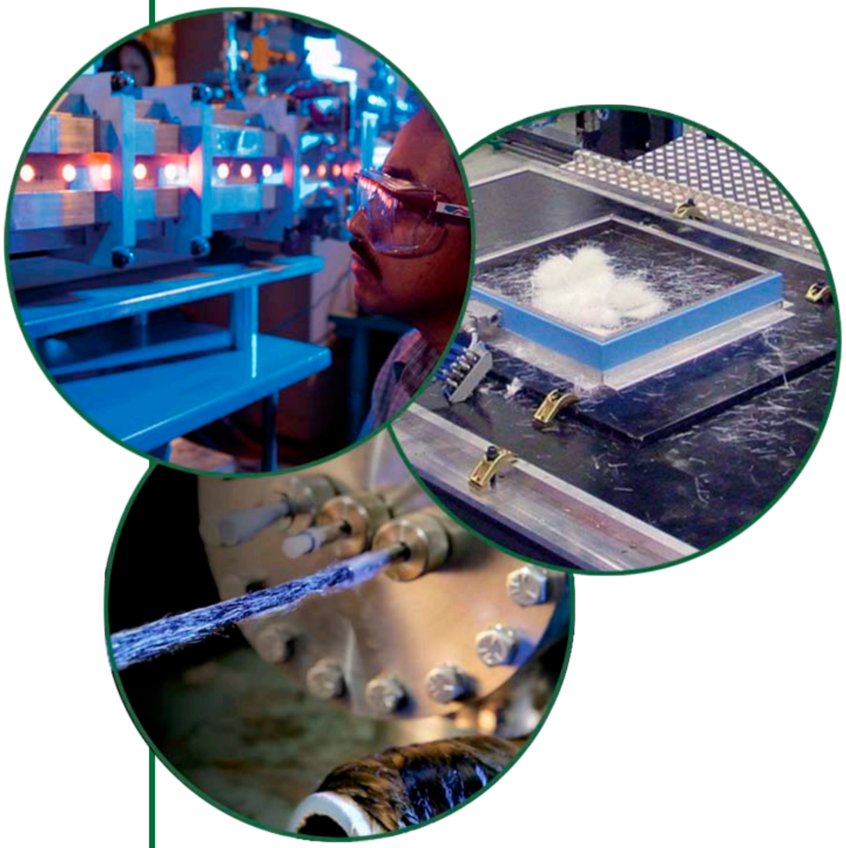
Advanced Oxidation & Stabilization of PAN-Based Carbon Precursor Fibers

9 June 2010



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Project ID: LM006

U.S. DEPARTMENT OF ENERGY

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Overview

Timeline

Phase **I**
- Start 2004
- End 2010

Phase **I** completion on 9/30/2010

Phase **II**
- Start 2010
- End 2015

Budget

- FY 2010 $1,150K

Barriers

- Barriers addressed
  A. High cost of carbon fiber
  B. Actual inadequate supply base for low cost carbon fibers (B)
  C. High volume manufacturing of carbon fiber

Partners

- ORNL (Host site), carbon fiber expertise
- Sentech Inc. (Experimental site), Atm. plasma and hardware development

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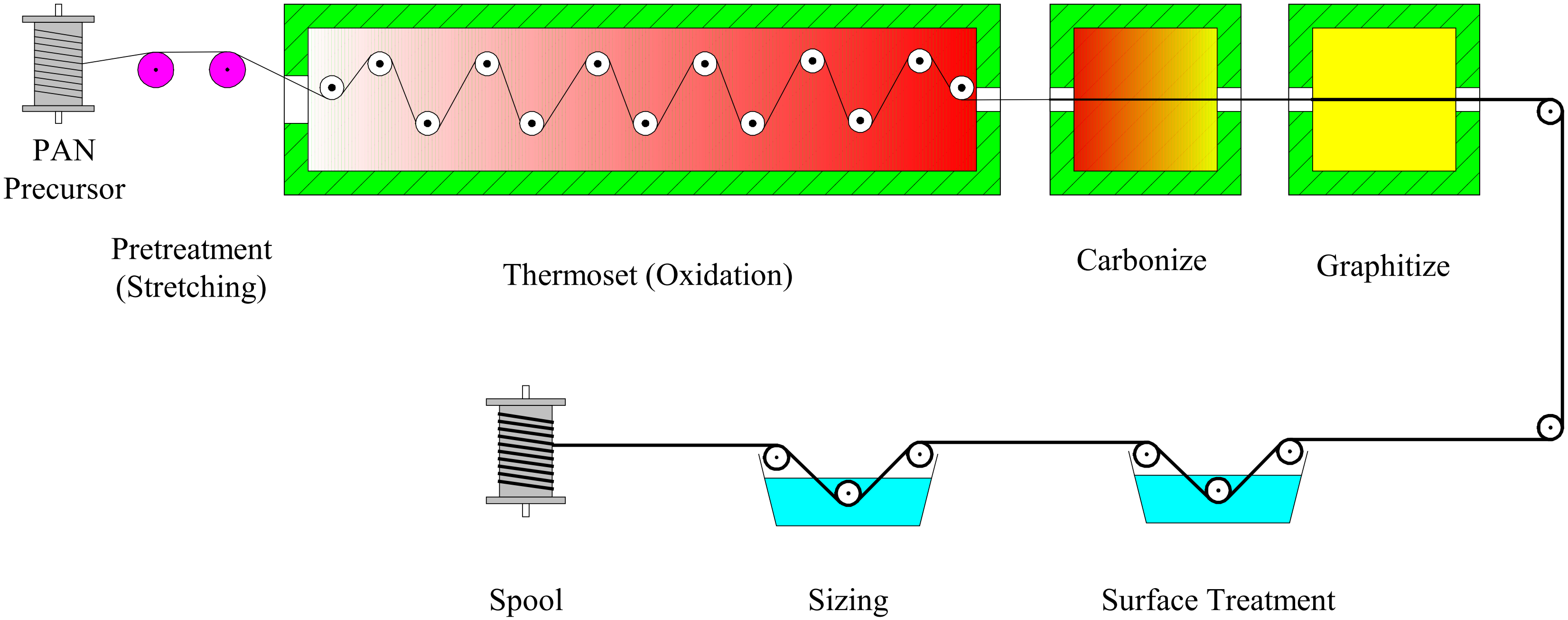
Objectives

- **Rapid stabilization and oxidation of PAN-based carbon fiber precursor**

- **Oxidative stabilization is the bottleneck in the production process often requiring 80 to 120 minutes. By developing a 2-3X faster oxidation of a precursor, higher throughput and significant cost reduction in the carbon fiber manufacturing can be achieved**

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

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Oxidation Interfaces

Virgin PAN

Stabilization

Plasma Oxidation

FOP "Fully"

White precursor

Yellowish to reddish-black

Black

Oxidized PAN Fibers (black)

Processing temperature (°C)

TBD

TBD

Stabilization

Stabilization-Oxidation interface TBD

Oxidation

Oxidation-Carbonization interface TBD

Bulk Density, g/cc

1.20 (virgin precursor)

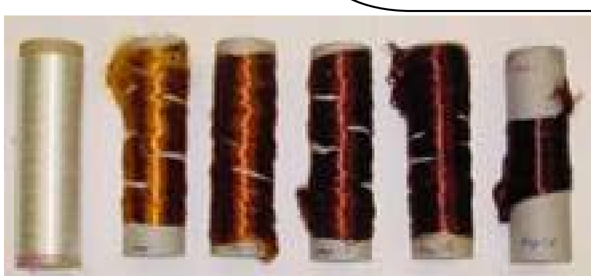
TBD

*

TBD *

Typ. 1.40/1.39 (commercial, commodity)

Diffusion Controlled Phase



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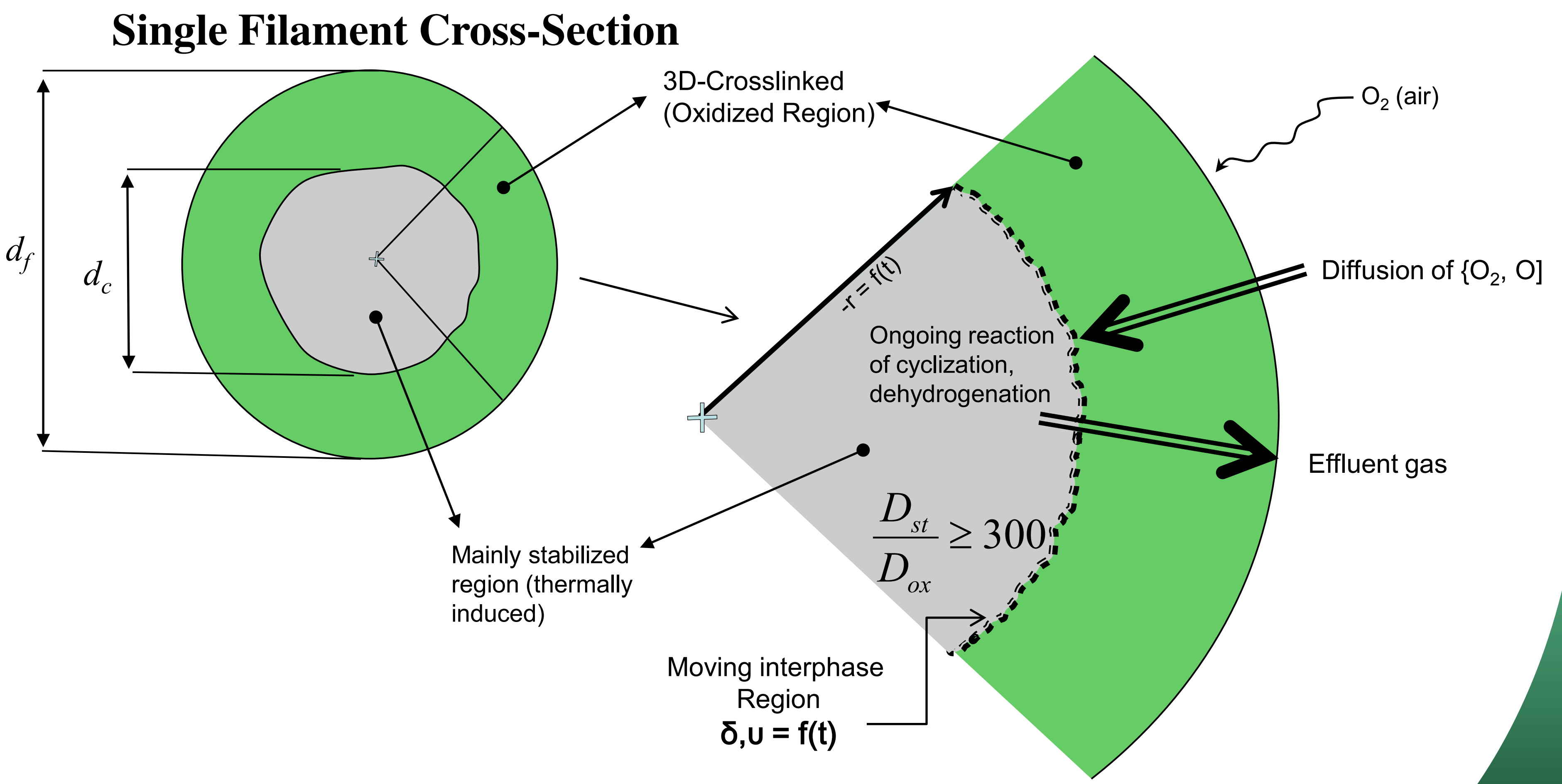
Approach: Reduce PAN-Oxidation Two Zones Morphology



- 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

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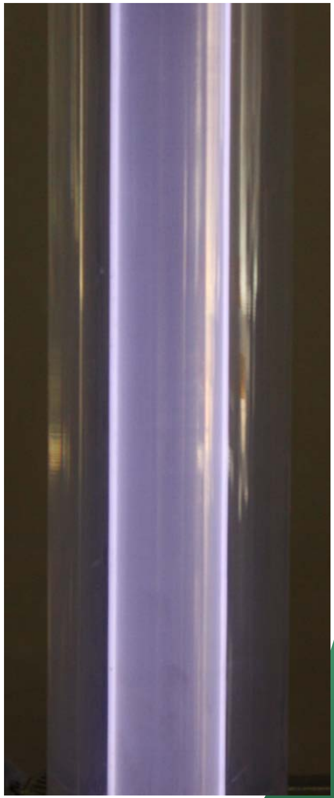
Approach: Advanced Oxidation

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



Plasma Discharge Device

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Milestones

Date	Milestone or Go/No-Go Decision
Dec-09	Analyze and report initial experimental results on materials compatibility
Mar-10	Report bulk density from initial experiments on advanced oxidation of textile PAN precursor. Density has to be >1.30g/cm^3
June 10	Report experimental data indicating that plasma oxidized, conventionally carbonized PAN tow (≥3k) satisfy program mechanical property requirements (Strength: 250Ksi and Modulus: 25 Msi)
Sep-10	Report updated evaluation of residence time and unit energy demand

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Technical Accomplishments

- Residence time reduced by $\geq$ 2 - 3X to date with 1 to 3 small tows (3k)
- Extensive testing of fiber properties, causes and effects, analysis led to improved fiber quality
- Comprehensive stoichiometry measurements and analysis completed to date; will lead to optimized oxidation
- Materials compatibility testing initial report completed; results will be used for construction of demonstration-scale reactor
- Began incorporating additional feed gases to further improve process results and process economics

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Technical Accomplishments

- Performed initial experiments with textile PAN. Results show that textile PAN can be successfully oxidized using the advanced oxidation process. Initial results showed density 1.32-1.33 g/cm^3

- Completed major design and process modifications to the Multiple Tow Reactor 1 (MTR1) resulting in more stable performance with enhanced safety, control, and data acquisition

- Construction started on the Materials Compatibility Test Stand (MCTS), which will allow long term exposure testing in the advanced oxidation

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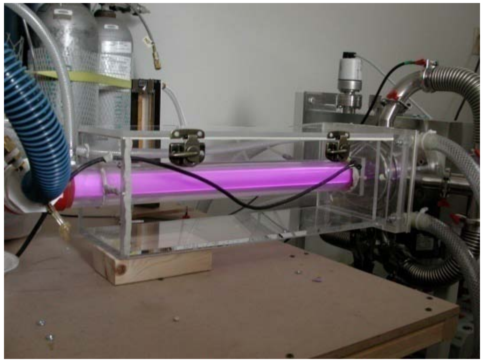
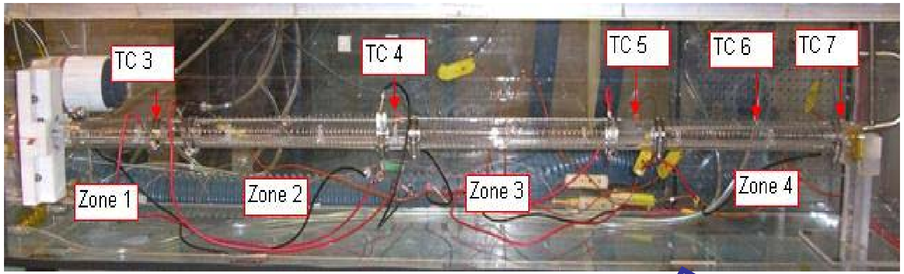
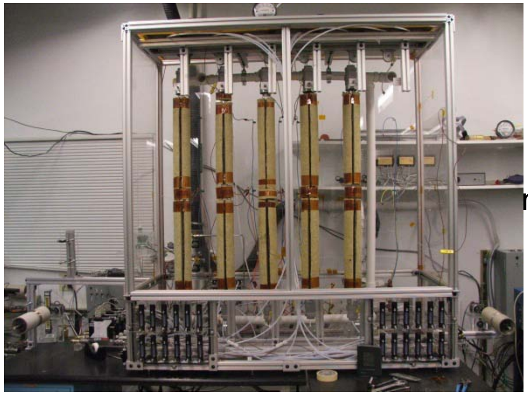
Reactor Development



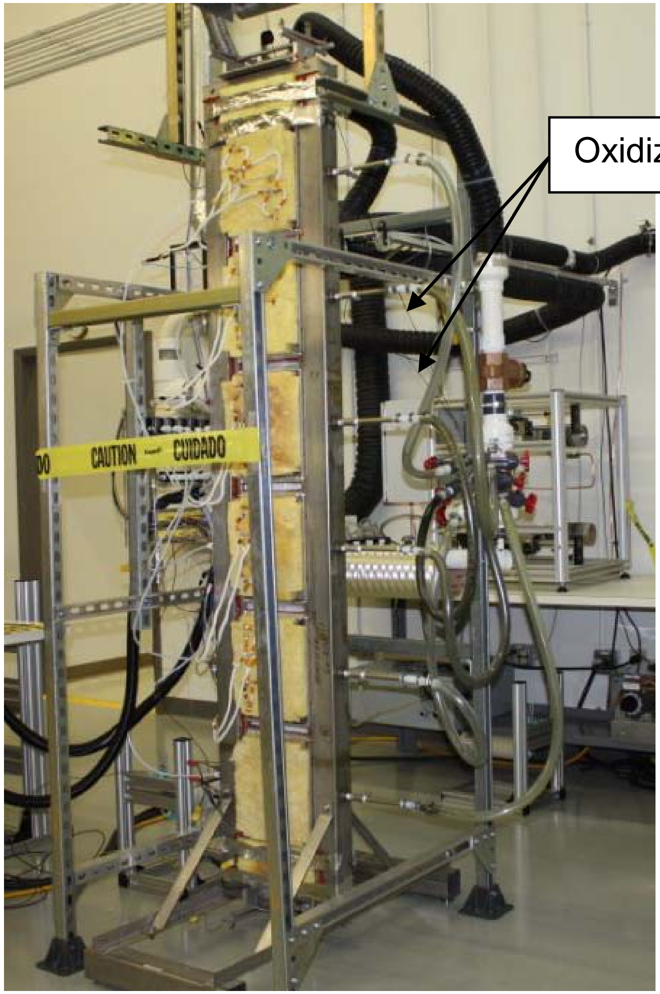
(thermal component added)



(longer reactor length, multiple injection points)



Single Tow Reactor 1 (STR1)



Multiple Tow Reactor 1 (MTR1)
Current state

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Technical Results

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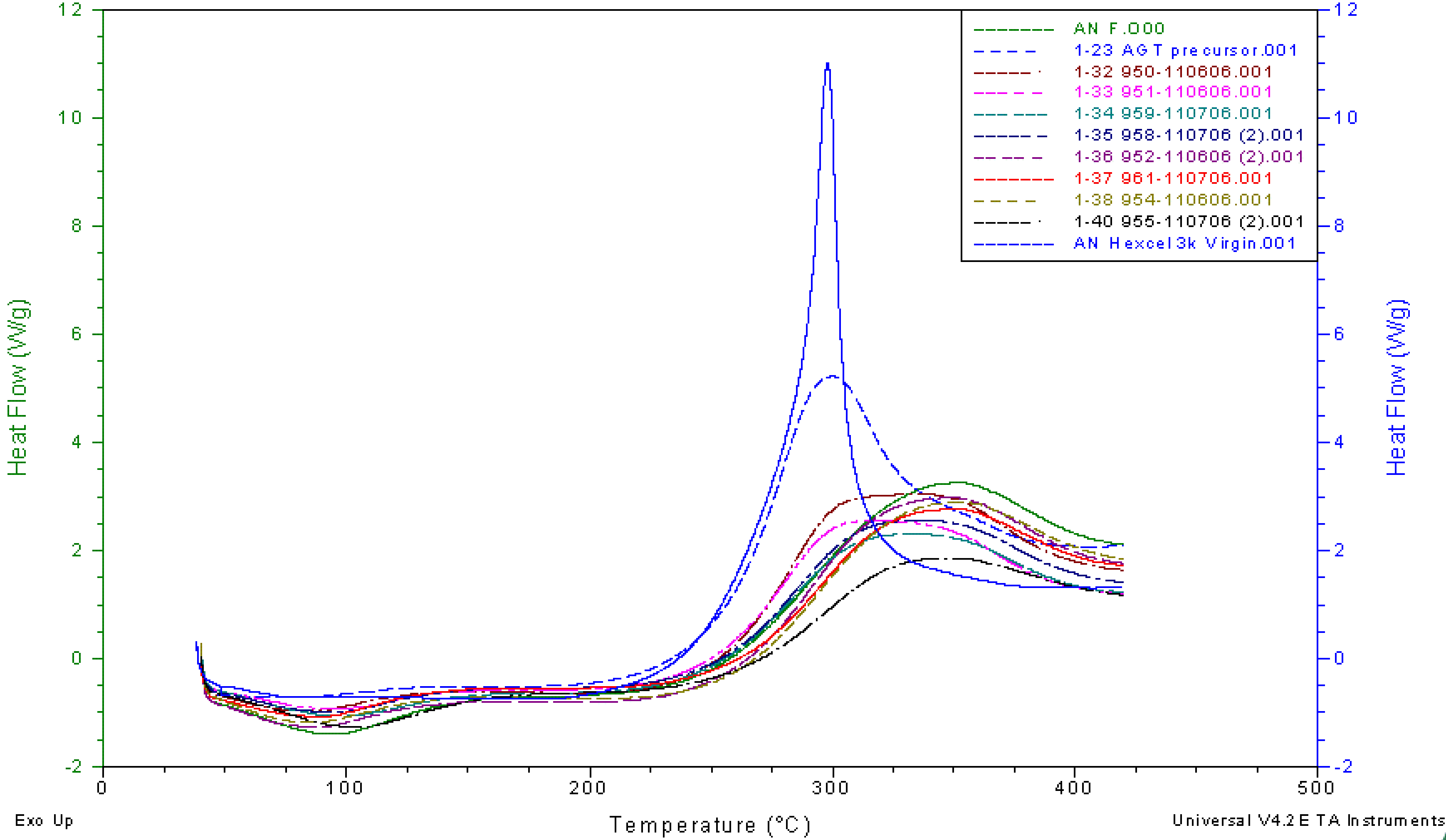
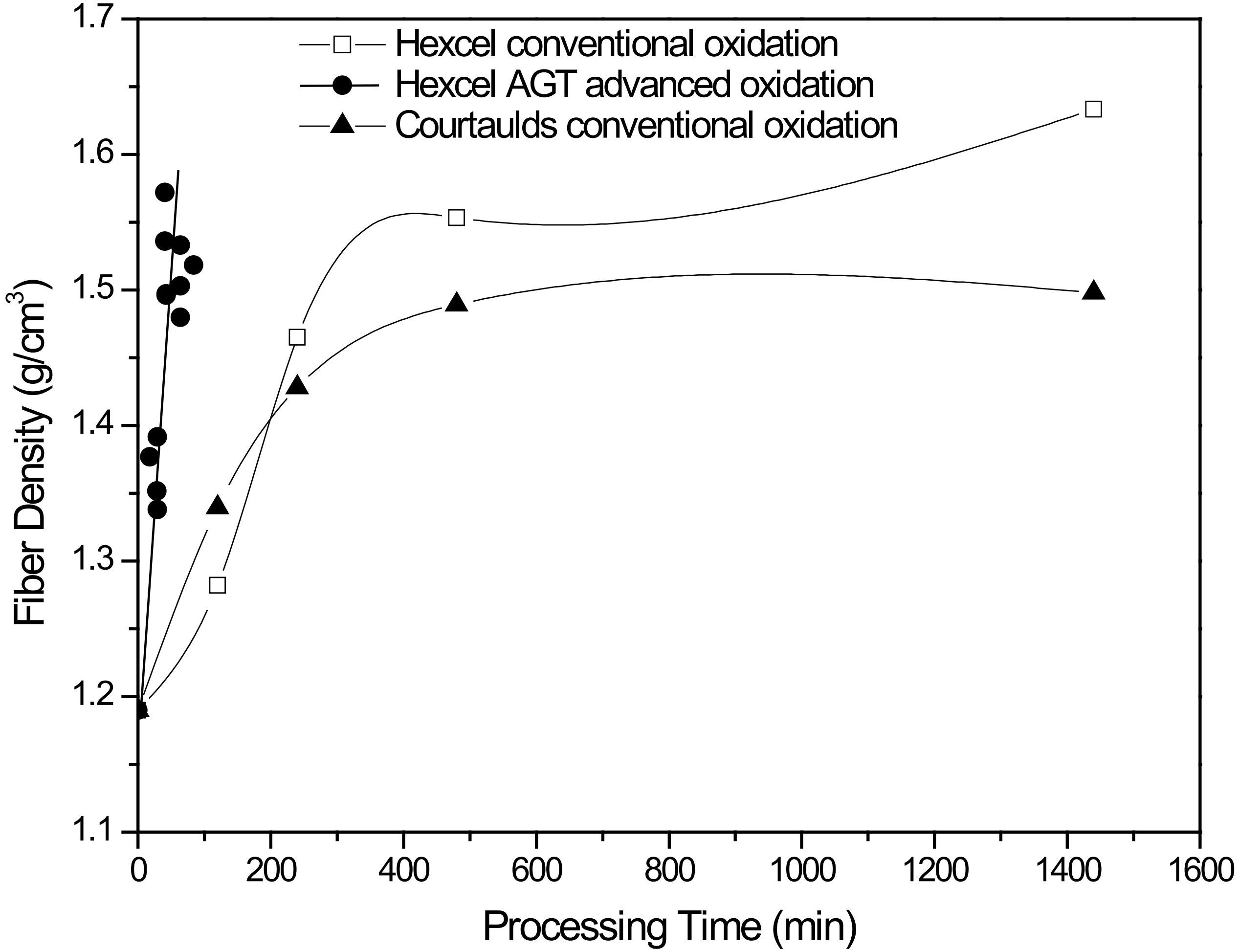


DSC thermograms of PAN fibers: comparison of plasma oxidized vs. virgin and conventionally oxidized. It is clear that plasma oxidized fiber had less remaining heat of reaction

Technical Results



Accelerated oxidation is demonstrated in processing time vs. density profiles for fibers in conventional and ORNL proprietary oxidation process

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Measured mechanical properties of single filaments from various oxidized tows

Date	Sample	Density* (g/cc)	Diameter Microscopy (µm)	Peak stress (ksi)	Strain at Peak Stress (%)	Modulus (Msi)	Damage (Qualitative microscopic observation)
Single Tow Reactor 1 (STR1). All 3k tows.							
07/20/2007	1427	1.338	N/A	31.7	6.10	0.88	N/A
10/02/2007	1586	1.377	N/A	35.1	18.02	0.82	N/A
03/31/2008	1750	1.503	N/A	20.0	3.15	0.70	N/A
04/02/2008	1754	1.518	N/A	17.1	3.27	0.60	N/A
Multiple Tow Reactor 1 (MTR1).). All 3k tows.							
01/29/2010	265	1.35-1.36	12.1	22.8	3.4	0.9	Moderate
02/01/2010	269	1.34-1.35	12.3	18.7	2.5	0.9	Severe
02/11/2010	281 #1	1.28-1.29	13.1	41.0	10.5	1	Minimal
02/12/2010	283 #1	1.29-1.30	13.1	29.5	4.5	1.1	Minimal
03/09/2010	292 #1	1.32-1.33	12.9	42.8	9.3	1.1	Moderate
03/10/2010	294 Textile	1.32-1.33	11.7	34.8	23.6	0.6	None
Conventional. All 26k tows, textile PAN.							
	F1045						
04/09/2010	4th Oxidized	1.374	10.2	33.3	15.2	0.8	None
04/16/2010	5th Oxidized	1.404	9.4	39.1	19.8	0.5	None
04/20/2010	6th Oxidized	1.382	10.3	37.0	20.6	0.5	None
	F1154C						
09/11/2008	Oxidized	1.382	11.9	27.6	14.4	0.9	None
Conventional. Fortafil fiber. 50K tow.							
06/02/2009	Oxidized	1.399	12.6	37.8	20.4	1.2	None
Conventional. 3k fiber.							
06/25/2008	Oxidized 4h	1.465	11.83	39.3	10.35	0.93	None
06/25/2008	Oxidized 24h	1.633	10.77	26.2	3.62	0.09	None

*If a range is given, this was determined by discrete density gradient column. Otherwise measured with pycnometer.

STRI: Single Tow Reactor 1

MTRI: Multi Tow Reactor 1

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Technical Results

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Measured mechanical properties of single filaments from various carbonized tows

Date	Sample	Density* (g/cc)	Diameter Microscopy (µm)	Peak stress (ksi)	Strain at Peak Stress (%)	Modulus (Msi)	Damage (Qualitative microscopic observation)
Test 227 Fiber #1 (MTR1)							
11/10/2009	Plasma Oxidized	1.37-1.38	12.55	17	2.92	0.6	Low/moderate
12/18/2009	CC† LT						
12/21/2009	CC HT2		7.9	137.4	0.6	22.1	Low/moderate
Test 228 Fiber #1 (MTR1)							
11/10/2009	Plasma Oxidized	1.38-1.39	13.06	26.5	5.24	1	Moderate
12/1/2009	CC LT						
12/2/2009	CC HT1		8.13	116.3	0.59	18.5	Moderate
12/18/2009	CC LT						
12/22/2009	CC HT2		8.53	99.8	0.51	20	Significant
Test 228 Fiber #2 (MTR1)							
11/10/2009	Plasma Oxidized	1.37-1.38	N/A	N/A	N/A	N/A	Significant
12/18/2009	CC LT						
12/22/2009	CC HT2		8.82	86.4	0.46	17.2	Significant

*Determined by discrete density gradient column.

† CC = Conventionally Carbonized. LT = Low Temperature. HT = High Temperature.

MTRI: Multi Tow Reactor 1

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Technical Results

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Damaged Filaments from MTR1

Damage from early stage experiments

Undamaged Filaments from MTR1

Damage minimized from process optimization

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Future Work

- **Rest of FY10**
  - Complete stoichiometry investigations
  - Refine oxidation process to satisfy program requirements for carbonized tow properties
  - Assess energy balance and demand
  - Conduct preliminary investigations with alternative precursors

Date	Milestone
Mar-10	Report bulk density from initial experiments on advanced oxidation of textile PAN precursor. Density has to be >1.30g/cm^3
Sept-10	Report updated evaluation of residence time and unit energy demand

- **FY11**
  - Continue processing and evaluation on PAN-based tows
  - Continue processing with alternative precursor, e.g. textile, large tows.
  - Further obtain energy and design data
  - Demonstrate plasma oxidation of large tow, multiple tows (24K to 80K/3)
  - Continue evaluation in hard-ware material compatibility

Date	Milestone
Mar-11	Demonstrate plasma oxidation of large tows (≥24K) achieving densities bigger than 1.35 gr/cm^3
Sept-11	Report experimental data in large tow of plasma oxidized and conventionally carbonized, achieving programmatic mechanical properties (250ksi, 25 Msi)

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Long term Milestones and Deliverables

- Demonstrate program property requirements satisfied, with low variability, in processing multiple large tows.
- Demonstrate plasma oxidation of multiple tows of alternative precursor
- Deliver, install, and checkout first plasma oxidation reactor module.
- 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
- 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

- This work directly supports petroleum displacement via improved fuel economy from vehicle weight reduction
- This work addresses the very important 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
- Major performance measures are good
  - Cut 3k tow residence time by ~ 2 to 3X vs. conventional oxidation
  - Considerable improvement made in reducing fiber damage due to excessive plasma exposure
  - Single-filament oxidized mechanical properties encouraging
  - Major advancements in multi-tow reactor operation and optimization
  - Met material delivery milestones
- Process and equipment scaling will constitute the majority of future work

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Thank you for your attention.

Ball
Lightening

Questions?

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