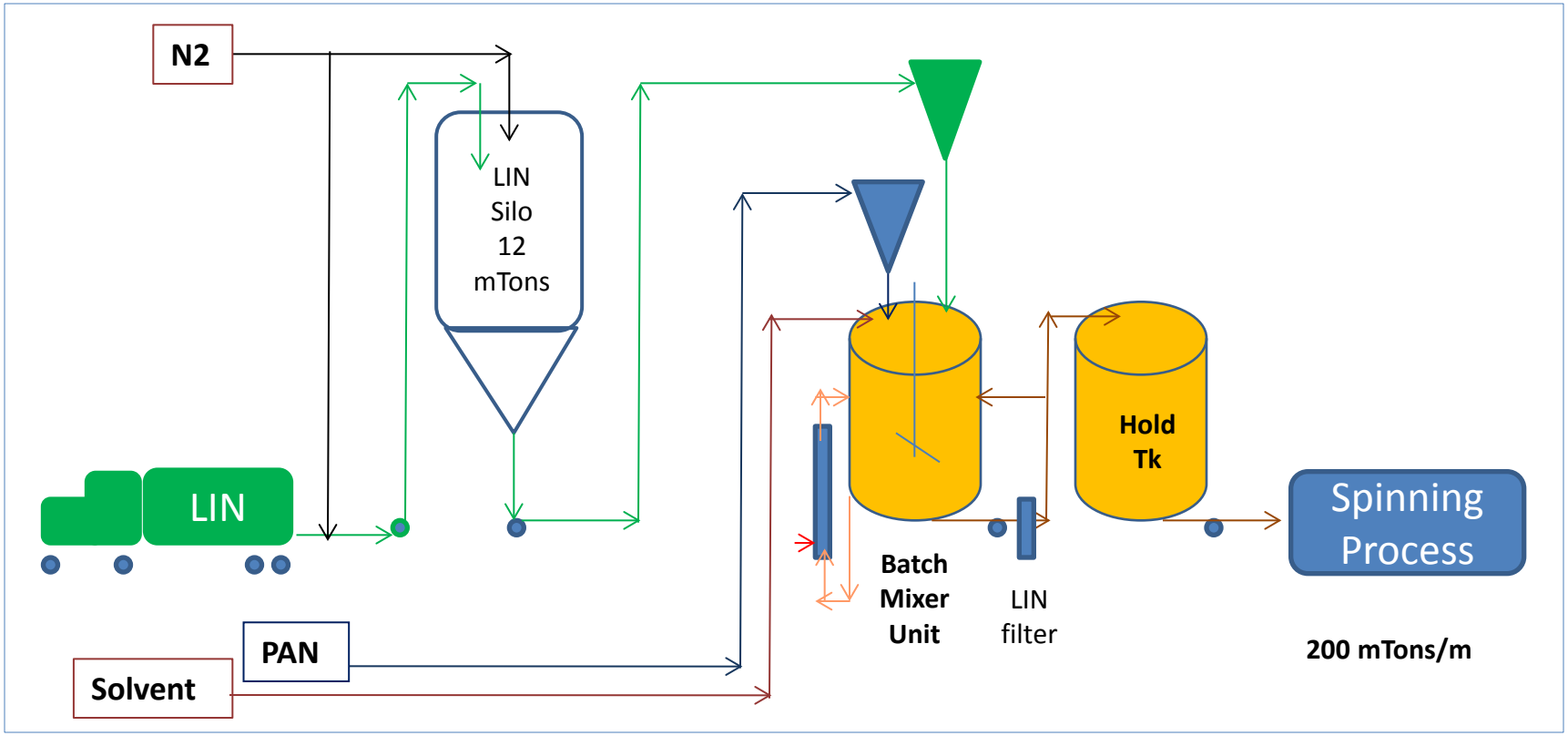
For Comparison
Precursor Spool # 96; POL # 7
35% L / HMWP



Weyerhaeuser Lignin Pilot Plant Process



Large Scale Mixing Facility



Zoltek Pilot Spinning Line

Zoltek Pilot Oxidation Line