Development and Commercialization of a Novel Low-Cost Carbon Fiber

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Zoltek Companies, Inc.

May 16, 2012

Project ID #
LM048

Overview

Timeline

- Start Date – Oct 2011
- End Date – Dec 2014
- ~ 15% Complete

Budget

- Total project funding
  - DOE - $3,748,865
  - Contractor - $5,221,798
- Budget Period 1 Funding (10/1/11 – 12/31/12)
  - $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 / $256,382 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
- strength > 250,000 psi
- modulus of elasticity >25,000,000 psi
- 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.

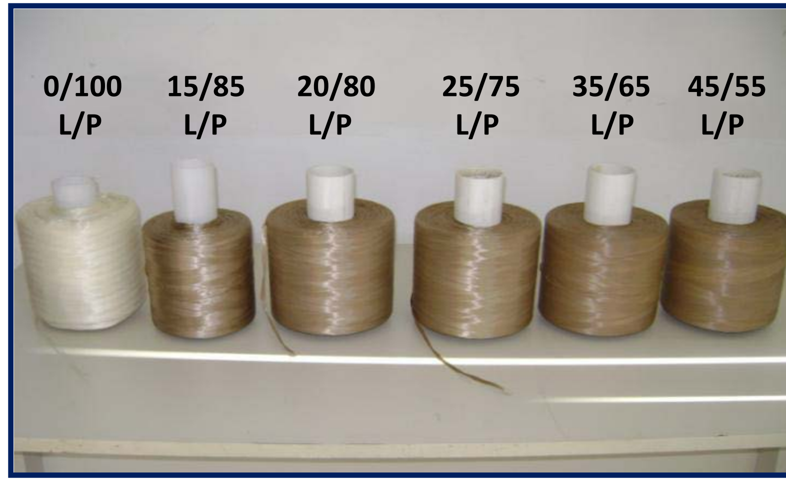
The commercial validation objective of this project will address the Inadequate Supply Base Barrier by demonstrating commercial scale production using existing manufacturing assets and approaches that have proven rapid capacity expansion capabilities.

Approach

Primary Technical Approach:
<u>Development of Lignin / PAN precursor using solution spinning process</u>

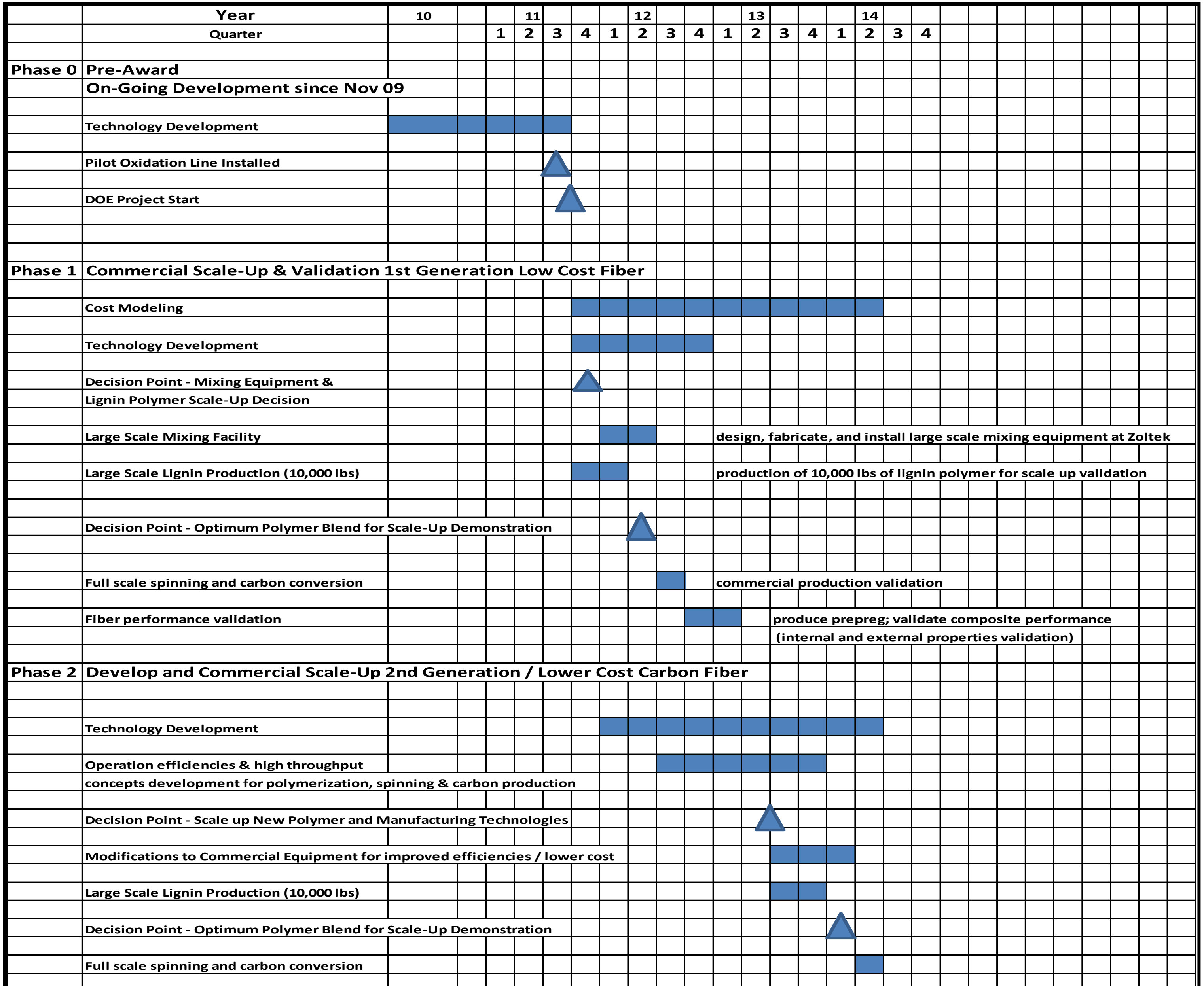
Strategy:

- Different from prior developments with lignin; wet spinning vs. hot melt
- Allows use of existing production equipment; immediate commercialization
- Limit 45% lignin content; reduced reliance on PAN; provides significant 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



Lignin / PAN Precursor Fibers

Schedule / Milestones

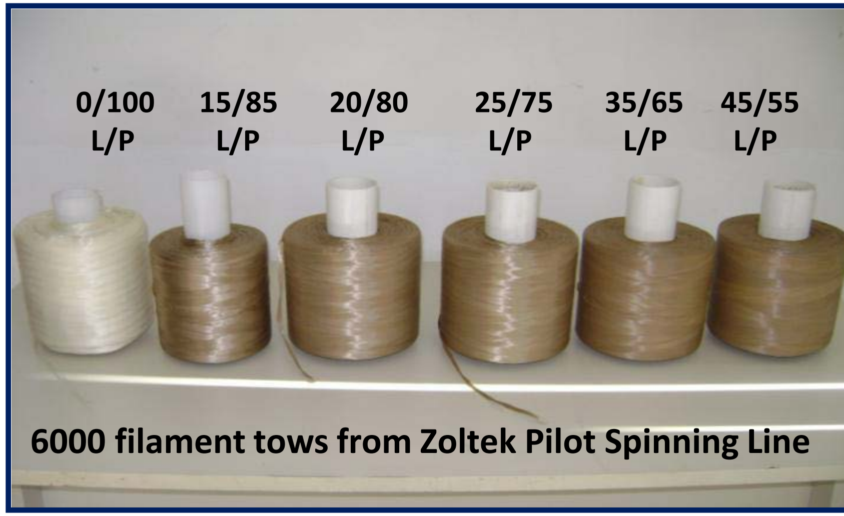


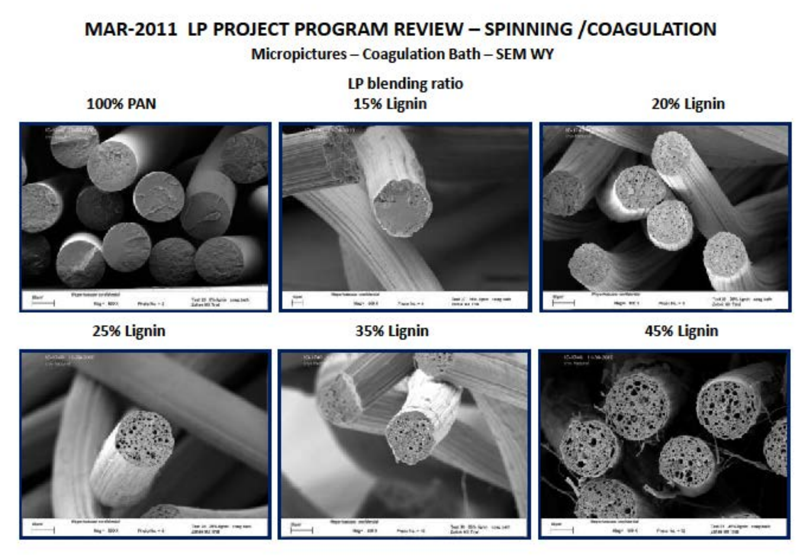
Schedule / Milestones

Month / Year	Milestone or Go / No-Go Decision
• Dec 2011	Go Decision to design and fabricate large scale lignin / PAN polymer mixing facility based on successful precursor spinning and conversion results; required for commercial scale-up; $75,000 investment
• May 2012	Go / No-Go Decision to define polymer blend, solution parameters, spinning process parameters, and conversion processing conditions for scale up validation
• Jul 2012	Milestone – first commercial scale demonstration of carbon fiber made from Lignin / PAN precursor; this will validate scale-ability of materials and processing technologies, provide data for cost model validation, and provide fibers for composite data validation and manufacturing demonstrations
• Jul 2013	Go / No-Go Decision for modifications to commercial processes and equipment for production of Lignin / PAN based commercial carbon fiber
• Feb 2014	Go / No-Go Decision to define polymer blend, solution parameters, spinning process parameters, and conversion processing conditions for scale up validation and commercial product introduction
• May 2014	Milestone – commercial process validation; produce carbon fiber for industry evaluation; commercial product introduction

Results Prior to Contract Award

- Weyerhaeuser & Zoltek began joint development of Lignin / PAN wet-spun precursor development in March 2010
- Solution behavior of Lignin / PAN (L/P) polymer blends limit lignin content to 45%
- By March 2011 spinning processing technologies were developed and precursor fibers produced
- Unacceptable macro-voids were obtained with lignin contents above 20% due to low solution viscosities and low solids achievable in spinning dopes
- Thermal analysis studies and batch oxidation studies showed subtle but significant differences in stabilization process for lignin containing precursor, defining need for Pilot Oxidation Line; installed Sept 2011
- Contract award Oct 2011

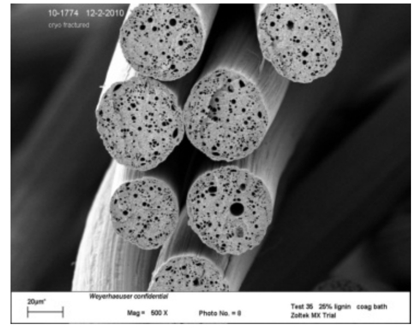




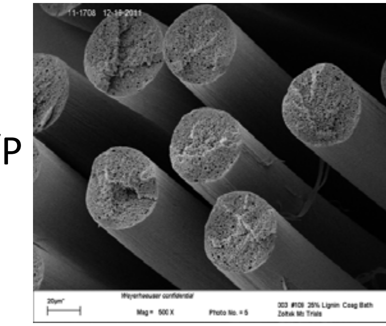
Accomplishments & Progress
Polymer & Fiber Spinning

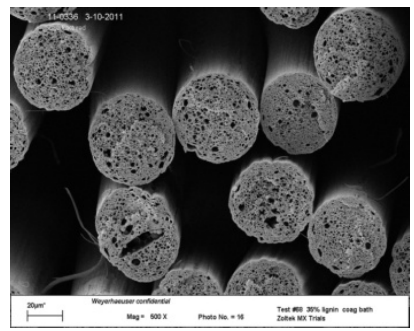
- PAN polymers were developed with higher molecular weights to achieve higher solution solids and viscosities for L/P spinning solutions
- Spinning trials were performed with different molecular weight PAN, L/P blend ratios, and solution solids to evaluate precursor fiber spin ability, quality, tenacity, and elongation
- Results indicated that PAN molecular weights 5 – 40% greater than standard PAN polymer achieved best spin ability and fiber quality
- SEM results are shown for 25, 35, & 45% lignin precursor fibers compared to March 2011 results; <u>current 25 & 35% fibers are good</u>
- Evidence of some macro-voids still present in 45% lignin fibers indicates need for further optimization for maximum lignin content

March 2011 Results | Current Results

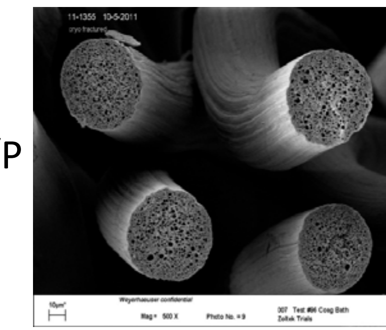


25% L/P

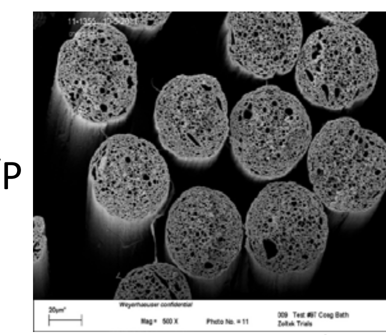




35% L/P

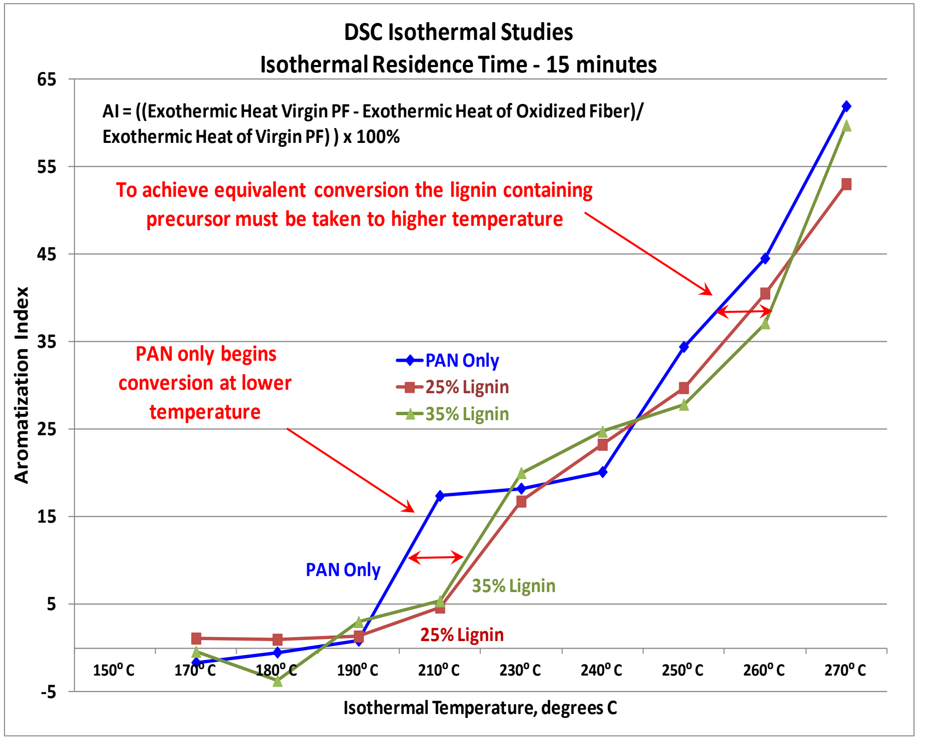


45% L/P



Accomplishments & Progress
Precursor Stabilization

- First step in conversion of precursor is stabilization or oxidation of the polymer fiber; this is typically done in an oxygen environment at temperatures of 200 – 300 ^{0}C
- Extensive thermal analysis is being done throughout the project on material variations to develop an understanding of the stabilization reactions and kinetics and to determine optimum time and temperature conditions to produce acceptable stabilized fibers
- The aromatization index (AI) vs. temperature data shown is generated from a series of isothermal differential scanning calorimeter tests; the AI is a good indicator of degree of stabilization of the precursor fiber; this data indicates a significant difference in the stabilization reaction of the lignin containing precursor fibers



Thermal analysis data is being used to determine stabilization process conditions for the Lignin / Pan precursor fibers compared to the 100% PAN reference conditions

ZOLTEK

Accomplishments & Progress
Precursor Stabilization

Weyerhaeuser

Pilot Oxidation Line

- The Pilot Oxidation Line (POL) was commissioned in October 2011 and is being used extensively to evaluate stabilization of the various precursor fibers being developed
- Data shown is from Oct – Dec 2011 (1^{st} quarter); 2^{nd} quarter data was not tabulated at time of this slide; each test run takes 24 – 48 hours to generate sample length required for carbonization studies
- Oxidized fiber samples are carbonized using furnaces on operational commercial lines

POL Spool #	Precursor		Density	Tenacity	Elongation
	Spinning Spool #	LP Content %	Ox Oven Pass 3	cN/Tex	%
POL-1	98	45	1.341	144	5.81
POL-2	95	35	1.333	142	6.40
POL-3	93	25	1.409	181	6.89
POL-4	98	45	1.290	149	7.61
POL-5	95	35	1.301	178	11.98
POL-6	93	25	1.358	167	7.68
POL-7	96	35	1.374	167	8.21
POL-8	96	35	1.394	190	8.23
POL-9	97	45	1.355	142	7.46
POL-10	88	0	>1.40	178	6.12
POL-11	97	45	1.355	121	4.37
POL-12	88	0	>1.40	193	7.7
POL-13	58	0	>1.40	154	9.16
POL-14	64	25	<1.170	134	6.64
POL-15	58	0	>1.40	217	16.1
POL-16	58	0	>1.40	169	10.42
POL-17	65	35	<1.170	133	6.16

Results are focusing in on density & tenacity requirements to produce successful carbon fiber

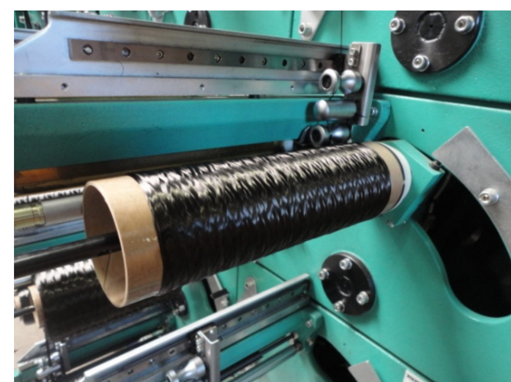
Accomplishments & Progress
Carbon Fiber

Parameter	Sample 100% PAN			Sample 35/65 % LP POL#7
Trial type	Industrial Oxidized & Carbonized			POL Oxidized & Industrial Carbonized
Tensile Strength (KSI)	389 - 456			244
Tensile Modulus (MSI)	32.55 - 36.10			29.2
Elongation (%)	1.052 - 1.178			0.76
Density (gr/cc)	1.777			1.77

- Many of the POL oxidized fibers produced during 1st quarter of the project were successfully carbonized by passing through furnaces on industrial carbon lines; POL Sample #7 (35% lignin) resulted in the highest and most uniform tensile properties shown above and compared to similarly produced 100% PAN fiber

- Based on known property reductions due to pilot scale precursor spinning and non-optimum stretching in conversion process, <u>POL Sample # 7 should result in higher property set when produced by commercial process; expected properties: Strength > 350 KSI; Modulus > 30 MSI; Elongation > 1%</u>

Oxidized sample fed through commercial line furnace; carbon fiber wound using commercial winder



Accomplishments & Progress
Cost Model

- Initial spreadsheet Cost Model has been developed to calculate cost reduction possibilities from standard PAN based carbon fiber
- % reduction is highly dependent on market price for acrylonitrile, which has varied in the past few years from $1500 / metric ton to $3000 / metric ton
- Carbon fiber cost reduction (assumed AN price @ $2500 / mt) solely due to material substitution @ 45% lignin content is approximately 11%
- Including expected increase in conversion efficiency of 45% lignin precursor (2.2 $\rightarrow$ 1.75), the cost reduction would increase to 21%
- Adding potential production speed increase of 1.5, the cost reduction would increase to 25%
- Phase 2 of this project will focus on defining modification to process and equipment for Zoltek's commercial production to achieve higher operational efficiencies and reduced energy consumption to try to achieve or exceed the $5.00 / pound target.

Collaborations

- Zoltek and Weyerhaeuser have been working together as close partners in the development of Lignin / PAN precursor technology under a joint development agreement signed in March 2010; this agreement established technical goals and milestones for joint development and outlined business relationship for product commercialization; the current project has focused and accelerated those goals and milestones
- 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

- Efforts during project quarters 2 & 3 (Jan – Jun 2012) will focus on further development and optimization of PAN and lignin polymers, spinning solutions, spinning process parameters, and oxidation process parameters in order to completely define these parameters for the May decision point for the commercial scale validation. Definition of these parameters will be based on demonstrated carbon fiber properties exceeding project goals.

- Commercial scale validation milestone remains scheduled for July 2012; a detailed plan for this trial will be prepared in June; 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; thermoplastic, epoxy, vinyl ester compatible sizings)

- In April 2012, Phase 2 cost and process modeling will begin to evaluate every step of current commercial production process to define opportunities for improvements in operational efficiencies and energy efficiencies; these studies will define recommendations and justifications for commercial line process and equipment modifications for the July 2013 decision point

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

In the first five months of this project, significant progress has been made in the materials and processing technologies demonstrating feasibility to meet and exceed project objectives:

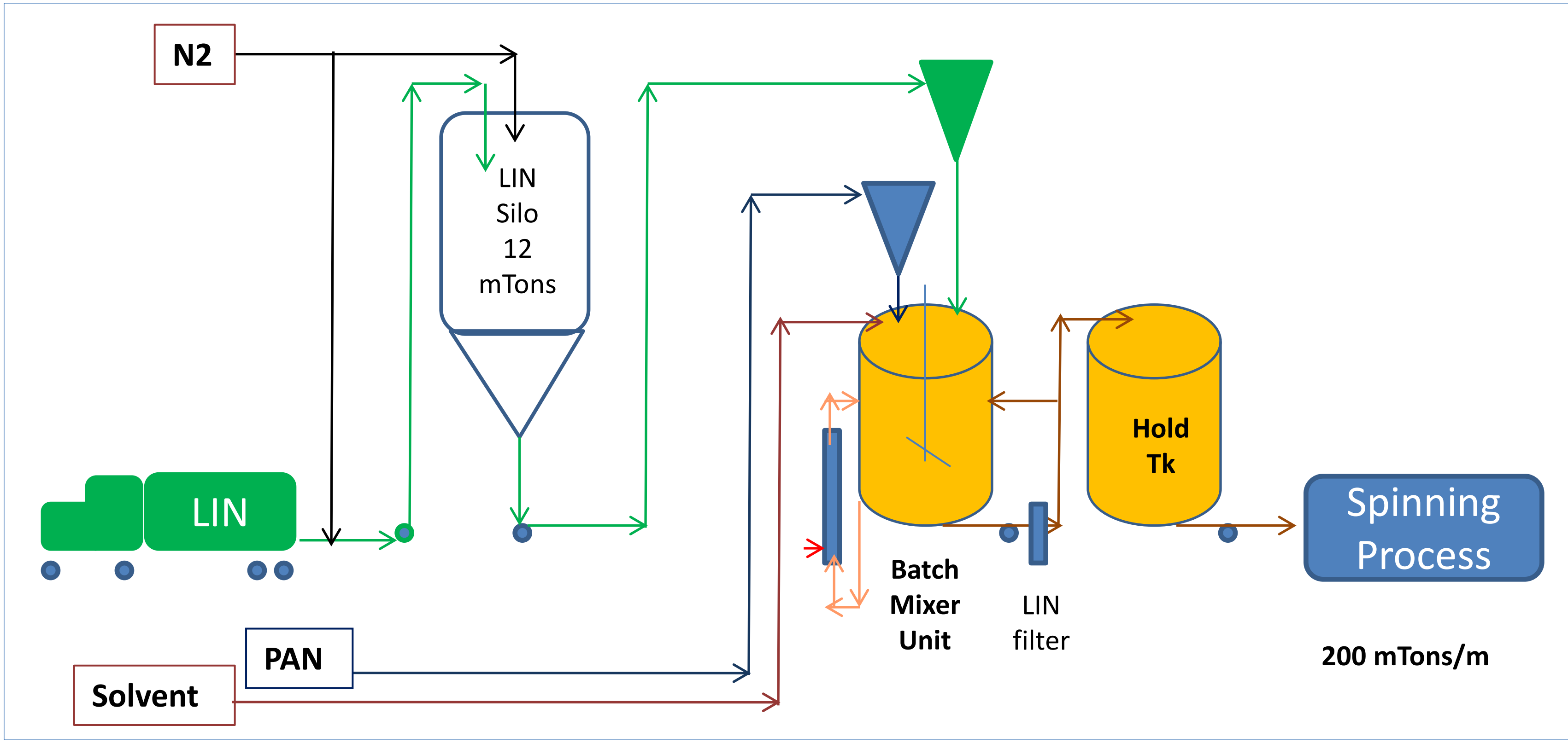
- polymer, solution, and spinning technologies to achieve high quality, high lignin content precursor fibers
- pilot scale continuous oxidation parameters have been developed and demonstrated resulting in carbon fibers with properties that can exceed project targets
- initial cost modeling has demonstrated potential to approach project cost target
- near-term commercial scale up validation on schedule

Technical Back-Up Slides

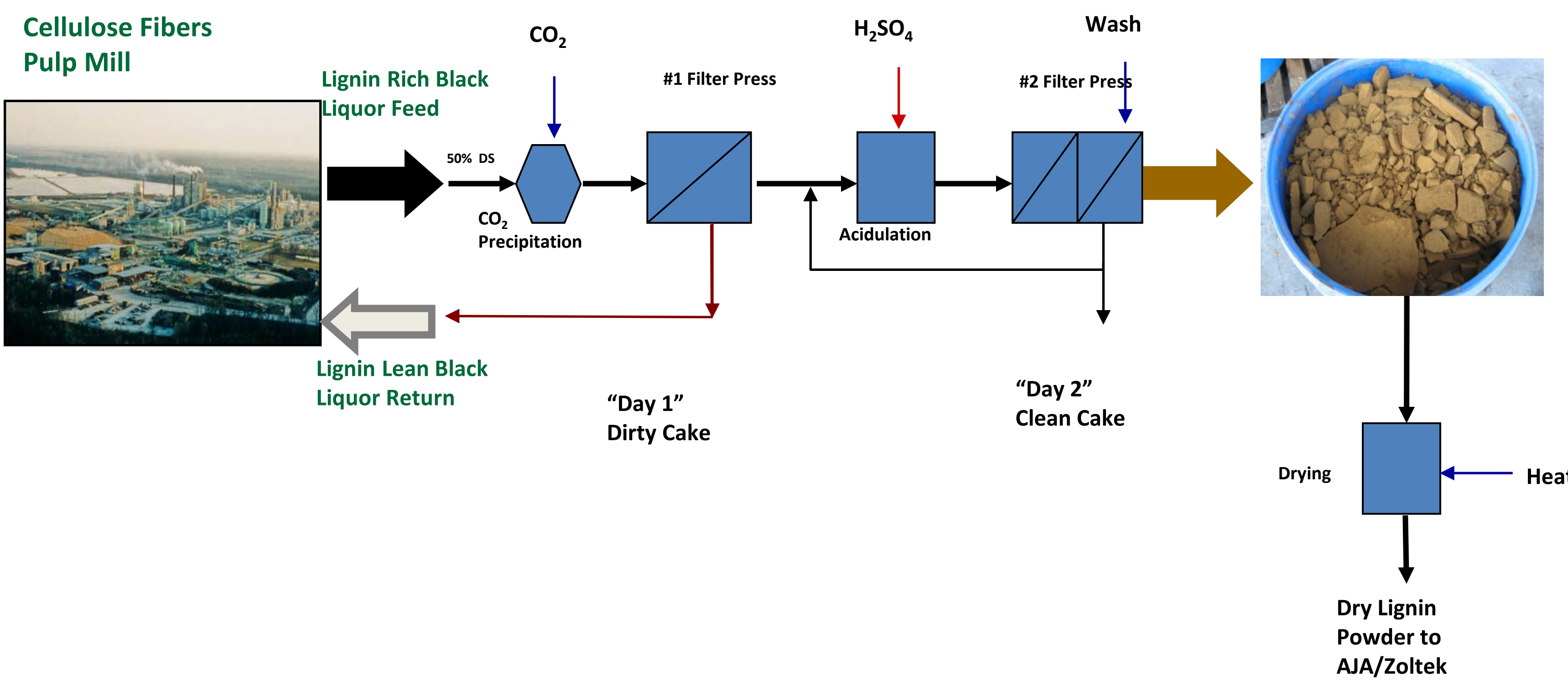
LP PROJECT

Zoltek Pilot Spinning Line

Large Scale Mixing Facility



Weyerhaeuser Lignin Pilot Plant Process



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Accomplishments & Progress
Polymer & Fiber Spinning

Weyerhaeuser

PAN Polymer	Lignin Content vs total solids	Solids	Dynamic Viscosity, Poise		
			60 ºC	50 ºC	40 ºC
Standard PAN	0%	20%	55.1	74.5	100.9
+5% MW	0%	20%	62	81	108
+25% MW	0%	20%	69	91	120
+40% MW	0%	20%	98	130	177
+60% MW	0%	20%	363	461	605
+75% MW	0%	20%	593	710	1026
+24% MW	45%	24%	41	57	Gel
+24% MW	45%	25%	61	85	Gel
+24% MW	45%	26%	Gel	Gel	Gel
+40% MW	45%	24%	23	27	34
+40% MW	45%	25%	29	Gel	Gel
+40% MW	45%	26%	Gel	Gel	Gel
+60% MW	45%	24%	59	66	78
+60% MW	45%	25%	84	104	158
+60% MW	45%	26%	Gel	Gel	Gel
+75% MW	45%	24%	198	270	Gel
+75% MW	45%	25%	Gel	Gel	Gel

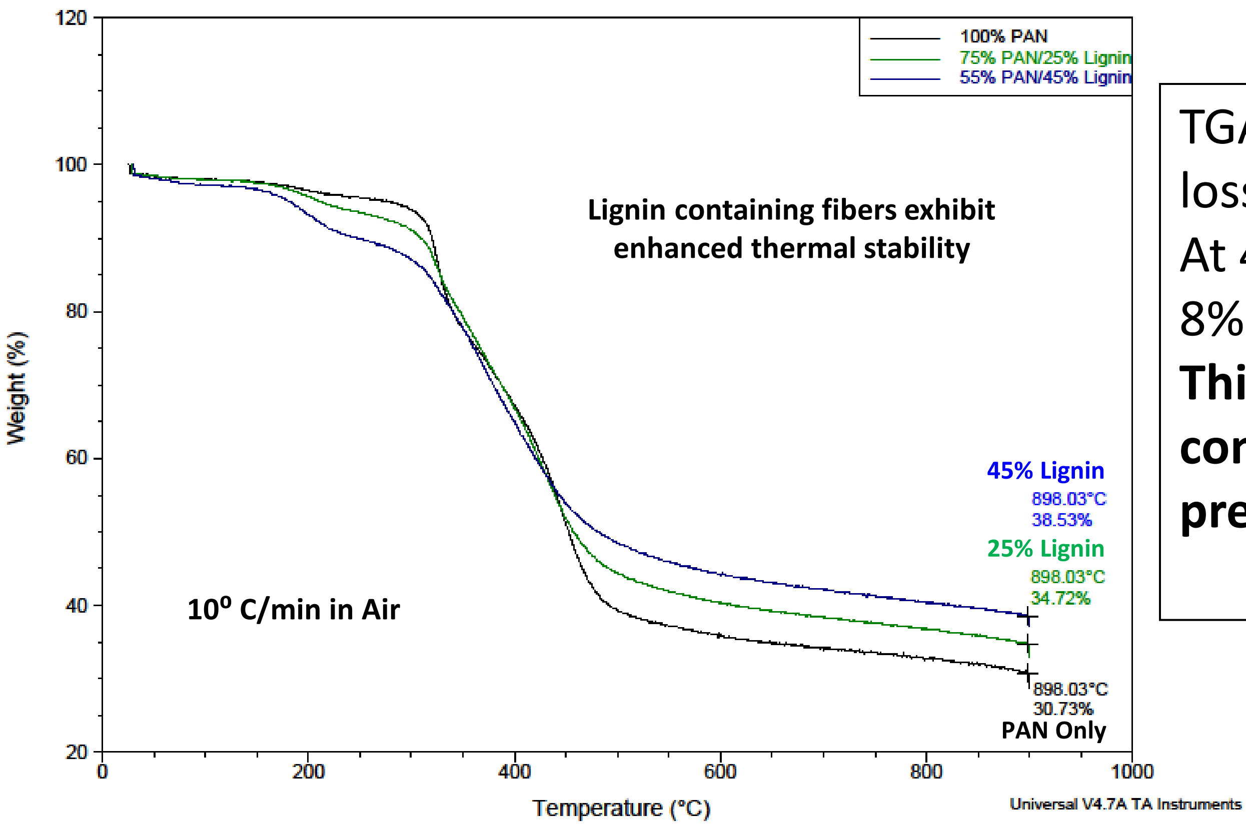
PAN polymers were developed with higher molecular weights to achieve higher solution solids and viscosities for spinning

% MW Increased	Spinning Process
5	Good
25	Good
40	Good
60	Bad
75	Bad

Test ID	92	93	109	110		100	96	95	107	111		72	97	98	112
PAN content	75%	75%	75%	75%		65%	65%	65%	65%	65%		55%	55%	55%	55%
Lignin content	**25%**	**25%**	**25%**	**25%**		**35%**	**35%**	**35%**	**35%**	**35%**		**45%**	**45%**	**45%**	**45%**
Solid Content Calculated	27.0 %	23.0 %	23.0 %	21.0 %		27.0 %	23.0 %	24.0 %	23.0 %	23.0 %		24.5 %	27.0 %	24.0 %	25.0 %
Dynamic. Viscosity . @ 25 ºC (poise)	ND	89	584	584		198	560	225	512	528		35	179	1120	544
Solid Content Analyzed	26.0 %	22.6 %	22.6 %	19.9 %		25.9 %	21.4 %	23.3 %	22.5 %	21.5 %		20.0 %	24.1 %	19.5 %	20.8 %
Tenacity (mN/Tex)	331	322	370	377		255	317	318	392	354		349	329	340	348
Elongation (%)	34.6	40.5	31.6	31.6		33.9	37.9	40.7	32.7	28.6		33.0	32.9	38.5	30.0
Spec. Viscosity Polymer	Base	+5%	+60%	+75%		Base	+5%	+40%	+60%	+75%		Base	+5%	+40%	+75 %

Spinning trials were performed with different solids and lignin blend ratios

Carbon Yield Analysis



TGA indicates lower mass loss as % lignin increases. At 45% lignin, mass loss in 8% lower.

This indicates that conversion for 45% L/P precursor may be ~ 1.72