High Strength Carbon Fibers

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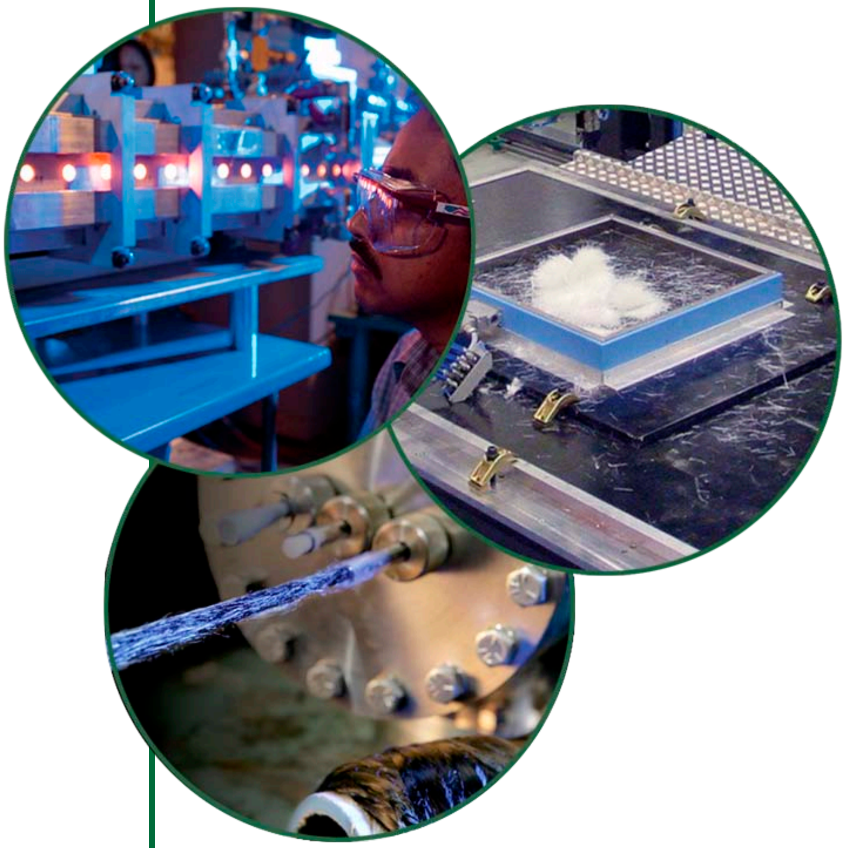

Project ID: ST093

Overview

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Timeline

- Start 2007
- Project End date: 2015
- 10% completed

Barriers

- High cost of high strength carbon fibers
- Carbon fiber account for ca. 65% of the cost of the high pressure storage tanks

Budget

- FY07 $600K
- FY08 $0
- FY09 $200K
- FY10 $200K

Partners

- ORNL (Host side)
- Virginia Tech - VT

Relevance

Objective: to reduce the manufacturing cost of high-strength carbon fibers by means of:

- **Significant reduction in the production cost of the PAN-precursor via hot melt methodology**
- **Later on, the application of advance carbon fiber conversion technologies (in) development at ORNL.**

This melt-spun PAN precursor technology has the potential the reduce the production cost of the high strength carbon fibers by > 30%. The additional application of advanced conversion technologies (ORNL) could further reduce this cost by another ~20%.

Melt-Spun PAN Precursor - Introduction

- Currently, ALL commercial PAN precursor is wet spun
  - Pure PAN has a lower degradation temperature than melt temperature
  - Formulation to render PAN melt spinnable generally reduces the finished fiber strength
  - ORNL and its partners are exploring novel approaches to render PAN melt spinnable with minimum copolymer content
- Wet spinning is capital intensive due in part to the solvent handling and recovery systems
  - Wet spinning solvents may be highly corrosive and environmentally hazardous
  - Wet spinning plants have very high "plant holdup" and pumping requirements to move the solvent
- Wet spun fibers are more likely to have flaws or bubbles
- Very complicated/cost intensive to produce flow-free, high purity PAN filaments
- Melt spinning is a higher throughput process

Melt-Spun PAN Precursor is partially Proven Technology

- BASF developed melt-spun PAN precursor in the 1980's
  - Carbon fibers were qualified for B2 bomber
  - Demonstrated 400 – 600* ksi fiber strength and 30 – 40 Msi modulus; even better properties were thought to be achievable
  - PAN content was 95% - 98% (consistent with high strength)

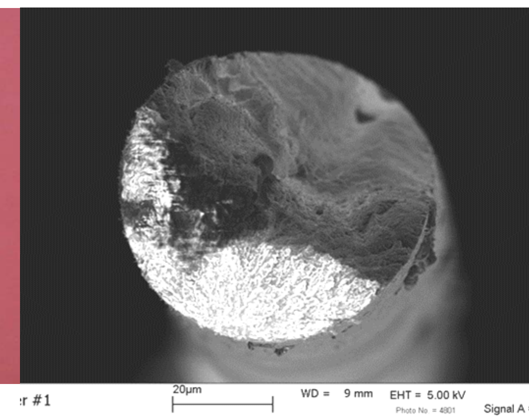
*Future HS-CF will need values around 700ksi

Melt-Spun PAN Precursor (cont'd)

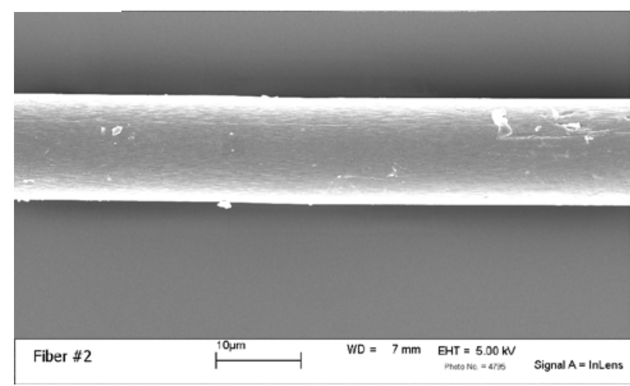
– Significantly lower production cost than wet-spun fibers
  • ~ 30% lower precursor plant capital investment
  • ~ 30% lower precursor plant operating cost
  • Typical precursor line speed increased by ≥ 4X at winders
– Program was terminated in 1991 due to carbon fiber market collapse at cold war's end, a forecasted long (~10yr) recovery period, and solvent issues (acetonitrile, nitroalkane)
– Information provided by Joe Venner of BASF
  • Co-inventor of BASF melt spinning technology
  • Key member of BASF development team
– Various US Patents and publications are available from this BASF development time.

Mechanical Accomplishment - Progress Status

- Demonstrated feasibility of using benign plasticizers to melt spin PAN and promote higher degree of drawing
- Novel comonomers were successfully incorporated
  - Initially produced: Foamed PAN fibers and high molecular weight "fibrous" materials (4/08)
- First (low-quality) fibers were melt spun (2008 to mid 2009)
- Actual, produced PAN filaments:
  - Moderate quality
  - Large diameters
  - Need increase AN contain, > 95%



- Key technical issue: Improve melt stability by reducing Tm below the PAN degradation temperature.



FY10 Milestones

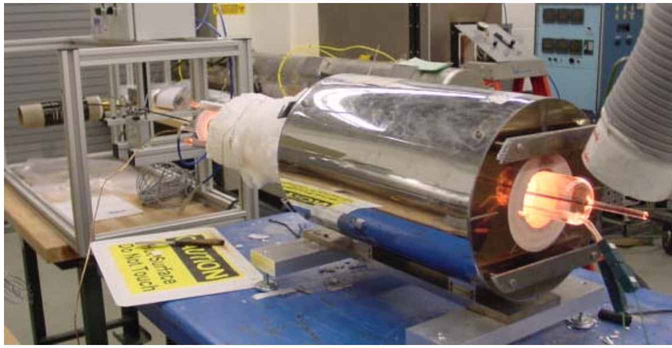
Task/ Subtask	Title	Milestone/Deliverable Description	Planned Completion Date
Precursor Development	Melt stable PAN filaments	Single filaments drawn from melt stable polymer with 92 – 95 mol% AN	12/2009
	Multi-filament precursor tow	Make > 10-foot long "micro-tow" w ≥ 10 filaments, with 10 – 20 μm filament diameter and ≤ 1 vol% filament porosity	03/2010
	2nd generation multi-filament precursor tow	Make > 10-foot long "micro-tow" w ≥ 10 filaments, with chemistry and process modified to increase carbon fiber mechanical properties	07/2010
Conversion	150 ksi multi-filament carbon tow	Melt spun PAN fibers converted with mean single-filament or tow tensile properties 15 Msi modulus and 150 ksi ultimate strength	05/2010
	200 ksi multi-filament carbon tow	Melt spun PAN fibers converted with mean single-filament or tow tensile properties 18 Msi modulus and 200 ksi ultimate strength	09/2010

Leveraging

- The H_2 high strength carbon fiber program is a major beneficiary of a decade of prior investments in carbon fiber R&D at ORNL
  - Successful in developing revolutionary new approaches to precursor and conversion technology (Advanced Oxidation and MAP)
  - Unique physical resources specific to carbon fiber R&D
  - Access to ORNL's extensive materials processing and characterization capabilities
  - Development of extensive intellectual expertise including an established network of university and industry partners

Unique ORNL Capability – Precursor Evaluation System

- **Designed for development of conventional processing recipes with limited quantities of precursor**
  - Residence time, temperature, atmospheric composition, and tension are independently controlled in each furnace
  - Can process single filament up to thousands of filaments
  - Precise tension control allows tensioned processing of ~20-filament tows



Unique ORNL Capability – Conventional Pilot Line

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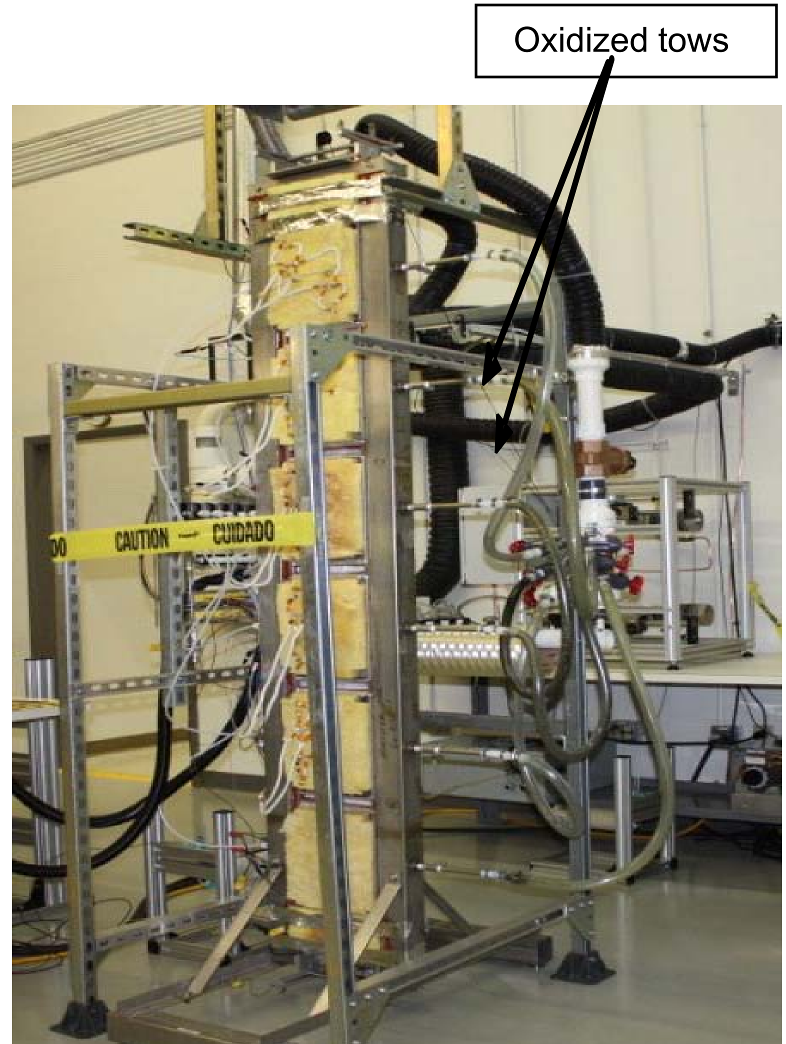
- 1:20 scale of a commercial grade production line
- Capacity for 8 tows
- Upgrades underway for automated operation and production of high strength carbon fiber
- Unique capability among FFRDC’s and universities

Textile PAN Precursor

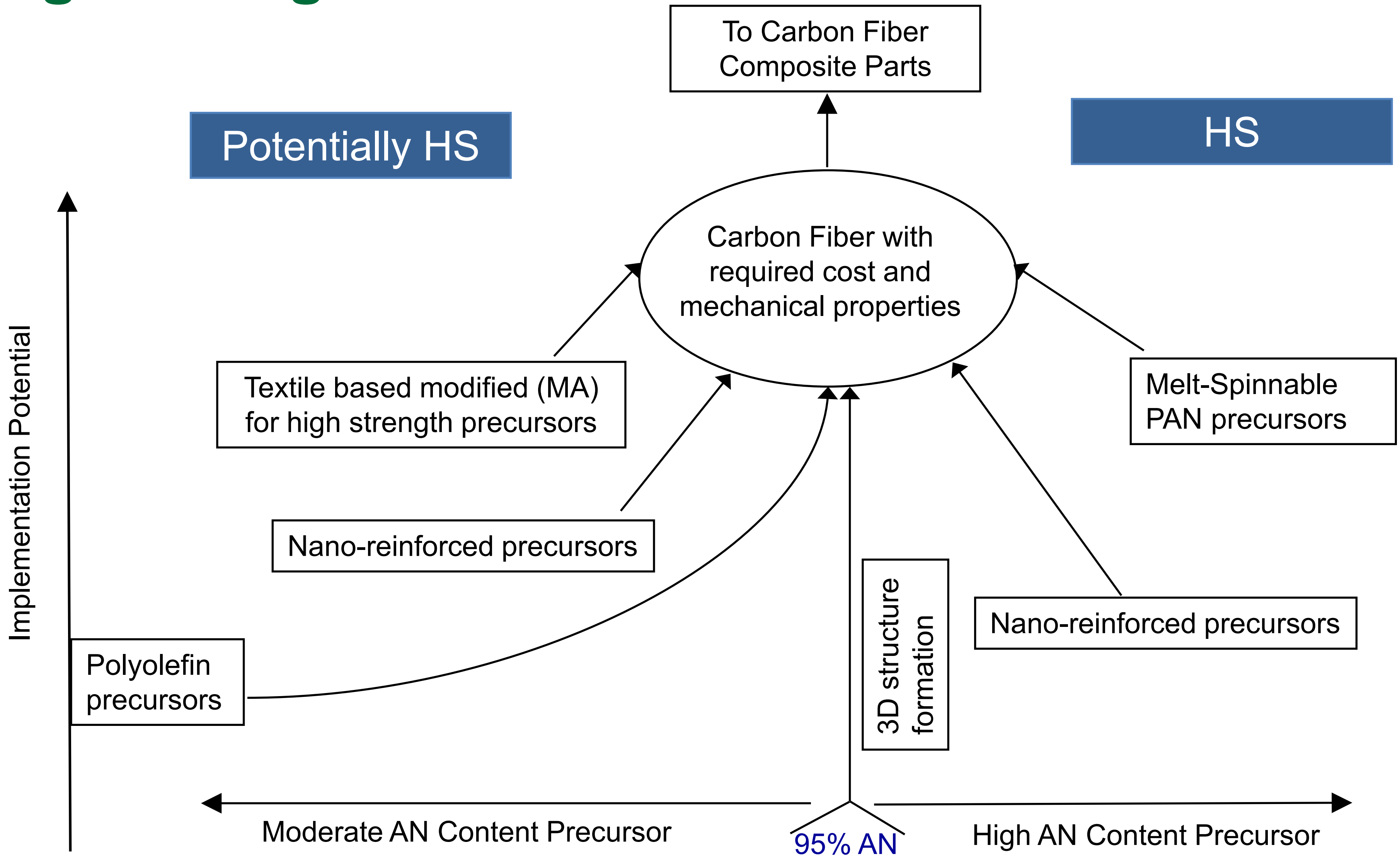
- ORNL and FISIPE have conducted extensive work on commodity grade fibers from textile PAN precursor and are currently evaluating large carbon fiber tows
- Modified textile PAN with methyl acrylate (MA) comonomer should enable a moderate- to high-strength fiber at lower cost
- FISIPE is aggressively pursuing the development of a new textile PAN precursor that may be applicable for high strength carbon fibers

ORNL Advanced Conversion

- Oxidation / Stabilization
  - Cross-links and oxidizes the fibers; conventionally requires 70 – 120 minutes, diffusion controlled process (O_2)
  - Principal development based on atmospheric pressure plasma
    - Demonstrated ~ 30 minute residence time, scalable.
    - Current scale is one 3k tow oxidized at 0.3 m/min
    - Process scaling to commence soon
- Microwave-assisted plasma carbonization
  - Demonstrated single large tow line speed ~ 5 m/min
  - Demonstrated 3-tow processing at > 1 m/min
  - Satisfied property targets for automotive structural applications



High-Strength Carbon Fiber – Potential Routes



Cost Modeling

- Kline and Company has been cost modeling carbon fiber manufacturing for the Automotive Composites Consortium since 2003
- Kline has completed models on high strength carbon fibers made from wet-spun PAN (baseline) and melt-spun PAN
- Kline's models are fairly rigorous and moderately conservative
- The appropriate use of the Kline model results is for comparison and trending
  - select the most promising research approaches
  - identify critical cost sensitivities
  - establish scaling targets
- *Cost* is the manufacturer's cost to produce; *price* is highly dependent on carbon fiber market conditions

Estimated Precursor Cost

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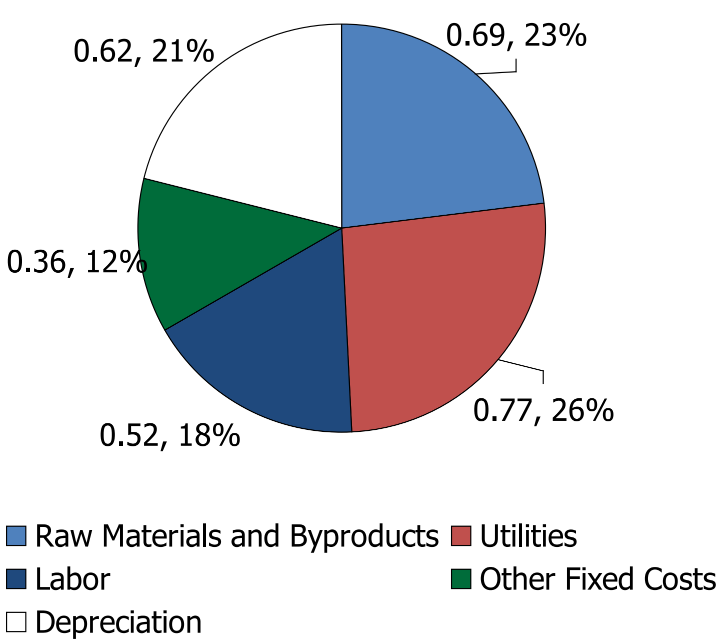
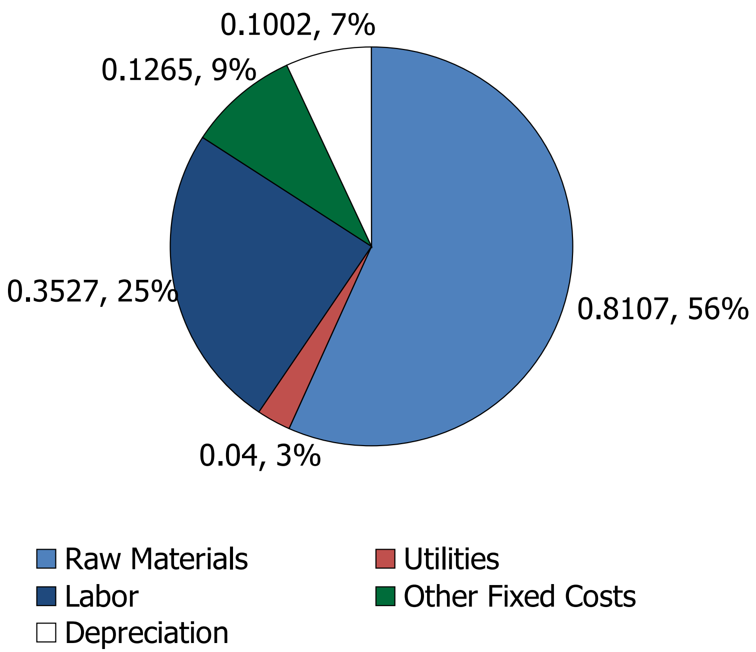
Wet-Spun PAN Cost Structure
$2.97/lb of Precursor



Line speed ~ 200 m/min

3x Melt-Spun PAN Cost Structure
$1.43/lb of Precursor

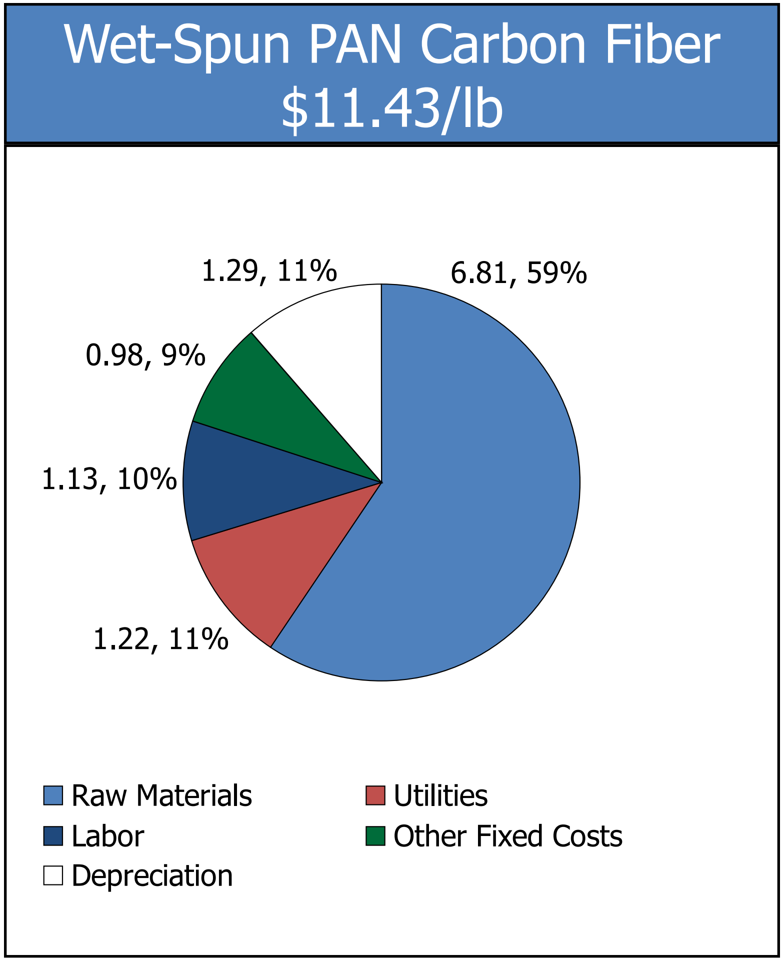


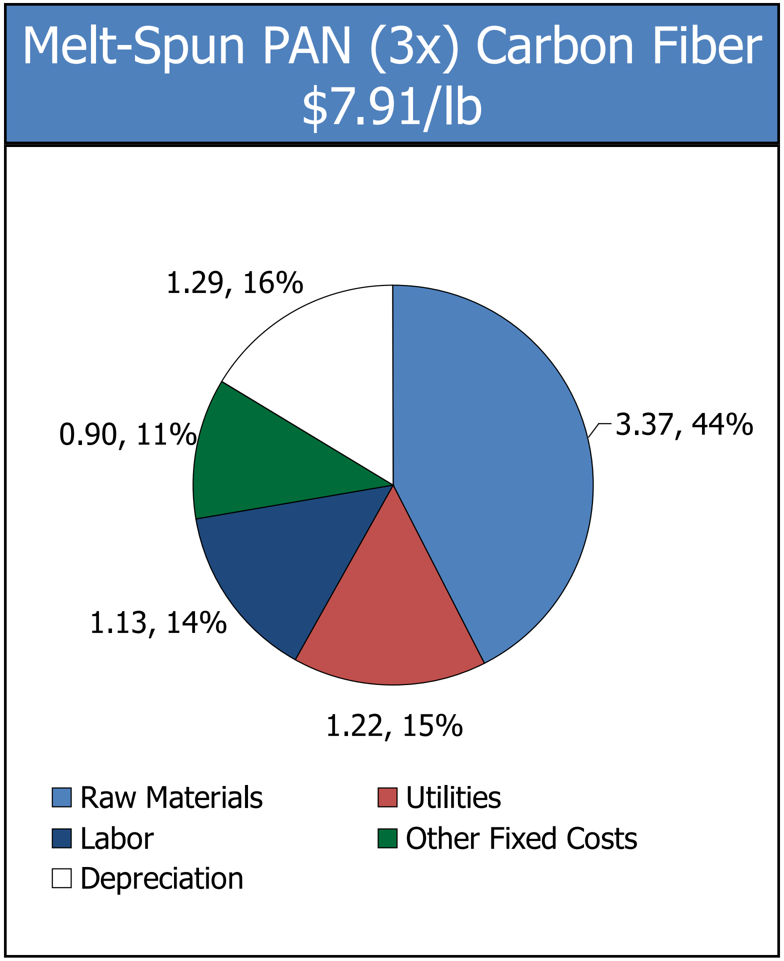
Line speed ~ 1,800 m/min

Precursor plant scale is 12M lb/yr of precursor fibers. Melt spinning rate is assumed to be 3X that of pitch.

Source: Kline and Company, November 2007; estimates based on oil at $60/bbl

Estimated Finished Carbon Fiber Cost





Conversion plant scale is 5M lb/yr of finished carbon fiber.

Source: Kline and Company, November 2007; estimates based on oil at $60/bbl

Potential CF Cost Matrix

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Estimated cost based on implementation of IP from ORNL program

Precursor and Conversion	Mill Cost $/lb CF
Baseline **– Wet spun PAN precursor conventionally converted**	**$11.43**
Melt spun PAN precursor conventionally converted	**$ 7.91**
Melt spun PAN, advanced oxidation, conventional carbonization	**$ 6.83**
Melt spun PAN, advanced conversion	**$ 6.11**

Mill cost is the manufacturer's to produce finished carbon fibers. These cost estimates are derived primarily from the 2007 Kline reports and are based on petrochemical prices in CY2007Q1

Collaborations and Partnerships

- Virginia Tech
  - A leading US university in synthesis and processing of PAN-based polymers
  - Polymer development team led by Professor James McGrath, an “icon” in the polymer science community
  - Spinning development team led by Professor Donald Baird, who is also highly respected by his peers
  - Main subcontractor
- University of Tennessee
  - Extensive fiber, materials, and process characterization support
- Sentech, Inc.
  - An important contributor to the development of advanced oxidation and stabilization processes
  - Leading expertise and IP rights in unique atmospheric pressure plasma processing technology
- FISIPE
  - A leading supplier of textile PAN fibers
  - Portuguese company; there are no textile PAN fiber producers active in the US
- Nanomaterials providers; several companies
  - Some do their own R&D in their material to satisfied costumer request

Future Work

Rest of FY10

- Continue efforts for the generation of acceptable hot-melt PAN-filaments/tows

FY11

- Improve process efficiency and parameters to achieve a better PAN precursor
- Continue conversion of these PAN filaments/tows into carbon fibers and their evaluations
- Consideration towards scalability, more and longer filaments

Summary

This year accomplishments:

- Single filament drawn from stable melt polymer (12/2009)
- First long filament generation was achieved by PAN-Melt Spinning process (3/2010)

Overall Project Impact:

- This work addresses a very important barrier in the application of carbon fiber
- This work is developing a new approach for the generation of carbon fiber PAN-precursor. This method offers a higher potential for achieving a significant cost reduction up to 30 to 50% in the generation of this precursor for carbon fiber when compared to PAN wet-spinning

Thanks!

Questions?