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Manufacturing Carbon Fiber from Pitch – Equipment Scale and Considerations

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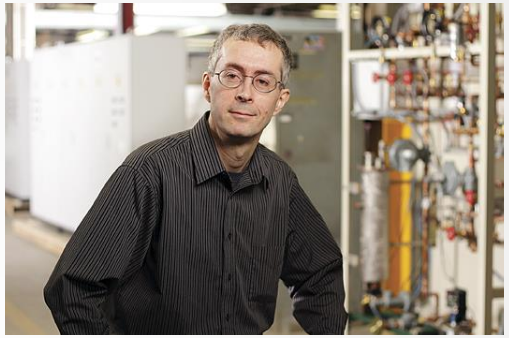
About Harper

- An Employee-Owned Company
- Headquartered in Buffalo, NY
- On Site Technology Center
- Multi-Disciplined Engineering Talent
  - Chemical
  - Ceramic
  - Mechanical
  - Electrical
  - Industrial
  - Process & Integration



About Harper

- Established Leader in Thermal Processing Systems
- Key Partner in Carbon Fiber Scale Up
- Primary focus:
  - New / Challenging / Advanced Material Processing
    - 200^oC - 3000^oC
    - Batch and Continuous Processing
    - Precise Atmospheric Controls
      - Inert, Hydrogen, Halogen, CVD
    - High Purity Requirements
    - Complex gas-solid interactions

The “Pitch” for Coal Tar Pitch

- Huge demand from automotive market → low cost light weight materials; potential enabler/accelerator for Electric Vehicles (EV’s)
- Abundance of Coal
  - No excess capacity to produce more constituents of PAN (propylene and ammonia)
- “Green” use for coal that is not power generation → reduction in carbon emissions
- Redeployment of coal miners (U.S. coal production, consumption and employment are at lowest levels in 40 years) → re-energize the market
- Less utilities to process into Carbon Fiber → lower kW/kg
- Cost advantage of Pitch precursor compared to PAN precursor (raw material ~$0.75/kg versus $2-$3/kg)
- Lower kW/kg + Lower precursor cost = Low cost carbon fiber → high value

Why is Pitch making a Comeback?

- Increasing world capacity of carbon fiber not enough – need to lower $/kg
  - 50k industrial grade PAN fiber can be obtained for $15 - $18/kg
  - Low carbon steel coil $1.10/kg
  - Recycled aluminum $2.27/kg
- Large (massive) scale production is needed in order to meet demand and lower cost
  - Alternate precursors such as lignin have has had limited success and long road ahead

Pitch versus PAN

- **Pitch**
- Polycyclic aromatic hydrocarbon
- CF yield >70%
- High modulus, moderate tensile strength, excellent conductivity
- Tows < 1.5k
- Raw material ~$0.70/kg
- Typically cannot support its own weight

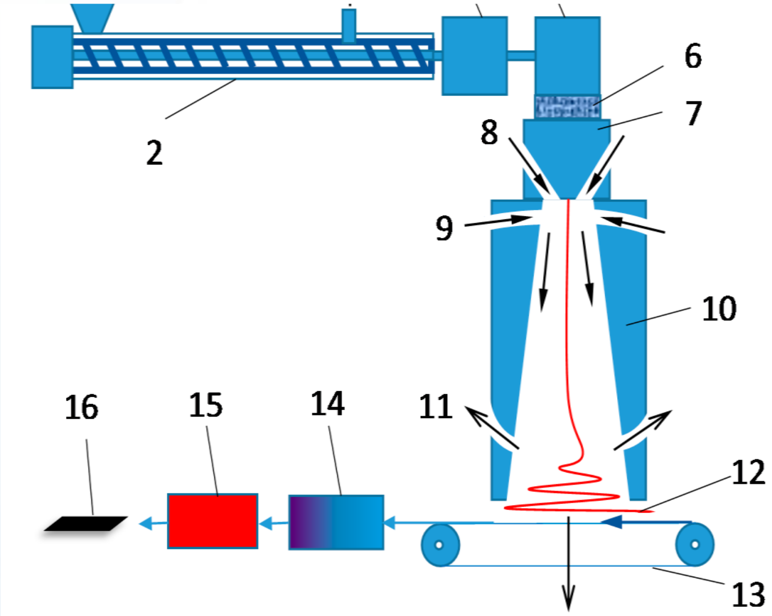
- **PAN – Polyacrylonitrile**
  - Vinyl polymer
  - CF yield 50-55%
  - High tensile strength, moderate modulus, good conductivity
  - Tows 1k – 600k
  - Raw material $2-$3/kg
  - Can support its own weight

Pitch Precursors – Basic Introduction

- Higher carbon fiber yield >70% versus 55% for PAN
- Two types → Isotropic and Anisotropic (Mesophase)
  - Isotropic Pitch – weak structural orientation of carbon atoms and underdeveloped graphite crystallinity result in carbon fiber with a low modulus
  - Mesophase Pitch – highly orientated molecular structure and high crystallinity results in carbon fiber with a higher modulus than conventional PAN fibers
    - Majority of carbon fiber made from pitch is made from mesophase pitch
      - Can achieve a high degree of orientation of hexagonal layers along fiber axis during spinning so stretch during thermal processing is not required

Pitch Carbon Fiber Process – Simplistic View

- A schematic diagram of a melt blown fiber spinning apparatus and thermal processes for manufacturing pitch-based CFs.[1]



1-pitch feeding
2-extruder
3-exhaust vent
4-ballast pump
5-spinning pump
6-filter
7-spinneret head
8-primary air stream
9-secondary air stream
10-diffuser
11-air exhaust
12-spun fiber web
13-moving belt collector
14-stabilization oven
15-carbonization furnace
16-CF web

[1] "*Meltblown Solvated Mesophase Pitch-Based Carbon Fibers: Fiber Evolution and Characteristics*", Zhongren Yue, Chang Liu and Ahmad Vakili in Journal of Carbon Research. C 2017, 3 (26).

Pitch Carbon Fiber Process - Reality

- In order to have good carbon fiber you need good pitch precursor
  - Mixture of several thousand aromatic hydrocarbons
  - Composition primarily reliant on processing temperature and distillation time during purification
  - Conversion of Isotropic Pitch to Mesophase Pitch – pyrolysis or solvent treatment
    - If using solvent then the solvent needs to be removed

Pitch Precursor - Reality

- Non-textile → non self-supporting
- Scale-up target
  - How thick, how long, how fast…
  - Process window – how fast CAN things be driven in the thermal processing steps?

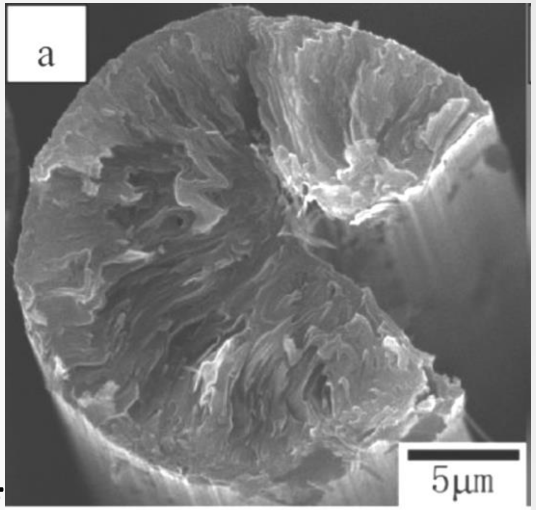
Pitch Carbon Fiber Manufacturing Process

Spinning → Stabilization → Carbonization

Spinning:

- Melt-spun or melt-blown through a circular nozzle spinneret
- Mesophase pitch can be melt spun, but flow characteristics make it difficult. Add solvents but need to be removed → Solvated Mesophase

- Melt spinning process affects internal structures and resulting fiber properties
  - If not controlled properly → significant carbon fiber defects, Example is "pac-man split" during carbonization[2]



[2] "*Effect of Liquid Crystalline Texture of Mesophase Pitches on the Structure and Property of Large-Diameter Carbon Fibers*", Guanming Yuan, Baoliu Li, Xuanke Li, Zhijun Dong, Wanjing Hu, Aidan Westwood, Ye Cong, and Jiang Zhang in ACS Omega 2019, 4, 1095-1102

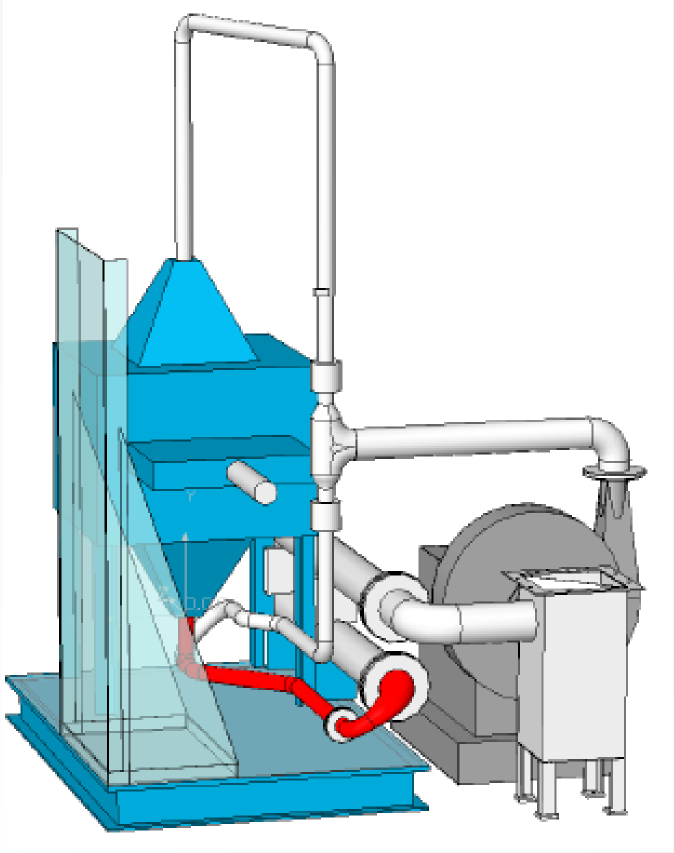
Pitch Carbon Fiber – Stabilization

- Cross-link fibers so they cannot be melted or fused together during carbonization
- For solvated mesophase precursor, devolitization of precursor important step
  - Is this step performed before stabilization equipment or is it part of equipment?
  - Will there be solvent recovery?
- Unlike PAN fiber tows, majority of pitch processes need a belt to support the fiber during stabilization
- Belt design to minimize “turn-around” losses and maintain product uniformity critical

Pitch Carbon Fiber – Stabilization

- Thermal and Air Velocity Uniformity
  - Typically material is spun onto a belt and a down flow air configuration
  - Critical how air is delivered to and through material as well as air velocity uniformity to prevent localized crushing of material
  - Simulation and Testing can help in design stages
    - Thermal and Velocity Uniformity Modeling
    - "Square Foot Furnace" testing
    - Test Module

Square Foot Furnace



- Air or Nitrogen - 1400^{o}C
- Convection and/or Radiation
- 12" x 12" up to 3" mat

THERMO, CHEMICAL, PROCESS MODEL OF NON-TEXTILE REINFORCING FIBER PRECURSOR

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ABSTRACT

One of the formats used for making advanced reinforcing fibers including non-PAN based carbon fiber has the precursor as a non-woven mat. The conversion process involves drying, curing and chemical conversion. The processes are complex involving exothermic and endothermic processes and material property changes as the thermal treatment progresses. Harper's model provides a general treatment of the overall process. Each of the individual processes is characterized by two to four parameters that can be determined using lab scale instruments. The model can be used to analyze the heating of nonwoven mats of arbitrary reinforcing fiber precursor (generally polymeric) fibers. The model uses radiation, convection, gas-phase conduction and process thermodynamics to predict the thermal and chemical profiles over time. Examples are discussed showing the use of the model to provide commercially interesting results, such as allowable bed depths, relationship between parameters and process time (equipment size / capacity).

Evaporation Examples

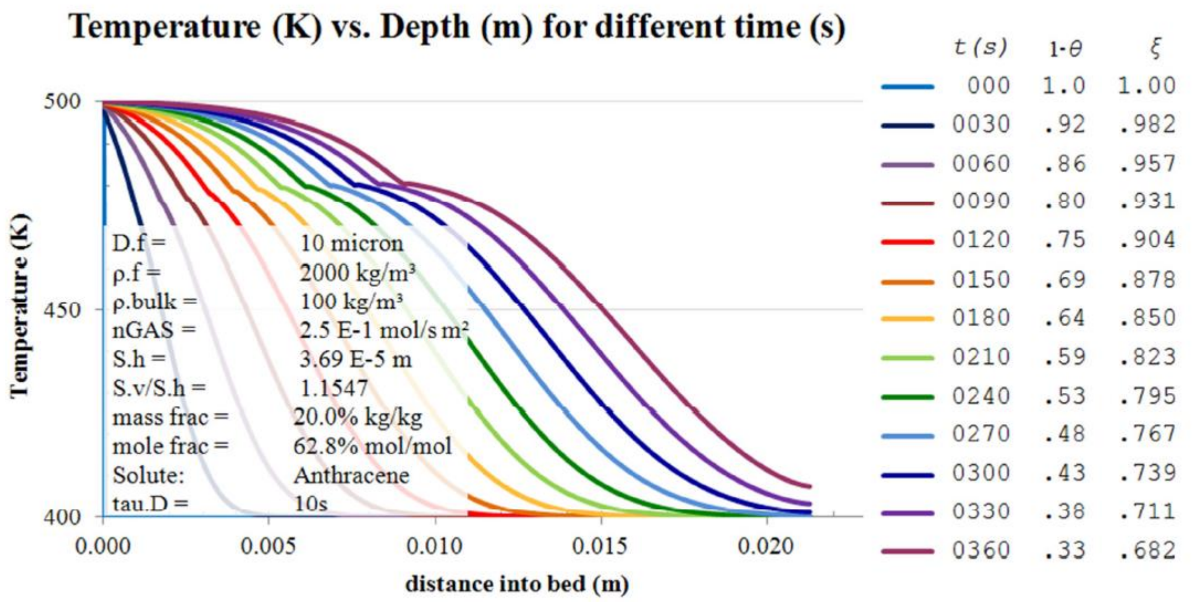

Figure 9: Comparison: dry (Figure 7, top, half-way point) and 20% volatile content.

Pitch Carbon Fiber – Carbonization

- Once fibers stabilized, heated >1250°C
- What the furnace looks like depends on the scale of production, precursor format and steps included (devolitization or not)
  - Will look vastly different from lab scale to research to pilot to production scale
- May need belt to support the mat
- How to transfer material from Stabilization to Carbonization? → Drums
  - Transfer drum from stabilization to carbonization then transfer drum from carbonization to cooling belt

Pitch Carbon Fiber – Carbonization

(12) **United States Patent**
Bencic

(10) **Patent No.: US 6,514,072 B1**
(45) **Date of Patent: Feb. 4, 2003**

(54) **METHOD OF PROCESSING CARBON FIBERS**

(75) Inventor: **David M. Bencic**, Batavia, NY (US)

(73) Assignee: **Harper International Corp.**, Lancaster, NY (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **09/862,928**

(22) Filed: **May 23, 2001**

(51) **Int. Cl.**[7] **F27B 9/28**
(52) **U.S. Cl.** **432/8**; 432/59
(58) **Field of Search** 432/59, 8; 226/97.3

(56) **References Cited**

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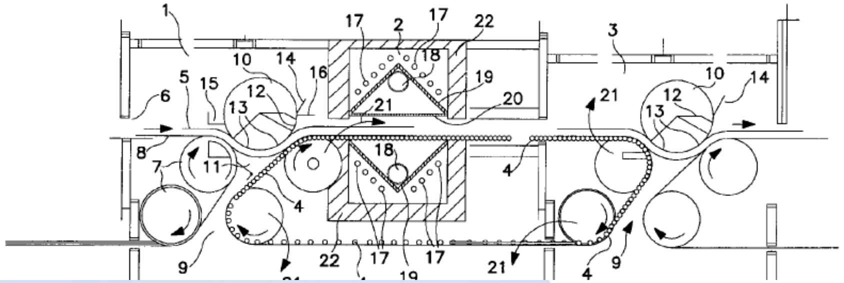
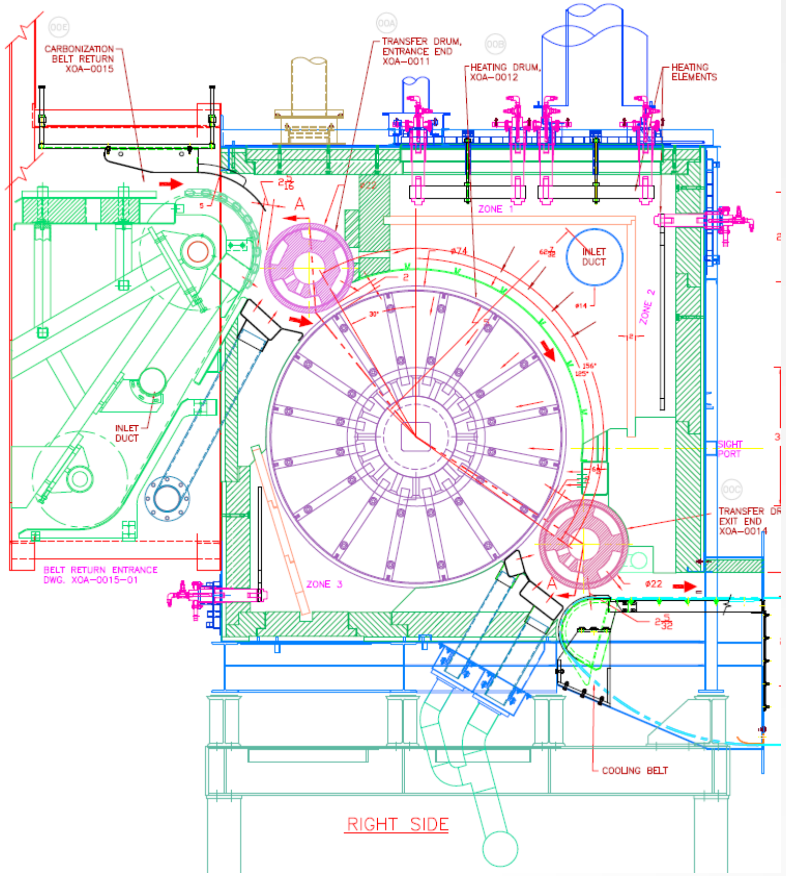
Primary Examiner—Jiping Lu
(74) *Attorney, Agent, or Firm*—Jaeckle Fleischmann & Mugel, LLP

(57) **ABSTRACT**

This invention is for a novel method of treating carbon fiber. Carbon fiber is a very unique material and its processing requires high temperatures. Also since carbon fibers are lightweight and porous, heating is accomplished in this process by radiation with a heated gas flowing through the material. Also a float is used to transfer the material from one process station to another so as to prevent delaminating of the carbon fiber.

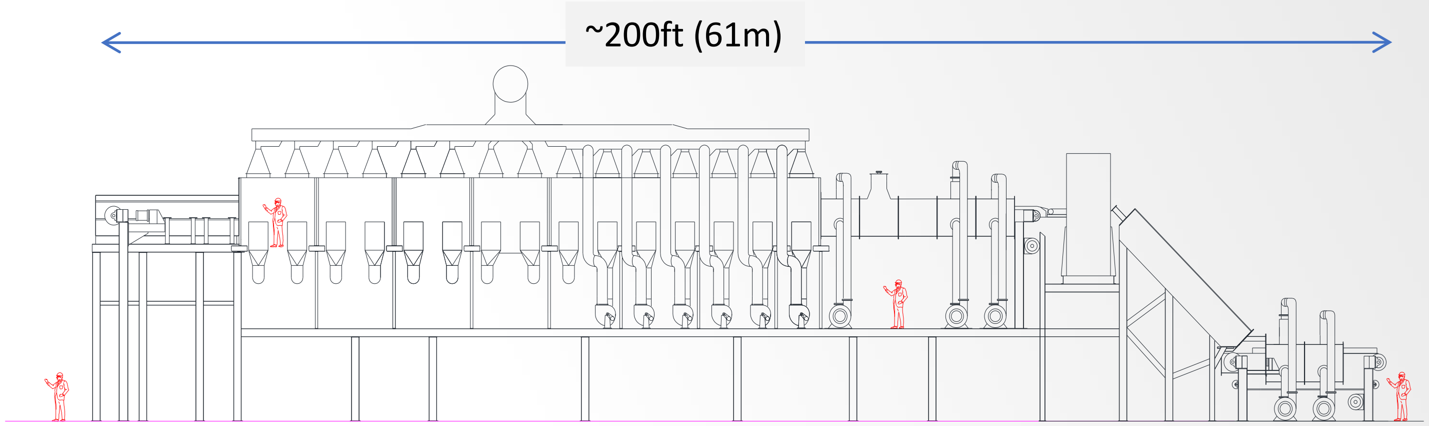
19 Claims, 1 Drawing Sheet

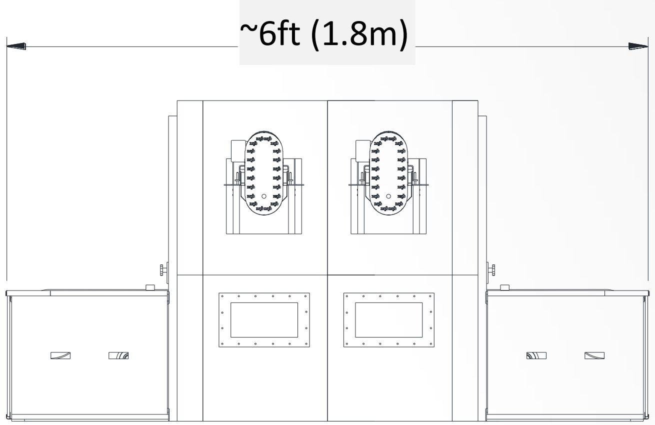




Carbon Fiber Manufacturing Process - Scale

- “Production” Scale:
  4-5m wide belt
  100 – 500kg/hr
  1m/min line speed
- Research Scale:
  150 – 450mm wide belt
  0.05 – 1kg/hr
  4 – 15 mm/min line speed
- Lab Scale: Batch





Pitch Carbon Fiber – Lab Scale Batch Equipment

- A small, simple batch oven and furnace can be used to investigate:
  - Residence time required vs. mat height
  - Property variances vs. height within the mat
  - Laydown mass per area
  - Stability of filaments under loading
- Furnace can have tunnel for pushing a sample into and out of the furnace

Steps for New Entrant to Pitch Carbon Fiber

- Future – what are you trying to achieve?
  - Bigger, faster, cheaper
  - Research and Development – “Sanity Check”
    - Specialized
    - Expensive
    - Complex
- Need to concentrate on:
  - Perfecting pitch process and spinning
  - Need to be able to test small batches
  - Lab scale/Research Scale → Pilot Scale → Production Scale

Final Comments for New Entrant to Pitch Carbon Fiber

- Early recognition of the composite part process(es) (since pitch formats are not apt to be tows.) and derive the carbon fiber form and mechanical properties from these downstream composite applications
- Take open-minded approach to performing unit operations in a batch or continuous manner
- Scale up factors should be 10x or less
- Generational cycles 2 years or more ← it takes time to develop your process and make continuous improvements

Thank you for your time!
We welcome any questions…

Harper International

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