Coal to Carbon Fiber (C2CF)
Continuous Processing for High Value Composites

DE-FE0031796

matt.weisenberger@uky.edu

Center for Applied Energy Research
Disclaimer

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Koppers (with UK) is developing a spinnable mesophase pitch from coal tar recovered from metallurgical coke production at integrated steel mills.

UK is developing stable multifilament melt spinning and continuous thermal conversion.

Prototype composite parts will be demonstrated with the carbon fiber.

Cost and technology gap analyses for the carbon fiber will be evaluated, for new markets and industries for US coal.
Overview

• Project rationale and goals

• Task Updates: Successes & Challenges
  1. Coal Tar to Mesophase Pitch
  2. Melt Spinning & Thermal Conversion (oxidation)
     • The “spinnability” problem: “the ease of stable filament formation”
  3. Tensile Properties

• Future Direction & Challenges
Rationale: Source Compounds in Coal

I. Mochida et al. / Carbon 38 (2000) 305 –328

Integrated, Domestic Steel Mill

Coal Tar

Coking

COAL

Steel

Novel Low QI Coal Tar Pitch Production

Mesophase Pitch Production

Continuous Multifilament Tow (Green) Melt Spinning

Continuous Oxidation, Carbonization & Graphitization

Weaving

Thermoplastic Compounding

Carbon Fiber Filament Characterization

MSC

Weaving

Composites Fabrication

UK
Initial Economics: Case Study Value Add

Approximate Coal Tar Composition
- Water 5%
- Light Oils 2%
- Naphthalene 10%
- Creosote 33%
- TS 41%
- Beta Resin 2%
- QI 7%
- Pitch 50%

1570 KT COAL
- Pitch 80 kt $400/t $32M
- Mesophase 40 kt $800/t $32M
- Carbon Fiber 16 kt $110/kg $1.76B

- Value add relative to the isotropic CTP
  - 55x ($50/lb)
  - 5.5x ($5/lb)
Carbon Fiber Economics: Pitch is cheaper

- Pitch based CF
  - Could be:
    - 2-3x cheaper than PAN
- Why?
  - Cheaper precursor
  - 30% better yield
  - Melt, not solution spun
  - No tension during ox/carb
- 160 kt/yr capacity
  - Only ~ 5% is pitch based CF → 5 -10 kt/yr
    - Mitsubishi
    - Nippon
    - Solvay

### DISCLAIRE: Approximate Costs

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Precursor cost ($/kg)</th>
<th>CF Yield (wt.%)</th>
<th>*Precursor CF cost ($/kg) (not price)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AN</td>
<td>2.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PANa</td>
<td>4.00 – 9.17</td>
<td>50 %</td>
<td>8.00 - 18.34 (13.17)</td>
</tr>
<tr>
<td>Coal Tar</td>
<td>0.40</td>
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<td></td>
</tr>
<tr>
<td>Mesophase pitch</td>
<td>3.30 – 5.00</td>
<td>80 %</td>
<td>4.13 – 6.25 (5.19)</td>
</tr>
</tbody>
</table>

*Carbon 142 (2019) 610-649

Fiber $/lb per modulus
- Glass Fiber: $0.01/lb-GPa
- SM PAN CF: $0.03/lb-GPa
- IM PAN CF: $0.06/lb-GPa
- HM Pitch CF: $0.07/lb-GPa

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Project Goals: ... To maximize the coal value chain

- Develop and scale efficient processing technology to produce coal tar derived, spinnable, mesophase pitch
  - ultra-low quinoline insolubles (QI) precursor
- Clarify and simplify tedious continuous multifilament spinning and thermal conversion
  - Efficient production of high performance carbon fiber products (woven carbon fiber preforms, continuous, and chopped tow)
- Demonstrate and characterize representative composite parts
- Economic & Technological Gap Analyses
# Gantt Chart

We are here: April 2021

<table>
<thead>
<tr>
<th>Task and Subtask</th>
<th>BP1</th>
<th>BP2</th>
<th>BP3</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1 Project Management and Planning</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 Coal to Monophase</td>
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<td></td>
<td></td>
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<tr>
<td>2.1 Production of Low QI Isotropic Coal Tar Pitch</td>
<td>✔️</td>
<td></td>
<td></td>
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<tr>
<td>2.2 Production of Monophase Pitch</td>
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<td>✔️</td>
<td></td>
</tr>
<tr>
<td><strong>3 Continuous Spinning and Thermal Conversion</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.1 Melt Spinning</td>
<td></td>
<td></td>
<td>✔️</td>
</tr>
<tr>
<td>3.2 Continuous Oxidation</td>
<td>✔️</td>
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<td>✔️</td>
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<tr>
<td>3.3 Weaving and Chopping of Oxidized Fiber</td>
<td>✔️</td>
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<td>✔️</td>
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<tr>
<td>3.4 Continuous Carbonization</td>
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<td></td>
<td>✔️</td>
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<tr>
<td><strong>4 Composite Fabrication</strong></td>
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<td></td>
<td>✔️</td>
</tr>
<tr>
<td>4.1 Representative Composite Fabrication (Woven and Injection Molded)</td>
<td>✔️</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>5 Analysis</strong></td>
<td></td>
<td></td>
<td>✔️</td>
</tr>
<tr>
<td>5.1 Materials Characterization</td>
<td>✔️</td>
<td></td>
<td>✔️</td>
</tr>
<tr>
<td>5.2 Economic Analysis/Technological Gap Analysis</td>
<td></td>
<td>✔️</td>
<td>✔️</td>
</tr>
</tbody>
</table>
## Milestone Chart

<table>
<thead>
<tr>
<th>Task/Subtask</th>
<th>Milestone Title/Description</th>
<th>Planned Completion Date</th>
<th>Actual Completion Date</th>
<th>Verification method</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.2</td>
<td>Production of ≥ 1 kg pitch containing ≥ 90% (60 wt.%) mesophase and a softening point ≥ 300 °C (≤ 315 °C)</td>
<td>03/31/2020</td>
<td>04/10/2020</td>
<td>Topical Report</td>
</tr>
<tr>
<td>3.1</td>
<td>Continuous melt spinning of ≥ 90% mesophase pitch, with ≥ 100 filaments, for ≥ 10 minutes</td>
<td>09/30/2020</td>
<td>11/04/2020</td>
<td>Quarterly Report</td>
</tr>
<tr>
<td>3.2</td>
<td>Production of non-fused oxidized mesophase pitch fiber with high strain-to-failure</td>
<td>03/31/2021</td>
<td>03/31/2021</td>
<td>Quarterly Report</td>
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<tr>
<td>3.3</td>
<td>Production of a plain weave sample from oxidized mesophase pitch fiber with ≥ 100 warp ends and produce ≥ 100 g of chopped oxidized mesophase pitch fiber</td>
<td>09/30/2021</td>
<td></td>
<td>Quarterly Report</td>
</tr>
<tr>
<td>4.1</td>
<td>Production of continuous fiber composite using mesophase pitch derived carbon fiber through resin infusion and curing, as well as a ≥ 10 wt.% thermoplastic and injection molded sample, and report thermal and mechanical properties for both</td>
<td>03/31/2022</td>
<td></td>
<td>Quarterly Report</td>
</tr>
<tr>
<td>5.2</td>
<td>Final Report for project</td>
<td>09/30/2022</td>
<td></td>
<td>Final Report</td>
</tr>
</tbody>
</table>
Tasks Updates
Task 2: Coal Tar to Mesophase

- Low QI coal tar pitch production
- 1 kg/batch mesophase production
- Coal tar derived mesophase pitch

1s of kg scale currently

Mesophase = 62%
Tsp = 310 ºC
Making Mesophase

Example

START: Coal Iso Pitch:
- Tsp ~ 100 °C
- C/H = 18.62 wt.%
- QI = 0.36 wt.%
- TI = 19.83 wt.%
- THFI = 11.61 wt.%

FINAL: Mesophase
- ~ 51 wt.% yield
- ~ 60 vol% mesophase
- Tsp ~ 300 °C
- C/H = 26 wt.%
- QI = ~ 50 wt.%

Post processing:
- Vacuum distillation
  - < 1 Torr
  - 340 °C
  - 5 min
  - ~ 3 wt.% volatiles

- Heat soaking [Singer(1977), Lewis (1977), Chwastiak and Lewis (1978)]
- Solvent-extraction [Diefendorf and Riggs (1980)]
Development of Mesophase

~ 30% Mesophase

Isotropic

Mesophase

~ 60% Mesophase

ASTM D4616-95.
Concentration of mesophase

• Isotropic binder inclusions lower Tsp, which facilitates spinning
  • 100% mesophase from coal tar pitch is difficult to spin (will not flow) because the Tsp is too high (> 320 °C)
• Up to ~ 40% binder inclusions of isotropic pitch spins well
  • Should be homogeneously dispersed and small (~ 10 micron)
  • Tsp ~ 305 °C
### Capillary Rheology

The shear rate constant at 4362 1/s is given by the equation:

\[ \eta = \eta_0 e^{\frac{E_a}{RT}} \]

### Table of Data

<table>
<thead>
<tr>
<th>Sample</th>
<th>Q1 (%)</th>
<th>% Mesophase</th>
<th>Tsp (C)</th>
<th>Ea (kJ/mol)</th>
<th>Estimated viscosity at pressure spinning T (Pa s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2CF-20-0425</td>
<td>58.84</td>
<td>72.83</td>
<td>317</td>
<td>154.1</td>
<td>20 to 60</td>
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<tr>
<td>C2CF-20-0425 HM</td>
<td>58.4</td>
<td>55.5</td>
<td>330</td>
<td>153.5</td>
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<tr>
<td>KCTP-038-HT7</td>
<td>55.86</td>
<td>90.05</td>
<td>308</td>
<td>235</td>
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<td>KCTP-051-HT7</td>
<td>52.97</td>
<td>57.72</td>
<td>286</td>
<td>232.4</td>
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<tr>
<td>KCTP-052-HT6</td>
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<td>77.5</td>
<td>315</td>
<td>208.5</td>
<td>-64</td>
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<tr>
<td>KCTP-058-HT21</td>
<td>47.47</td>
<td>60.3</td>
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<td>62.59</td>
<td>306</td>
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<td>-26</td>
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<tr>
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<td>67.93</td>
<td>64.65</td>
<td>302</td>
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<td>-11</td>
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<td>C2CF-20-1162</td>
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<td>240</td>
<td>219.4</td>
<td>-</td>
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<td>KCTP-063-HT23</td>
<td>68.4</td>
<td>68.4</td>
<td>308</td>
<td>222.6</td>
<td>-</td>
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<tr>
<td>KCTP-060-HT23</td>
<td>67.93</td>
<td>64.65</td>
<td>302</td>
<td>201.8</td>
<td>-11</td>
</tr>
<tr>
<td>C2CF-20-1245</td>
<td>47.16</td>
<td>62.1</td>
<td>306</td>
<td>132.5</td>
<td>-</td>
</tr>
<tr>
<td>C2CF-20-1260 HM</td>
<td>52.81</td>
<td>60.5</td>
<td>310</td>
<td>187.3</td>
<td>-31</td>
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<tr>
<td>KCTP-036-038 Mix</td>
<td>55.24</td>
<td>90</td>
<td>310</td>
<td>220.1</td>
<td>-73</td>
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<tr>
<td>KCTP-067-HT23</td>
<td>100</td>
<td>100</td>
<td>328</td>
<td>177.8</td>
<td>-83</td>
</tr>
<tr>
<td>KCTP-068-HT22</td>
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<td>100</td>
<td>329</td>
<td>181.2</td>
<td>-</td>
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<tr>
<td>C2CF-20-1288</td>
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<td>79.6</td>
<td>302</td>
<td>165.0</td>
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<tr>
<td>SP271</td>
<td>12.93</td>
<td>100</td>
<td>256.72</td>
<td>296.4</td>
<td>-87</td>
</tr>
<tr>
<td>M-AR</td>
<td>30.85</td>
<td>100</td>
<td>263.65</td>
<td>307.2</td>
<td>-16</td>
</tr>
<tr>
<td>KCTP-034-HT7</td>
<td>48.5</td>
<td>80.56</td>
<td>299</td>
<td>237.5</td>
<td>-22</td>
</tr>
</tbody>
</table>
Tsp and QI decrease with increasing Ea
C2CF-20-0425 (58.84%)  
KCTP-036-038 Mix (90%)  

C2CF-20-1245 (62.1%)  
KCTP-053-HT21 (77.5%)  

C2CF-20-1260 HM (60.5%)  
KCTP-063-HT23 (68.4%)
What is a “spinnable” coal tar mesophase?

Initial target of > 10 min of uninterrupted melt spinning

- **Mesophase content**
  - ~ 60 to 80 vol%
  - Well-dispersed, small (~10 micron) isotropic binder inclusions

- **Softening point temperature**
  - ~ 305 °C, or < 320 °C

- **Capillary rheology**
  - Activation energy of flow of ~ >190 kJ/mol

- **Viscosity stable with time at temperature**
  - 10s of min

- **Issues for further investigation**
  - Spinnability association with chemistry of mesophase
    - aromaticity, Mw distribution, etc.

We are working to build charts like this

![Spinnability vs DDR](chart.png)
Subtask 3.1 – Melt Spinning
AJ Extruder System
Operational Winter 2020 - 2021

1” Extruder
Metering pump
Spin pack: 100 hole spinneret
100 filament mesophase spinning

• Multifilament melt spinning is a major milestone of the project

• Spinnability:
  • Relative ‘ease’ of fiber formation
  • Complex interplay of temperature and rate dependent flow of mesophase pitch
  • Stability of the process to proceed for 10s of minutes to hours, uninterrupted

• Important measurable factors
  • Softening point temperature (QI)
  • Viscosity(T)
    • $E_a$ of flow
Spinning Stability: Green Fiber Luster

PS325-Green
KCTP-20-0425-HM2

PS324-Green
Mitsubishi “SP271”

“matte”
Duller grey

“glossy”
Shinier black

Matte
Unstable

Glossy
Stable
Oxidation Studies of AJ13 Pitch Fiber

Current oxidation method is designed for isotropic (not mesophase) pitch fiber, and requires extensive time at temperature.

- Ramp 5°C/min to 170°C
- Ramp 0.15°C/min to 310°C
- Isothermal 30 min

3X reduction in requisite oxidation time

Oxidized coal tar mesophase fibers
No interfilament fusion observed

3X reduction in requisite oxidation time
### Oxidized Pitch Fiber - Resilience

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Mesophase</th>
<th>Break Load (gf)</th>
<th>Break Stress (MPa)</th>
<th>Modulus (GPa)</th>
<th>Break Strain (%)</th>
<th>Resilience (kPa)</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS309 Green</td>
<td>KCTP-076 Coal tar mesophase</td>
<td>0.40</td>
<td>16.8</td>
<td>5.39</td>
<td>0.34</td>
<td>28.5</td>
<td>22</td>
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<tr>
<td>PS309 Ox</td>
<td></td>
<td>0.77</td>
<td>26.9</td>
<td>5.25</td>
<td>0.54</td>
<td>72.7</td>
<td>24</td>
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<tr>
<td>PS307 Green</td>
<td>SP271 Baseline</td>
<td>0.65</td>
<td>22.3</td>
<td>4.65</td>
<td>0.50</td>
<td>55.8</td>
<td>23</td>
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<tr>
<td>PS307 Ox</td>
<td></td>
<td>1.91</td>
<td>66.6</td>
<td>7.10</td>
<td>1.52</td>
<td>506.8</td>
<td>18</td>
</tr>
</tbody>
</table>

Green Fiber is incredibly FRAGILE. Oxidized fibers demonstrate an increased strain to failure and resilience, relative to green fiber. Important for weaving.
Radial texture of graphitized fibers
## Carbon Fiber Tensile properties

<table>
<thead>
<tr>
<th>% Mesophase</th>
<th>Fiber</th>
<th>Diameter (um)</th>
<th>Stdev (um)</th>
<th>Stress At Break (MPa)</th>
<th>Stdev (MPa)</th>
<th>Modulus (GPa)</th>
<th>Stdev (GPa)</th>
<th>Strain at Break (%)</th>
<th>Stdev (%)</th>
<th>N</th>
<th>CY %</th>
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<tbody>
<tr>
<td>59.4</td>
<td>PS252a-052-GF671</td>
<td>17.70</td>
<td>0.75</td>
<td>1061</td>
<td>297</td>
<td>624</td>
<td>42</td>
<td>0.17</td>
<td>0.05</td>
<td>40</td>
<td>79</td>
</tr>
<tr>
<td></td>
<td>PS252b-052-GF671</td>
<td>17.62</td>
<td>0.95</td>
<td>1022</td>
<td>379</td>
<td>592</td>
<td>67</td>
<td>0.17</td>
<td>0.06</td>
<td>40</td>
<td>79</td>
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<tr>
<td>77.5</td>
<td>PS253a-053-GF671</td>
<td>15.18</td>
<td>2.21</td>
<td>882</td>
<td>201</td>
<td>609</td>
<td>40</td>
<td>0.14</td>
<td>0.03</td>
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<td>PS253b-053-GF671</td>
<td>15.18</td>
<td>2.21</td>
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<td>61</td>
<td>0.15</td>
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<td>60.3</td>
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<td>79</td>
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<td>PS267b-059-GF678</td>
<td>12.90</td>
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<td>366</td>
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<td>77.5</td>
<td>PS270-053-GF678</td>
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<td>986</td>
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<td>390*</td>
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<td>60.3</td>
<td>PS275a-059-GF674</td>
<td>15.61</td>
<td>1.52</td>
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<td>215</td>
<td>464*</td>
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<td>0.05</td>
<td>39</td>
<td>80</td>
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<td>60.6</td>
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<td>0.61</td>
<td>1607</td>
<td>215</td>
<td>448</td>
<td>29</td>
<td>0.36</td>
<td>0.05</td>
<td>40</td>
<td>72</td>
</tr>
</tbody>
</table>

*Pacman defects observed

37% ‘missing’ area for PS270: 390 → 619 GPa

- Most had moduli ~ 600 GPa (87 MSI)
- Most ~ 80% CY
- Working to improve strength (strain to failure)
Review of Progress

- Coal tar derived mesophase production at 1s kg scale
  - Progress defining a ‘spinnable’ mesophase

- Multifilament melt spinning achieved
  - Rheological insight
  - Faster oxidation achieved

- Single filament tensile properties measured
  - Moduli at approximately 600 GPa (87 MSI)
  - Strength still low at ~ 1 GPa (145 ksi)
    - strain to failure low at 0.15 – 0.25%
Future

• Stable multifilament melt spinning
  • Challenges:
    • Spinnable mesophase supply
    • Start up
    • Stability
    • Spinneret cleaning

• Build spinnability charts
  • # of minutes of uninterrupted spinning vs. draw down ratio

• Investigate chemistry of spinnable and non-spinnable mesophase
  • Mw distribution (mass spectroscopy)
  • Aromaticity (H NMR)
  • QS fraction of mesophase

• Tasks 3.2 – 3.4 requiring continuous multifilament tow
  • MS 3.3 – Weaving oxidized fiber (Sept. 2022)
C2CF  Coal to Carbon Fiber: Continuous Processing for High Value Composites

Koppers (with UK) is developing a spinnable mesophase pitch from coal tar recovered from metallurgical coke production at integrated steel mills.

UK is developing stable multifilament melt spinning and continuous thermal conversion.

Prototype composite parts will be demonstrated with the carbon fiber.

Cost and technology gap analyses for the carbon fiber will be evaluated, for new markets and industries for US coal.

matt.weisenberger@uky.edu