Melt-Spun PAN Precursor for Cost-Effective Carbon Fibers in High Pressure Compressed Gas Tankage

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Oak Ridge National Laboratory

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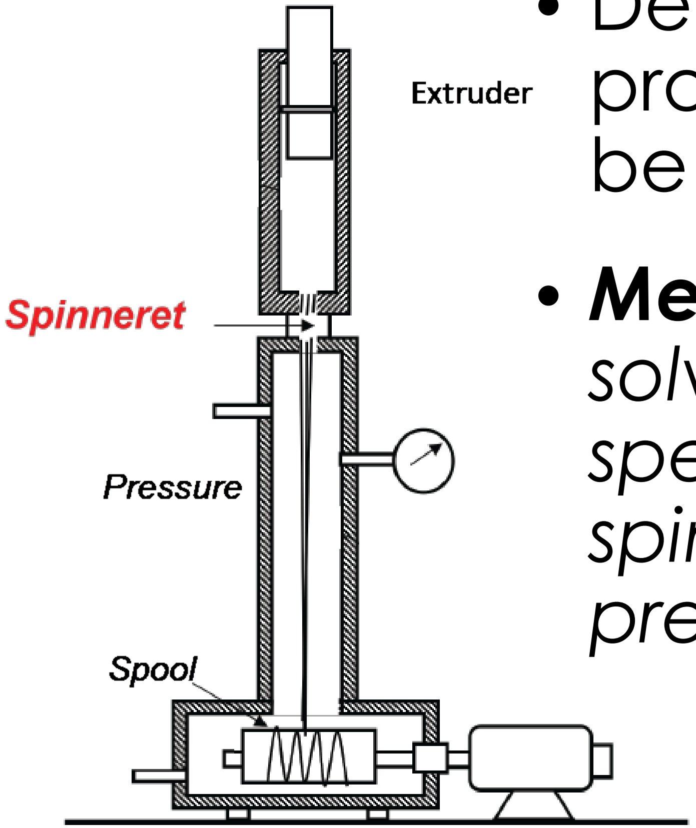
Project ID # ST239

Project Goal



- Demonstrate that melt spun PAN precursor can reduce 700ksi carbon fiber cost by 25% vs conventional solution spinning
- Demonstrate the process effectively scales to pre-production levels necessary to make finished CF to be validated in multiple high pressure tanks.
- ***Melt spinning*** *of PAN offers significantly reduced solvent utilization/ recovery advantages, faster line speeds, potential higher quality and much smaller spinning equipment footprint vs conventional precursor production*

Partner Prescott Composites plans to commercialize this technology for producing economically advantaged CF

Overview

Timeline and Budget – Phase 1

- Project Start Date: 10/15/21
- Project End Date: 9/30/23
- Total Project Budget: $4,898,084
  - DOE Share: $2,697,522
  - Cost Share: $2,200,562
  - DOE Funds Spent*: $135,545
  - Cost Share Funds Spent*: $276,923

    * As of ~ 03/01/2022

  - Total Federal Spent**: $149,901

    ** As of ~ 03/31/2022

Partners

- Project lead – Felix Paulauskas, PI ORNL
- Program Management – Erin Brophy, Collaborative Composites Solutions
- Partner organizations
  - Virginia Tech -precursor dope formulations
  - JR Automation - design/fabrication of key equipment
  - High Energy Sales, LLC –consulting based on BASF experience
  - Hexagon R&D –high pressure tank design and manufacturing requirements - makes and tests tanks In Phase II
  - Prescott Composites –leading evaluation of Commercial Feasibility and ensuring along with the Technical Viability of this development that our team's focus is on the end goal of commercialization

Relevance/Potential Impact

Cost-effective high pressure compressed gas storage is critical for widespread utilization of Hydrogen in Vehicles

- CF cost accounts for approximately 50% of total vehicle high pressure storage system cost
- Toray T700S, the baseline commercial fiber in high pressure storage ranges ***from $26-30/kg CF -*** DOE storage system targets require dropping this to ***$13-15/kg***

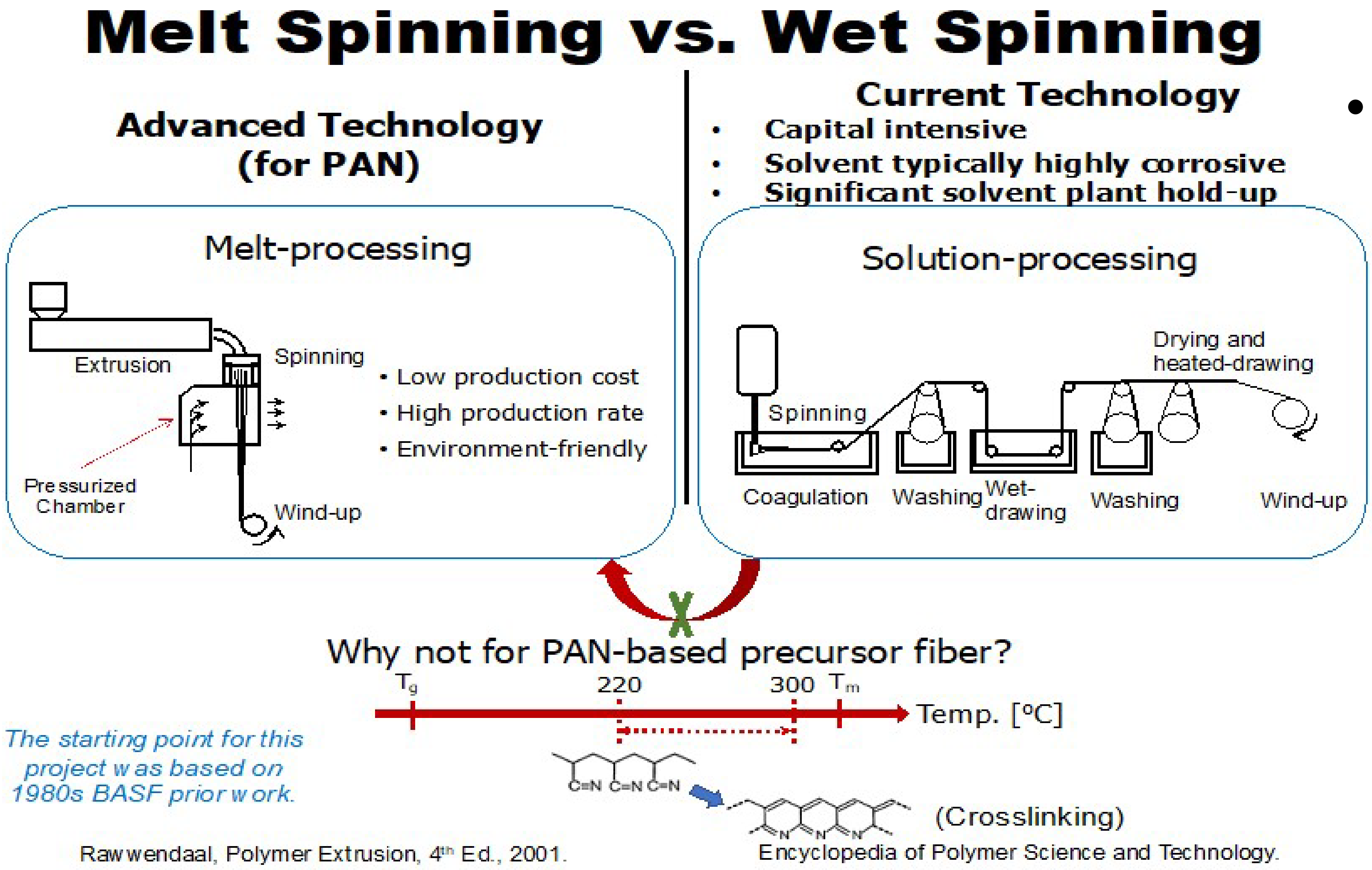
Cost of CF is split between the precursor fiber and conversion

- DOE has previously supported R&D on novel advanced conversion processes with potential to produce low-cost, high-strength CF and reduce energy use.
- High-tensile strength CF is exclusively produced from PAN precursor made via solution spinning requiring extensive capital investment for fiber formation and solvent recovery.

Large cost reductions will be required in <u>both</u> the precursor <u>and</u> conversion processes.

Project Approach

- Our team will develop and demonstrate a novel approach for melt spinning PAN precursor fiber to replace solution spinning.



- Melt spinning
  - Slashes amounts of solvent utilized along with energy and equipment associated with solvent recovery
  - Enhances spinning speed
  - Reduces fiber defects incurred in solvent removal
  - Is more attractive economically and for the environment

Project Builds on Significant Background and Prior Work

- BASF developed melt-spun PAN precursor in the 1980s.
  - CF’s were qualified for B2 bomber
  - Demonstrated 400 to ~600 KSI fiber strength and 30 – 40 MSI modulus; even better properties were thought to be achievable
  - AN content was 95% - 98% (consistent with high strength)
- Lower production cost than wet-spun fibers by ~30%.
  - Typical precursor line speed increased by ≥ 4X at winders
- Program was terminated in 1991 due to CF market collapse at cold war’s end, a forecasted long (~ 10 yr) recovery period, and solvent issues (acetonitrile, nitroalkane).

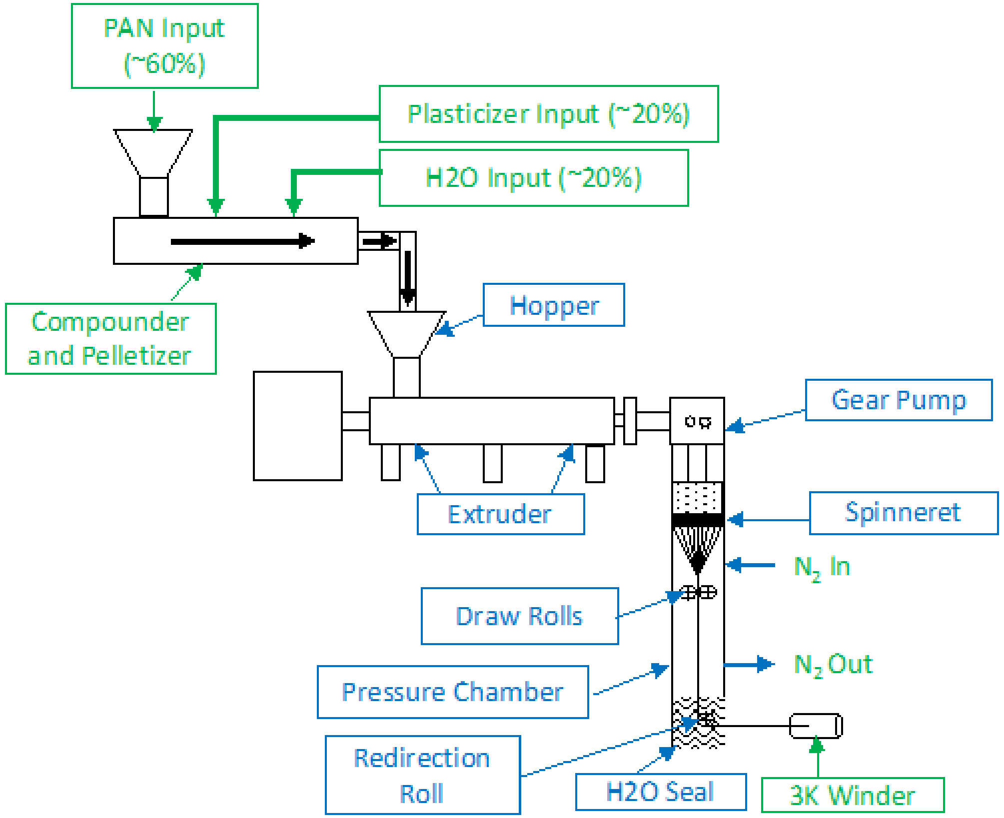
We are recently drawing even more heavily on this experience!

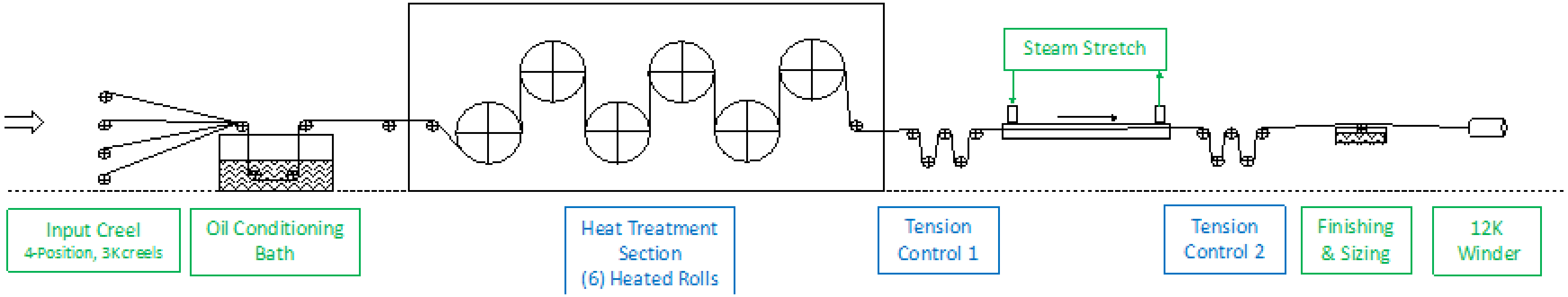
Our Approach is Driven by this Assessment

Metric	Prior Accomplishments	End of Phase I Plan	End of Phase II Plan
Precursor Formulation	Acceptable for small batch production for process feasibility only	Capable of being continuously spun at small-scale, achieving 700ksi property level	Capable of being continuously spun at pre-production-scale, achieving 700ksi
Melt Spinning Equipment	Slightly modified off-the-shelf equipment for bench-top small batch (250g/day runs) for feasibility only. Could not retain plasticizers.	Purpose built for plasticizer retention and continuous runs (~5kg/day) and achieving high performance properties	Purpose built for plasticizer retention, semi-production scale (>25kg/day) runs achieving high performance properties
Spun Amount	100 filament/100g batches	100 filament/100m continuous tow	>100kg 12K continuous tows
Converted Amount	50g/90 filament batches	250g of 100 filament samples for testing	>50kg 12K tows for tank manufacturing/testing
Level of Demonstration	Single filaments in small batches	100 filament tows, >100m continuous mfg	12K tows used to make 5 tanks
Converted Properties	250ksi best achieved in single filament testing	700ksi in single filament testing	700ksi via strand testing & tank performance data

Project Accomplishments – System Responsibilities and Interfaces Detailed

- ORNL, High Energy, and JRA collaborate on system design
- JRA to provide extrusion system including extruder, metering pump, spin packs, and pressurized quench chamber
- ORNL provides pelletized PAN and fiber handling equipment





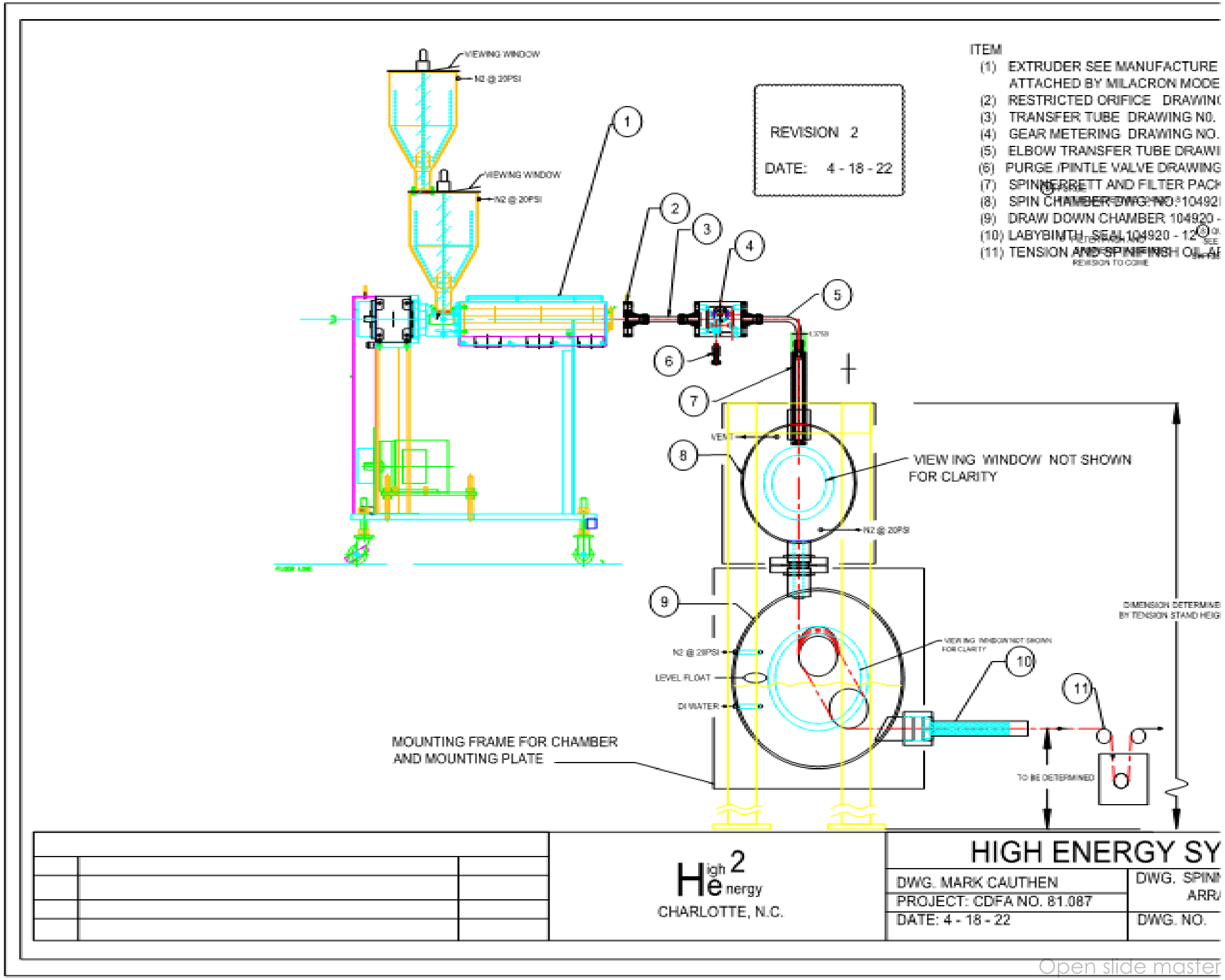
Project Accomplishments (cont)

ORNL has recently obtained 2 large quantities of scarce PAN powder for systems checkout and basis for plasticization development (either material may be suitable as purge materials base as well)

- Starting material is a less expensive PAN/VA formulation that will be appropriate for equipment checkout
- Second material is a higher quality PAN/MA formulation to serve as baseline for plasticized dope being developed by Virginia Tech
- Both materials were provided through exclusive partnerships with non-traditional foreign acrylic suppliers since acrylic sources in the US are captive to CF manufacturers

Project Accomplishments (cont)

Preliminary design layout schematic provides more functional relationships



Project Accomplishments (cont)

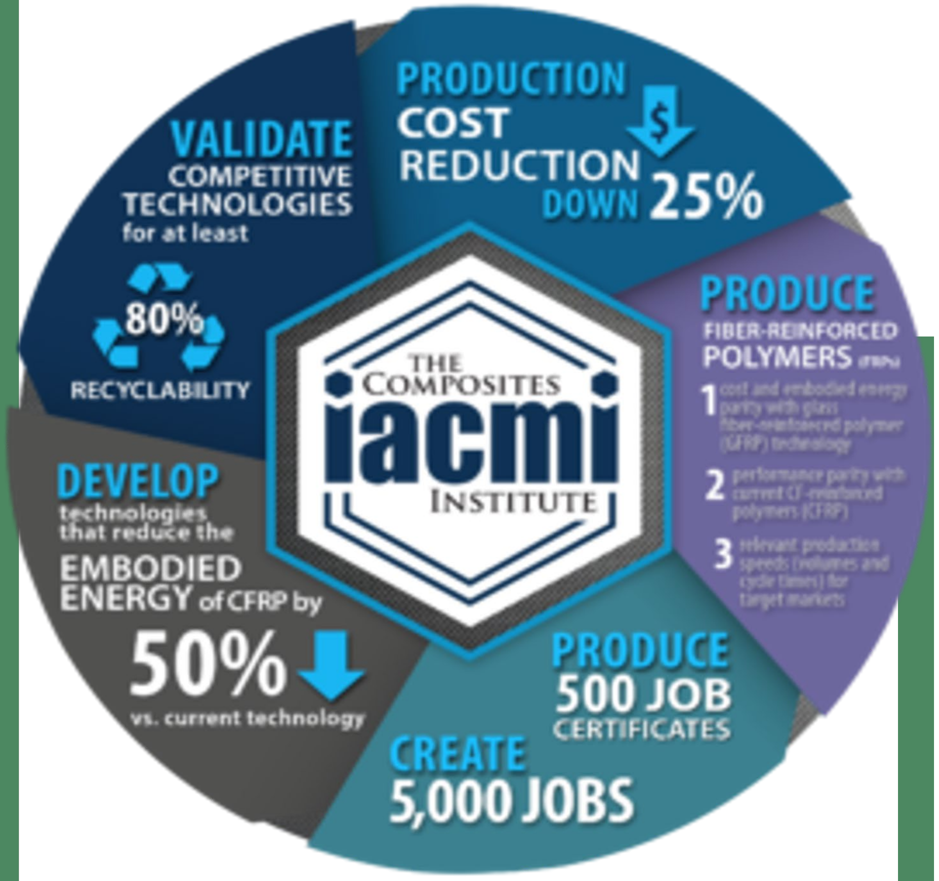
Specifications and/or preliminary designs have been completed for the following equipment:

- Heat Treatment/Dryer chamber with multiple stretching rollers
- Tensioning system at the exit of the obove heating/dryer chamber:
- Steam stretcher: already here, from prior projects,
- Take-off winders: already here, from prior projects.
- Basis design of the Double Feed Hopper System (for JRAuto.).
- Primary Extruder
- Restricted Orifice
- Transfer Tube Will Pick Up From The Orifice To The Pump Block Manifold
- Pump Block Manifold
- Spin Pump
- Elbow Transfer Tube
- Spin Pack (Filter) And Spinneret
- Spin Chamber (Quench Chamber)
- Labrynth Seal
- Exit Roll Stand
- Acrylic Bath
- Dryer
- Exit Roll Stand
- Stretch Chamber
- Stretch Roll Stand
- Peddling Stand
- Cleaning Chamber

Responses to Previous Year Reviewers' Comments

- This project has not been previously reviewed.

Project Team Leadership



CCS Corporation (IACMI) – Prime Contractor
Erin Brophy - Program Manager

Dr.-Eng. Paulauskas is the Principal Investigator

ORNL's Carbon Fiber Capabilities/Activities

Mission Overview: The Oak Ridge National Laboratory's Carbon and Composites Group develops and transitions innovative science and technology impacting U.S. energy security. ORNL works closely with industrial partners throughout the value chain to effectively transition technologies and enable successful commercial deployment.

Carbon Fiber Development
ORNL is presently leading a major DOE initiative to develop disruptive technologies for producing low cost carbon fiber. Major focal areas are (i) alternative precursors, (ii) advanced, energy efficient processes, and (iii) scaling for technology transition. ORNL processing capabilities range from single filament to tens of tons annually. Key pieces of the unique equipment suite for developing and demonstrating new approaches for lower cost carbon fiber are the ORNL Precursor Evaluation System and Carbon Fiber Technology Facility.

Organizations Addressing Key CF Technical Issues

Virginia Tech, Department of Chemistry

The laboratories of Prof. Robert Moore are fully equipped with polymerization facilities and all required analytical tools for polymer characterization:

- GPC for MW determination,
- NMR for copolymer composition,
- Thermal Analysis for melting point depression, thermal stability, and thermomechanical relaxation studies,
- Melt Rheology,
- Raman spectroscopy /Raman microscopy for fiber conversion and chain orientation studies).

The Virginia Tech effort will build upon recent ORNL/VT successes with new capabilities in polymer-solvent interactions.

Virginia Tech 1

Dr. Robert B. Moore

JR Automation's Fibers & Composites Experience

40+ Years of Experience in Fibers & Composites

JR Automation offers advanced fiber solutions for many applications. We aim at enabling our customers to implement their proprietary processes and manufacturing technologies from concept to start-up while maintaining complete confidentiality.

Industries Served

- PAN & Carbon Fiber Lines
- Staple & Filament Yarns
- Web Handling
- Advanced Fibers

Specific Machine and Process Experience in Carbon Fiber

- PAN Fiber - Wet spun, Air Gap, Melt Spun & Mesophased (Pitch) Spinning Lines
- Carbon Fiber - Creeling, Carbonization, Coating/Sizing, Winding
- Post Processing of Carbon fiber - Prepreg Machines

JR Automation will lead design, fabrication, and installation of critical extrusion and drawing systems for this initiative based on world class experience with similar operations.

JR AUTOMATION

Jeff Franklin

Project is Driven by End User Requirements

HIGH-ENERGY

High-Energy brings
Over 35 years of experience
in melt spinning systems.
our energy brings your product to life"

Mark Cauthen

Hexagon R&D LLC (R&D) is Part of Hexagon Composites ASA (Hexagon)

Hexagon is ***the*** global market leader in lightweight composite cylinders storage and transport of pressurized gases:

- Have delivered over 17 million Type 4 tanks,
- Storage tank product size ranges from 10 liters to more than 11,500 li
- Tanks are used in a variety of gas transportation, vehicle or stationary applications,
- More than 400,000 tanks have been delivered for light, medium or heavy-duty vehicles.

HEXAGON

Hexagon will utilize existing laboratory facilities to evaluate fibers with short beam shear specimens and burst testing using a Standard Test and Evaluation Bottle (STEB) that is well characterized at 250 bar and/or 700 bar operating pressure.

Dylan Winter

Prescott Composites Utilizes Low-Cost Materials to make Low-Cost Intermediate Products and Light-Weight (L-CW) Composite Products.

To achieve Prescott Composites' L-CW Composite Products, Prescott Composites will utilize:

- ORNL's LCCF Technologies to develop Light-Weight Composites
- ORNL's Additive Manufacturing Technologies to prototype L-CW Composites and Proprietary Internal Processes for Prototyping and Specific Application level testing, leading to
- High-Rate Production utilizing Prescott's Proprietary Low-Cost Processes.

PRESCOTT COMPOSITES

Not only will these L-CW Composites weigh less, they will offer higher application performance capabilities at more competitive pricing compared to metal counterparts.

Jay Batten, CTO

Team Members/Responsibilities

- ORNL – Dr.-Eng. Felix Paulauskas as Principal Investigator leads melt spinning equipment/process development, conversion process development, and scaleup of precursor production at ORNL and conversion at CFTF in Phase II as well as characterization of fiber properties and economic analyses in both Phases. Bob Norris focuses on technical coordination.

- CCS Corporation (IACMI) – Erin Brophy - Program Management of the contract and all contracting requirements, facilitating project communications and equipment acquisitions

- Virginia Tech, Dr. Robert B. Moore, Department of Chemistry – Lead and execution of precursor and purge material formulations development and optimization

- JR Automation – Jeff Franklin- detailed design/fabrication of extruders along with integrated polymer production and solvent extraction systems for development and scaleup in Phases I and II.

- High Energy Sales, LLC – former BASF employee, Mark Cauthen, will consult and provide design assistance on unique equipment and process approaches found successful by BASF.

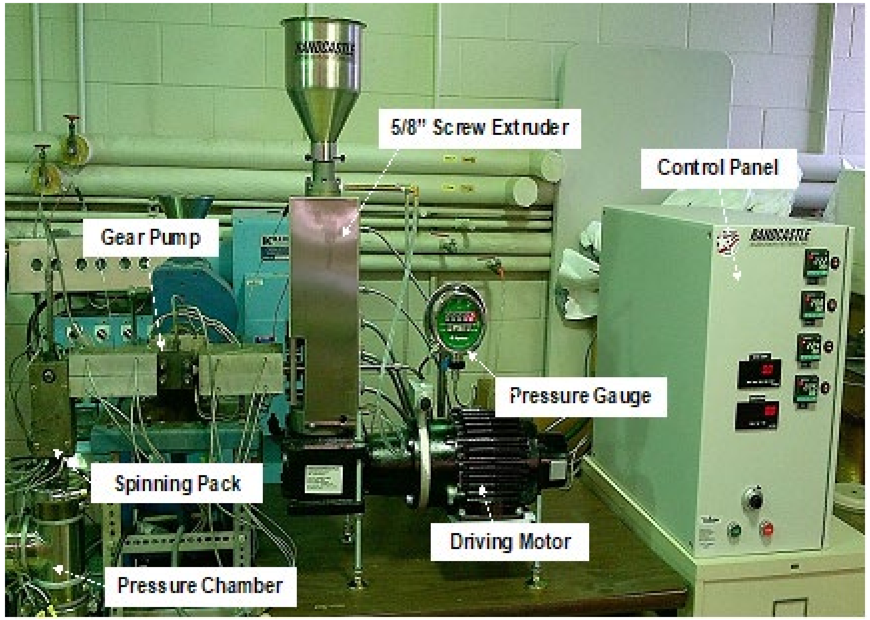
- Hexagon R&D – Dylan Winter consults on design and manufacturing requirements for high pressure tank construction based on world leadership position in Phase 1, makes and tests tanks In Phase II

- Prescott Composites – Jay Batten – Prescott Composites leads the team’s evaluation for Commercial Feasibility and is ensuring the utilization of high-capacity low-cost fiber in support of this and other composite market opportunities.

Key Challenges in Pathway Forward

Although earlier ORNL/VT work demonstrated significant progress with enhancing “science” background with chemistry advances and demonstrating the equipment characteristics needing in going forward, significant engineering improvements are necessary:

- Optimally plasticized formulations
- Improved purge materials
- Better handling formats (pellets?)of the above
- Enhanced pressurization of spinning and controlled solvent removal
- Superior injection techniques



These activities still require significant design and process innovation!!!

Proposed Future Work

- Phase 1
  - New pressurized extruder, quench system, and transition interfaces from pressurized extraction to open drawing system designed and built
  - Enhanced formulations for spinning dope and compatible purge materials created and tweaked in spinning trials with new equipment
  - Conversion recipes developed and optimized
  - ***Properties matching T700 achieved/cost analyses demonstrated for:***

Phase1/Phase 2 Down-selection

- Phase 2
  - Spinning equipment redesigned and built along with precursor production and conversion processes scaled for tank demonstrations
  - Tanks built and tested meeting DOE requirements
  - Alternative uses identified and assessed for materials at end of life

"Any proposed future work is subject to change based on funding levels."

Proposed Work Plan for Phase 1 and Phase 2

Tasks and Supporting Activities	Phase 1								Phase 2											
	Year 1				Year 2				Year 3				Year 4				Year 5			
	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
T1: Precursor and Purge Formulations																				
T2: Spinning of Modified Precursor																				
T3: Conventional Conversion of Melt-Spun Precursor																				
T4: Techno-Economic Modeling and Commercialization of Carbon Fiber Production																				
T5: Scale-up of Precursor Production																				
T6: Assessment of Potential Impact of Advanced Conversion Technologies																				
T7: Assessment and implementation of Post Treatments for Demonstration																				
T8: Scale up of Fiber Conversion and Production of CF at CFTF for Composite Tank Trials																				
T9: Manufacturing and Testing of High-Pressure Tanks																				
T10: Assessment of End-of-Life Recycling Approaches for Tank Material																				
T11: Final report issued to sponsor																				
Go/No-Go Decision								G												
Milestones	M1.1.1	M2.1.1	M2.1.2	M3.2.1	M3.2.2	M3.2.3	M3.2.4	M3.2.5	M5.1.1	M5.1.2	M5.1.3	M5.2.1	M5.2.2	M6.4.1	M7.2.1	M8.1.1	M8.3.1	M9.1.1	M9.2.1	M10.1.1 M11.0.1
Monthly teleconferences	X X X	X X X	X X X	X X X	X X X	X X X	X X X	X X X	X X X	X X X	X X X	X X X	X X X	X X X	X X X	X X X	X X X	X X X	X X X	X X X
Quarterly reports	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X

"Any proposed future work is subject to change based on funding levels."

Summary and Conclusions

- Melt spinning of PAN precursor offers potential cost savings largely via less solvent utilized overall and less capital and operating costs.
- Earlier work at BASF established manufacturing processes with ES&H issues; ORNL team leveraging/building on this initial pathway
- Key equipment and formulation advancements are needed to improve plasticization formulations, handling in spinning, and extraction
- Team responsibilities restructured specifically to address those needs
- Hexagon brings tank manufacturing perspective and Prescott is driving carbon fiber manufacturing business plans

Technology Transfer Activities

Overall partner cost share amounts to over 28% of the total $12.5M budget, including the following key commitments:

- Partner *Prescott Composites plans to commercialize Carbon Fiber Composites utilizing this* economically advantaged CF with performance competitive with T700
- *Prescott has already arranged licensing with ORNL for related carbon fiber technology.*
- *Prescott has pledged $2M in cash contributions along with significant additional in-kind contributions to accelerate this effort*

Summary and Conclusions

- Melt spinning of PAN precursor offers potential cost savings largely via less solvent utilized overall and less capital and operating costs associated with solvent recovery
- Earlier work at BASF established manufacturing processes with less desirable ES&H features that ORNL and partners have modified and demonstrated as pathway towards compressed tankage requirements.
- Key equipment engineering and formulation advancements are still necessary to improve plasticization formulations, handling in spinning, and extraction
- Team responsibilities restructured specifically to address those needs
- Hexagon brings tank manufacturing perspective
- Prescott is driving carbon fiber composites commercialization plans

Thank you for
your attention.