The Carbon Fiber Conversion Process and Future Market Potential and Optimizations

Presented at TECHNICAL SESSION A4: CARBON FIBERS & COMPOSITES
CCM 12 – Mumbai, November 2, 2012
Agenda

• Fiber Production & the Role of Carbonization
• Thermal Conversation Process
  - Flowsheet and Layouts
  - Unit Operations Overview
  - Utilities
• Scale of Operations
• Impact of Precursors
• The Road Towards Optimization
Goals and Objectives

1. Give all attendees a strong base-level understanding of CF Conversion
2. Understand the state-of-the-art with regard to Scales of Operation
3. Understand the Role of utilities, influents and effluents at each Unit Operation (Understand Environmental Impact)
4. Stimulate discussion about where the industry is going
About Harper
About Harper

- Headquartered outside of Buffalo, NY
- Established in 1924
- 45,000 ft\(^2\) manufacturing facilities
- 5,500 ft\(^2\) dedicated Technology Center
- Multi-disciplined engineering talent
  - Chemical
  - Ceramic
  - Mechanical
  - Electrical
  - Industrial
  - Process & Integration
Core Skills:

- Scale up of New or Challenging Processes
  - 200°C – 3000°C
  - Atmospherically Controlled
  - Continuous Processing

- Construction Techniques in Metallic > Ceramic > Graphitic
- Integrated Systems Design – Plant Supply
- Complex Flows of Advanced Materials
- Precise Control of Gas - Solid Interactions
About Harper

Carbon Fiber Market
Advanced Thermal Systems for Fiber Processing

- PAN based C-fiber
- Pitch based C-fiber
- Rayon based C-fiber
- Alternative Precursor Development
- Carbon Nano Tubes
- Carbon Fiber Recycling

A Broad Experience Base in a Range of Carbon Processes
About Harper

Services to the Carbon Fiber Market

- **Equipment Supply (~40 Years)**
  - LT Furnaces, HT Furnaces and UHT Furnaces
  - Atmospherically Controlled Oxidation Ovens
  - Surface Treatment & Drying
  - Material Mass Transport & Waste Gas Treatment

- **Complete System Supply (~15 Years; >10 contracts)**
  - Systems Integration and Energy Recovery

- **Feasibility Studies & Modeling**
- **Retrofits, Revamps & Upgrades**
- **Business Development & Consulting**
- **Training & Optimizations**
About Harper
Harper International
CF Line Full Line Scope of Supply

Leaders in the Supply of Complete Carbon Fiber Systems
Historical Development of CF, CF Precursors and Precursor Processes
Carbon Fiber Process Overview

- Polymerization
- Spun Fiber
- Stabilization / Oxidation
- Carbonization
- Graphitization
- CF
Total Carbon Fiber Process
Precursor to Application

Conversion is but a part of the overall process
PAN Carbonization

Chemistry of the Process:

- Oxidation (200°C – 300°C) Aligns and Closes Polymer Rings and Forms Off Gas
- LT (<1000°C) Interconnects Polymer Chains Off Gas and Remove Impurities
- HT Further (1400°C – 1800°C) Interconnects Polymer Chains Off Gas and Remove Impurities
- UHT (2400°C – 2800°C) delivers higher modulus

Ovens & Furnaces are required to make Carbon Fiber
Historical Development of Carbon Fibers

**Graph:**
- Specific Tensile Strength vs. Specific Young's Modulus for various materials:
  - Int. Mod. Pan-based Carbon (Type II)
  - HM Pan-based Carbon (Type I)
  - S glass
  - Boron
  - Sic (Nicalon)
  - Al₂O₃
  - HM Pitch based Carbon

**Table:**

<table>
<thead>
<tr>
<th>Major Constituent</th>
<th>Strength (MPa)</th>
<th>Tensile Modulus (GPa)</th>
<th>Tensile Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina (1)</td>
<td>1750</td>
<td>154</td>
<td>2.7</td>
</tr>
<tr>
<td>Alumina (2)</td>
<td>2275</td>
<td>224</td>
<td>3.0</td>
</tr>
<tr>
<td>Silicon carbide (3)</td>
<td>3920</td>
<td>406</td>
<td>3.0</td>
</tr>
<tr>
<td>Boron (4)</td>
<td>3600</td>
<td>400</td>
<td>2.5</td>
</tr>
<tr>
<td>Glass (5)</td>
<td>4580</td>
<td>86</td>
<td>2.5</td>
</tr>
<tr>
<td>Carbon (6)</td>
<td>5500</td>
<td>330</td>
<td>2.7</td>
</tr>
</tbody>
</table>

(1) Nextel 312, 3M, Minneapolis, MN
(2) Nextel 400
(3) Avco SCS 6, Textron Inc. Lowell, MA
(4) Avco Boron
(5) S-Glass, Corning Glass, Corning, NY
(6) MS-40, Grafil, Sacramento, CA
## CF Precursors & Recovery

<table>
<thead>
<tr>
<th>Chemistry</th>
<th>Maximum</th>
<th>Typical</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAN</td>
<td>68% max</td>
<td>(50% typical)</td>
</tr>
<tr>
<td>Cellulose</td>
<td>44% max</td>
<td>(20% - 30% typical)</td>
</tr>
<tr>
<td>Lignin</td>
<td>67% max</td>
<td>(typical ?)</td>
</tr>
<tr>
<td>Pitch</td>
<td>85% max</td>
<td>(w/o solvent)</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>85% Max</td>
<td>(25% - ?? w/ solvent)</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>85% Max</td>
<td>(typical ?)</td>
</tr>
</tbody>
</table>

The Precursor can have a significant impact on Plant Economics
Carbon Fiber Polymerization

Common Solvents for PAN Precursor

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Chemical Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaSCN</td>
<td>Sodium ThioCyanante</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethylformamide (CH₃)₂NC(O)H</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethyl Sulfoxide (CH₃)₂SO</td>
</tr>
<tr>
<td>DMAC</td>
<td>Dimethylacetamide CH₃C(O)N(CH₃)₂</td>
</tr>
</tbody>
</table>

Even within the predominate Precursor type (PAN), there are significant differences in the Precursor process, Plant Economics, and Product Quality.
# Historical Development of Carbon Fibers

<table>
<thead>
<tr>
<th>Date</th>
<th>Precursor</th>
<th>HTT (°C)</th>
<th>Strength (MPa)</th>
<th>Modulus (GPa)</th>
<th>Density (g cm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1957</td>
<td>Rayon</td>
<td>1000</td>
<td>275</td>
<td></td>
<td>1.3</td>
</tr>
<tr>
<td>1959</td>
<td>Rayon</td>
<td>2500</td>
<td>350–1000</td>
<td>40</td>
<td>1.5</td>
</tr>
<tr>
<td>1961</td>
<td>PAN</td>
<td>—</td>
<td>550–700</td>
<td>170</td>
<td>—</td>
</tr>
<tr>
<td>1965</td>
<td>Hot stretched rayon</td>
<td>2500</td>
<td>1250</td>
<td>170</td>
<td>—</td>
</tr>
<tr>
<td>1965</td>
<td>Isotropic pitch</td>
<td>1000</td>
<td></td>
<td>70</td>
<td>—</td>
</tr>
<tr>
<td>1966</td>
<td>PAN-HT</td>
<td>1400</td>
<td>2000</td>
<td>250</td>
<td>1.76</td>
</tr>
<tr>
<td>1966</td>
<td>PAN-HM</td>
<td>2600</td>
<td>1600</td>
<td>480</td>
<td>1.91</td>
</tr>
<tr>
<td>1970</td>
<td>Hot stretched rayon</td>
<td>2600</td>
<td>2600</td>
<td>520</td>
<td>1.90</td>
</tr>
<tr>
<td>1971</td>
<td>Stretched pitch</td>
<td>2500</td>
<td></td>
<td>480</td>
<td>2.0</td>
</tr>
<tr>
<td>1973</td>
<td>Mesophase pitch</td>
<td>2800</td>
<td>1900</td>
<td>380</td>
<td>2.0</td>
</tr>
<tr>
<td>1976</td>
<td>Mesophase pitch</td>
<td>3000</td>
<td>2200</td>
<td>700</td>
<td>2.15</td>
</tr>
<tr>
<td>1980</td>
<td>PAN-IM</td>
<td>—</td>
<td>4000</td>
<td>300</td>
<td>1.81</td>
</tr>
<tr>
<td>1985</td>
<td>5µ PAN-HT</td>
<td>—</td>
<td>5000</td>
<td>260</td>
<td>1.80</td>
</tr>
<tr>
<td>1986</td>
<td>5µ PAN-HM</td>
<td>—</td>
<td>3400</td>
<td>400</td>
<td>1.88</td>
</tr>
<tr>
<td>1990</td>
<td>Mesophase pitch</td>
<td>3000</td>
<td>2000</td>
<td>840</td>
<td>2.15</td>
</tr>
</tbody>
</table>
### Historical Development
Recent Production Capacities (2010)

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Small tow (metric tonnes)</th>
<th>Small tow (lb)</th>
<th>Large tow (metric tonnes)</th>
<th>Large tow (lb)</th>
<th>ID# *</th>
</tr>
</thead>
<tbody>
<tr>
<td>AKSA</td>
<td>1,800</td>
<td>4,000,000</td>
<td></td>
<td></td>
<td>27262</td>
</tr>
<tr>
<td>Cytec Industries</td>
<td>2,300</td>
<td>5,000,000</td>
<td></td>
<td></td>
<td>24960</td>
</tr>
<tr>
<td>Dalian Xingke Carbon Fiber</td>
<td>600</td>
<td>1,320,000</td>
<td></td>
<td></td>
<td>27750</td>
</tr>
<tr>
<td>Formosa Plastics</td>
<td>7,300</td>
<td>16,000,000</td>
<td></td>
<td></td>
<td>27264</td>
</tr>
<tr>
<td>Grafil</td>
<td>2,000</td>
<td>4,400,000</td>
<td></td>
<td></td>
<td>26890</td>
</tr>
<tr>
<td>Hexcel</td>
<td>7,300</td>
<td>16,000,000</td>
<td></td>
<td></td>
<td>25238</td>
</tr>
<tr>
<td>Kemrock</td>
<td>650</td>
<td>1,430,000</td>
<td></td>
<td></td>
<td>26142</td>
</tr>
<tr>
<td>Mitsubishi Rayon</td>
<td>6,150</td>
<td>13,530,000</td>
<td>2,750</td>
<td>6,060,000</td>
<td>27836</td>
</tr>
<tr>
<td>SGL Carbon</td>
<td></td>
<td>6,500</td>
<td>14,300,000</td>
<td></td>
<td>25642</td>
</tr>
<tr>
<td>Toho Tenax</td>
<td>13,500</td>
<td>29,620,000</td>
<td></td>
<td></td>
<td>26204</td>
</tr>
<tr>
<td>Toray Industries</td>
<td>17,900</td>
<td>39,440,000</td>
<td>300</td>
<td>660,000</td>
<td>26964</td>
</tr>
<tr>
<td>Yingyou Group</td>
<td>220</td>
<td>484,000</td>
<td></td>
<td></td>
<td>72402</td>
</tr>
<tr>
<td>Zoltek Corp.</td>
<td></td>
<td>8,750</td>
<td>19,300,000</td>
<td></td>
<td>26150</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>59,700</strong></td>
<td><strong>131,240,000</strong></td>
<td><strong>18,300</strong></td>
<td><strong>40,320,000</strong></td>
<td></td>
</tr>
</tbody>
</table>

A list of the world’s current carbon fiber manufacturers, compiled by HPC. Capacity estimates for the year 2010 are based on public information about ongoing expansions that was available to HPC in December 2008. Source: CompositesWorld
The Carbon Fiber Thermal Conversion Process

- Flowsheet
- Unit Operations
- Scale of Operations
Carbon Fiber Thermal Conversion Process

Precursor (typically PAN)

Nitrogen
CW
Energy
Natural Gas
Oils & Electrolytes
Resins
DI Water

Pretreatment
Oxidation 300C
Low Temperature Carbonization (800-1000C)
High Temperature Carbonization (1600-1800C)
After Treatment: Stage 1
After Treatment: Stage 2
Online Winding

Waste Gases
CO, CO₂
N₂ gases (HCN, Nox NH₃)
Sox, Tars, Misc.

Reject Heat & CW

Wastewater
Spent Aq. Soln.
Spent Agents

Carbon Fiber

Online Winding
Carbon Fiber Conversion Process

- Complexity and Cost added through Waste Gas Treatment
- Significant Opportunity for Energy Recovery and Cost Reduction; through further Flowsheet sophistication
Harper International
General Arrangement / Layout

Complete Industrial Scale Pilot Line
Typical Plant Layout
Facility Layout – General Overview

- Line Widths (Width of Tow Band) 300mm – 4200mm
- Facility Widths 10x – 20x Tow Band
  - 2m Wide Research Lab
  - 10m Wide Pilot Plant
  - 30m Wide Industrial Line
- Facility Lengths 10x – 15x Facility Width
  - Long Linear Layout Typical
- Exclusive of OSBL Items N2 Plant, Electrical Substation, Cooling Tower
Scale of Operations
### Review of Scales of Operations

<table>
<thead>
<tr>
<th>Scales</th>
<th>Size Range (mm Width)</th>
<th>Capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Production</td>
<td>1000mm-4200mm</td>
<td>100tpy to more than 4000tpy</td>
</tr>
<tr>
<td>Industrial Scale Pilot</td>
<td>300mm-1000mm</td>
<td>20tpy-100tpy</td>
</tr>
<tr>
<td>Micro Scale (University, Institute)</td>
<td>&lt;100mm</td>
<td>Less than 3 tpy</td>
</tr>
</tbody>
</table>
Review of Scales of Operations

Capacity Expansion 2011 - 2012 Based on Faster Line Velocities; Higher Production Rates from 3m Single Muffle
Scale of Operations

• Modern Line Speeds
  At 10m/min – 20 m/min for a state of the art line

• Oxidation Oven Capacities
  More Than 500 – 750 kg/hr feed of PAN
  More than 500 m – 1000m Overall Heated Length
  4 Zones Minimum; Typically 6 – 8 Zones
  Widths up to 4m -- 3m wide designs are becoming more common
  Unsupported Heated Lengths typically less than 15m

• LT and HT Furnaces Understand Your Process and the Impact of Technical Specifications
  Widths up to 4m -- 3m wide designs wide are dominant state of the art
  Unsupported Heated Lengths 15 m – 20m
  HT Temperatures Regimes <1450C, 1600C, and 1800C or greater
Carbon Fiber Systems
Cost Versus Capacity

Refined Model:
Carbon Fiber Thermal Conversion
Historical Growth Trends
& Future Optimization
Five Important Historical Steps Towards Efficiency that have Supported Carbon Fiber Capacity Expansion:

1. Increase of Scale (Wider and Longer)
2. Treatment of Oxidation Oven Exhaust & Potential for Energy Recovery
3. Closed Pipe Treatment of Furnace Exhausts & Potential for Energy Recovery
4. Low Profile Furnace Muffles for Reduced Gas Consumption
5. Movement Towards Sealed Oxidation Oven Design
Challenges in Carbon Fiber Operations to Capturing Projected Growth

Cost Dynamics as a Function of Scale-Up

Asymptote Indicative of Diminishing Returns
Closed Pipe Treatment of Furnace Exhaust

TOX capable of also treating LT & HT Process Exhausts as well the Ventilation Hoods (LT Hoods, HT Hoods, Oven Vestibules)
Low Profile Muffle Design
To Reduce Nitrogen Consumption

Nitrogen Consumption Model Reduction Based on Muffle Design
Treatment of Oxidation Oven Exhaust:
Integration & Heat Recovery
2m and 3m (6 Zone Designs)

<table>
<thead>
<tr>
<th>Line Width</th>
<th></th>
<th>2m Wide</th>
<th>3m Wide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidation Oven Zones</td>
<td>#</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Exhaust Rate</td>
<td>Nm³/hr</td>
<td>20760</td>
<td>43200</td>
</tr>
<tr>
<td>Exhaust Temp</td>
<td>°C</td>
<td>260</td>
<td>260</td>
</tr>
<tr>
<td>Ambient Temp</td>
<td>°C</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>Delta T</td>
<td>°C</td>
<td>235</td>
<td>235</td>
</tr>
<tr>
<td>Energy Lost</td>
<td>kw</td>
<td>1633</td>
<td>3399</td>
</tr>
</tbody>
</table>
Shift Towards Sealed Oxidation Oven Design

Integration & Heat Recovery 2m and 3m (6 Zone Designs)

<table>
<thead>
<tr>
<th>Line Width</th>
<th>m</th>
<th>2m Wide</th>
<th>3m Wide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidation Oven Zones</td>
<td>#</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Total Exhaust Rate</td>
<td>Nm3/hr</td>
<td>20760</td>
<td>43200</td>
</tr>
<tr>
<td>Exhaust Temp</td>
<td>C</td>
<td>260</td>
<td>260</td>
</tr>
<tr>
<td>Ambient Temp</td>
<td>C</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>Delta T</td>
<td>C</td>
<td>235</td>
<td>235</td>
</tr>
<tr>
<td>Energy Lost</td>
<td>kw</td>
<td>1633</td>
<td>3399</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>% MakeUp to Exhaust</th>
<th>%</th>
<th>0.75</th>
<th>0.75</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preheated Make Up</td>
<td>Nm3/hr</td>
<td>15570</td>
<td>32400</td>
</tr>
<tr>
<td>Make Up Temperature</td>
<td>C</td>
<td>260</td>
<td>260</td>
</tr>
<tr>
<td>Ambient Temp</td>
<td>C</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>Offset</td>
<td>kw</td>
<td>1225</td>
<td>2549</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Hours Per Year</th>
<th>kw</th>
<th>&gt;7000</th>
<th>&gt;7000</th>
</tr>
</thead>
<tbody>
<tr>
<td>USD$ / kw-hr</td>
<td>$</td>
<td>$0.10</td>
<td>$0.10</td>
</tr>
<tr>
<td>USD$ / year</td>
<td>$</td>
<td>$903,150</td>
<td>$1,879,385</td>
</tr>
</tbody>
</table>
Carbon Fiber Expansion: Challenges to Capturing Growth
Challenges in Carbon Fiber Operations to Capturing Projected Growth

- Diminishing returns in optimization of current scale systems
- Development costs associated with next generation technology
- Need for increased efficiency of chemical reaction
- Reducing carbon footprint
Harper Beacon

Challenges:
1) **Diminishing Returns**: The Opportunity for Increased Efficiency In Scale is Declining
2) **Consumer Market Adoption**: At Higher Volumes a Better Understanding of Environmental Impact is Required (Automotive)

Opportunities:
1) **Create Tool** to Rank Environmental Impact of Various Production Schemes
2) **Understand Impact** of Scale and Configuration on Environmental as well as Cost
3) **Use the Tool to Identify** Opportunities for Greater Total Efficiency
CO2 Emissions Modeling

**Theoretical CO2 Emission for CF Production***:
- Polymer Losses (Footprint of Polymer Production Ignored)
- Sensible Heat of Reaction (Polymer and Purge Gases)
- Source of Energy

**Actual CO2 Emission for CF Production***:
- Polymer Losses (Footprint of Polymer Production Ignored)
- Sensible Heat of Reaction (Polymer and Purge Gases)
- Energy Summarized by Unit Operation
- Thermal Losses
  - Heat Rejected to Atmosphere
  - Heat Rejected To Cooling Water
- Waste Gas Abatement Technology (Major Schemes Considered)
- Source of Energy

* Energy Requirement to Produce Purge Gas Ignored
## CO2 Emissions Modeling

**Primary Results from Sample Evaluation:**

<table>
<thead>
<tr>
<th></th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Production Rates:</strong></td>
<td>500 – 2250</td>
<td>TPY</td>
</tr>
<tr>
<td><strong>Line Sizes:</strong></td>
<td>1750 &amp; 3000</td>
<td>mm Wide</td>
</tr>
<tr>
<td><strong>CO2 Emissions</strong>:</td>
<td>9.7 – 23.4</td>
<td>kg CO2 Per kg CF</td>
</tr>
<tr>
<td><strong>Theoretical CO2</strong>:</td>
<td>2.7 (average)</td>
<td>kg CO2 Per kg CF</td>
</tr>
</tbody>
</table>

(*Energy to Produce Purge Gas Ignored*)

<table>
<thead>
<tr>
<th></th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CAPEX</strong></td>
<td>$2.17 – $4.55</td>
<td>USD / kg of CF</td>
</tr>
<tr>
<td><strong>OPEX</strong></td>
<td>$6.27 – $14.58</td>
<td>USD Per kg CF</td>
</tr>
</tbody>
</table>

Sample Data from [www.harperbeacon.com](http://www.harperbeacon.com)
Sample Data from www.harperbeacon.com
Beacon Summary

Plan to capture greater opportunities ahead must include continued equipment improvements with a holistic perspective of the process & operating economics.
Building a Carbon Fiber Business
Navigating the Challenges
Optimizing the Project Development Timeline

• How to Establish a Technology Position
  
  Buy, Joint /Venture, License Technology, Develop Technology
  What about a Process Design Package

• First Target Fiber Type, Properties and Capacity
  
  Led By Business Planning and Market Development Efforts

• Understand Your Process and the Impact of Technical Specifications
  
  Empirical Investigation of Material Packing Density (Tow Spacing is Critical)
  Empirical Investigation of Residence Time and Each Process Step

  Market Size and Empirical Data Will Determine Line Size and Unit Op. Design

• Consider Capacity and Other Needs – Is a Single Line Enough?
  
  Capacity Limitations of Single Lines
  How is Product Development Handled
  How Is Training and Staff / Operations Development Handled
  Industrial Pilot and MicroLine Options
Typical Development Timeline

• Precursor Development & Bench Scale Investigation
  0 – 60 Months in Duration (Buy, Develop, License)

• Pilot Scale Investigation, Scale Up, Validation & Training
  3 – 24 Months in Duration (Test at Harper Facility – vs- Own)

• Production Scale Project Execution
  15 – 30 Months in Duration (Experience & Execution Plan)

• Operations Fine Tuning
  3 – 24 Months in Duration (Oper. Experience & Training)

• Production Scale Operation: Total Time Line

Total Time Line for Reaching Production Scale Operation

20 Months to More than 10 Years
Typical Development Timeline

Timeline to Production Scale Operations for Emerging Producers

- Precursor Development
- Bench Scale Investigations
- Pilot Scale & Training
- Production Plant Project Execution
- Operations Fine Tuning
- Optimized Production Scale Operation

Time Line (Months)

- Bench Scale Investigations
- Pilot Scale
- Production Scale
- Optimized Operations (Nameplate)
Harper International Carbon Fiber MicroLine

Complete Thermal Conversion System
For Research and Development of Carbon Fiber
On a Continuous Processing Basis
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