ST099

Development of Low-Cost, High Strength Commercial Textile Precursor (PAN-MA)

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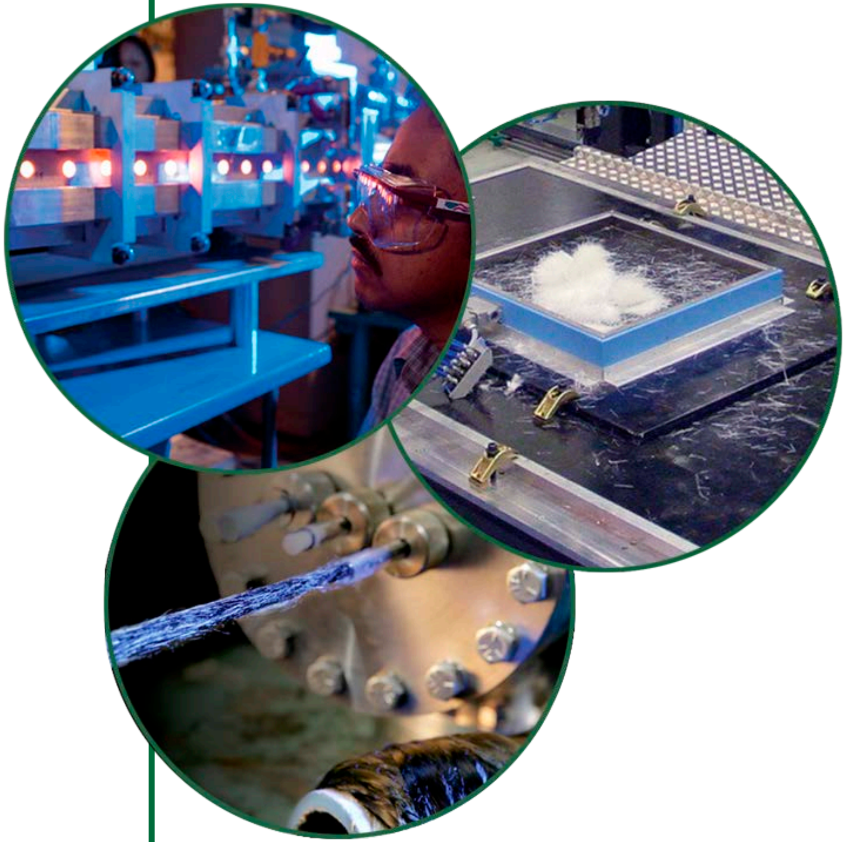
June 2014

Status as of mid April 2014



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U.S. DEPARTMENT OF ENERGY

OAK RIDGE NATIONAL LABORATORY

MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

Project Overview

Timeline

- Start April 2011
- End December 2014

Budget

- FY 2011: $350K
  ($125k from VT)
- FY 2012: $300K
- FY 2013: $550K
- FY 2014: $0
- DOE Total: $1200K
- FISIPE & SGL Cost Share: $1,277K
- Cost Share: 52%

Barriers

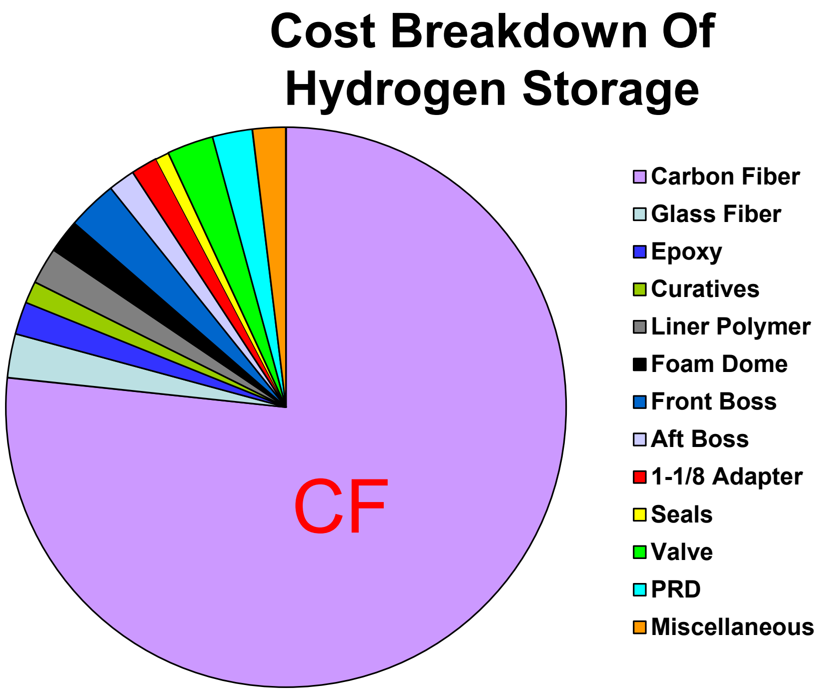
- Barriers addressed
  - High cost of carbon fiber
  - CF largest cost component of high pressure storage tanks.
  - Inadequate supply base for low cost carbon fibers

Partners

- ORNL: carbon fiber conversion, precursor characterization, carbon fiber characterization
- FISIPE: Precursor formulation, precursor spinning
- SGL: Carbon fiber conversion

Relevance - Background

- The CF material represents a significant portion of the overall cost of pressure vessels (60-80%).
- There is a strong need for a reduction in the cost of CF.
- **Precursor is 55% of the cost of the Carbon Fiber.**
- Target properties: **35-38 MSI Modulus; Strength ~650 - 700 KSI.**



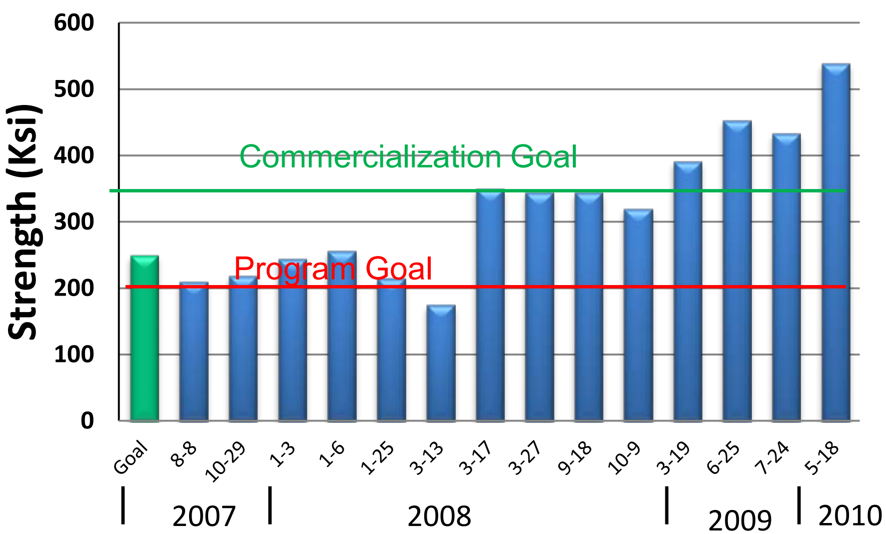
	Strength (KSI)	Modulus (MSI)	Estimated Production Costs
Current Market Fibers (Aerospace Grade)	700	35-38	$15-20/lb
Project Target	650-700	35-38	$10-12/lb
Current Status	592-619	35-39	$10-12/lb

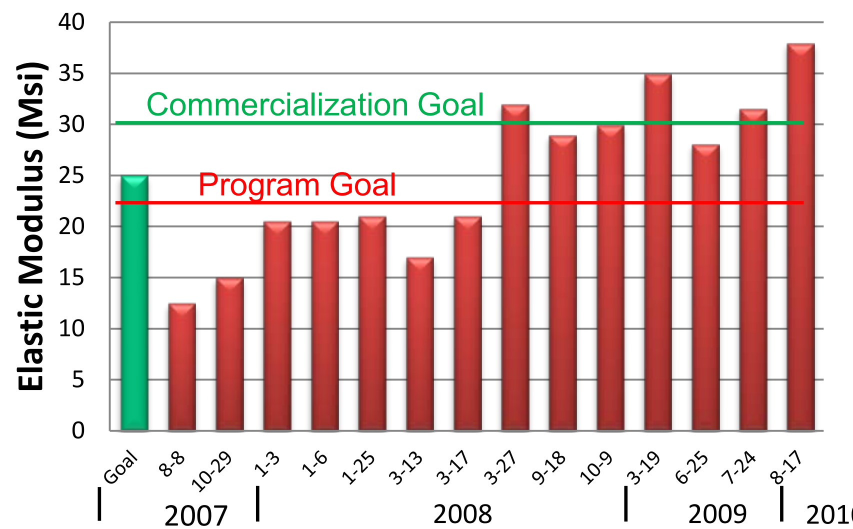
Relevance – Project History

Project built off 2 previous projects funded by Vehicle Technologies.

1st was conducted by Hexcel: Feasibility of using "textile" grade PAN (carpet and sweater fiber) as a precursor. Properties: 20 MSI, 240 KSI.

2nd was conducted by ORNL and FISIPE (Lisbon, Portugal): Develop a textile based precursor for vehicles.





Target Properties:
250 KSI and 25 MSI

Final properties:
540 KSI and 38 MSI

Past - Milestones

Date	Milestone	Status
July 2011	Down select to most promising precursor formulation.	Complete
August 2011	Conduct first chemical pretreatment trials.	Determined not Needed
September 2012	Achieve carbonized fiber properties of at least 150KSI strength and 15MSI modulus.	Complete
March 2012 Go/No-Go	Achieve carbonized fiber properties of at least 300 KSI strength and 30 MSI modulus.	Complete
October 2012	Downselect to the most promising precursor.	Complete
April 2013	Carbonize tows and achieve 450 KSI and 31 MSI.	Complete

FY2014 Milestones

Date	Milestone	Status
December 2013	Carbonize tows and confirm that material properties meets performance requirements of > 500 KSI & 30 MSI modulus.	Complete 1/13/2013
March 2014 Go/No/Go	Carbonize tows and confirm that material properties meets performance requirements of > 550 KSI & 31 MSI modulus.	Complete 1/13/2013
June 2014	Carbonize tows and confirm that material properties meets performance requirements of > 600 KSI & 32 MSI Modulus.	Complete 3/30/2014
July 2014	Complete cost report and estimate the cost savings if the precursor under development were used to manufacture carbon fiber as compared to the precursors that are currently used by industry. Metric: Cost savings in carbon fiber manufacturing cost of at least 25% when compared to precursors currently used by industry.	Phase I Baseline 6/30 Phase II 7/31

FY2014 Milestones

Date	Milestone	Status
September 2014	Carbonize tows and confirm that material properties meeting performance requirements of > 650 KSI & 33 MSI modulus.	In Process
October 2014	Issue final project report which will include identification of other potential commercialization routes, materials and possible corporate entrants to achieve the same goals as this project (i.e. high strength at minimal cost and a good commercial pathway).	Not Started
October 2014	Deliver 20 Kg of fiber for evaluation to a tank manufacturer selected by DOE.	In Planning
November 2014	Commitment by a carbon fiber manufacturer to use the fiber developed in this project in production.	Scale-Up has begun.

Two Reference Cost Models (Industrial not Aerospace)

H_2 Storage

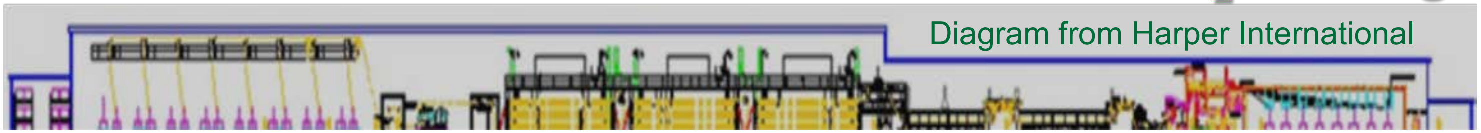


Diagram from Harper International

Cost Per Pound of Carbon Fiber	Precursors	Stabilization & Oxidation	Carbonization/ Graphitization	Surface Treatment	Spooling & Packaging	
NEW TRJ - $12.31 High Volume Not Done	$6.61	$1.61	$2.65	$0.93	$0.50	TRJ Model 2014
Baseline Today - $10.20	$5.56	$1.78	$1.41	$0.80	$0.65	ORNL Model 2012
High Volume Today - $9.35	$5.23	$1.62	$1.27	$0.72	$0.49	

Baseline: 3M lb/yr line
High Volume: 12-15M lb/yr line

NEW Textile Research Journal (TRJ) Model
- 24 K
- Industrial Grade
- Based on Moses Lake Facility

ORNL Model
- 48K
- Industrial Grade
- Based on Multiple Manufacturers

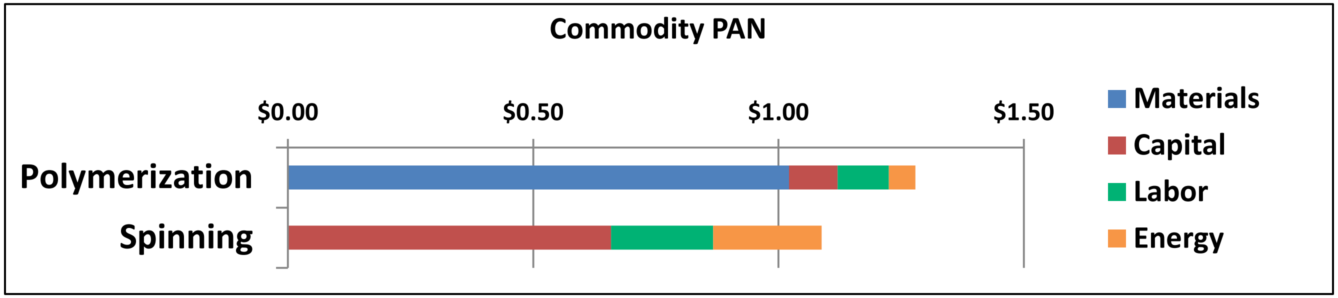
Precursor Cost is by far the Greatest (55%) followed by Oxidation and Carbonization

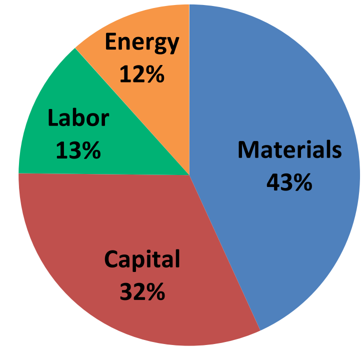
Oxidation is the rate limiting step and thus mass throughput limiting step.

ORNL 2012 Model – Precursor Cost (Industrial Grade)

Current CF Precursors

- Cost drivers are polymerization materials (i.e. acrylonitrile) and high spinning equipment cost

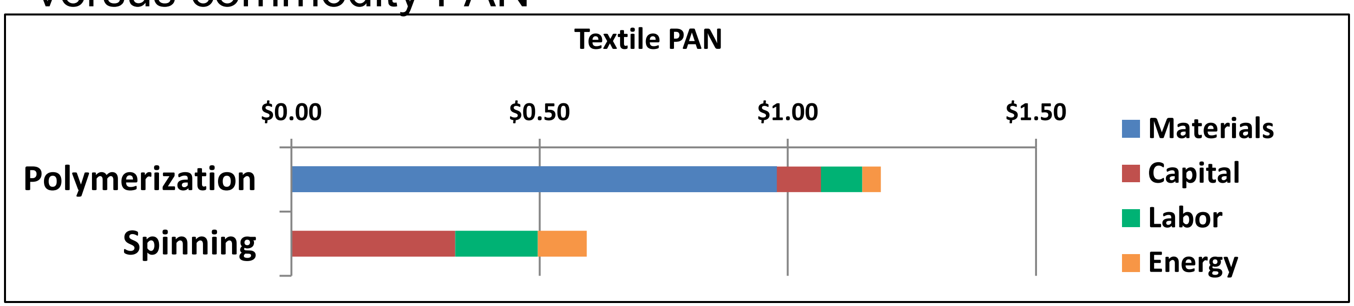


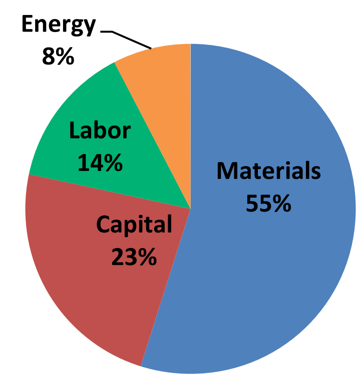


Tex. PAN 7500 t/y Plant	Com. PAN 7500 t/y Plant	Savings
$1.78 /lb	$2.37 /lb	$0.58 (25%)

Textile Precursors

- Cost savings driven by substantially higher mass throughput per $ invested in spinning equipment versus commodity PAN



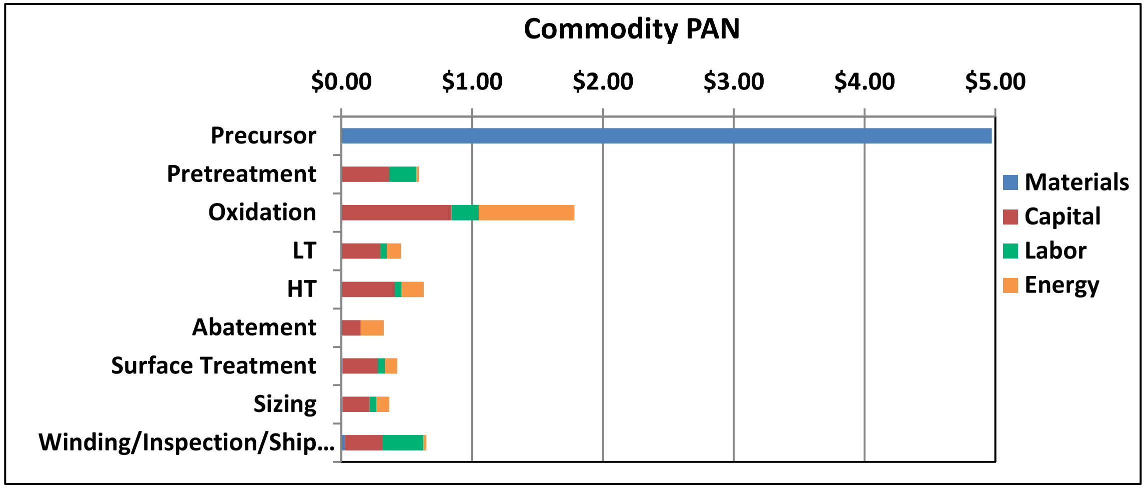


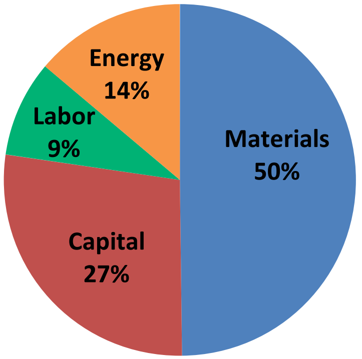
ORNL 2012 Model – Carbon Fiber Cost (Industrial Grade)

H_2 Storage

Current Commercial Carbon Fiber

Cost drivers are high precursor cost and with low conversion yield (47.6%)

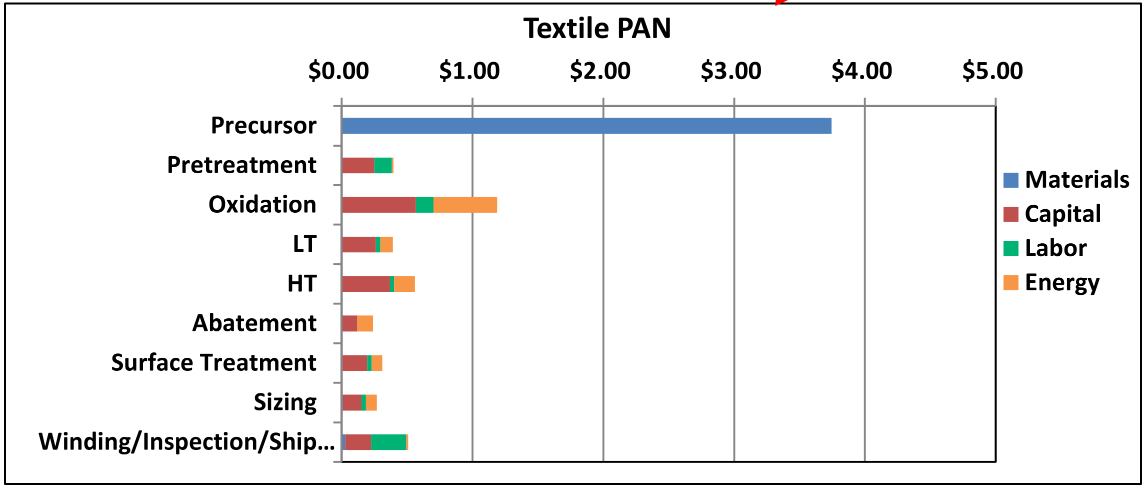


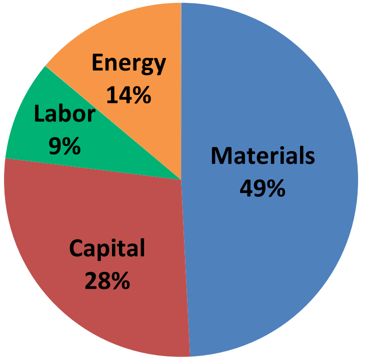


Tex. PAN 2250 t/y Plant	Com. PAN 1500 t/y Plant	Savings
$7.61 /lb	$10.20 /lb	$2.59 (25%)

Textile Based Carbon Fiber

Cost savings over commodity PAN mostly from lower cost precursors.





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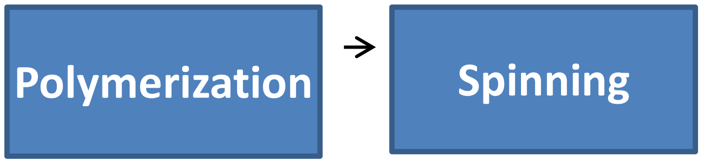
ORNL 2014 Model (700 Ksi) – Preliminary Baseline Results

Developing a 700 KSI Fiber production cost model in two phases:

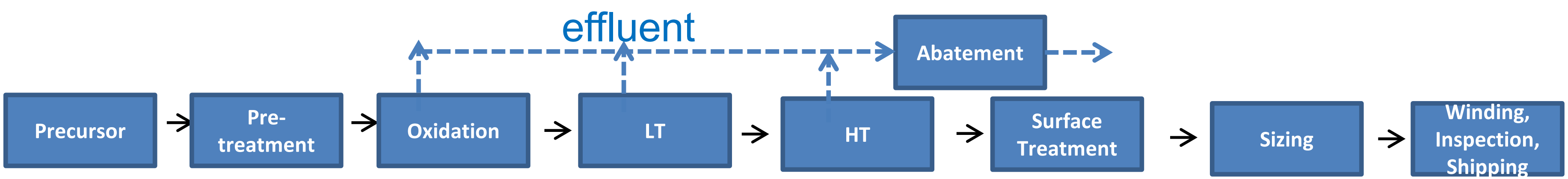
- Phase I: Baseline **Completion: 30 June 2014**
- Phase II: Project Benefit **Completion: 31 July 2014**

- Precursor model (7500 t/year line capacity)

  Evaluate precursor manufacturing at the level of two major process steps



- CF model (1500 t/year line capacity) Evaluate carbon fiber manufacturing at the level of nine major process steps



ORNL 2014 Model (700 Ksi) – Preliminary Baseline Results

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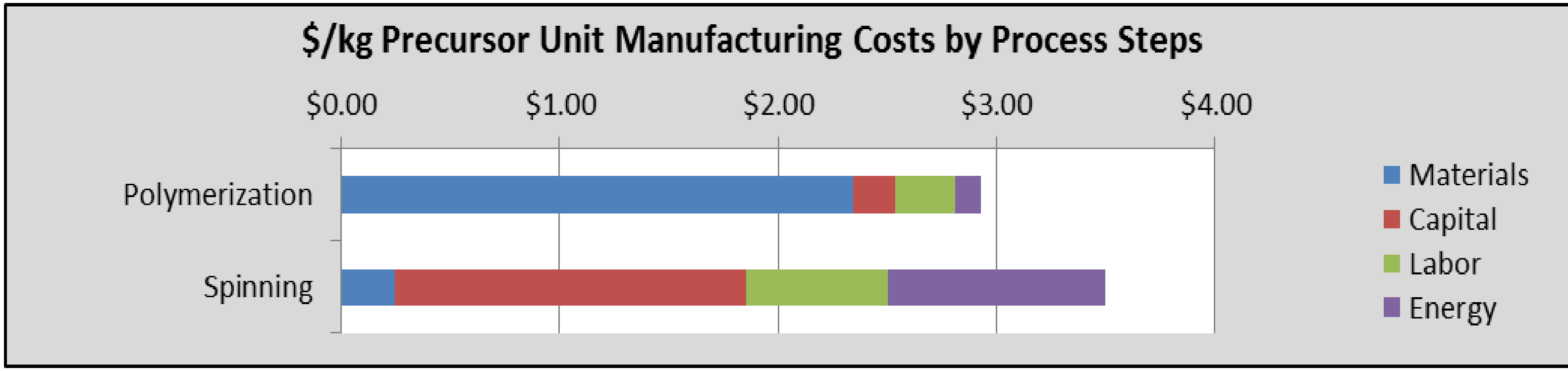
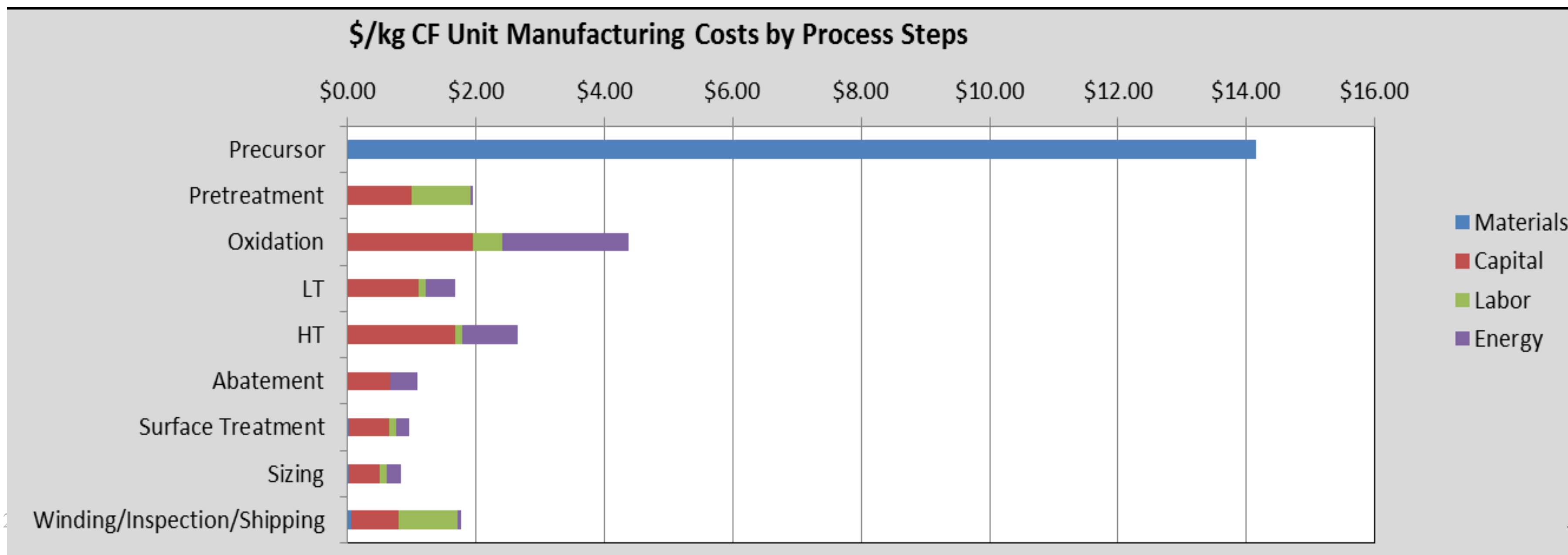
Precursor Cost $6.40/Kg ($2.91/pound)



Carbon Fiber Cost $29.40/Kg ($13.36/pound)



Project Approach

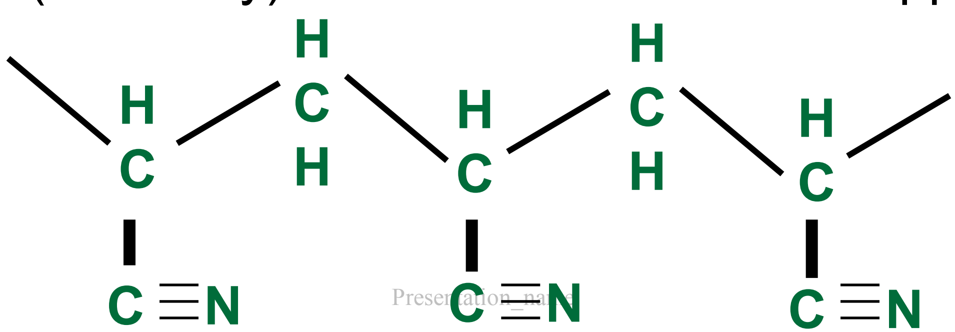
1. Identify candidate PAN-MA resins.
2. Determine fiber spinning parameters. (Purity level, molecular weight, AN concentration, 3rd components such as itaconic acid, temperature, solvent concentration, etc.)
3. Down Selection from 11 polymers to 3 candidate fibers to 1 final fiber.
4. Improve fiber purity and "roundness"
5. Determine the conversion protocol.
6. Optimize all above parameters.

Fiber formulation being done in Portugal.

Fiber conversion optimization being done in two teams:

- ORNL (US) – High tension oxidation approach.
- SGL (Germany) – Low tension oxidation approach.

PAN:



$T_g \approx 120°C$

FY11-12 Status

FY 2011

Kick-off Telecon 21 April 2011. Several months of retrofit to produce a PAN-MA precursor. Downselected from numerous potential formulations.

11 polymer compositions sent to ORNL for screening.

3 were selected for further development using analytical techniques.
(critical: high molecular weight, high AN content, uniform exotherm during oxidation, etc.)
First trial: 282 KSI, 28.4 MSI with F1921.

FY 2012

Preliminary Conversion Trials were held with all 3 Precursors

Go/No-Go MILESTONE 3/31/12: Achieve properties of at least 300 KSI strength and 30 MSI modulus.

F1921 Precursor: 324.7 KSI; 26.9 MSI
F2350 Precursor: 372.8 KSI; 36.0 MSI
F2027 Precursor: 252.7 KSI; 27.2 MSI

The F2350 Precursor was downselected for further development.

FY13-14 Status – Accomplishments

Precursor → Prestretching → Oxidation 1 → Oxidation 2 → Oxidation 3 → Oxidation 4 → Carbonization 1 → Carbonization 2 → Carbon Fiber

200-300C 80-120 min

400-1800C; 4-14 min

Completed **In Process**

Optimization through iterative optimization of Temperatures, Exposure Times and Tension (Stretch %) in each of 7 stages of conversion.

Once process is optimized, produce 20 Kg of fiber and send to Hexagon Lincoln for testing.

Sample Data Analysis

T1	T2	T3	T4	T5	?	
Oxi 1	Oxi 2	Oxi 3	Oxi 4	LT	HT	ST/Size
Time 1	Time 2	Time 3	Time 4	Time 5	Time 6	
Hi% 1	Hi% 2	Hi% 3	Hi% 4	?	?	
Low% 1	Low% 2	Low% 3	Low% 4			

A-I, S-U
J-R

Sample Run	UTS (KSI)	E (MSI)	STF (%)
A-B	576.9	39.8	1.7
B	493.0	38.5	1.6
C	543.1	37.9	1.7
D	471.6	36.1	1.5
F	308.6	34.9	1.2
G	408.1	34.6	1.4
H	446.2	35.2	1.4
K	491.1	34.7	1.7
L	499.3	34.2	1.7
P	552.9	35.7	1.9
R*	307.0	34.5	0.8
S*	499.8	37.2	1.5
T*	488.7	37.9	1.4
U	545.2	38.3	1.6

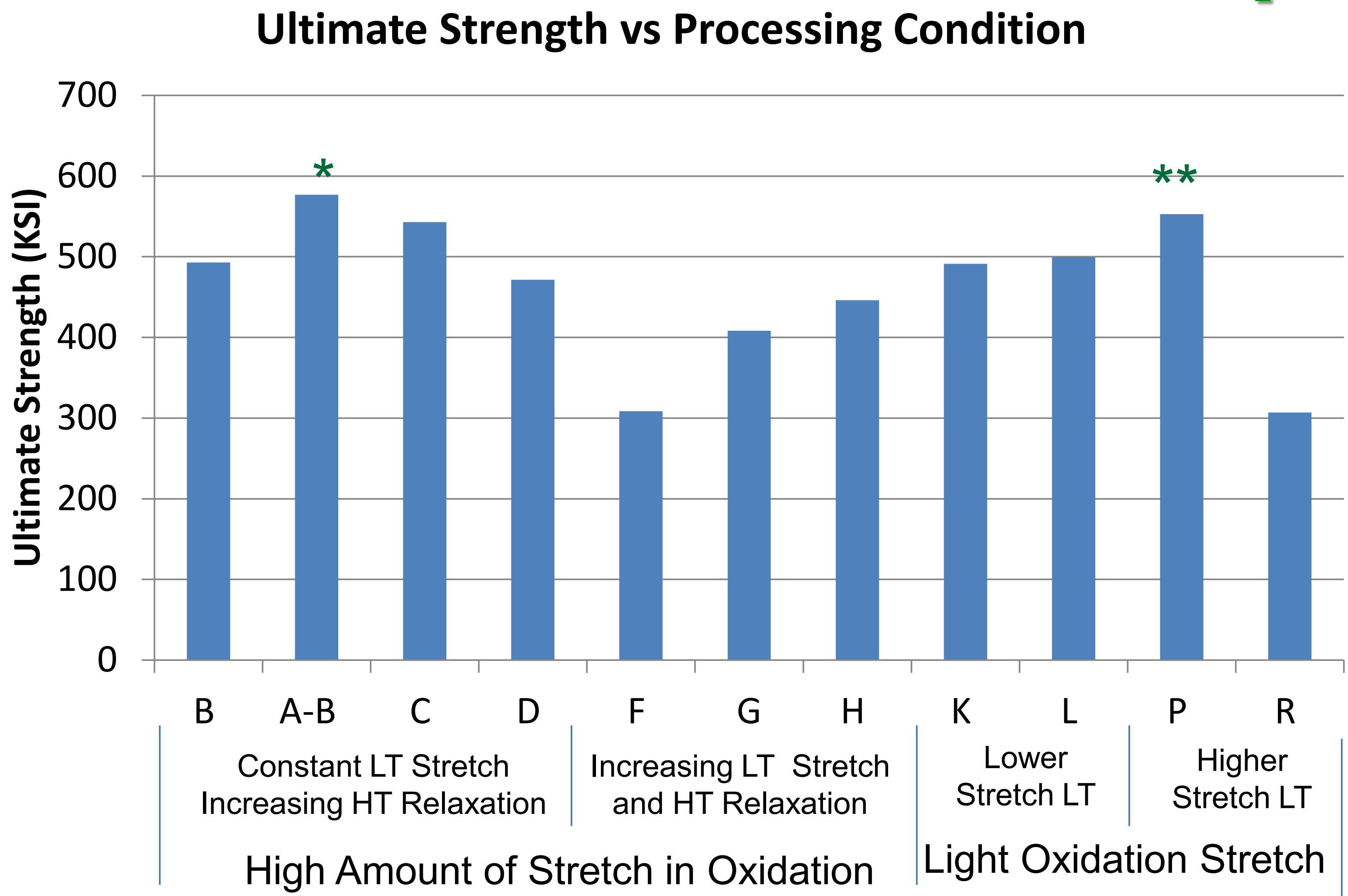
Completed In Process

Processing Conditions Systematically Varied

Strand Tests conducted using ASTM4018 at the Oak Ridge Carbon Fiber Technology Facility

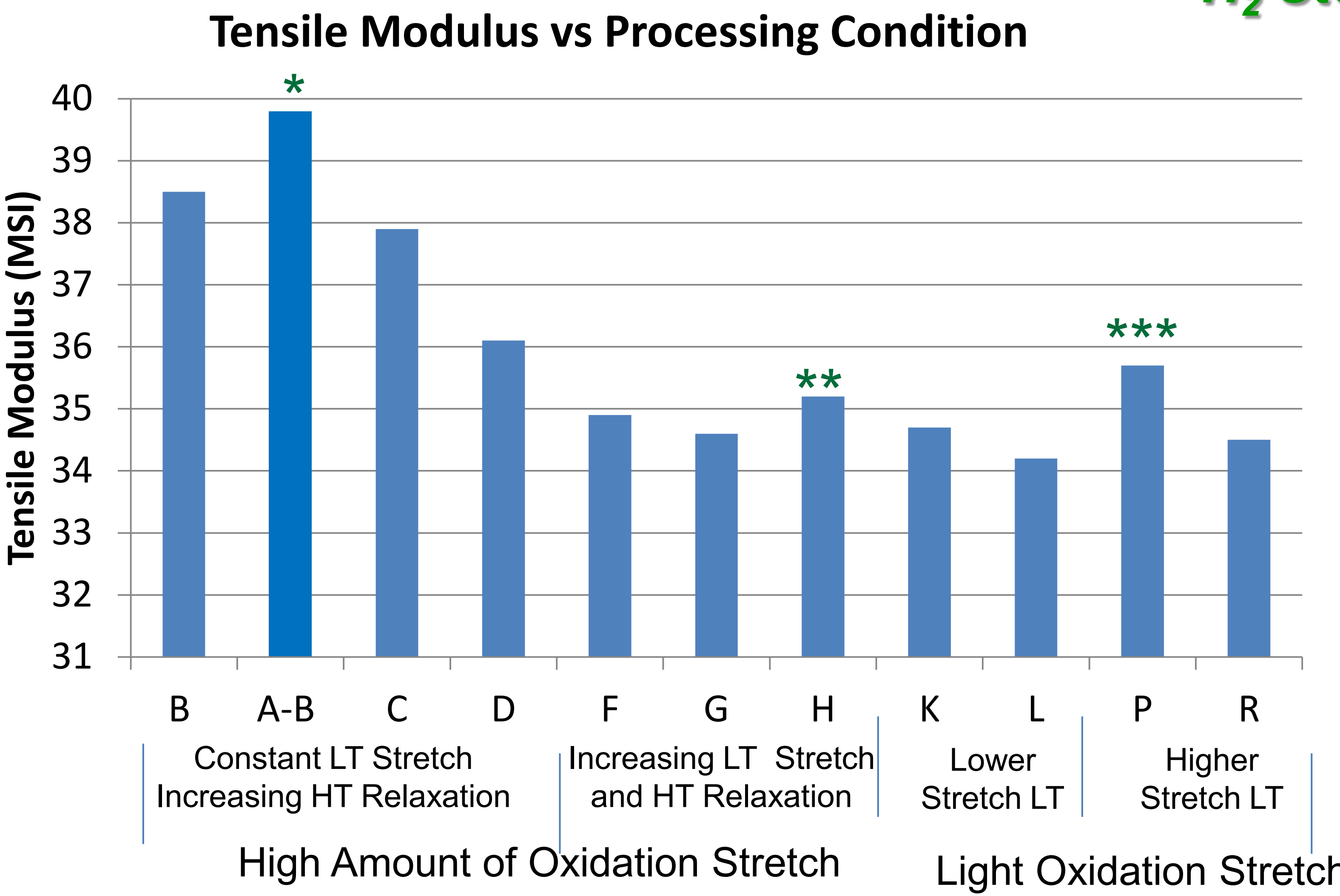
Processing Conditions Omitted for Export Control Compliance

Sample Data Analysis



Conclusion: Optimum HT Relaxation Identified*, Optimum LT Stretch Identified**

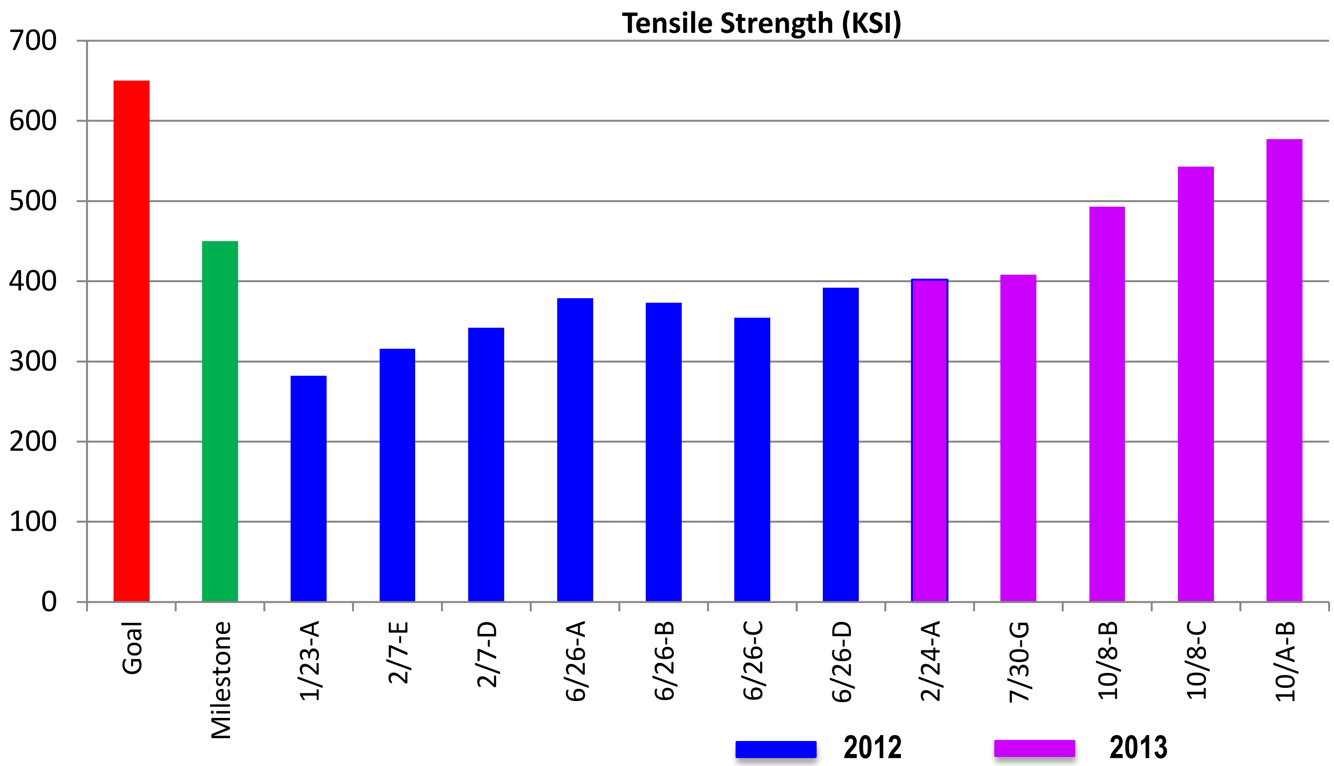
Sample Data Analysis



Conclusion: High Amount of Stretch in Oxidation* & Increased Relaxation in HT Carbonization & Increase Stretch in LT*****

Go/No-Go Milestone Completion

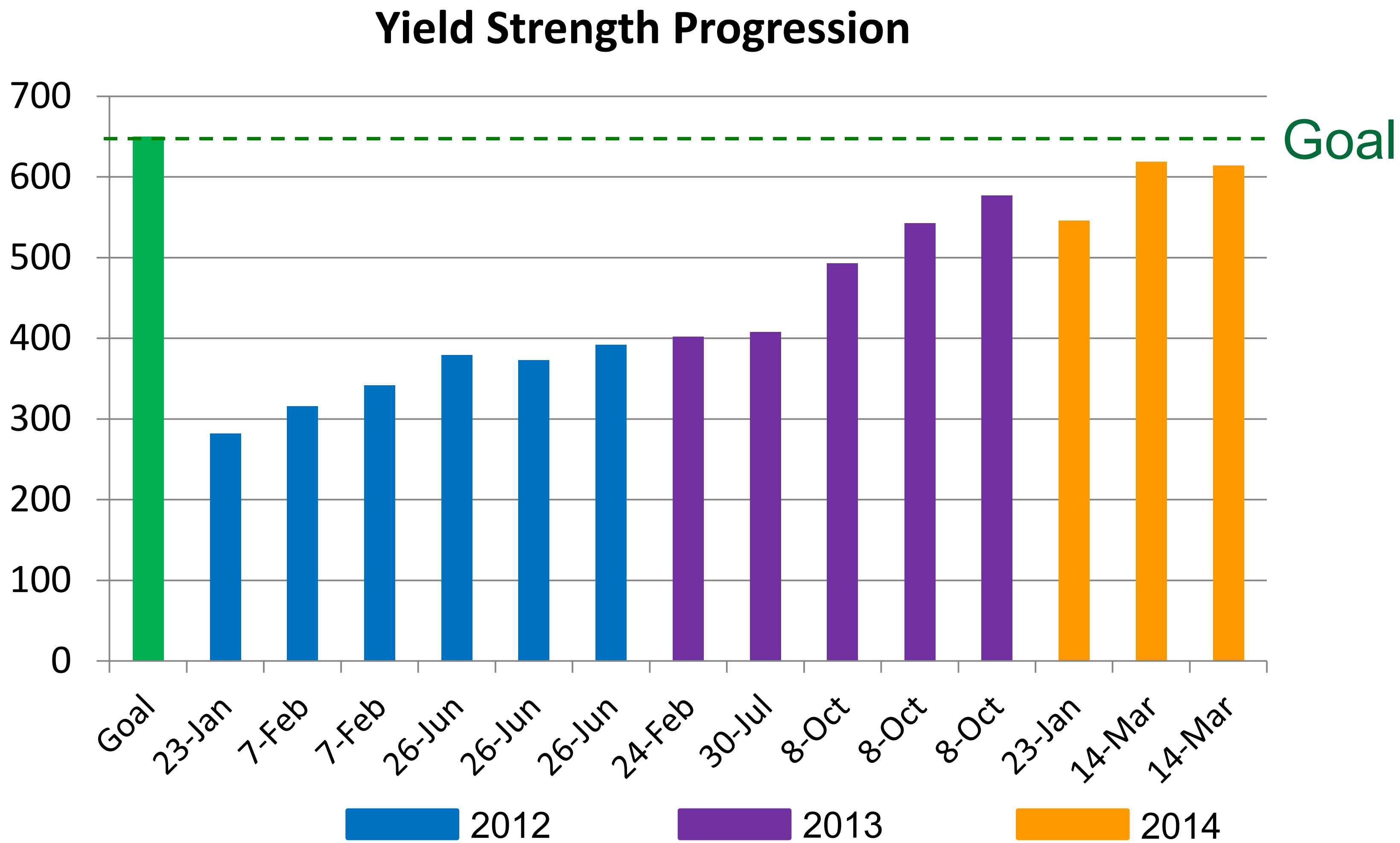
FY13Q4 Milestone: Reach an intermediate goal of 450 KSI tensile strength and 33 MSI modulus. Milestone exceeded.



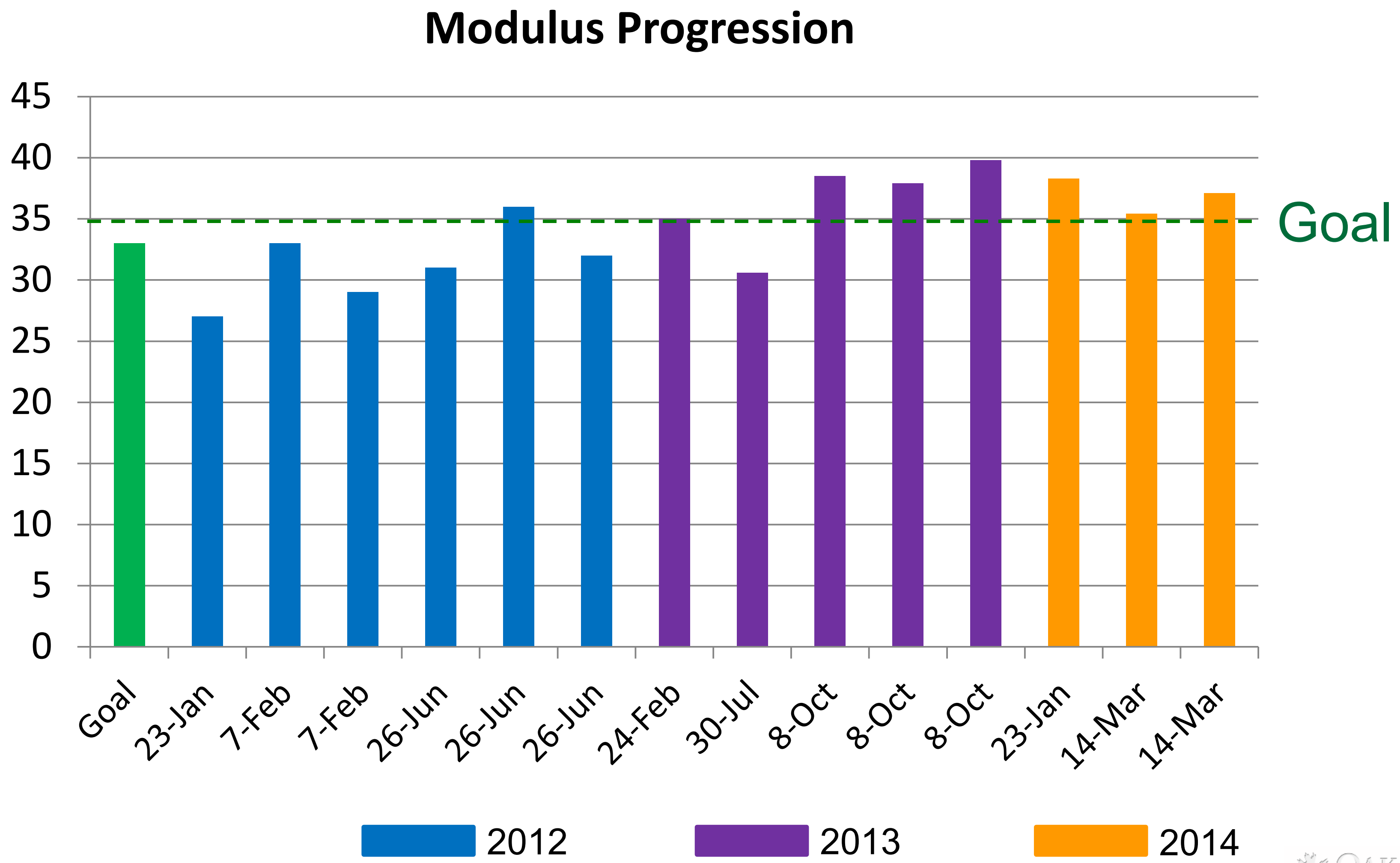
Intermediate milestone of 450 KSI Strength and 33 MSI modulus exceeded. Current properties: 576.9 KSI strength and 39.8 MSI modulus. Verified using ASTM4018 at ORNL CFTF.

FY13-14 Status – Accomplishments

Strength over Project Duration



Modulus over Project Duration



FY13-14 Status - Accomplishments

Major Issues Resolved:

Fiber fuzzing

(Diameters: 11-13 as a precursor)

Consistency along the Tow

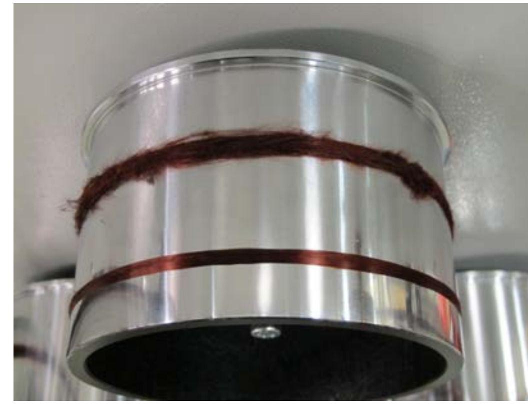
(< 8% Variability)

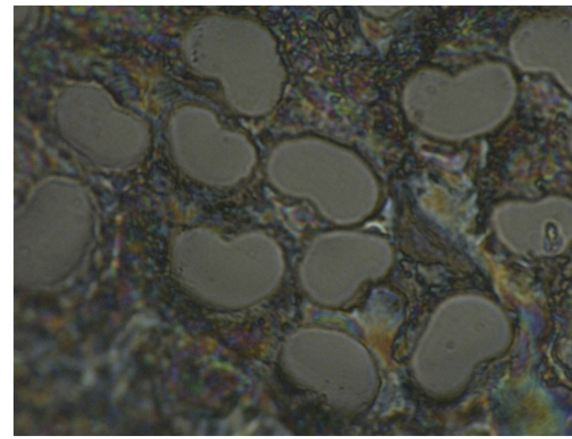
Tow to Tow Variability

(<5% in filament count)

Fiber Uniformity in Roundness

(width/thickness ratio: 1.1-1.4)





Resolved by optimization of spinning conditions, such as temperature, spin rate, solvent concentration, etc.

ORNL identified issues that are critical for CF precursors but not textile fiber. FISIPE resolved those in their process.

Their process conditions are proprietary.

FY13-14 Status - Accomplishments

We have completed optimization of all 4 oxidation zones and most of the way through the carbonization.

15 of 18 Processing Parameters Completed: 83%
(6 Zones – Temperature, Time, Stretch % in Each)
Remaining: LT Stretch %, HT Stretch % & HT Final Temperature

Current Test Matrix:

- 2 Different Oxidation Profiles
- 5 Low Temperature Carbonization Stretch Conditions
- 3 High Temperature Carbonization Stretch Conditions
- 3 Different High Temperature Carbonization Temperatures
- 90 Combined Condition Variations

Collaboration

ORNL:

- Conducts conversion from precursor to carbon fiber. (multiple profiles)
- Develops relationships between processing conditions and fiber properties.
- Precursor characterization and advises on modification.
- Carbon fiber characterization.
- Composite characterization and coordinates activities.

FISIPE:

- Formulates the polymer.
- Spins the polymer into precursor fiber.
- Analyses of the precursor.

SGL:

- Conducts conversion from precursor to carbon fiber for multiple applications.
- Carbon fiber characterization.

Hexagon Lincoln:

- Will evaluate the finished fibers for composite (tank) applications.

Proposed Future Work

Future Plans

1. Complete refinement of conversion protocol. Time – Temperature – Tension.

2. Scale-up ability to make precursor to an industrial scale. (Transfer process from pilot precursor line to industrial fiber line.)

3. Complete cost model & brief to DOE & HSTT.

4. Deliver fiber to a tank manufacturer (Hexagon Lincoln) and conduct preliminary composite coupon testing, will also conduct parallel testing at ORNL

5. Make preliminary composite samples. Test and compare to baseline industrial fibers.

Past Reviewer Comments

1.The research team should add a partner or effort in the area of cost estimating. It should also consider including others in the fiber industry beyond FISIPE to ensure that precursor development will have a wider impact rather than simply to SGL Group before the project is complete.

In FY 14 the team has added a cost estimating effort. While additional partners would be eagerly welcomed, the proprietary nature of the work dictates that each project be conducted with a single precursor manufacturer. We have developed similar efforts with 2 additional textile manufacturers targeting lower fiber strengths.

2. It would be good to develop a better understanding of the impact on final materials properties of polymer dope filtration as well as other aspects of the spinning process that could reduce the number of large-scale pilot trials. It is unclear if SGL Group plays a role in the project. If so, its role should be described. It has manufacturing expertise that can be brought to bear on this project.

The polymer processing details are understood but highly proprietary and cannot be presented in this forum. SGL is also conducting conversion trials.

Past Reviewer Comments (Continued)

3.The project team needs to include specific metrics for developing a high-quality aerospace CF. The team needs to have an update on the cost estimate based on the current assumptions.

The project metrics are tied to the milestones and are basically to develop fibers with properties equivalent to lower cost aerospace carbon fibers. i.e. 700 KSI strength and >33 MSI modulus in a 24K tow size. A cost model is being developed.

Summary

Relevance

- Carbon fiber composites make up 60-80% of the hydrogen storage system and the cost of the fiber makes up the majority of that cost.

Approach/Strategy

- Developing lower cost precursors, building off of previous project, to meet performance requirements while preserving high production rate cost benefits.

Technical Accomplishments

- Chose 11 Formulations, down selected to 3 candidate fibers and then down selected to1 development system.
- About 83% through optimization

Collaboration and Coordination

- Building off Vehicle Technologies Work
- FISIPE (Precursor supplier) and SGL Carbon Fibers are partners

Future Work

- Complete Optimization of current formulation. Test fibers.


Thank you for your attention.
Questions?