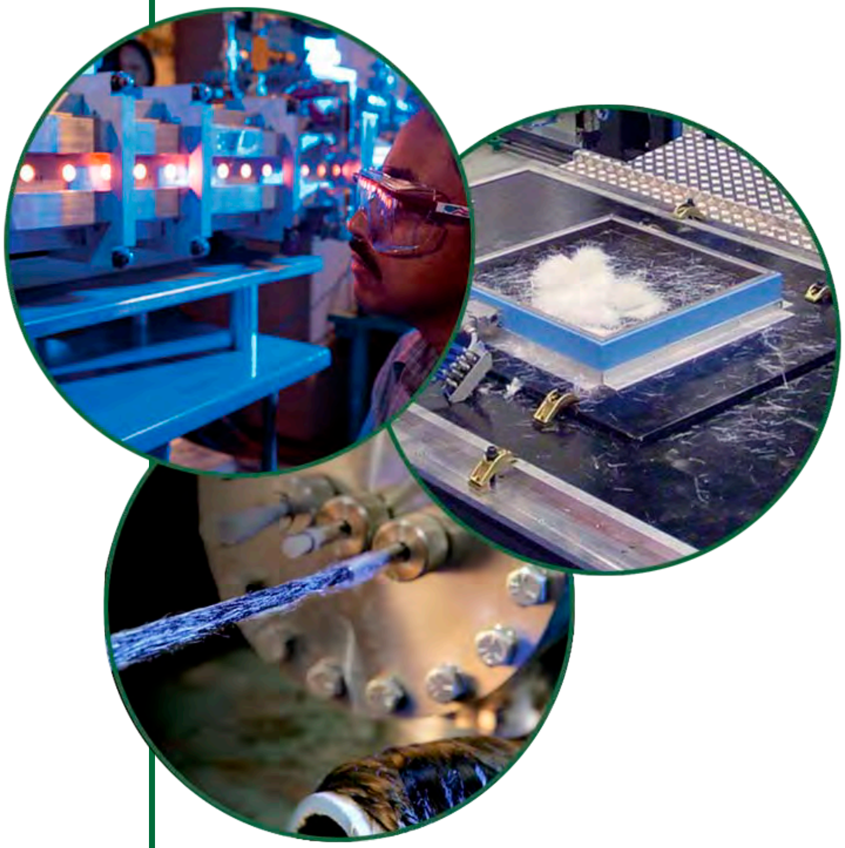
# Advanced Oxidation & Stabilization of PAN-Based Carbon Precursor Fibers

May 15, 2011



Dr.–Eng. Felix L. Paulauskas
MS&T Division

Oak Ridge National Laboratory
Phone: 865-576-3785
Email: paulauskasfl@ornl.gov

Project ID: LM006

U.S. DEPARTMENT OF ENERGY



OAK RIDGE NATIONAL LABORATORY
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# Project Overview

## Timeline

Phase **I**

- Start 2004
- End 2010

Phase **I** completed*

***anticipated shortly once strength is achieved**

Phase **II**

- Start 2011
- End 2015

## Budget

- FY 2011: $1,900K

## Barriers

- Barriers addressed
  - ➢ High cost of carbon fiber
  - ➢ Inadequate supply base for low cost carbon fibers
  - ➢ High volume manufacturing of carbon fiber

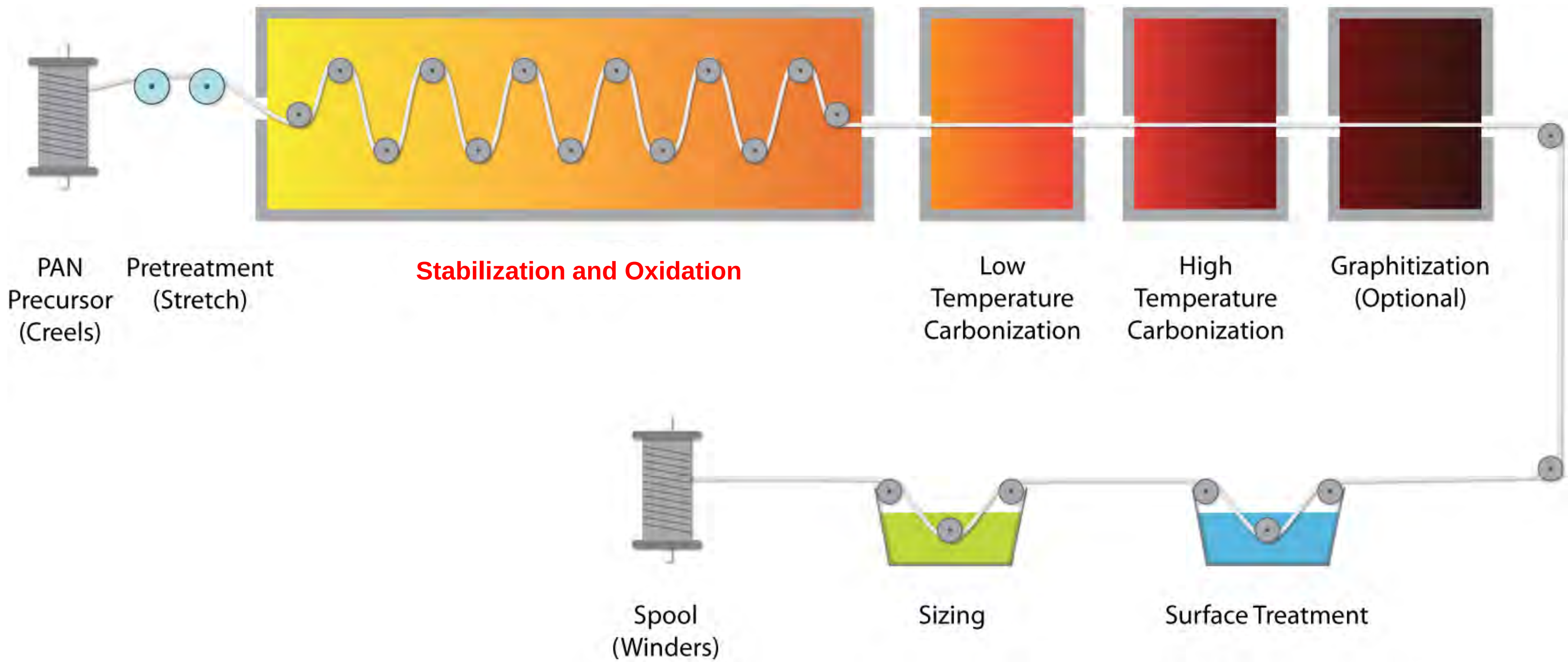
## Partners

- ORNL (Host site), carbon fiber expertise, characterization
- SRA, Int. (Experimental site), atmospheric plasma and hardware development

# Project Objectives

- **Phase I: Produce multiple tows of carbon fiber meeting minimum program specifications using oxidation residence time of 40 minutes or less.**
  - **Oxidative stabilization is the bottleneck in the production process often requiring 90 to 120 minutes. By developing a 2-3X faster oxidation process, higher throughput and significant cost reduction can be achieved. Completed**
- **Phase II: Demonstrate Phase I capability at pilot scale.**
  - **This will involve more tows and larger tows at less than 40 min residence time (increased throughput).**

# Conventional PAN Processing




**Typical processing sequence for PAN –based carbon fibers**

| Major Cost Elements | |
|---|---|
| Precursor | 43% |
| Oxidative stabilization | 18% |
| Carbonization | 13% |
| Graphitization | 15% |
| Other | 11% |

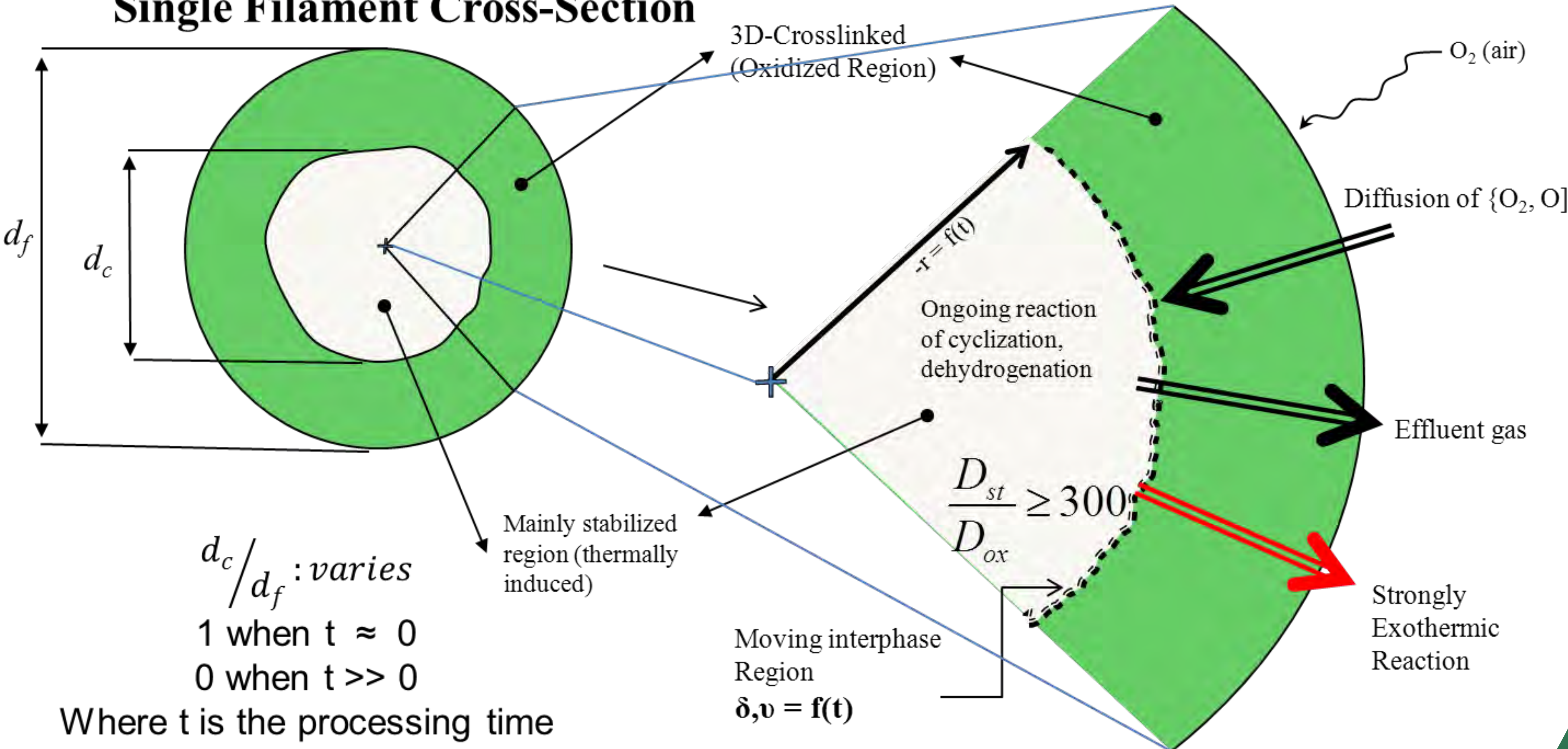
Automotive cost target is \$5 - \$7/lb

Tensile property requirements are 250 ksi, 25 Msi, 1% ultimate strain

ORNL is attempting major technological breakthroughs for major cost elements

# Approach: Reduce PAN-Oxidation Two Zones Morphology

## Single Filament Cross-Section




- Diffusion of oxygen to reactive sites is restricted, sequent reactions follow more slowly
- The limiting factor in the oxidative processing is the diffusion-controlled phase

# Approach: Advanced Oxidation

- Addresses diffusion-controlled stages of conventional oxidation
- Based on non-thermal, atmospheric pressure plasma processing
- Good physical and morphological properties; carbonization and mechanical property validation underway
- Residence time reduced by 2 - 3X (single tow)
- Fiber core better oxidized (digestion profiles)
- System design improvements and scale-up underway

**Plasma Discharge Device**

# Milestones

| Date | Milestone | Status |
| --- | --- | --- |
| June 2010 | Report experimental data indicating that plasma oxidized, conventionally carbonized PAN tow (≥ 3k) satisfy program mechanical property requirements. | Incomplete |
| September 2010 | Report updated evaluation of residence time and unit energy demand. | Complete |
| September 2010 | Document map of stoichiometry in MTR1 with ≥ 2 tows with ≥ 3k filaments per tow. | Complete |
| March 2011 | Demonstrate plasma oxidation of large tows (≥ 24K) achieving densities larger than 1.35 gr/cm$^3$. | Upcoming |
| September 2011 | Report experimental data in large tow of plasma oxidized and conventionally carbonized, achieving programmatic mechanical properties (250 KSI & 25 MSI, 1%). | Upcoming |

# Technical Accomplishments

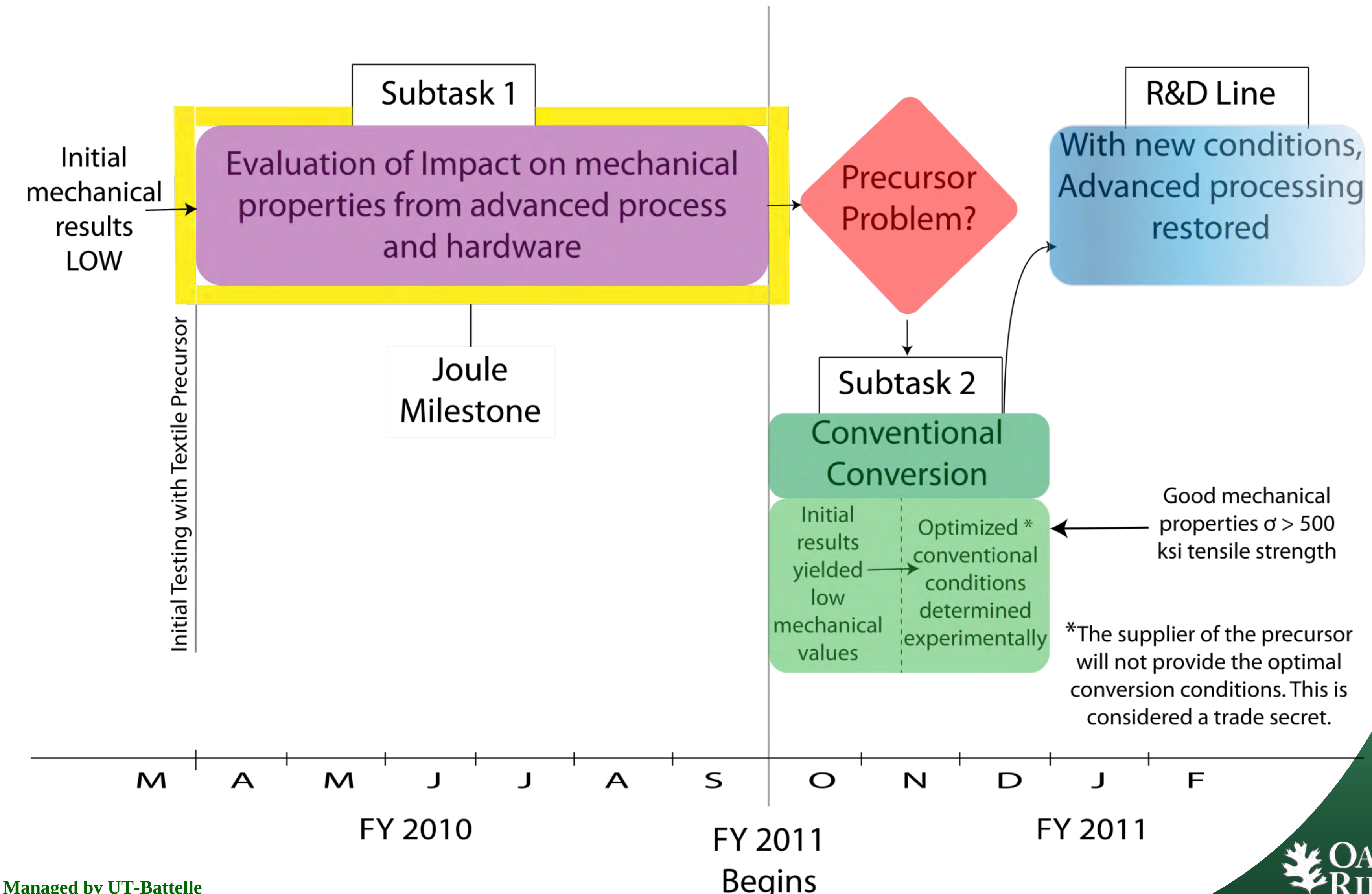
## JOULE Milestone Status

- **JOULE Milestone: The core focus recently for this project has been the achievement of the minimum program mechanical requirements:**
  - **Tensile Strength: 250 KSI**
  - **Modulus: 25 MSI**
  - **Strain: 1%**
- **The current status is that the Modulus requirement has been met, but the tensile strength and strain requirements have not.**
- **Significant work over many months isolated the cause and re-established baseline conditions for optimal fiber.**
- **The research team has been singularly focused on meeting the remaining requirements, and believes it will accomplish this shortly.**

# Technical Accomplishments

## Project Timeline: Subtask 1

MECHANICAL PROPERTY EVALUATION PROCESS FY 2010- FY 2011



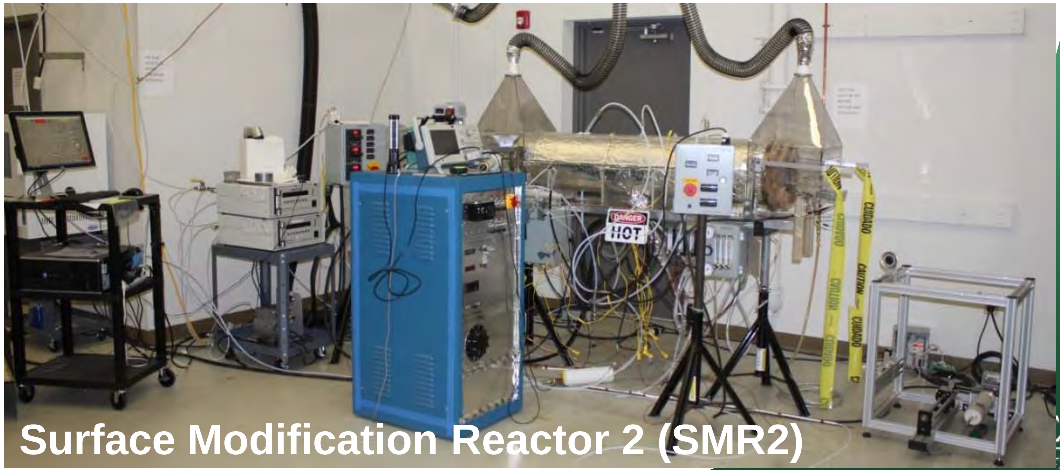
# Technical Accomplishments

## Subtask 1: Advanced Method/Apparatus Evaluation

## Apparatus Overview


- Processes up to 6 tows, 3000 filaments per tow.
- Core advanced technology demonstrator
- Vertical design
- Six heating zones
- Pre and Post treatment temperature control
- Fully automated via LabVIEW

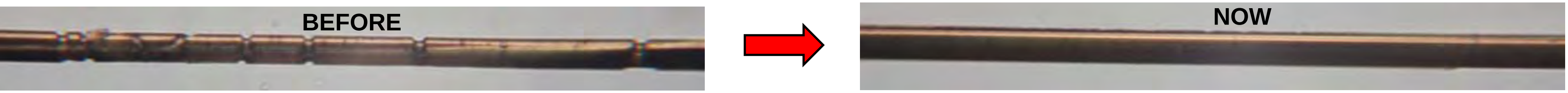
- Dual-use for surface treatment and oxidation
- Two temperature zones
- Large cross-sectional area for internal modifications
- Demonstrator for new surface discharge method
- LabVIEW automated



# Technical Accomplishments

## Introduction
## Investigation Areas and Issues

- **The type of damage being done to the fiber had never been seen before (based on observations from industry consultants).**




- **The mechanical properties of the plasma oxidized fiber yielded very good properties in density as well as mechanical and morphological properties. Once carbonized, the mechanical properties were inadequate; modulus was achieved, tensile strength not.**

- **An enhanced plasma application technique utilizing surface discharges significantly improved the fiber quality vs. density, but was not a solution to the damage problem.**

***Two side issues (reactor/process troubleshooting and precursor conversion recipes) needed to be resolved in order to continue with the main thrust of the R&D work.***

# Technical Accomplishments

## Subtask 1: Advanced Method/Apparatus Evaluation
## Investigation Areas

- **Reactive species concentration: Extensive work was done, looking at the relationship between damage and reactive species concentration and flow from the plasma generator. Parametric tests were performed**
- **Gas contamination, Water/humidity contamination, Inadequate temperature regulation, Flow control/configuration**
- **Overall process rate: Residence time and line speeds were varied to examine the effect this has on damage.**
- **Plasma geometry/position: Explored multiple internal flow configurations and reactive species enhancements.**

**This investigation did not turn up conclusive cause of the damage responsible for poor mechanical properties of carbonized fiber.**

**Due to this fact, attention turned to the precursor itself as a possible cause of the damage.**

# Technical Accomplishments

## Subtask 1: Advanced Method/Apparatus Evaluation

## Technical Results

| Sample | Sample No. | Delivered | Oxidized | | | Carbonized | | |
|---|---|---|---|---|---|---|---|---|
| | | | Peak Stress (ksi) | Modulus (Msi) | Strain @ Break (%) | Peak Stress (ksi) | Modulus (Msi) | Strain @ Break (%) |
| | | | Conventionally Oxidized | | | | | |
| Aerospace | REF 1 | ORNL | 43.7 | 1.4 | 13.0 | 427.2 | 25.9 | 1.58 |
| Commodity | REF 2 | ORNL | 37.8 | 1.2 | 20.4 | 543.9 | 30.7 | 1.60 |
| Textile | REF 3 | ORNL | 38.8 | 0.5 | 20.6 | 381.9 | 26.2 | 1.33 |
| | | | Plasma Oxidized | | | | | |
| Mutiple Tow Reactor 1 (MTR1) | | | | | | | | |
| SR349 | 2 | 6/18/2010 | 27.5 | 0.8 | 3.2 | 174.1 | 27.8 | 0.61 |
| SR370 | 16 | 7/8/2010 | N/M | N/M | N/M | 181.6 | 22.6 | 0.74 |
| SR400 | 39 | 8/17/2010 | 47.4 | 0.8 | 21.5 | N/M | N/M | N/M |
| SR401 | 40 | 8/17/2010 | 46.2 | 0.7 | 19.7 | N/M | N/M | N/M |
| SR408-5.5 | 47 | 8/17/2010 | 35.7 | 0.8 | 12.4 | 186 | 23.2 | 0.75 |
| SR409 | 49 | 8/17/2010 | 50.3 | 0.8 | 17.0 | N/M | N/M | N/M |
| SR415 | 55 | 8/23/2010 | 27.9 | 0.6 | 8.3 | 142.5 | 24.5 | 0.59 |
| Surface Modification Reactor 2 (SMR2) | | | | | | | | |
| SR415 SMR2 | 56 | 10/25/2010 | 35.4 | 0.6 | 13.9 | 176.8 | 23.9 | 0.74 |
| SR419 SMR2 | 59 | 10/25/2010 | 37.7 | 1.0 | 13.9 | 177.8 | 20.9 | 0.83 |

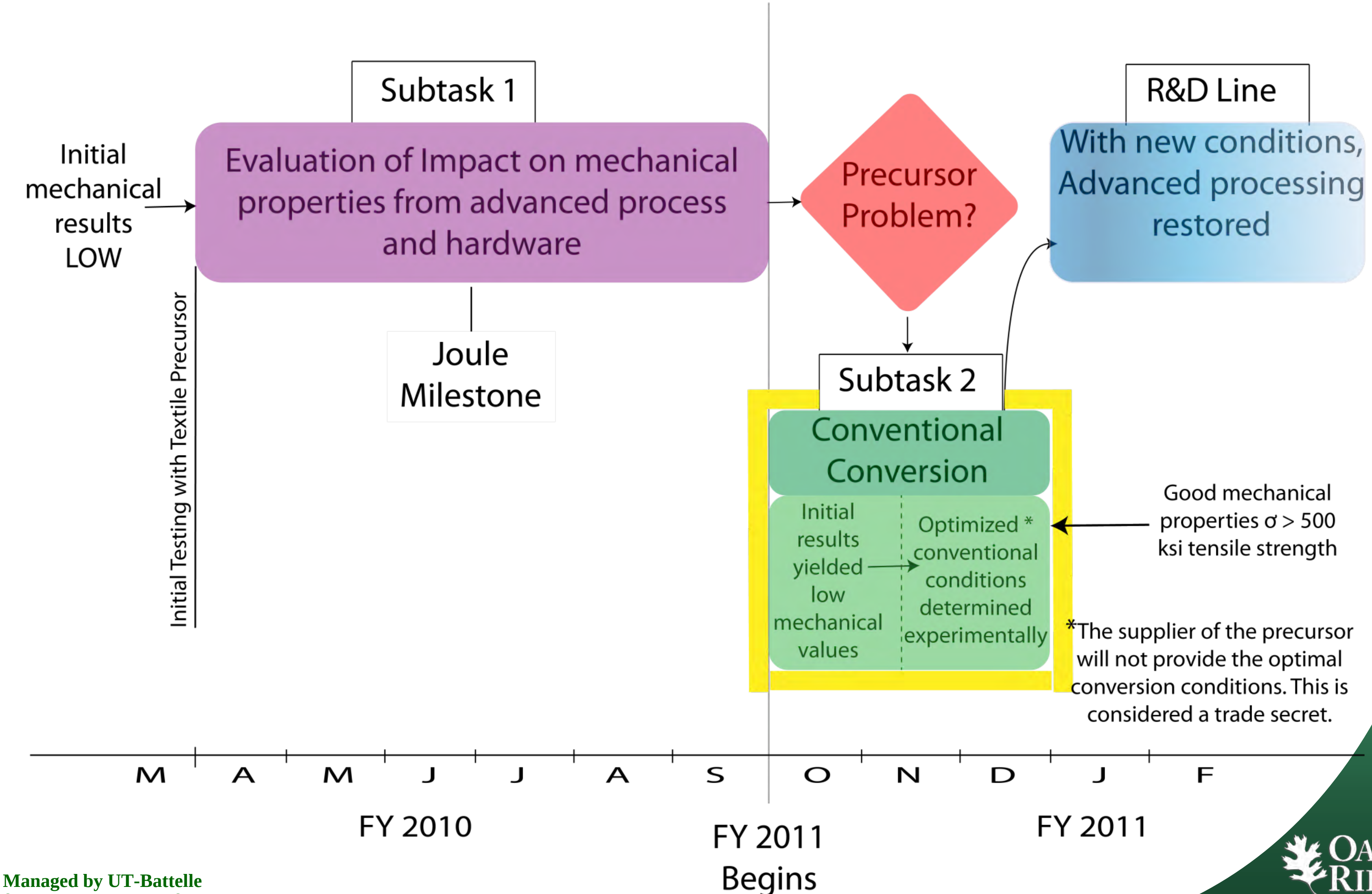
Program Minimum: Peak Stress, 250 ksi; Modulus, 25 Msi, Strain, 1 %

**Selected results from Step 1 work. Results are close to program minimums, but still needs improvement.**

# Technical Accomplishments

## Project Timeline: Subtask 2

MECHANICAL PROPERTY EVALUATION PROCESS FY 2010- FY 2011



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# Technical Accomplishments

## Subtask 2: Conventional Conversion/Analysis of Precursor Investigation Areas

- **The ORNL precursor evaluation line was utilized for conventional conversion.**
- **Initial conventional testing showed poor mechanical properties.**
- **Contamination of the precursor stock was considered, but ruled out.**
- **The optimal process parameters were not available from the manufacturer.**
- **The optimal process parameters were determined experimentally.**

**New baseline conditions were established that produced mechanical properties greatly exceeding the minimum program requirements.**

# Technical Accomplishments

## Subtask 2: Conventional Conversion/Analysis of Precursor
## Technical Results

### Initial Conventional Conversion
### Aerospace 3k processed at ORNL. Four Methods of conversion.

| | Oxidized | | | | Carbonized | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Sample | Density (g/cc) | Peak Stress (ksi) | Modulus (Msi) | Strain @ Break (%) | Density (g/cc) | Dates | Peak Stress (ksi) | Modulus (Msi) | Strain @ Break (%) |
| Baseline PL | 1.4089 | 42.7 | 1.0 | 14.69 | | 9/2010 | 217.9 | 21.6 | 1.00 |
| | | | | | | | 234.6 | 22.6 | 1.00 |
| | | | | | | | 244.0 | 22.2 | 1.00 |
| Despatch | 1.3796 | 45.0 | 1.0 | 17.6 | 1.8413 | 9/2010 | 168.2 | 20.5 | 0.80 |
| | | | | | | | 195.8 | 20.0 | 0.90 |
| | | | | | | | 214.0 | 20.0 | 1.00 |
| PES 1 pass | 1.4014 | 44.1 | 0.9 | 16.6 | 1.8428 | 9/2010 | 140.2 | 19.0 | 0.70 |
| PES 4 pass | 1.4133 | 46.5 | 1.0 | 15.7 | 1.8391 | 10/2010 | 153.0 | 20.1 | 0.74 |

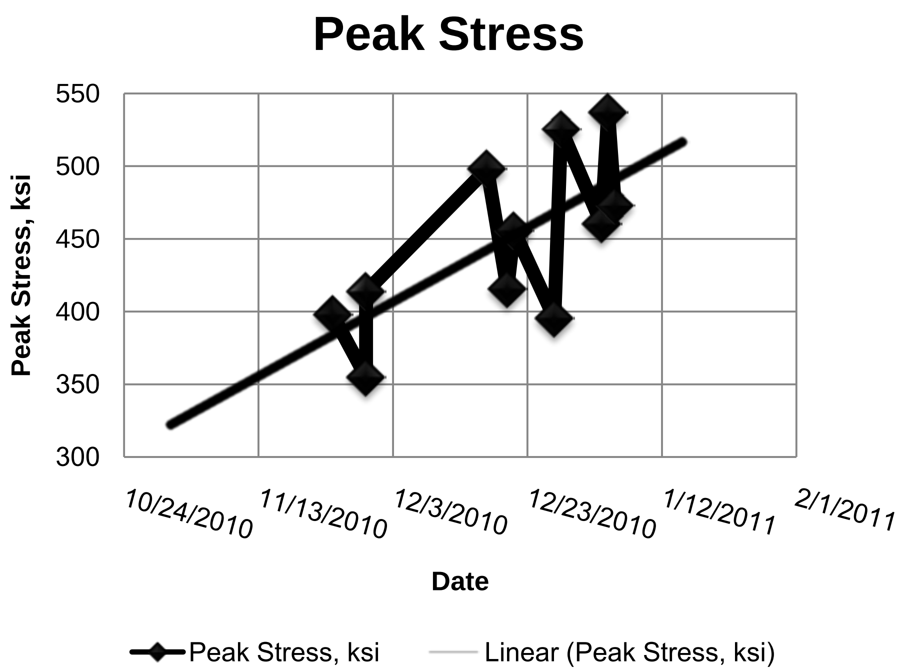
Program Minimum: Peak Stress, 250 KSI; Modulus, 25 MSI, Strain, 1 %

***In spite of the usage of aerospace grade precursor, the obtained mechanical values of the CF are unacceptable.***

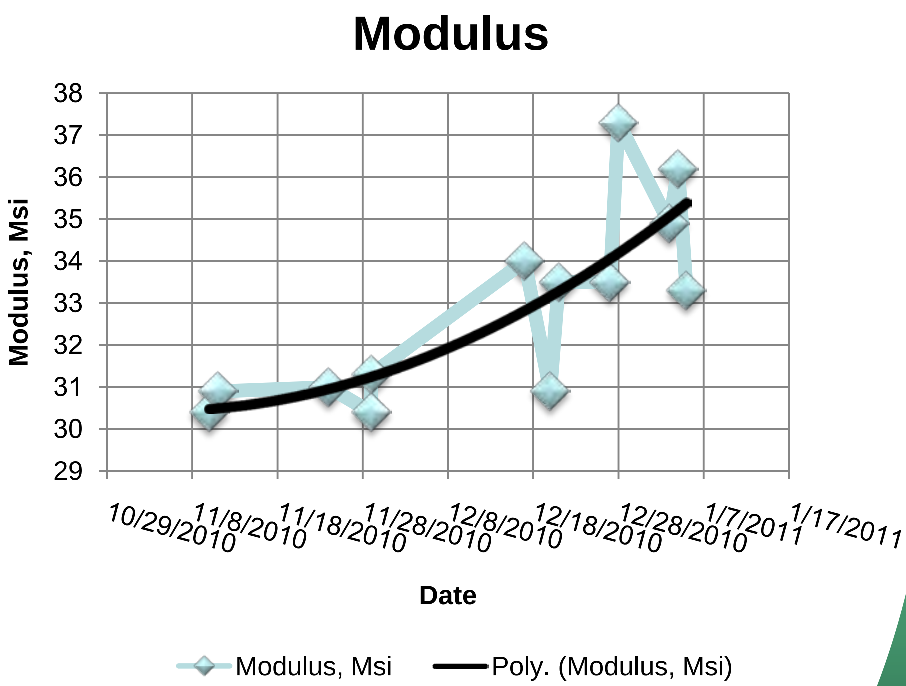
# Technical Accomplishments

## Subtask 2: Conventional Conversion/Analysis of Precursor Technical Results

### Final Evaluations of Conventional Conversion after optimization Aerospace 3k processed at ORNL.




**Program Minimum: 250 ksi (below scale)**



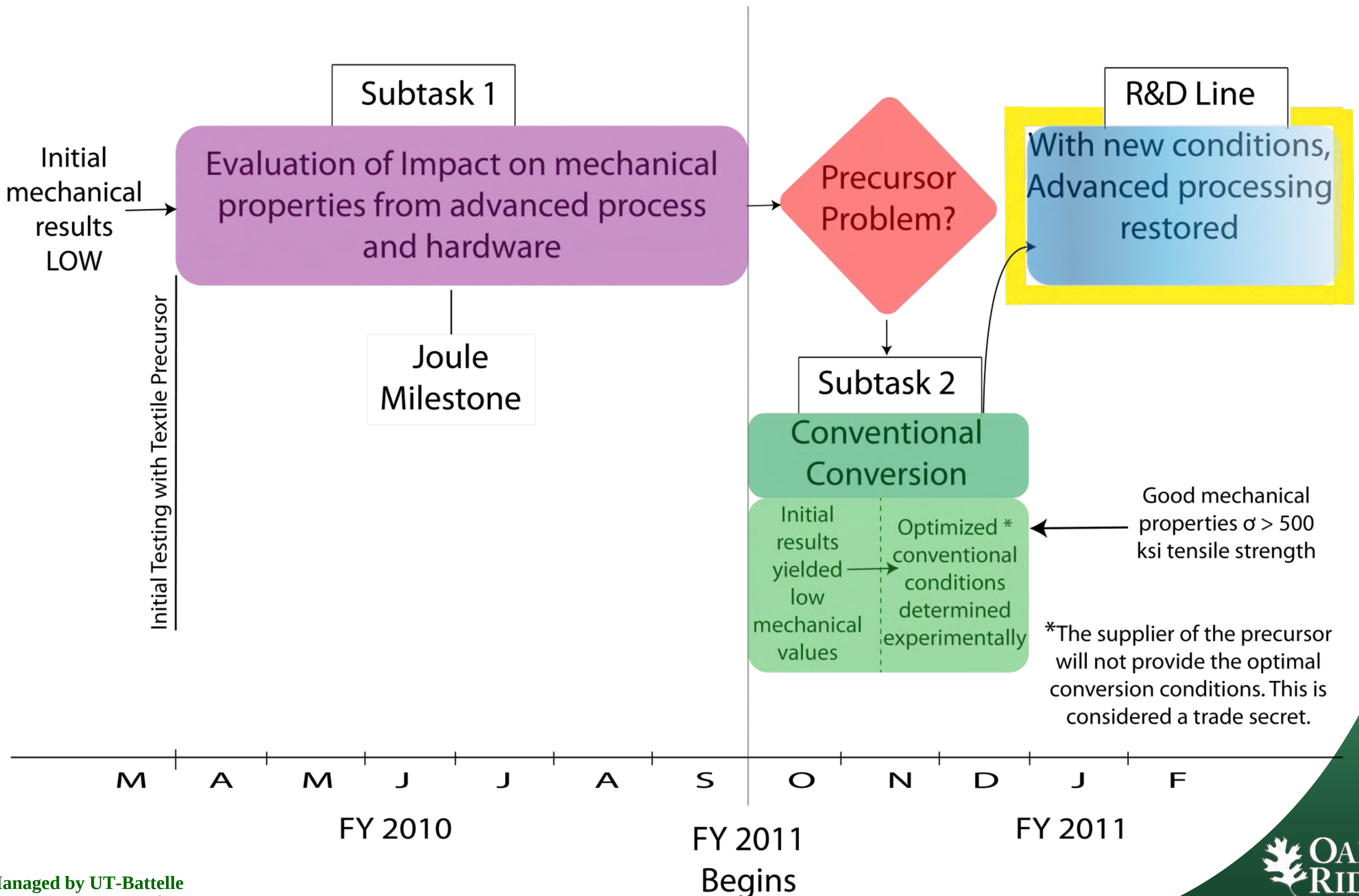

**Program Minimum: 25 Msi (below scale)**

***Mechanical values show a dramatic improvement over the previous table.***

# Technical Accomplishments

## Project Timeline: Back to R&D Line

MECHANICAL PROPERTY EVALUATION PROCESS FY 2010- FY 2011



# Technical Accomplishments

## Resumption of Main Advanced Method - Baseline Conditions

- **The initial phase in reestablishing baseline parameters in the advanced method was the replication of ORNL conventional testing in the MTR1, without plasma assistance, to generate a set of control results to ensure accurate comparisons. This phase has been completed.**
- **The next phase is the activation of the advanced method with the new baseline parameters established from above. This phase is currently being implemented.**

**It is anticipated that the minimum program mechanical requirements will be reached utilizing the plasma-based method will be achieved shortly.**

# Future Work

- **Rest of FY11**
  - **Refine oxidation process to satisfy program requirements for carbonized tow properties**
  - **Begin scale-up work and transition to Phase II (anticipated mid-year)**
  - **Design, Construct, and Operate MTR2 (pre-pilot-line oxidation oven)**
  - **Demonstrate rapid plasma oxidation of large tow, multiple tows (24K to 80K/3)**

- **FY12**
  - **Complete stoichiometric analysis of MTR2 process.**
  - **Complete scaling effects impact on process**
  - **Obtain scaled energy consumption data**
  - **Begin design and construction of MTR3 (pilot-line full scale oxidation oven)**

| Date | Milestone |
|---|---|
| June 2010 (1) | Report experimental data indicating that plasma oxidized, conventionally carbonized PAN tow (≥ 3k) satisfy program mechanical property requirements. |
| March 2011 (2) | Demonstrate plasma oxidation of large tows (≥ 24K) achieving densities bigger than 1.35 gr/cm3. |
| Sept 2011 (3) | Report experimental data in large tow of plasma oxidized and conventionally carbonized, achieving programmatic mechanical properties (250 KSI & 25 MSI, 1%). |

| Date | Milestone |
|---|---|
| Sep 2012 (4) | First runs of pre-industrial advance oxidation unit. This will be more advanced unit that the actual lab-multiple tow reactor. |

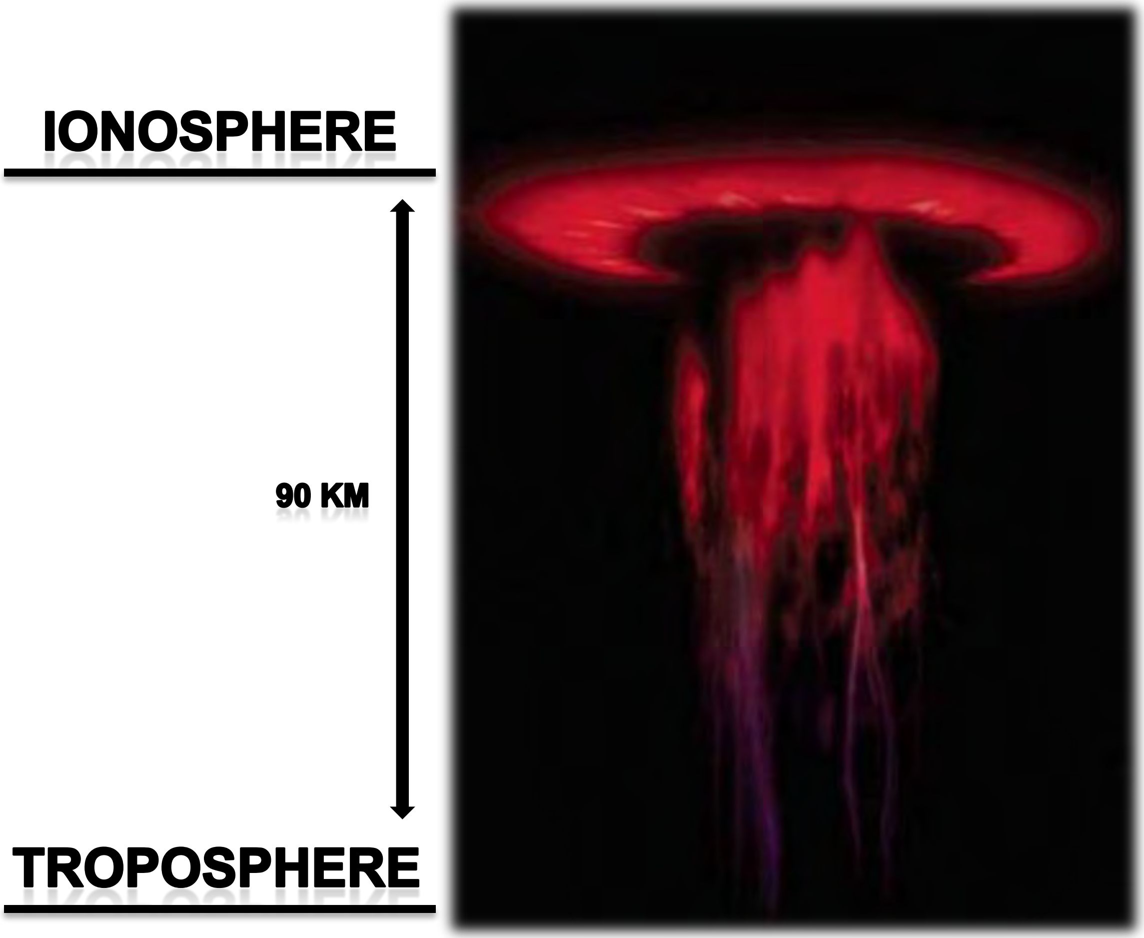
# Long Term Milestones/Deliverables

- Demonstrate program property requirements satisfied, with low variability, in processing multiple large tows.
- Demonstrate plasma oxidation of multiple tows of alternative precursor
- Demonstrate program property requirements satisfied, with low variability, in processing multiple large tows in plasma oxidation reactor module
- Optimize oxidation reactor module hardware and controls as required
- Deliver, install, and checkout first plasma oxidation reactor module.
- Review and update key technical and economic drivers for this technology specifically including residence time, projected equipment costs, and energy consumption per unit mass (go/no-go decision gate)
- Deliver equipment specification for a plasma oxidation module for an advanced technology/demonstration pilot line (principal project deliverable).
- Deliver, install, and commence operations of plasma oxidation module in the advanced technology pilot line (likely as part of an integrated technology demonstration follow-on project).

# Summary and Conclusions

- Residence time reduced by 2 - 3X to date with one 3k tow (in the Single Tow Reactor 1 – Tube Reactor)
- New surface-plasma processing method refined and improved.
- Materials compatibility testing to determine optimal construction materials of future furnaces is ongoing (not presented here).
- Stoichiometry analysis completed on current chemistry mechanisms.
- Unit energy analysis estimate completed (not presented here).
- Conventional baseline testing resulted in new basic optimal processing parameters. This parameters are currently being incorporated into the advanced method.
- This work directly supports petroleum displacement via improved fuel economy from vehicle weight reduction
- This work addresses the barrier of carbon fiber cost
- The approach is to develop a revolutionary new method for converting carbon fiber, which offers much higher potential for achieving significant cost reduction than evolutionary improvements to existing conversion technology
- Process and equipment scaling will constitute the majority of future work

# Thank you for your attention.




# Questions?



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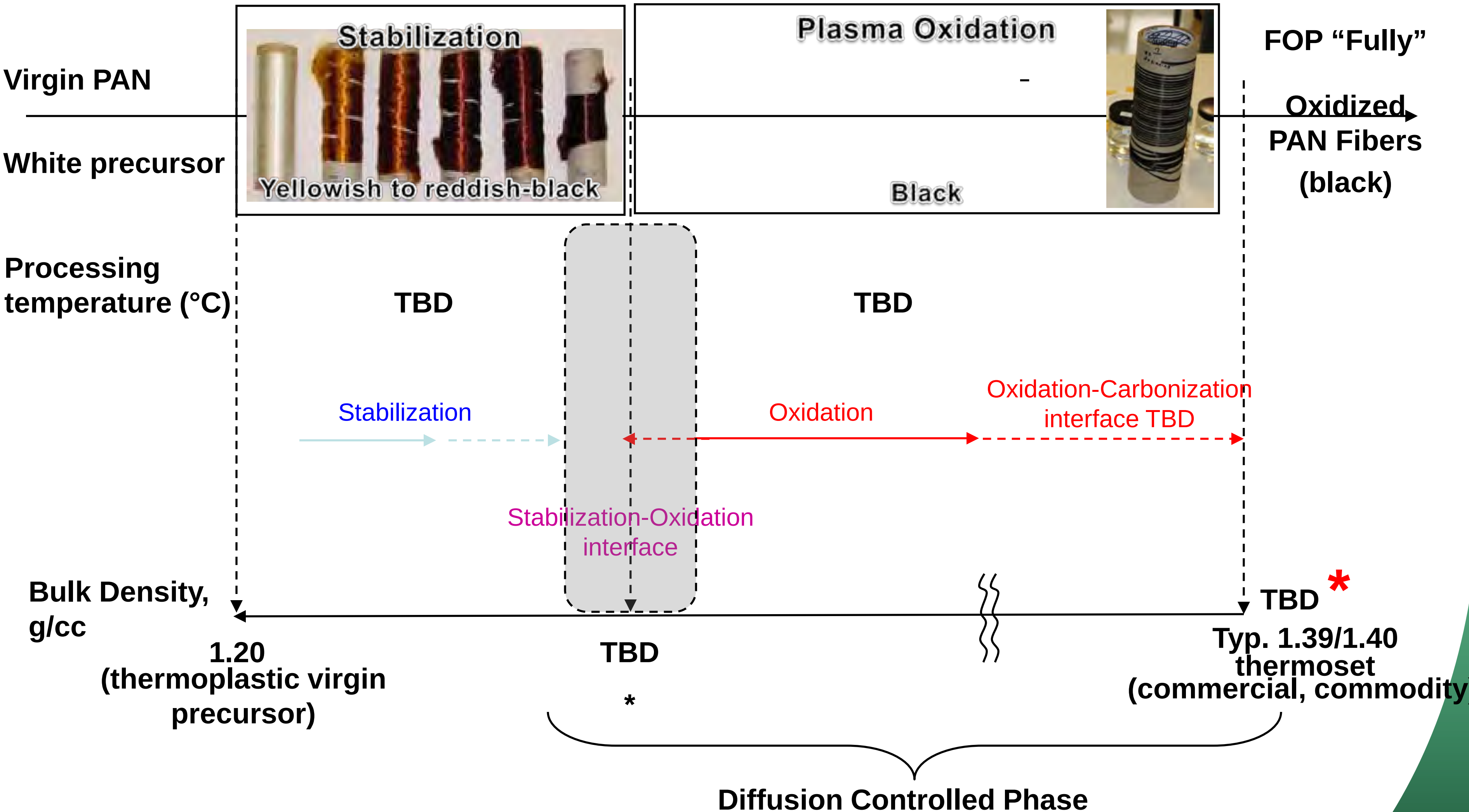
# Backup Materials

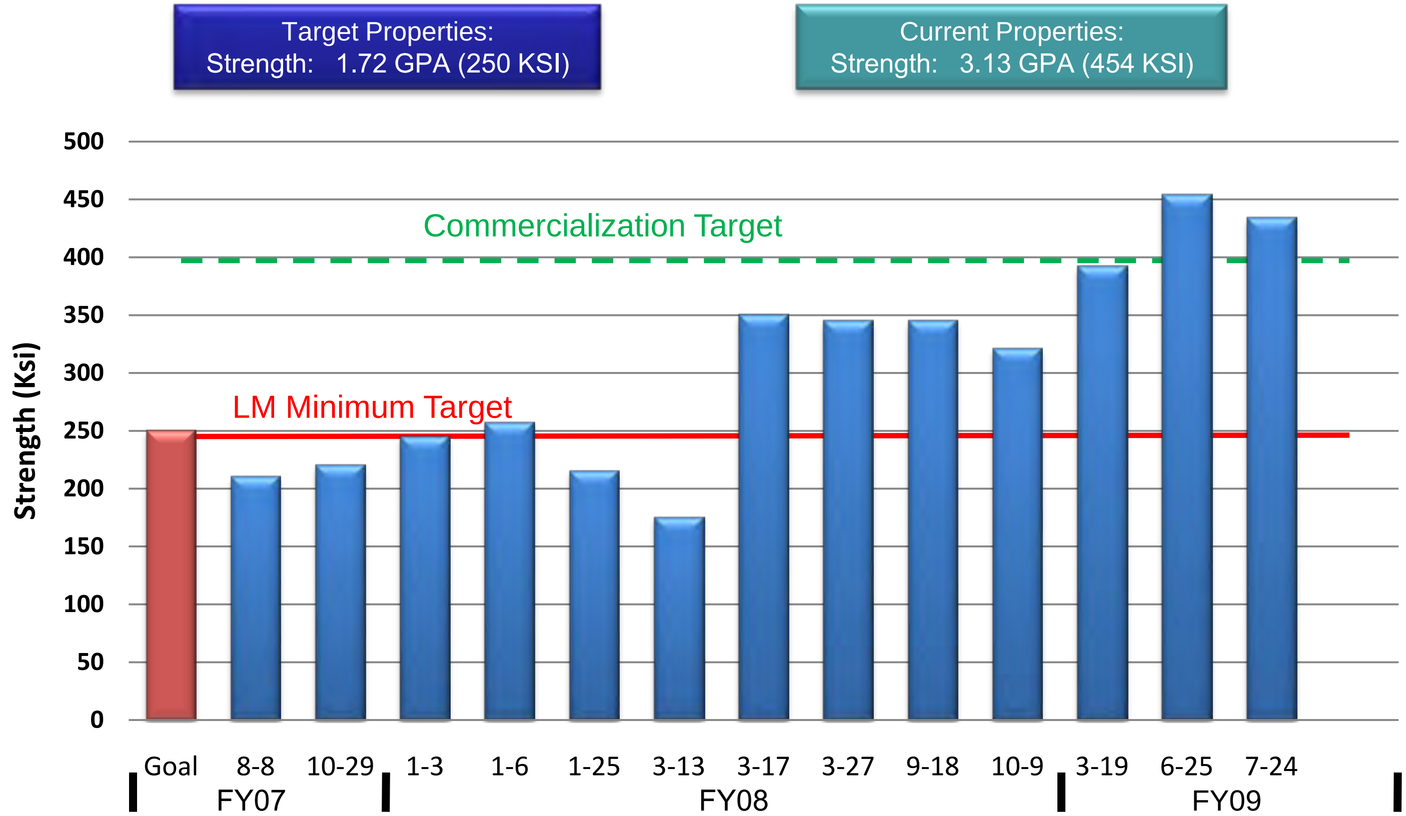
# Oxidation Interfaces



# Technical Accomplishments

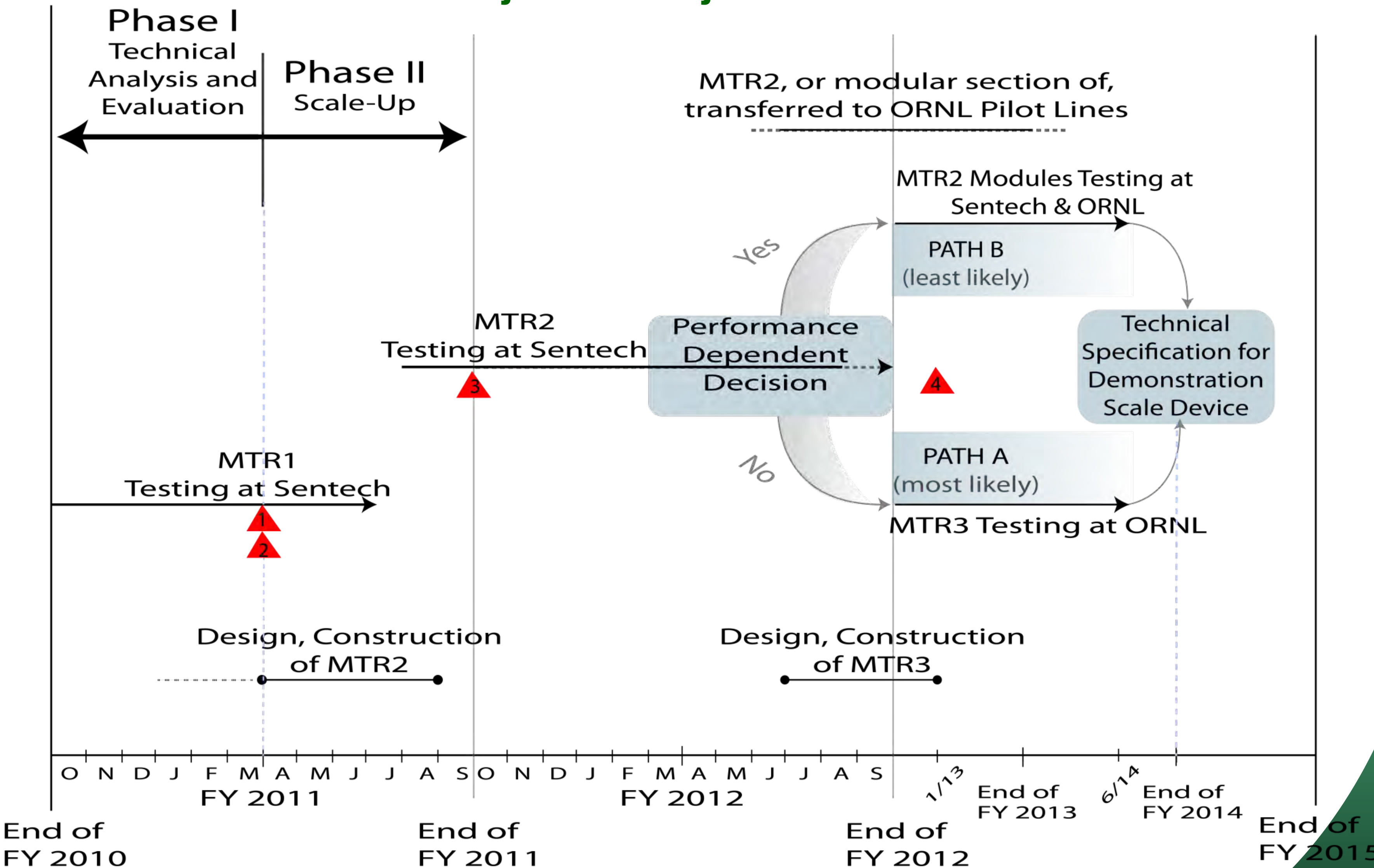
## Subtask 2: Conventional Conversion/Analysis of Precursor Investigation Areas

**As a reference, it took over two years to find the proper conversion conditions for the textile precursor. For the aerospace fiber, this time was reduced significantly (~3 months).**



# Future Work

## Projected Project Timeline




▲ **Denote Milestones (see next slide)**