C4WARD: Coal Conversion for Carbon Fibers and Composites: Project FEAA155

2021 Advanced Coal Processing Review Meeting

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Penn State — Jonathan Mathews

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Project funded by DOE’s Fossil Energy Program’s Advanced Coal Processing Program
Outline

• Background
• Objectives
• Approach
• Results
• Summary and Future Work
Outline

• Background
Converting Coal into Value-Added Products
Finding use for every molecule that is mined. No molecule left behind!

Developing the underlying and translational science to enable the development and deployment of energy-efficient and cost-effective processes for: recovering rare-earth elements from coal and converting coal into high value-added products thus supporting the creation of new manufacturing industries and well-paying jobs in coal communities across the U.S.

Converting Coal into Value-Added Products
Finding use for every molecule that is mined. No molecule left behind!

Developing the underlying and translational science to enable the development and deployment of energy-efficient and cost-effective processes for: recovering rare-earth elements from coal and converting coal into high value-added products thus supporting the creation of new manufacturing industries and well-paying jobs in coal communities across the U.S.
Carbon Fiber Composites are widely used in Aerospace Technologies... and are expected to be widely used in highway transportation.
Potential of Carbon Fiber Composites Market Growth

Current market size (2014)

* Size of the bubble describes market size in 2020

Lara-Curzio et al. (2016)

But it is not only about stiffness and strength!
Low thermal conductivity carbon fibers could be used for building insulation

There is a need to replace rayon-derived carbon fibers for aerospace applications
Outline

• Background

• Objectives:
  • To develop the underlaying and translational science to establish processing-structure-properties relationships for coal-derived carbon fibers that will enable energy-efficient, cost-effective and environmentally sustainable processes for manufacturing carbon fibers with tunable properties.
  • This project will address challenges associated with coal processing, variability in coal feedstocks, and with scaling up carbon fiber manufacturing from the laboratory bench to semi-production scale at ORNL's Carbon Fiber Technology Facility.
Established in 2013, the CFTF is the Department of Energy’s only designated user facility for carbon fiber innovation.

- 42,000 sq. ft. facility
- 390 ft. long processing line, capable of custom unit operation configuration
- Up to 25 tons per year
The ORNL-UK Partnership to Develop Coal-Derived Carbon Fibers

Not all coals are the same

Bringing new Industries to coal communities

Together, ORNL and UK bring complementary and unparalleled capabilities in fundamental science and translational research and development expertise in:

- coal processing
- separation science and technology
- carbon science & technology
- computational chemistry and high-performance computing
- advanced characterization
- advanced manufacturing

to develop scalable, efficient, cost-effective, and environmentally sustainable processes for manufacturing coal-derived carbon fibers with tunable properties. A key element of this project is enabling scaling up fiber production from the laboratory benchtop level up to semi-production scale at ORNL's Carbon Fiber Technology Facility. This project will demonstrate a clear path for competitive industrialization of coal-derived carbon fibers and composites for a wide range of applications.
Outline

• Background
• Objectives
• Approach
Advanced Coal Processing at UK-CAER
Overview – COAL & PITCH Processing

**SOLVENT EXTRACTION PROCESS**

- **DIGESTION**
  - Pulverized Coal + Solvent
  - 400°C, 200 psi, 0.5 hr
  - Stirred

- **FILTRATION**
  - N₂ over-pressure
  - Fine meshes
  - Sintered elements

- **DISTILLATION**
  - Remove light components
  - Target softening point of the bottom material (pitch) of ~ 100°C

**MESOPHASE PROCESS**

- **HEAT SOAKING**
  - Isotropic pitch + heat + time
  - 415°C, atm pressure, 8 hr
  - N₂ purge stream
  - Stirred

  - Mesophase Pitch
  - High Performance Carbon Fiber
  - Industrial Carbon Fiber

**Light gases**
- Solids
  - Minerals, IOM

**Light gases**
- Make-up Solvent
  - Condensables

**Isotropic Pitch**
- Distillates
Coals and Solvents of Initial Interest

- **Bituminous**
  - Central Appalachian Basin
    - Blue Gem seam (low ash ~ 1 wt.%)
  - Illinois Basin
    - Springfield seam (Western Kentucky No. 9, Illinois 5, Indiana V)
    - Herrin seam (Western Kentucky No. 11, Illinois 6)

- **Sub-bituminous**
  - Powder River Basin – Wyoming and Montana

- **Solvents**: (heavy aromatics)
  - Anthracene Oil (from coal tar)
  - Creosote (from coal tar)
  - Decant Oil (from FCC of petroleum)
  - Make-up solvent → Condensates from our processing

Cost of solvents ~ $500 - $1000/tonne
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Data Management

EDX will be the repository for all data generated in this project.
Solvent Efficacy (microreactors)

<table>
<thead>
<tr>
<th>Coals</th>
<th>Solvent</th>
<th>Solvent:Coal (g/g)</th>
<th>Temp. (°C)</th>
<th>Time (min.)</th>
<th>Coal Conversion (wt.% daf coal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blue Gem</td>
<td>FCC Slurry oil (decant oil)</td>
<td>2:1</td>
<td>400</td>
<td>30</td>
<td>42.7%</td>
</tr>
<tr>
<td>Blue Gem</td>
<td>Coal Tar Distillate (Koppers)</td>
<td>2:1</td>
<td>400</td>
<td>30</td>
<td>44.3%</td>
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<tr>
<td>Blue Gem</td>
<td>Creosote (Lone Star)</td>
<td>2:1</td>
<td>400</td>
<td>30</td>
<td>61.7%</td>
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<tr>
<td>Blue Gem</td>
<td>Coal Tar Distillate (Coopers Creek)</td>
<td>2:1</td>
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<td>30</td>
<td>90.0%</td>
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<tr>
<td>Blue Gem</td>
<td>Anthracene Oil (Rain Carbon)</td>
<td>2:1</td>
<td>400</td>
<td>30</td>
<td>82.2%</td>
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<tr>
<td>Blue Gem</td>
<td>Petroflux (Rain Carbon)</td>
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<td>400</td>
<td>30</td>
<td>83.3%</td>
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<tr>
<td>Blue Gem</td>
<td>New FCC Slurry Oil (decant oil)</td>
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<td>400</td>
<td>30</td>
<td></td>
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<tr>
<td>Springfield</td>
<td>FCC Slurry oil (decant oil)</td>
<td>2:1</td>
<td>400</td>
<td>30</td>
<td>60.0%</td>
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<tr>
<td>Springfield</td>
<td>Coal Tar Distillate (Koppers)</td>
<td>2:1</td>
<td>400</td>
<td>30</td>
<td>98.0%</td>
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<tr>
<td>Springfield</td>
<td>Creosote (Lone Star)</td>
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<td>30</td>
<td>70.4%</td>
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<tr>
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<td>30</td>
<td>89.0%</td>
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<tr>
<td>Springfield</td>
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<td>70.7%</td>
</tr>
<tr>
<td>Springfield</td>
<td>Petroflux (Rain Carbon)</td>
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<td>400</td>
<td>30</td>
<td>86.4%</td>
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<tr>
<td>Springfield</td>
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<td>30</td>
<td></td>
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<tr>
<td>Herrin</td>
<td>FCC Slurry oil (decant oil)</td>
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<td>30</td>
<td>94.1%</td>
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<td>96.1%</td>
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<tr>
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<td>88.3%</td>
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<td>Anthracene Oil (Rain Carbon)</td>
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<td>Herrin</td>
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<td>72.4%</td>
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<td>30</td>
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</tr>
<tr>
<td>Monarch</td>
<td>FCC Slurry oil (decant oil)</td>
<td>2:1</td>
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<td>30</td>
<td></td>
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<td>400</td>
<td>30</td>
<td></td>
</tr>
</tbody>
</table>

Coopers Creek coal tar distillate shows promising conversions with three coals

Herrin coal is the best performing in conversion to liquid – at this point–

- Work continues towards completion of study
- Replicates are planned to ensure reproducibility
- Based on results, solvent-coal combination will be down selected.
Distillation of Coal Liquids

- Currently running distillation of coal liquids on a 2L scale reactor
- Have successfully achieved softening points exceeding 100°C using decant oil

Summary of recent distillation runs

<table>
<thead>
<tr>
<th>Run</th>
<th>Sample</th>
<th>Final Vapor T (°C)</th>
<th>DMA Softening Point (°C)</th>
<th>Mass Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C4-dist-4</td>
<td>FCC decant oil</td>
<td>364</td>
<td>104</td>
<td>20</td>
</tr>
<tr>
<td>C4-dist-5</td>
<td>FCC decant oil</td>
<td>360</td>
<td>105</td>
<td>21</td>
</tr>
<tr>
<td>C4-dist-7</td>
<td>Blue Gem : FCC DO (1:3 ratio)</td>
<td>332</td>
<td>84</td>
<td>19</td>
</tr>
</tbody>
</table>
Advanced Characterization

The project is leveraging unique capabilities available at ORNL, UK, and DOE User Facilities to obtain descriptions of coals at different length scales from the mesoscale down to the molecular level.

• X-ray and neutron computed tomography
• Small-Angle Scattering (neutron and X-ray)
• X-ray Photoelectron, Raman, Infrared, Laser-Induced Breakdown Spectroscopy
• High-resolution Electron Microscopy
• Nuclear Magnetic Resonance
• Other
X-rays and neutrons are sensitive to different components in coal structure

X-rays are more heavily absorbed by mineral matter in the coal structure (green in the 3D image).

A 2D slice image reveals the layered structure of Herrin coal.

A neutron radiograph from a recent experiment at ORNL's HFUR.

Neutrons are more sensitive to hydrogen.

A comparison of XCT and NCT data of the same coals will help illustrate the distribution of the organic and inorganic compounds in the coals.
XPS data provides elemental quantification as well as quantification of organically bound O, N and S.

### Surface Composition (at.%) – Analysis Area 1

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>O</th>
<th>N</th>
<th>Si</th>
<th>S</th>
<th>Al</th>
<th>Cl</th>
<th>Fe</th>
<th>Na</th>
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</thead>
<tbody>
<tr>
<td>Blue Gem</td>
<td>88.4</td>
<td>9.2</td>
<td>1.5</td>
<td>0.3</td>
<td>0.2</td>
<td>0.3</td>
<td>0.1</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Herrin</td>
<td>85.5</td>
<td>10.4</td>
<td>1.1</td>
<td>0.9</td>
<td>1.3</td>
<td>0.7</td>
<td>0.1</td>
<td>0.1</td>
<td>0.0</td>
</tr>
<tr>
<td>Springfield</td>
<td>83.4</td>
<td>12.1</td>
<td>1.3</td>
<td>1.3</td>
<td>0.8</td>
<td>0.9</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

C 1s  
O 1s  
N 1s  
S 2p
Chemical Characterization — Why do some solvents convert coal to liquids better than others?

ACP Decant Oil

Coopers Creek Coal Tar Distillate
Chemical Characterization — Discrimination of pitch spinnability through Mass Spectroscopy

Mitsubishi Oil “SP 271” spinnable mesophase pitch

In-house coal tar-based non-spinnable mesophase pitch
Mesophase Formation

Reflected light, polarized optical micrographs of spinnable coal tar mesophase pitches. Recent pitches have achieved 100% mesophase at ~ 305°C softening point.
Correlation between Softening Point and QI for Mesophase Pitches
**Pitch Rheology and Structure**

- Pitch viscosity is highly dependent on pitch composition and on temperature.
- Viscosity also depends on shear rate and may vary with time.

<table>
<thead>
<tr>
<th>Source</th>
<th>Name</th>
<th>Type</th>
<th>Base</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mitsubishi</td>
<td>AR</td>
<td>Mesophase</td>
<td>Naphthalene</td>
<td>Reference.</td>
</tr>
<tr>
<td>Cytec</td>
<td>Mesophase</td>
<td>Mesophase</td>
<td>Petroleum</td>
<td>Reference.</td>
</tr>
<tr>
<td>Koppers</td>
<td>Mesophase</td>
<td>Mesophase</td>
<td>Coal tar</td>
<td>Reference.</td>
</tr>
<tr>
<td>Conoco</td>
<td>Mesophase</td>
<td>Mesophase</td>
<td>Petroleum</td>
<td>Reference.</td>
</tr>
<tr>
<td>Motorcarbon</td>
<td>Meso-C</td>
<td>Mesophase</td>
<td>Petroleum</td>
<td>Commercial product.</td>
</tr>
<tr>
<td>Lonestar</td>
<td>110 C SP</td>
<td>Isotropic</td>
<td>Coal tar</td>
<td>Commercial product.</td>
</tr>
<tr>
<td>Koppers</td>
<td>110 C SP</td>
<td>Isotropic</td>
<td>Coal tar</td>
<td>Commercial product.</td>
</tr>
<tr>
<td>Rain/Rutgers</td>
<td>Carbores</td>
<td>Isotropic</td>
<td>Coal tar</td>
<td>Commercial product.</td>
</tr>
<tr>
<td>Rain/Rutgers</td>
<td>250M</td>
<td>Isotropic</td>
<td>Petroleum</td>
<td>Commercial product.</td>
</tr>
<tr>
<td>Rain/Rutgers</td>
<td>270M</td>
<td>Isotropic</td>
<td>Petroleum</td>
<td>Commercial product.</td>
</tr>
</tbody>
</table>

Various commercial and reference samples have been screened. Focus on coal-based.

Minophase (anisotropic) structures in pitch show optically active domains under cross-polarized light. Isotropic structures do not.
Bench Scale Melt Spinning of Fibers

- Melt processing is not defined by one temperature or shear rate.
- Pitch materials are particularly challenging for melt spinning due to their heterogenous composition.
- Rheology (temperature and shear rate dependence), thermal stability (volatilization)

ARA-24 mesophase pitch
Carbores isotropic coal tar pitch
Carbores isotropic coal tar pitch
100% mesophase petroleum pitch
Petroleum pitch fibers melt blown at CFTF scale

- Initial trial with high-softening point petroleum isotropic pitch fibers melt blown at CFTF.
- Average fiber diameter ~ 10 microns
Recent Results

Melt-blown fibers from petroleum-derived isotropic pitch have been produced both at lab-bench scale and at the CFTF.
Objective: Perform predictive simulations to efficiently break down different coals to pitches and then to fibers

Modeling: Analysis, structure generation, structure creation

Characterization: MS, optical, vibrational spectroscopy (Task 8)

“Coal & Pitch Model DB”

Efficient conversion by understanding structure/reactivity:

- Energy efficient
- Atom efficient
- Recover solvents
HPC Method Development

NN Training: Intermolecular interactions – Test case CH₄ adsorption in B and N doped porous nanocarbons

Model system:

$$M\text{Ph}$$
$$X_1 = \{C, B, N\}$$

• Training NN potential requires high-level reference data, MN15+ is an economical DFT method for NN training!

Adsorption energy relative to pure C

More practical DFT: MN15+

Ab initio reference:

Irie et al, J. Phys. Chem. A, in revision
**HPC Method Development**

**NN Training:** Deformation & fracture of graphene with DFT and approximate DFT (density-functional tight-binding, DFTB)

**Various Deformation & Failure**

- Bond order
- Energy
- Forces

Fracture (Graphene) DFTB+/LAMMPS, in preparation
Database of Characteristic Spectra; Example: GC-MS

- IR and Raman simulations
- UV/Vis spectra simulations
- NMR spectra simulations
- GC-MS spectrum simulations

MS for anthracene
xTB-GFN2, 500 MD trajectories, T=500 Kelvin

Full QM calculations of EI-MS spectra
Analysis is in progress for solvent extraction process being developed by the University of Kentucky
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Summary

• Significant progress has been made to understand the effect of coal and solvent type on solvent extraction process to obtain spinnable pitches.
• Multi-scale chemical and structural characterization of coals and solvents continues using advanced characterization techniques.
• Scaling-up activities at the Carbon Fiber Technology Facility (melt-blowing) of petroleum-derived pitches are progressing with success.
• Interatomic potentials are being developed for molecular dynamics simulations towards the development of a virtual reactor. Preliminary results have successfully predicted mass spectra of relevant compounds.
• A technoeconomic analysis for coal tar pitch carbon fiber manufacturing has been completed.
Additional Slides
XRD data is supplemented by EDS in identifying the minerals present in the coals.

The coals are subjected to demineralization process to reduce/remove the minerals prior to FTIR and NMR measurements.

XRD will also be used to obtain structural parameters such as interlayer spacing, for each coal.

The XRD patterns are used to identify the mineral phases. Their distributions on the coals are illustrated through the EDS Maps on the right.
Preliminary Raman Spectroscopy results

The Raman spectra are currently still being collected. The fits will be used to obtain structural parameters related to different coals.

2D Raman maps are also being collected on all the coals being investigated.
Not all coals are the same!

<table>
<thead>
<tr>
<th>Type of Coal</th>
<th>Percentage of Fixed Carbon (Dry, Mineral-Matter-Free Basis)</th>
<th>Gross Calorific Value (kBTU/lb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthracite</td>
<td>100</td>
<td>16</td>
</tr>
<tr>
<td>Semi-Anthracite</td>
<td>98</td>
<td>14</td>
</tr>
<tr>
<td>Lignite</td>
<td>92</td>
<td>13</td>
</tr>
<tr>
<td>High-Volatile B bituminous</td>
<td>86</td>
<td>9.5</td>
</tr>
<tr>
<td>Low-volatile bituminous</td>
<td>78</td>
<td>8.3</td>
</tr>
<tr>
<td>Medium-volatile bituminous</td>
<td>69</td>
<td>7</td>
</tr>
<tr>
<td>High-Volatile C bituminous</td>
<td>60</td>
<td>6.6</td>
</tr>
<tr>
<td>Subbituminous B</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>Subbituminous C</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>Meta-Anthracite</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>Low-volatile bituminous</td>
<td>20</td>
<td></td>
</tr>
</tbody>
</table>

Coal – Stages of Formation

Fossil Fuels. Energy Information Association
The Molecular Structure of Coal

This project will develop molecular models for several coals of interest.
By using computational chemistry, machine learning and advanced characterization tools, it will be possible to establish processing-structure-properties relationships for coal and coal-derived pitch at the molecular and mesoscale levels. This will accelerate the development of processes for fabricating coal-derived products with specific properties and performance (e.g., structural fibers or fibers for thermal management applications).

Not all coals are the same

Melt spinning or blowing of Pitch

Continuous carbon fibers for structural applications

Short carbon fibers for thermal insulation

Composite Materials and Structures

Sensors for process monitoring

CFTF settings are selected based on the nature of the feedstock and desired final product

Process Control

86.6 Å

Molecular Structure of Coal

High-throughput characterization tools will be used to determine the molecular structure of any type of coal.

Lara-Curzio (2019)
Molecular weight distribution and elemental composition

- Molecular weight distribution measurements (by MALDI-TOF-MS) shows the variety of pitch compositions
- SEM/EDS can be used to screen before applying more detailed tools

SEM/X-ray Energy Dispersive Spectroscopy

<table>
<thead>
<tr>
<th></th>
<th>C at.%</th>
<th>O at.%</th>
<th>S at.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% mesophase naphthalene pitch</td>
<td>98.15 ± 0.18</td>
<td>1.70 ± 0.18</td>
<td>0.15 ± 0.00</td>
</tr>
<tr>
<td>100% mesophase Petroleum pitch</td>
<td>96.31 ± 0.05</td>
<td>3.35 ± 0.12</td>
<td>0.34 ± 0.08</td>
</tr>
<tr>
<td>~0% mesophase Coal tar pitch 1</td>
<td>96.32 ± 0.55</td>
<td>3.40 ± 0.57</td>
<td>0.28 ± 0.02</td>
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<tr>
<td>~0% mesophase Coal tar pitch 2</td>
<td>96.93 ± 0.28</td>
<td>2.11 ± 0.23</td>
<td>0.96 ± 0.06</td>
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