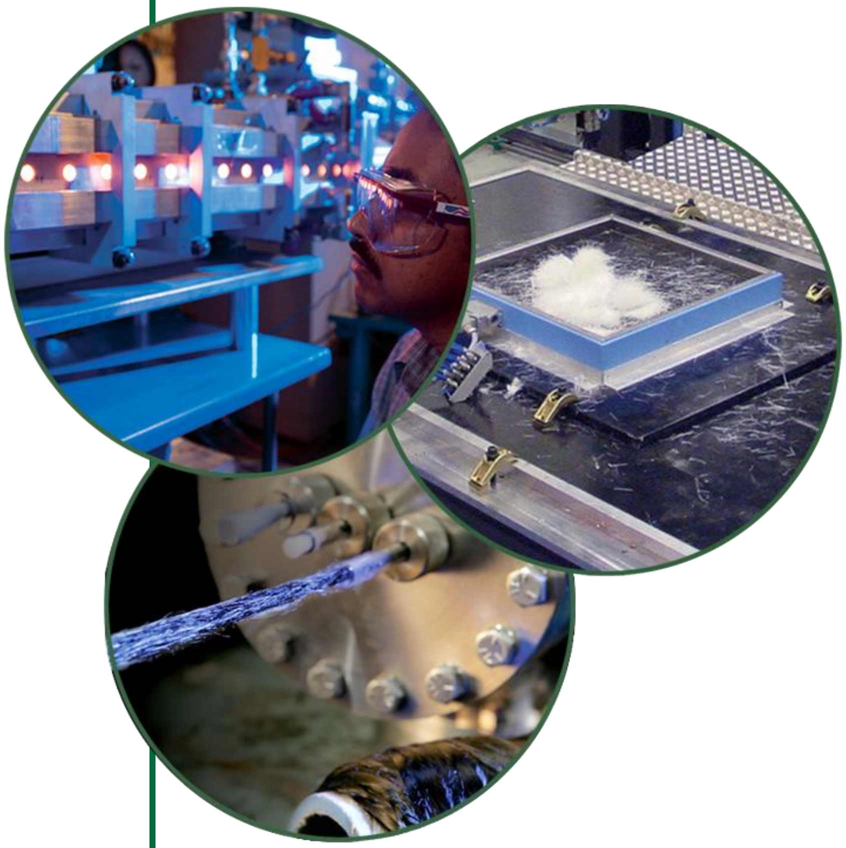
Carbon Fiber Precursors and Conversion



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U.S. DEPARTMENT OF ENERGY

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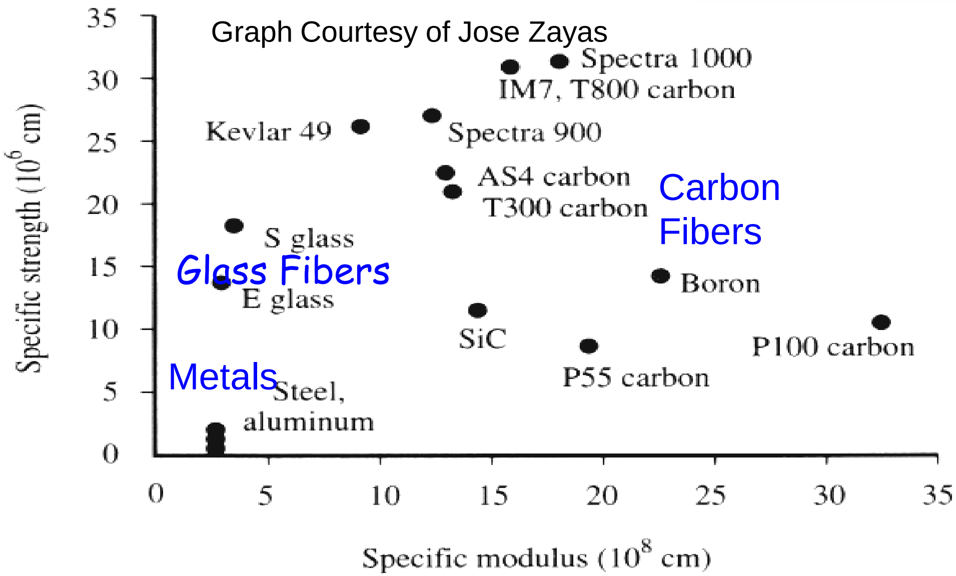
All Fibers are Not the Same



Reasons Carbon Fiber is Chosen

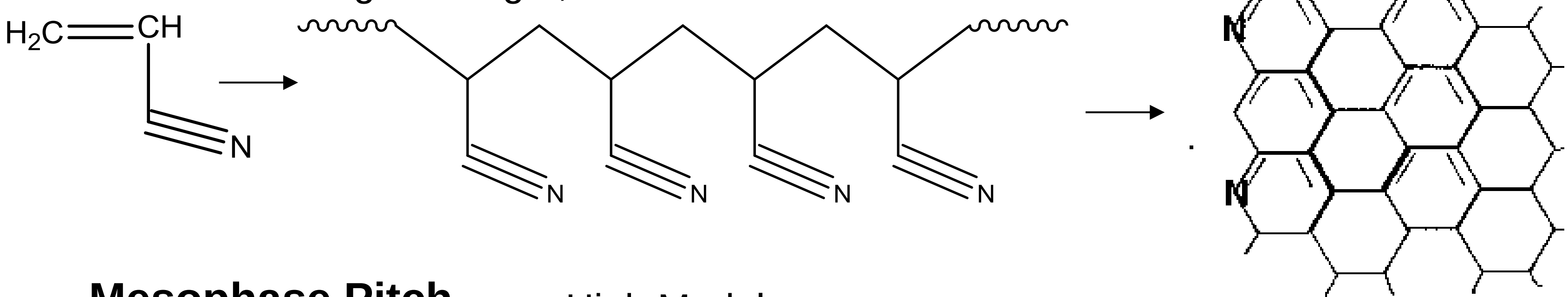
Low Density – Lightweighting
High Electrical Conductivity – Pitch is Best
Modulus – Pitch Based is Best
Near Zero Coefficient of Thermal Expansion
Strength – PAN Based is Best
Thermal Conductivity – Pitch is Best
Cost – PAN Based is Lower
Filtration Media – Pitch Based is Best
Design Flexibility of Composites
Chemical Resistance – Will not Corrode

Type	Strength (MPA)	Modulus (GPA)	Strain (%)	Density (g/cc)	Diameter (microns)
T-700 CF	4900	230	2.1	1.80	7
T-300 CF	3530	230	1.5	1.76	7
Pitch Based	2000	500-800	0.5-1.0	2.1	5-10
Rayon	580	59	1.0	2.1	6-7
E-Glass	2000	72-85	2.7	2.55	~20
S-Glass	4750	89	5.3	2.5	~20
Spectra 1000	3000	172	1.7	0.97	Varies
Basalt	2800-4800	86-90	3.2	2.7	Varies
Kevlar 149	3450	179	1.9	1.5	Varies

Potential Precursors

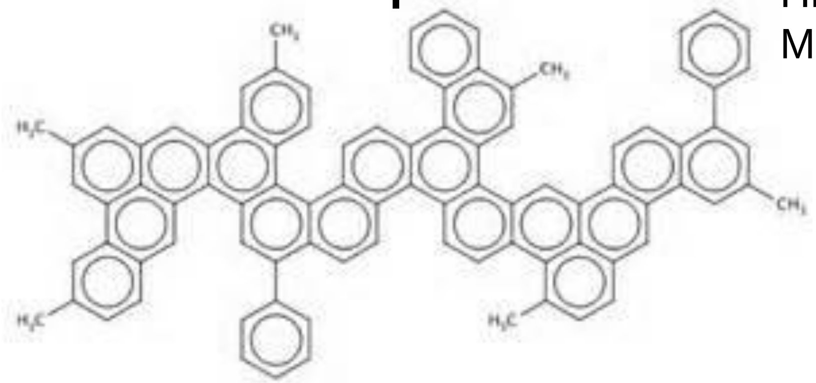
PAN

High Strength, Moderate Modulus



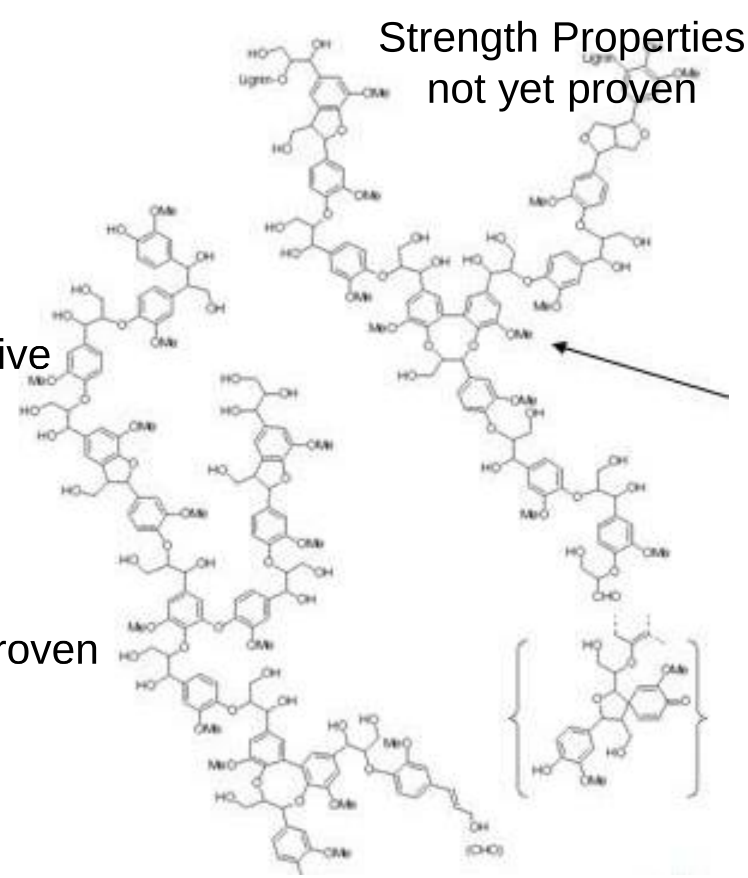
Mesophase Pitch

High Modulus,
Moderate Strength



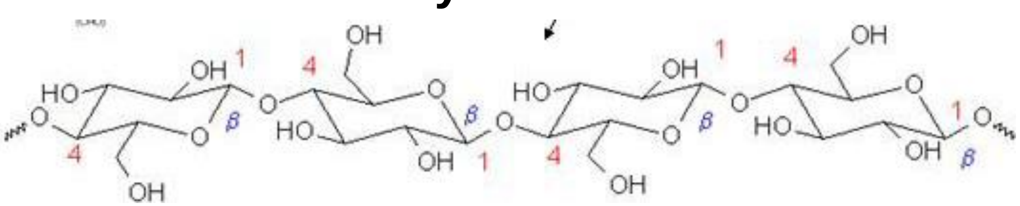
Lignins

Strength Properties not yet proven



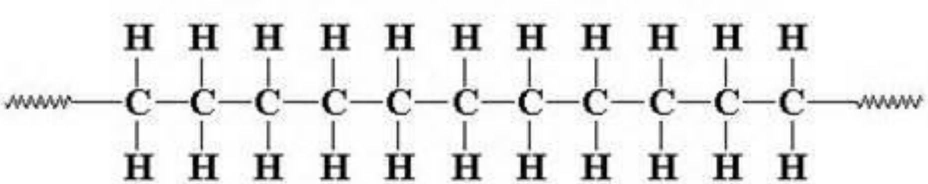
Rayon

Expensive and use for Ablative



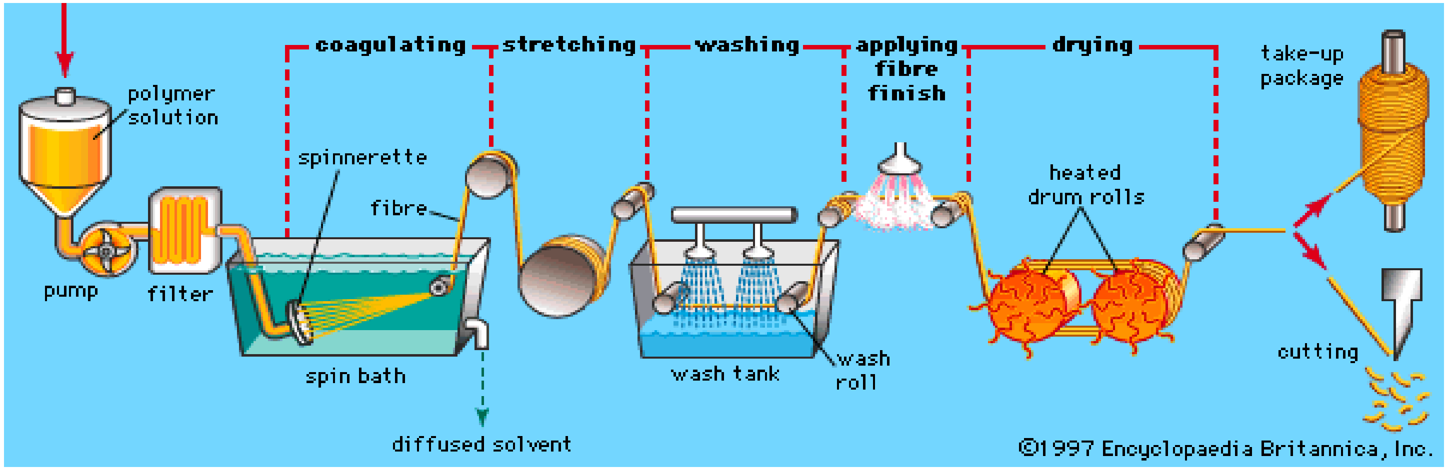
Polyethylene

Properties not yet proven

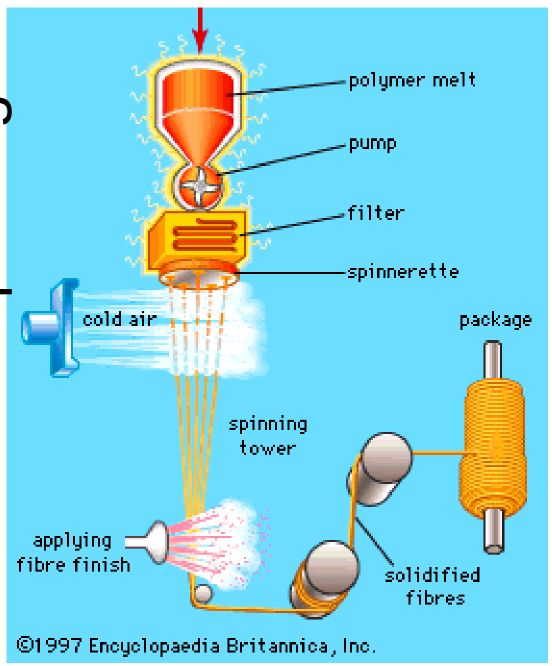


Fibers are Spun by 3 methods

Solution-Spinning

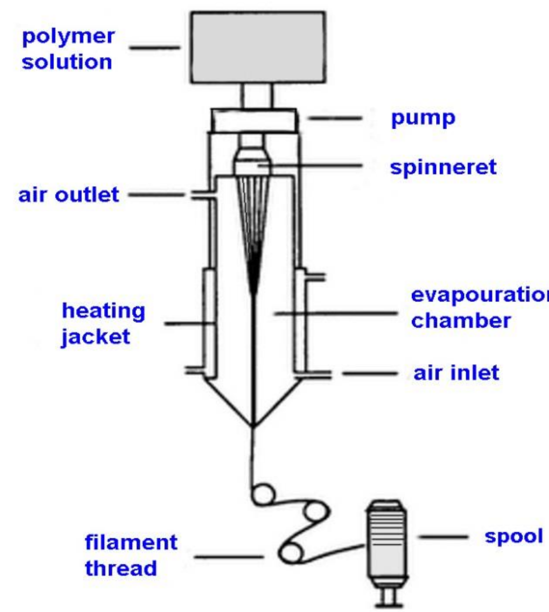


Melt-Spinning



12,000,000 lb/yr Precursor Plant		
	Wet-Spinning	Melt-Spinning
Spinning Speed	1X	3X
Capital Required	$77,750,000	$28,000,000
Raw Material	$0.69	$0.81
Utilities	$0.77	$0.04
Labor	$0.52	$0.35
Other Fixed	$0.36	$0.13
Depreciation	$0.65	$0.10
Total Per Pound of Precursor	$2.97	$1.43

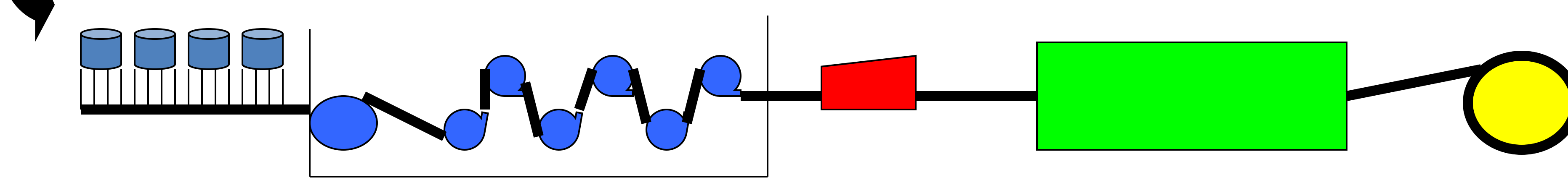
Dry-Spinning



It requires 2.1 lbs of PAN Precursor to make 1 lb of carbon fiber.

Precursor Manufacturing

Starts with a large “tank farm” which polymerizes PAN and other co-monomers



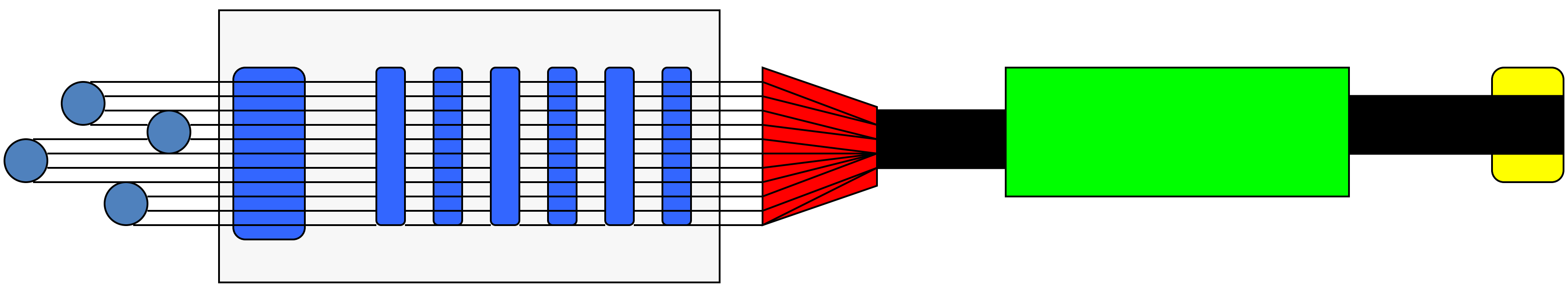
Multiple Spinnerettes

Solvent Extraction, Washing and Tensioning

Crimping

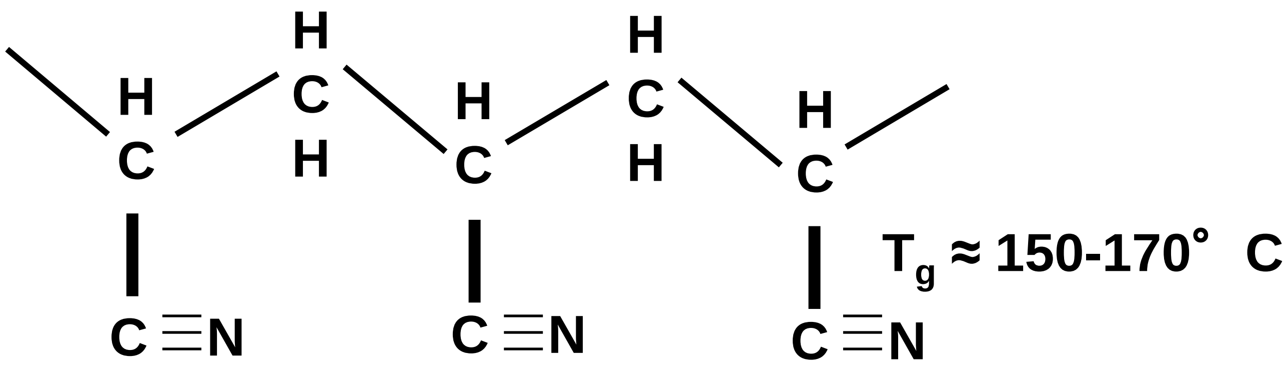
Drying with Tension

Spooling or Bailing in Bulk



Prestretch during Fiber Manufacturing

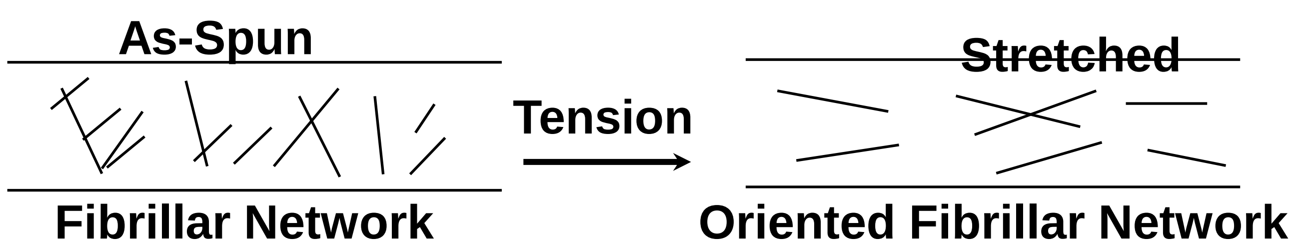
PAN:



PROCESS:

- Polymer solution
- Spun into coagulating bath
- Washed
- Stretched
- Dried

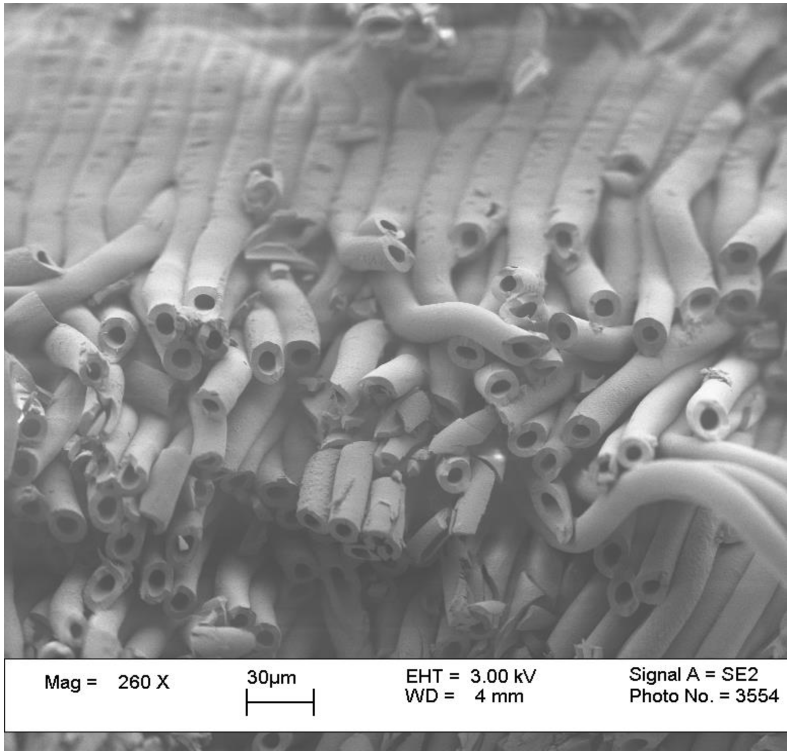
STRETCHING:

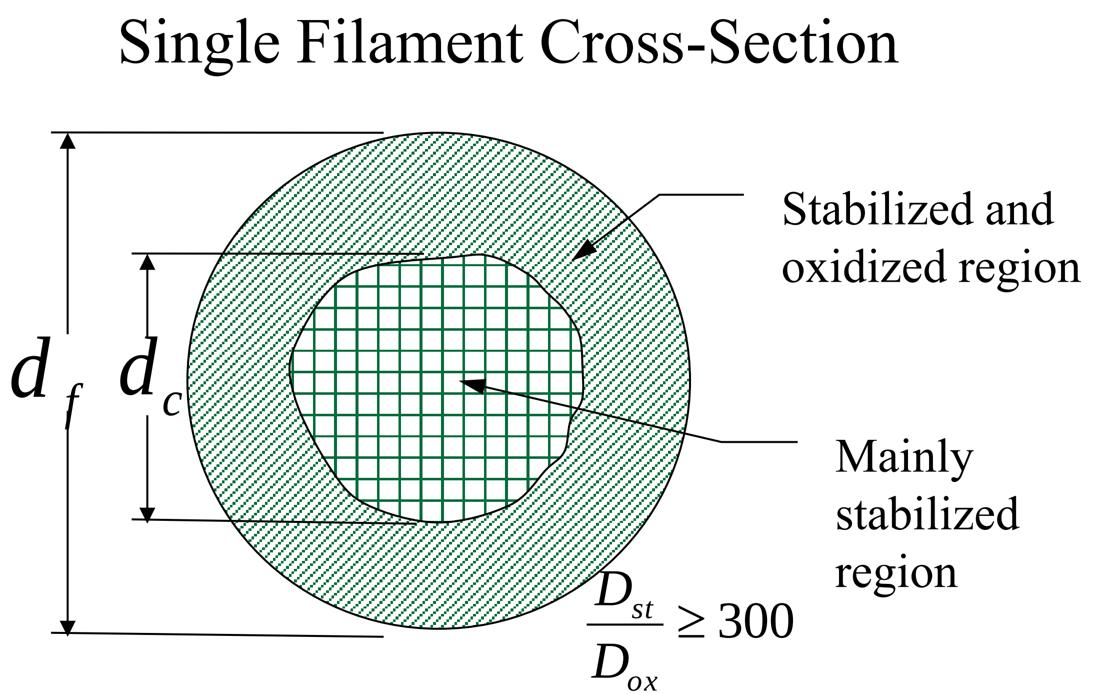


Majority of Carbon Fibers are PAN Based.

Stretching occurs below the T_g with H_2O as a plasticizer.

Conversion – Oxidative Stabilization



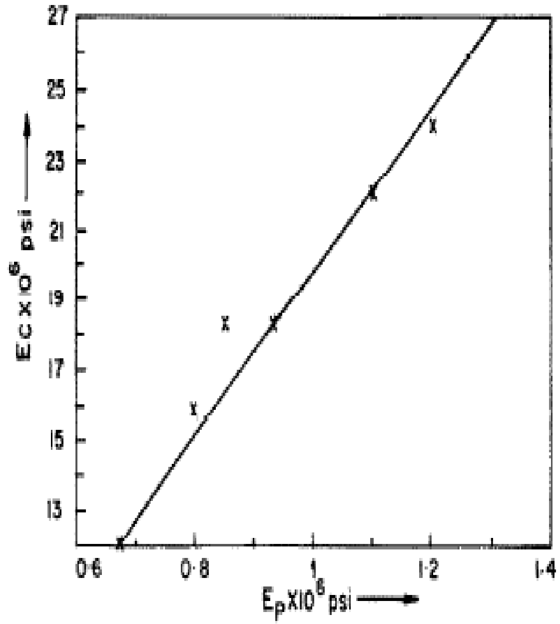


- **Oxygen and/or oxidative species need to diffuse through the oxidized "skin"**
- **Diffusion of oxygen to reactive sites is restricted, sequent reactions follow more slowly**
- **The limiting or controlling factor is diffusion**

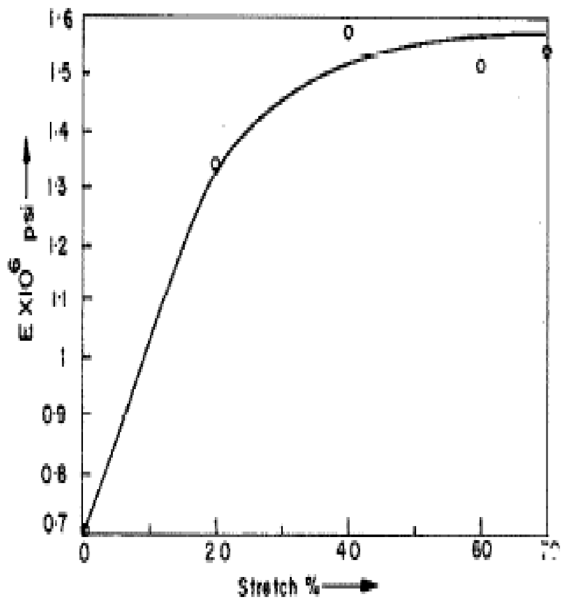
Conversion - Oxidative Stabilization

Stretching of Fibers during Stabilization

- **Stretching of filaments provides high molecular orientation and better mechanical properties.**
- **Dry PAN fibers are difficult to stretch (due to high Tg, strong dipole-dipole interaction**



Young's modulus of precursor fiber vs. resulting carbon fiber



Young's modulus of precursor fiber vs. precursor stretching

Mathur *et al*. carbon 1988

- Stretching is occuring while oxygen is diffusing in and crosslinking is occuring.
- Crosslinking results in resistance to further stretching and thus molecular alignment.
- A potential path to higher strength fiber would be to achieve the stretch prior to cross linking.

Carbonization

Usually two stages: Low and High Temperature

PAN fiber is pyrolyzed to carbon fiber

Process:
- **Inert atmosphere**
- **~ 300 - 1800° C**
- **Tow under tension**

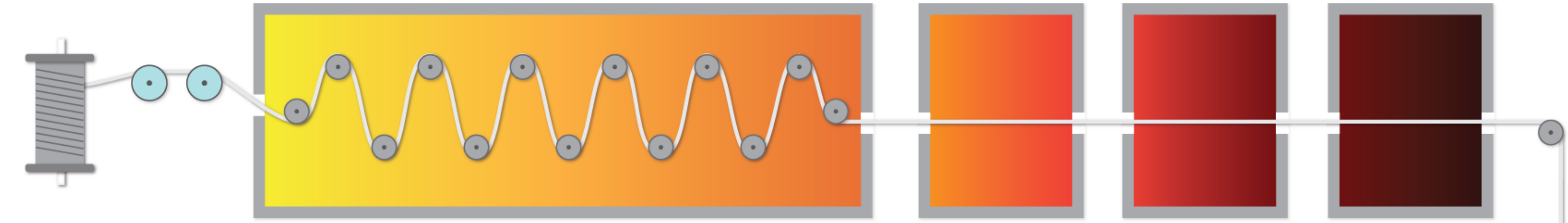
Key Features:

- Most non-carbon elements are driven from fiber
  - Generates corrosive, toxic, and carcinogenic effluents
- 50-60% of original PAN weight lost
- Carbon yield from PAN = 40-50% (Rayon = 10-30%; Pitch = 80-90%)
- PAN density = 1.2 g/cc - carbon fiber density = 1.8 g/cc
- Carbon fiber diameter ≈ 1/2 PAN fiber diameter
- Carbon content = 80-95%
- Carbon/Graphite fibrils or ribbons with “turbostratic graphite” structure

Graphitization

- Produces graphite fiber with higher carbon yield and more graphitic microstructure than carbonization step
  - Inert atmosphere
  - Tension – promotes correctly oriented morphology
  - 1500-3000° C
- Key features:
  - Carbon content > 99%
  - Density = 1.8 - 2.1 g/cc
  - More graphitic microstructure – increases tensile modulus, decreases tensile strength
  - Diameter = 5 -10 μm

Conventional PAN Conversion - process



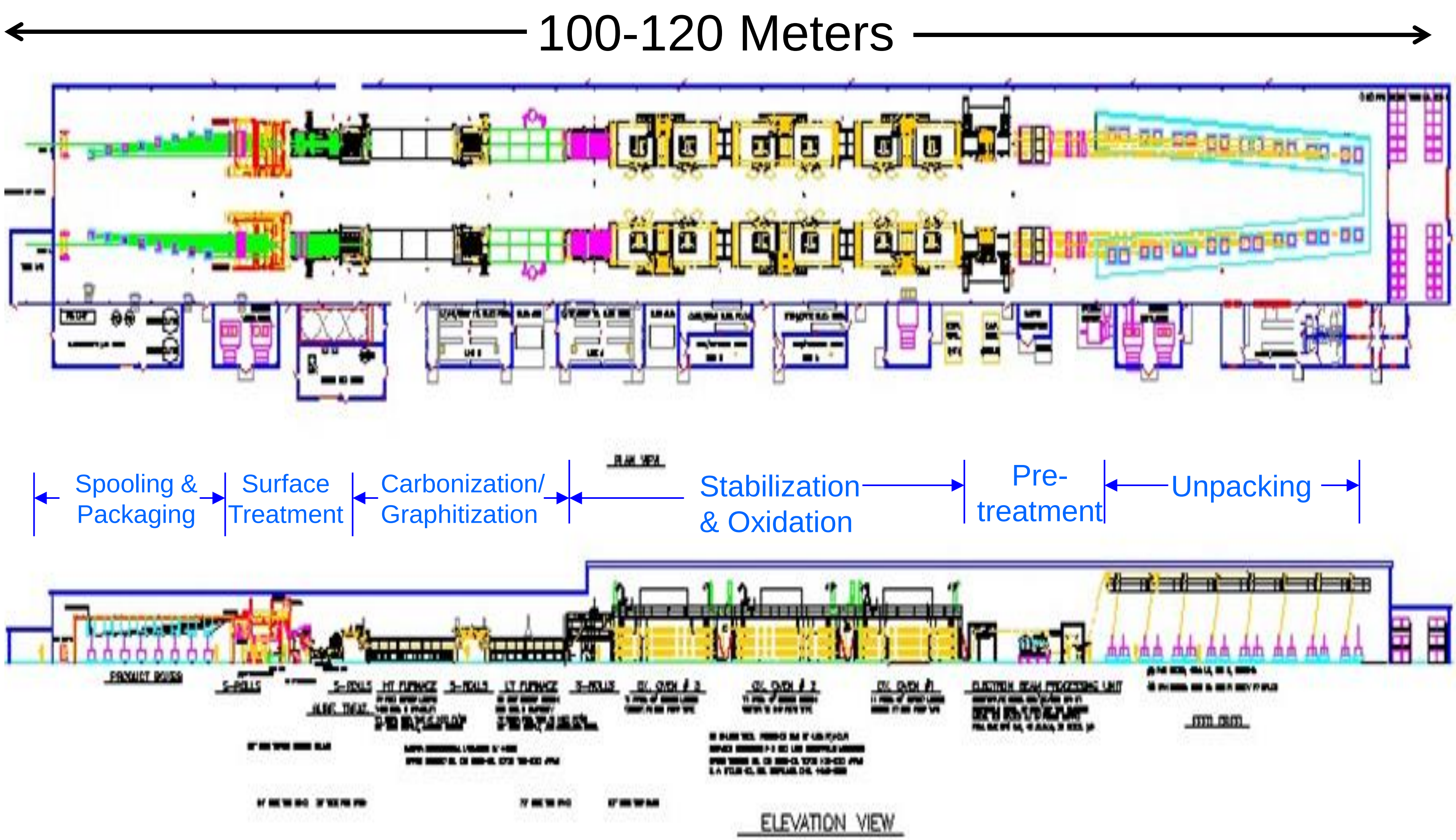
Typical processing sequence for PAN –based carbon fibers

Major Cost Elements

Precursor	~ 50%
Conversion	~ 40%
Other	~10%

ORNL is developing technological breakthroughs for major cost elements

Typical Carbon Fiber Manufacturing Facility



Staff of 5-8, 2 Lines Side by Side

Unpacking to Spooling Time = 2-3 hours

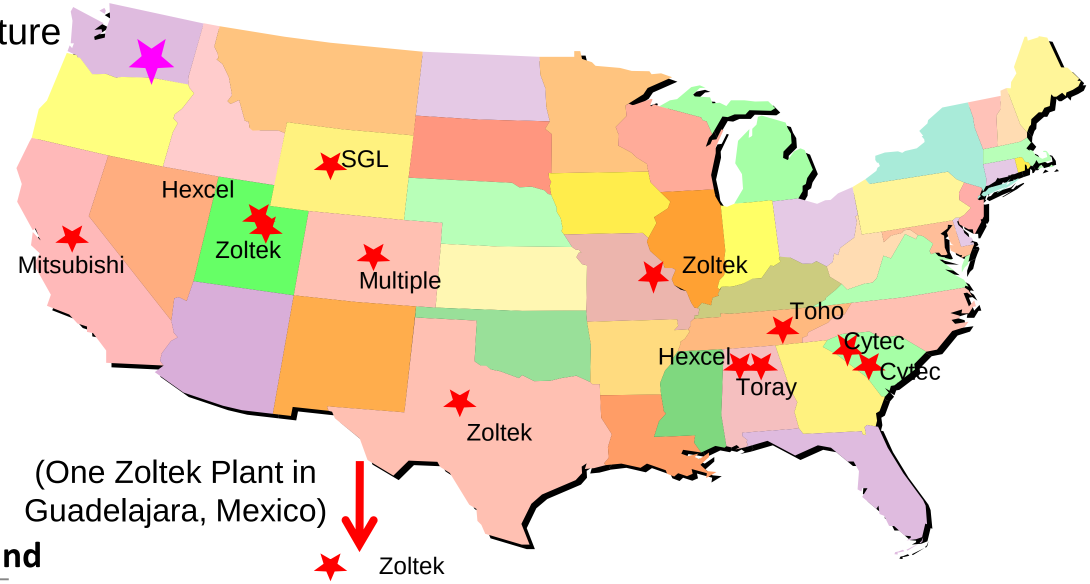
Aerospace vs Industrial Grade Carbon Fiber?

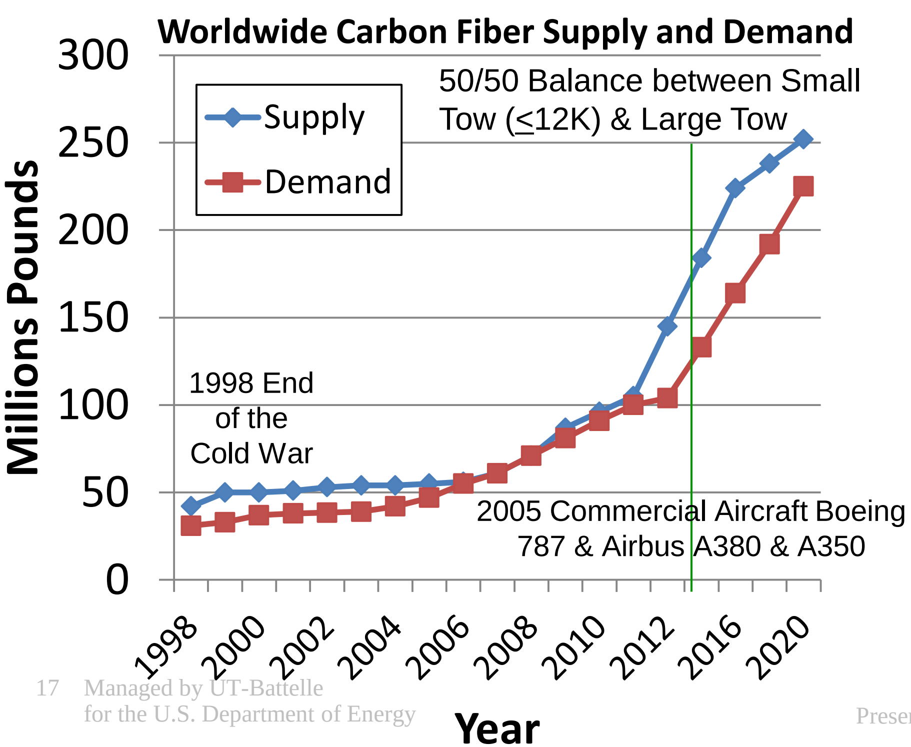
Attribute	Industrial Grade	Aerospace Grade	Cost Impact
Tow Size	12-80K Filaments	1-12K Filaments	Less material throughput
Precursor Content	< 92% AN, MA or VA	> 92% AN, MA	Little on raw material; slower oxidation
Precursor Purity	Can tolerate more impurity	Controls UTS	Slower spinning speed
Precursor Composition	Moderate MW	Higher MW yields Higher Properties	Significant increase in spinning and polymerization costs
Oxidation	Quicker due to lower AN	Slower due to higher AN	Time is money
Carbonization	Lower Temp	Sometimes Higher Temp	Small impact
Surface treatment	Same but utility affected	Same	None but Load Transfer affects amount of fiber needed
Packaging	Spooled	Small Spools	More Handling
Certification	None	Significant	Expensive; Prevents incremental Improvements.

Essentially the same process with slightly different starting materials. The traditional business model is for CF manufacturers to be specialty material makers, not high volume. That trend is shifting.

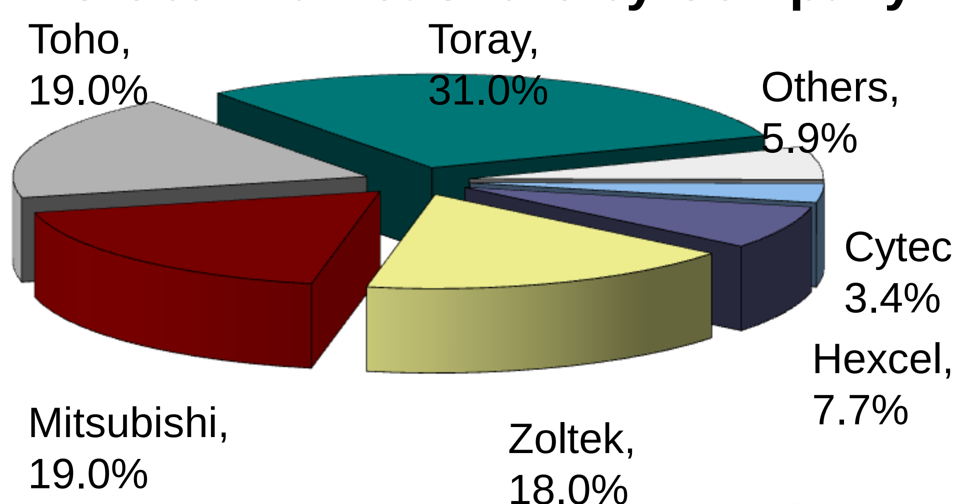
Domestic & International Carbon Fiber Production

North American Carbon Fiber Manufacturers





Global Market Share by Company



Competitors are entering the Market from China, Turkey, India and Russia

Carbon Fiber Production - United States

Company	US Facilities	Non-US Facilities
Hexcel (US)	Decatur, AL; Salt Lake City, UT	Spain
Cytec (US)	Greenville, SC; Rock Hill, SC	None
Toray (Japan)	Decatur, AL	Japan
SGL (Germany)	Evanston, WY, Washington	Scotland, Germany
Zoltek (US)	Abilene, TX; St. Louis, MO Salt Lake City, UT	Mexico, Hungary
Mistubishi (Japan)	Sacramento, CA	Japan
Toho Tenax (Japan)	Rockwood, TN	Japan, Germany

Source: Polyacrylonitrile (PAN) Carbon Fibers
Industrial Capability Assessment, Department of Defense

<u>United States Universities with significant research in Carbon Fiber production</u>

Clemson University
University of Kentucky
Virginia Tech
Georgia Tech

Note: Large efforts in carbon fiber <u>composite</u> development at many laboratories and universities.

Start with an Understanding of Where the Costs Are

Diagram from Harper International

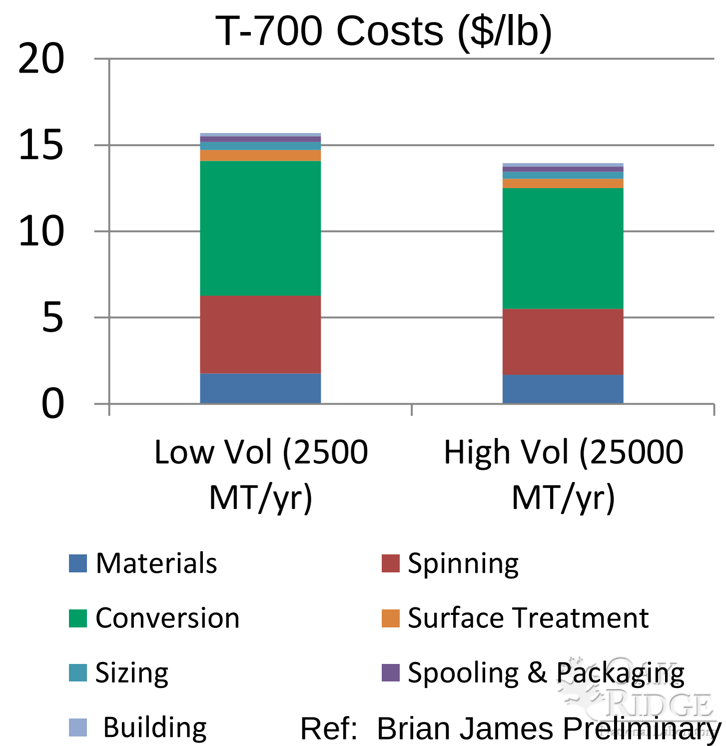
	Precursors Materials	Precursors Spinning	Stabilization & Oxidation	Carbonization/ Graphitization	Surface Treatment	Spooling & Packaging
Industrial Grade - $10.20	$2.78	$2.78	$1.78	$1.41	$0.80	$0.65
High Volume* - $9.35	$2.78	$2.45	$1.62	$1.27	$0.72	$0.49
Aerospace Grade - $13.35	$3.21	$3.21	$2.88	$2.45	$0.81	$0.80
High Volume* - $11.61	$3.21	$2.89	$2.54	$1.57	$0.80	$0.78

Ref: Das, S., ORNL Cost models 2012 and 2014.

- High Volume is 25,000 Tons/year. All Costs are $/lb

Not Captured is that Oxidation is the rate limiting step and thus mass throughput limiting step.

Precursor Materials:	24%
Precursor Spinning:	24%
Stabilization & Oxidation:	26%
Carbonization:	14%
Surface Treatment/Sizing:	6%
Spooling and Packaging:	5%



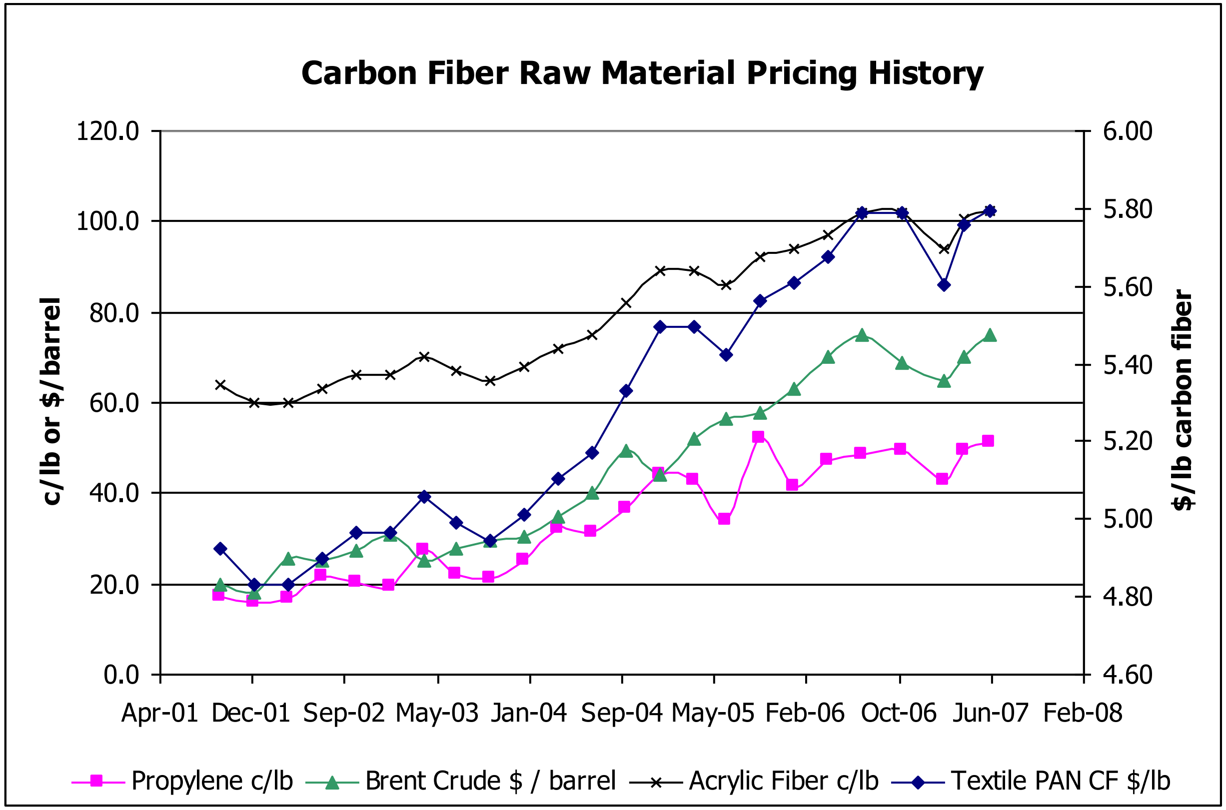
Ref: Brian James Preliminary Cost Model

6 Elements of Cost Reduction

1. Scale of Operations
2. Precursor Materials
3. Precursor Spinning
4. Stabilization
5. Manufacturing Composite
6. Carbonization

Raw Material - Cost Sensitivity to Oil Prices

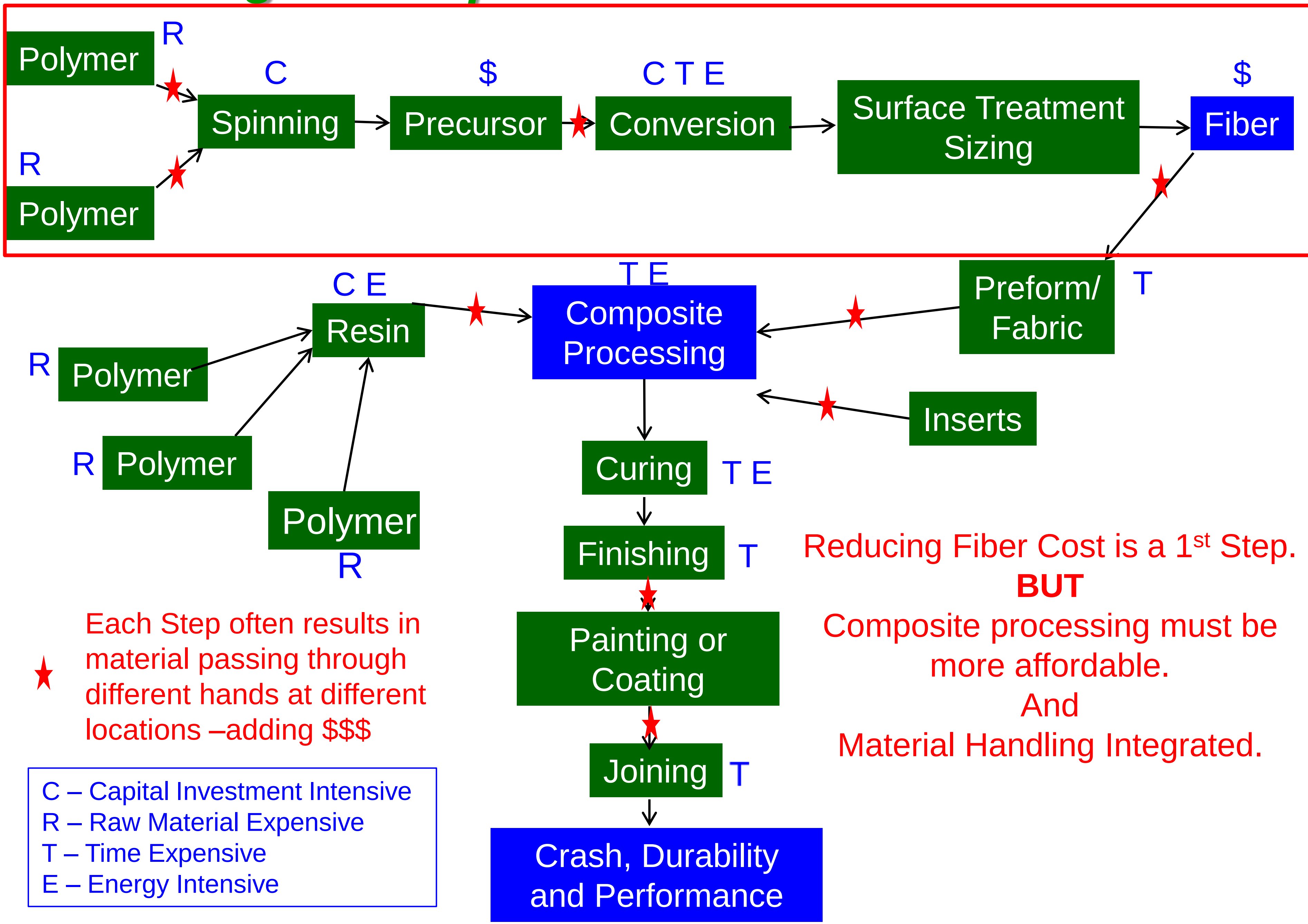
The precursor and thus CF manufacturing costs are sensitive to oil prices.



World Oil Price	Polypropylene	Acrylic Fiber	Textile PAN CF
$60/barrel	$0.48/lb	$0.90/lb	$5.55/lb
$75/barrel	$0.50/lb	$1.00/lb	$5.75/lb

Source: Kline (2007)

The Making of Composites – Fiber is Part of the Cost



Potential Elements of Cost Reduction for Reinforcement

Precursor Materials:	24%
Precursor Spinning:	24%
Stabilization & Oxidation:	26%
Carbonization:	14%
Surface Treatment/Sizing:	6%
Spooling and Packaging:	5%

Carbon Fiber Cost

1. Non-PAN precursors. (Pitch, Rayon, Lignin, Polyolefins, etc.)
2. Melt or Dry Spun PAN. (Melt spun being pursued, 1 source of dry spun)
3. Higher Molecular Weight Precursors.
4. High Rate Stabilization. (Developed under VTO program, not yet extended to high performance fibers)
5. Higher Volume Conversion Methods (i.e. Fiber Layering)
6. Pre-stretching above the Tg of the polymer to yield better molecular alignment.
7. Alternative Carbonization. (Early work being conducted.)
8. Alternative Surface Treatments and Sizings. (Work is dormant.)

Other Technologies

1. Full or Partial use of Alternative Reinforcements. (Some characterization or alternate fibers needed under long term operating conditions.)
2. Higher Rate Composite Manufacturing Methods. (IACMI)
3. Alternative Product forms (Tapes, Preimpregnated tow, etc.)
4. Improved Load Transfer (improved fiber/resin bonding)

Key Challenges – Requires a Multi-Prong Approach

Precursors
- Raw Materials are Commodity (Can we use other materials)
- Melt Spun PAN, Air-Gap Spun PAN, Increased MW of either.

Conversion
- Pre-stretching to achieve molecular alignment (new method)
- Advanced Oxidation to improve throughput (3X)
- Higher rate, lower energy carbonization
- Fiber Layering to increase throughput

Post Treatment
- Improved surface treatment and sizing
- Alternative Product forms

Design
- Alternate Fibers (in part or in whole)
- Higher Rate Manufacturing methods


Thank You
Mahalo
Dziekuje
Merci
Gracias
Achiu
Obrigado
Danke
Xie xie
Tesekkür ederim
Spasibo
Grazie
Arigato
Sas efharisto
Jag tackar
Toda

Backup Slides

History of Carbon Fiber Composites Industry

- **Early Composites: Wood, Adobe Bricks, Laminated Bow**
- **1900 -1970: Fiber glass, man-made fiber, and resin systems**

Year	Carbon Fiber Market Major Events
1970's	Golf Shaft & Fishing Rods
1974	DoD Filament Winding Rocket Motor Cases
1975	Satellite Applications
1976	Aerospace Structures
1980	Cold War Defense Boom
1980's	Boeing 757 & 767, Secondary Structures
1991	Defense Force Reduction
2003	Airbus 380
2004	Boeing 787
2009	Recession and Slow Down in Economy
2012	Increases in Wind and Industrial Sector

Current & Growing Applications of CFCs

<u>Current Traditional Applications</u>

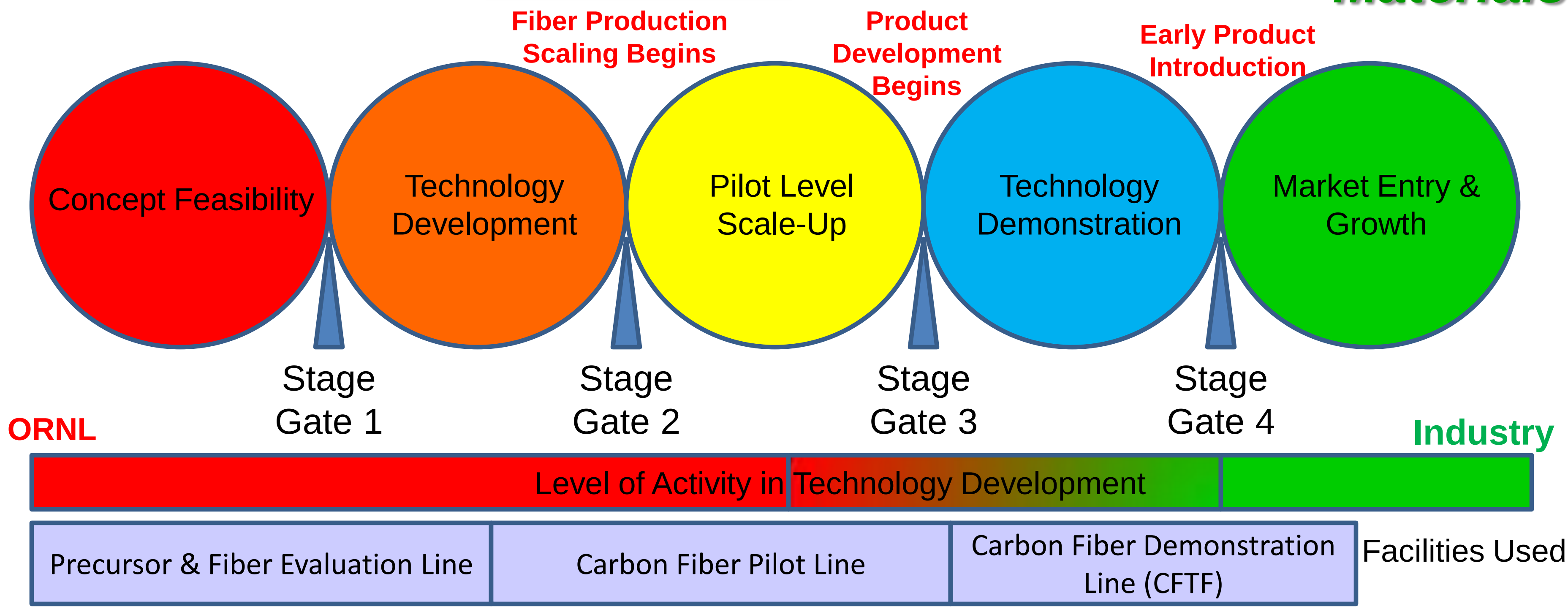
- Aerospace: Space, Military and Commercial (~30%)
- Industrial use (55%)
- Sport (15%)
- Energy Wind Blades
- Energy Storage: Flywheels, Pressure Vessels
- Medical implants (prostheses), x-ray and MRI equipment
- Space Travel

<u>Growing Applications</u>

- Unmanned Vehicles
- Wind Generator Blades
- Automotive, transportation and marine
- Batteries; EMI/RF, Ablative Applications
- Civil engineering: Bridges and bridge columns
- Offshore oil exploration and production
- Thermal Radiators
- Cell Phone and Computer Casings

Process for Carbon Fiber Technology Commercialization

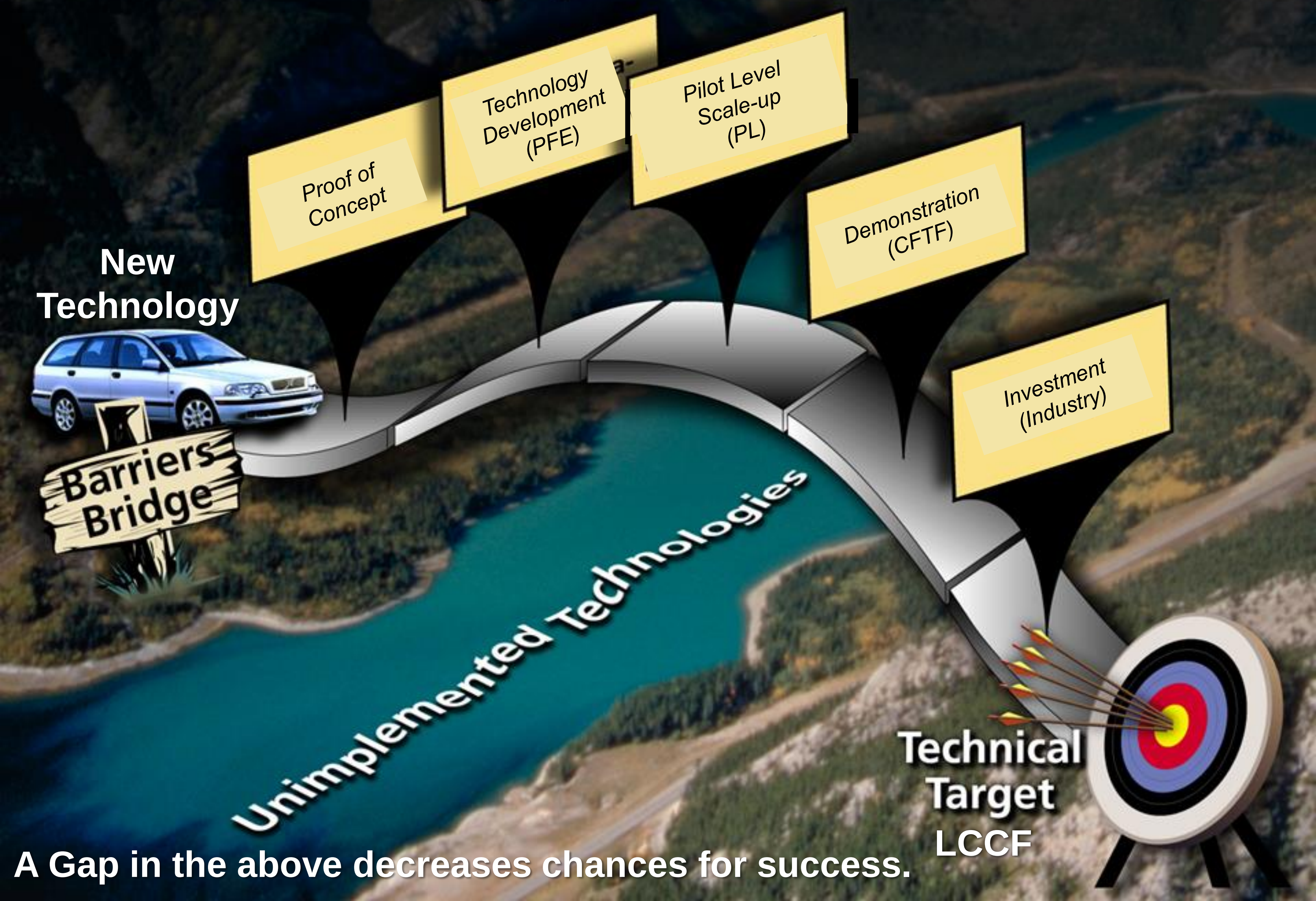
Materials



Approach:

1. Develop the Technologies at Lab Scale
2. Scale to Pilot Line
3. Work with CF Industry to Scale to Industrial Level. Reduce Risk.
4. Work with OEMs & Suppliers to incorporate in composite material systems. Reduce their risk.

To Reach Technical Targets, All Five Barriers Must Be Overcome



Critical Cost Reduction Pathways

The cost reduction goal can be accomplished by combining technologies.

Savings from $10.20 baseline. $0.85/lb additional savings available from volume scale-up.

Current Cost Model did not evaluate savings of combining technologies.

Precursors

- High PE Polyolefins ($5.65/lb)
- Polyolefin Blends ($2-$5/lb)
- **Kaltex Textile*** ($2.35/lb)
- PAN-VA Textile ($2.61/lb)
- Alternate Textile Precursor $?
- Lignin Blends ($.60-1.20/lb)
- High Content Lignin ($2.68-$5.98/lb)
- Bio-Mimicked Spider $?
- Other: Melt Spun PAN, PAN-MA for HS, DARPA Super Fiber

Stabilization & Oxidation

- Conductive Oxidation $?
- Disassociated Pre-Stretching $?
- **Advanced Oxidative Stabilization*** ($2.69/lb)

Carbonization/ Graphitization

- **Low Temperature Alternative Carbonization*** $0.50-2.00
- Microwave Assisted Plasma ($1.31)

ST/Sizing

Spooling & Packaging

All ($0.07- $2.50/lb)

- Interfacial Optimization
- Thermochemical Surface Treatment
- Plasma Surface Treatment

Current Technology Status

1. Early Stage Development (PFE Facility)
2. Initial Integration of Technologies (Pilot Scale)
3. Pre-Production Demonstration (Pre-Production Scale)

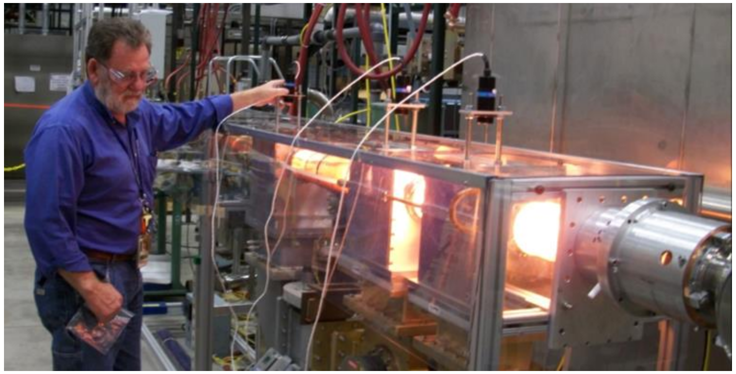
Advanced Oxidation

- **Phase I: Develop the technologies to reduce oxidation time by 2-3X (Lab Scale)**
- **Phase II: Demonstrate Phase I capability at Pilot Scale. Large tows and multiple tows. (Current)**
- **Future Phase III: Scale to Preproduction Level (CFTF)**

Currently Processing 2-24K tows with properties over 300 KSI.

	Conventional Technology	Advanced Oxidation	Savings*
1500 t/y Scale	$10.20	$7.51	$2.69 (26%)

Advanced Carbonization Using MAP



- **Microwave Assisted Plasma (MAP) Carbon Fiber Manufacturing is a technology for carbonizing carbon fibers at higher speeds and significantly lower costs than those achievable by present industrial practice**

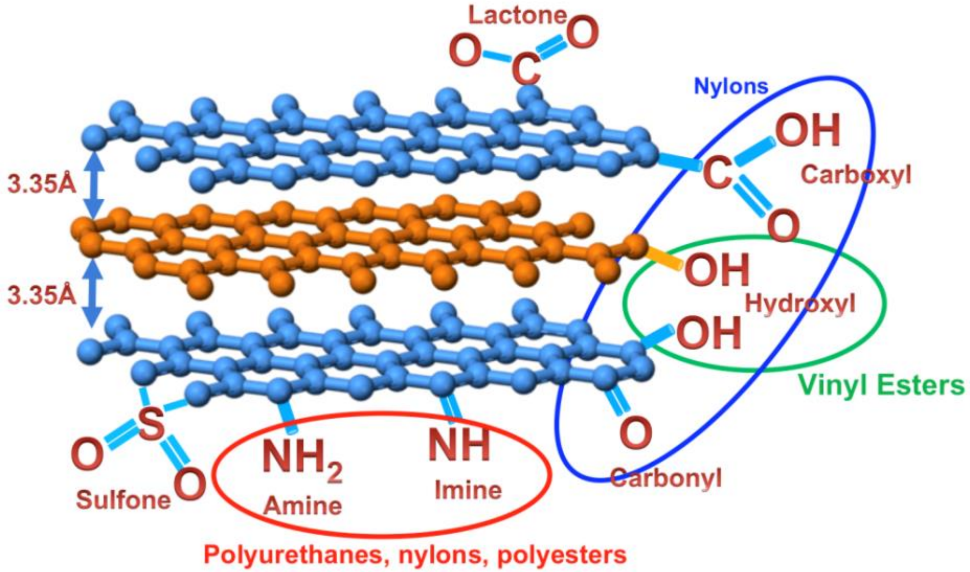
Substantial advances with MAP demonstrated:

- Demonstrated stable system in 8 hour continuous operation
- Successfully scaled from 3 to 5 tows meeting all property requirements
- Reduced effluents to enhance economic feasibility
- Low thermal inertia – rapid turnaround for maintenance, repair, and production set-up:
- 20 min for MAP vs. 12-40 hrs for conventional.
- Lower residence time enhances output and reduces energy consumption (smaller footprint)
- Lower temperature operation versus conventional process with equivalent fiber mechanical properties
- Cost savings driven by substantially reduced carbonization, abatement, and surface treatment processing costs

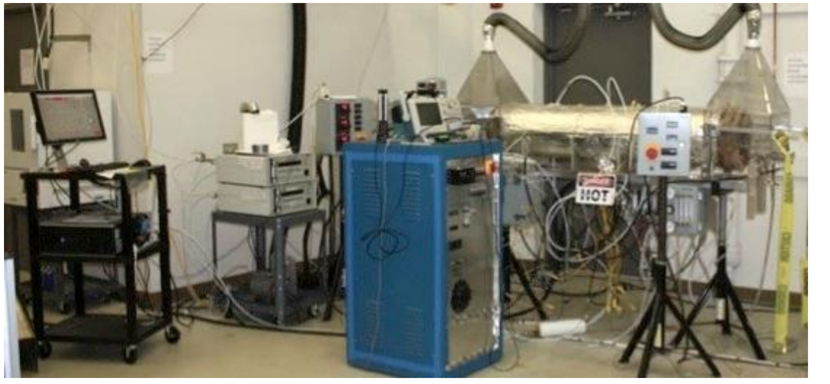
	Conventional Technology	Advanced Carbonization	Savings*
1500 t/y Scale	$10.20	$8.89	$1.31 (13%)

* From cost model

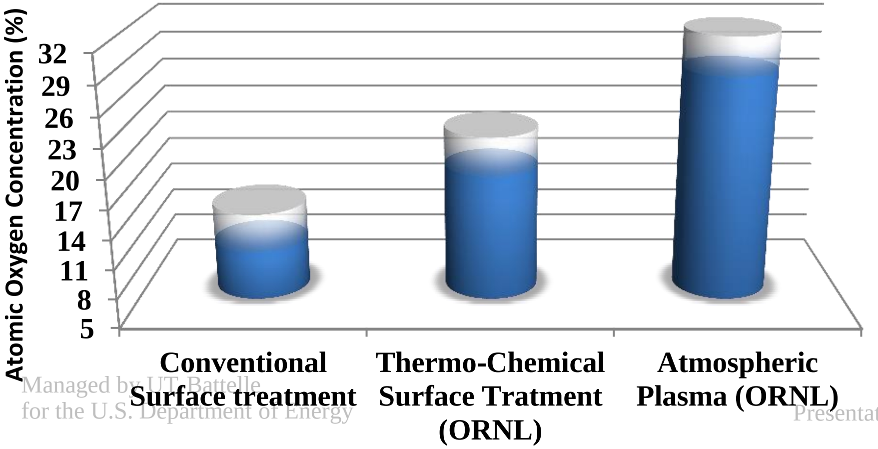
Thermo-chemical and Plasma Surface Treatment + New Sizings



Atmospheric Plasma



* Allows for the use of far less fiber in the composite which yields a significant per part cost reduction. 10-20% fiber use reduction possible reducing overall composite part cost. Example: 50% fiber / 50% resin part made of $12/lb CF and $1/lb resin would have $6.50 in material costs. A 20% reduction in fiber use would yield a 40% fiber / 60% resin part which would have $5.40 in material cost.



THERMOCHEMICAL

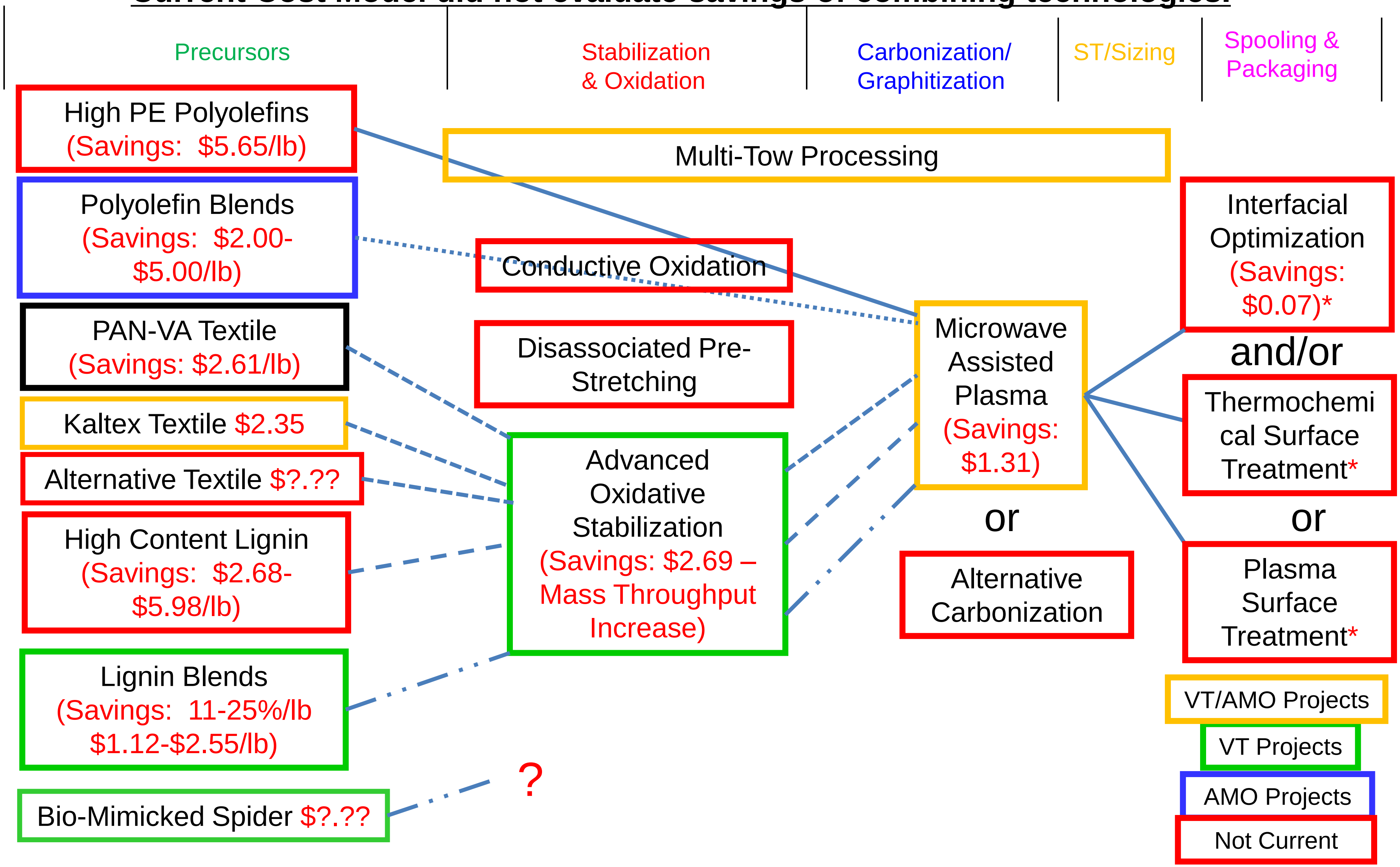
- Double the oxygen concentration on the carbon fiber surface as compared to Electrochemical industrial practice
- Very high volume of OH (15%) and COOH (5%) groups and no carbonyl,
- 20% higher short beam shear compared to industrial practice with VE

Critical Pathways for Achieving $5-7/lb Goal

The goal can be accomplished by combining technologies.

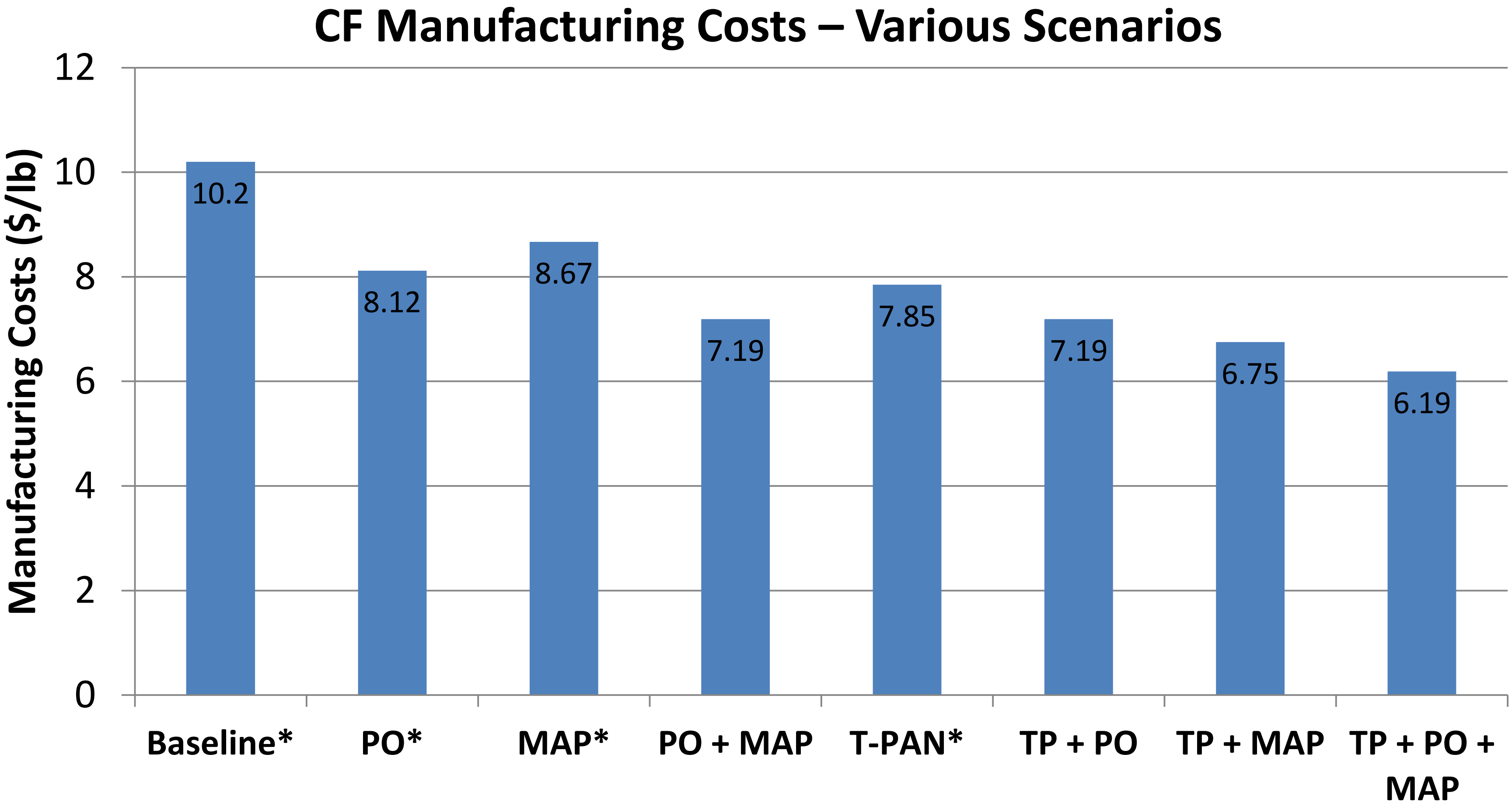
Savings from $10.20 baseline. $0.85/lb additional savings available from volume scale-up.

<u>Current Cost Model did not evaluate savings of combining technologies.</u>



Integrating Multiple Technologies

Savings from $10.20 baseline. $0.85/lb additional savings available from volume scale-up.



Note: Results for combined technologies from an Earlier cost Model (circa 2009) but the baseline, PO, MAP and T-PAN numbers were reconfirmed in the 2012 cost model.*

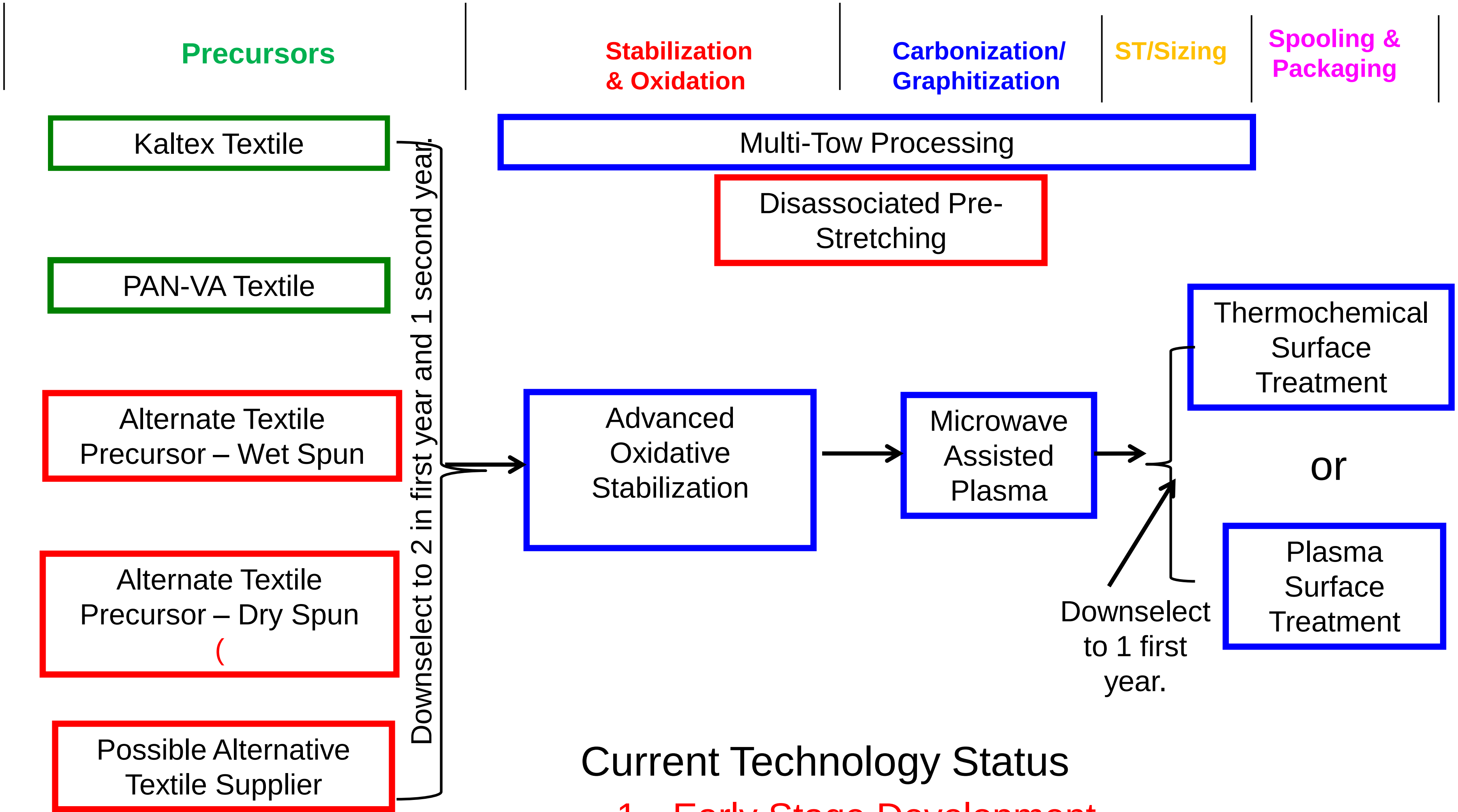
PO – Plasma Oxidation

T-PAN – Textile PAN

MAP – Microwave Assisted Plasma Carbonization

IF asked to Develop LCCF in the Shortest Time, Lowest Risk

Savings from $10.20 baseline. $0.85/lb additional savings available from volume scale-up.



Current Technology Status

1. Early Stage Development
2. Initial Integration of Technologies
3. Pre-Production Demonstration

Low Cost Carbon Fiber: Potential Applications

Materials

Civil Infrastructure
Rapid Repair and Installation, Time and Cost Savings

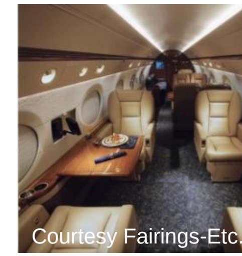
Bio-Mass Materials
Alternative Revenue
Waste Minimization

FUELING OUR FUTURE BIOMASS 2008

Non-Traditional Energy
Geothermal, Solar & Ocean Energy

Non-Aerospace Defense
Light Weight, Higher Mobility

Aerospace
Secondary Structures



Electronics
Light Weight, EMI Shielding

Other Industries have Interest. CF Manufacturers who adopt new technologies will do so only if they can sell into multiple markets with minimal risk.

Energy Storage
Flywheels, Li-Ion Batteries, Supercapacitors

Power Transmission
Less Bulky Structures
Zero CLTE

Oil and Gas
Offshore Structual Components

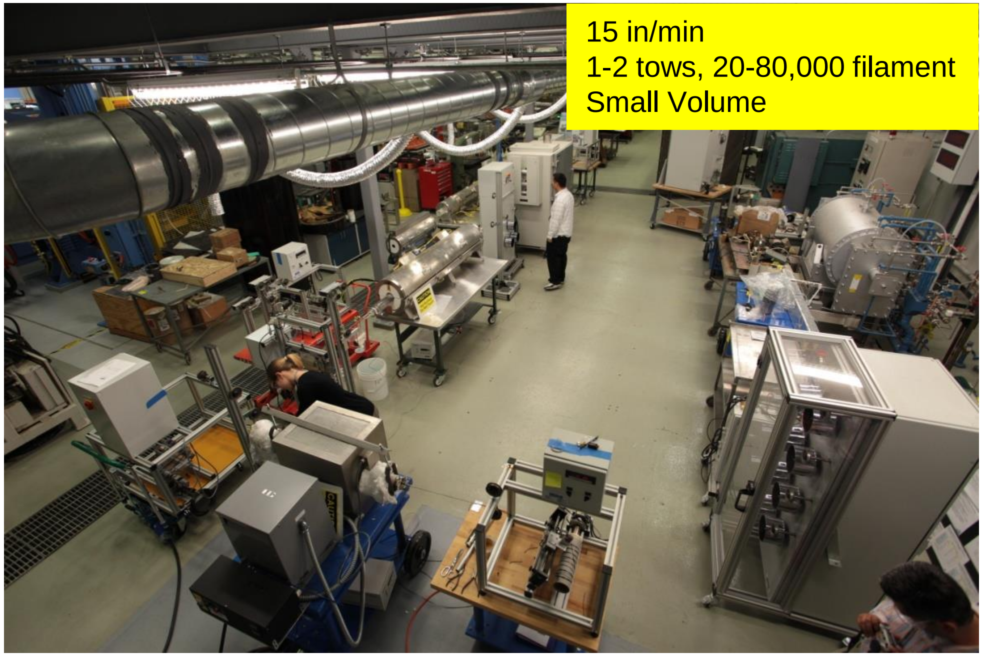
Vehicle Technologies
Necessary for 50+% Mass Reduction

Wind Energy
Needed for Longer Blade Designs

Pressurized Gas Storage
Only Material With Sufficient Strength/Weight

Carbon Fiber Research Facilities

15 in/min
1-2 tows, 20-80,000 filament
Small Volume



Precursor & Fiber Evaluation Lab

1:20 speed of a commercial grade production line
Capacity for 1-5 tows, 5000-80,000 filments
Preferred tow size ≥ 3k

Pilot Line

3 Scales of Development Lines + Analytical Labs

Full Speed Line
25 Tons/year Capacity, 3,000 – 620,000 Filaments/Tow
Fully integrated, Multi-format design

Carbon Fiber Technology Facility