Coal to Carbon Fiber – Novel Supercritical CO$_2$ Solvated Process (MUSCL)

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DE-FE0031800

Prepared for the 2021 NETL Annual Coal Processing Project Review Meeting
Who We Are

Ramaco Coal, founded in 2011, is a coal-based conglomerate with operations in five states. It consists of two main operating companies:

**Ramaco Resources**
A publicly traded met coal producer (METC-Nasdaq) with low cost, high quality production in West Virginia, Virginia and Pennsylvania.

Headquartered in Lexington, Kentucky.

[www.ramacoresources.com](http://www.ramacoresources.com)

**Ramaco Carbon**
The first vertically integrated resource, research and manufacturing coal technology platform focused on creating “Coal to Products”.

Headquartered in Sheridan, Wyoming.

[www.ramacocarbon.com](http://www.ramacocarbon.com)
Coal to Carbon Fiber – Novel Supercritical CO₂ Solvated Process (MUSCL)

DE-FE0031800

DOE Funding: $733,299
Cost Share: $323,500
Total Value: $1,056,799

Budget Period 1: 14 months
Budget Period 2: 10 months

MUSCL Multi-Ultra Supercritical Coal Liquefaction

- Brand New Process Never Attempted Before
- Closed Loop System > No Emissions
- Lower Cost > No Hydrogen Required
- Selective Extractions > Ideal for Upgrading to Mesophase
- More Ecologically Sound Than Traditional Processes (Greener)
Coal to Carbon Fiber – Novel Supercritical CO$_2$ Solvated Process

View of test space for sCO$_2$ pyrolysis loop.

Place coal here!

Supercritical CO$_2$ (sCO$_2$) test loop.

Test loop control station.

TerraPower
TerraPower’s pyrolysis test loop utilizes supercritical CO₂ in a closed loop.

CO₂ is heated up to 550°C, and acts as the heating fluid for the feedstock to reach pyrolysis temperatures and serves as a pyrolysis product solvent.

Kg batches of feedstock can be processed for testing various feedstock.

Pyrolysis energy recovered using efficient ‘reverse’ distillation process.

Pyrolysis Product Sample is Recovered in Condensate Collection 2 and 3 - “MUSCL oil”
Main technical focus area is on the **supercritical CO$_2$ processing steps**.

- MUSCL derived from established super critical extraction process technologies.
- Produces **on-purpose isotropic pitch** and valuable co-products.
- The other **non-sCO$_2$** processing steps are to be practiced mainly by conventional means.
Supercritical CO\textsubscript{2} separation of MUSCL-oil with sequential co-solvents

Modified Supercritical CO\textsubscript{2} extraction system (August 10, 2020)

- Reaction vessel: 100 mL
- 5 um stainless steel bag
- Sample loading: 17 g
- 50 °C and 20 MPa for Benzene Soluble fraction
- 70 °C and 30 MPa for Pyridine Soluble fraction

sCO\textsubscript{2} extraction system

100 mL sCO\textsubscript{2} vessel

Soxhlet extraction
Supercritical CO$_2$ separation of MUSCL-oil with sequential co-solvents

Results 1 – MUSCL sample produced on July 16-2020

Fraction yields between Soxhlet extraction and sCO$_2$ extraction are comparable

<table>
<thead>
<tr>
<th></th>
<th>Soxhlet extraction</th>
<th>sCO2 extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>MUSCL (July 16, 20)</td>
<td>MUSCL (July 16, 20)</td>
</tr>
<tr>
<td>Loaded amount (g)</td>
<td>11 g</td>
<td>17 g</td>
</tr>
<tr>
<td>Benzene soluble fraction (%)</td>
<td>49%</td>
<td>52%</td>
</tr>
<tr>
<td>Pyridine soluble fraction (%)</td>
<td>13%</td>
<td>12%</td>
</tr>
<tr>
<td>Residue (%)</td>
<td>25%</td>
<td>26%</td>
</tr>
<tr>
<td>Mass loss (%)</td>
<td>13%</td>
<td>10%</td>
</tr>
</tbody>
</table>
Supercritical CO₂ separation of MUSCL-oil with sequential co-solvents

Results 2 – Thermogravimetric analysis (TGA)

- Carbon yield at 900°C
  - MUSCL sample: 41%
  - Ramaco sample: 62%
- Decomposition temperature
  - Ramaco samples: offset 590°C
  - MUSCL sample: offset 540°C

Ramaco pyridine soluble fraction contains higher molecular weight compounds and structures than that of MUSCL sample.
Results 3 – Comparison with commercial mesophase coal pitch

- MUSCL sample produced on August 14, 2020 was fractionated
  - The sample contains less water content and has higher density
Supercritical CO$_2$ separation of MUSCL-oil with sequential co-solvents

Experimental Apparatus

- **Sample:** MUSCL oil produced on August 14, 2020
  - Sample ID: MRaw200814.
- **Extraction method**
  - Soxhlet extraction
  - Sample loading: 20 g
- **Solvents**
  - Benzene and Pyridine
- **Reaction time**
  - Benzene extraction: 16 hours
  - Pyridine extraction: 16 hours
Results and Discussion

- Benzene soluble fraction ranged from 59 – 62% whereas pyridine soluble was from 7 to 9%.
  - Low yield of Pyridine soluble fraction may be due to drying at 80 °C with vacuum to remove pyridine solvent.

- Mass loss was 9% which is attributable to water and volatile compounds in the sample.

<table>
<thead>
<tr>
<th>Experiment date</th>
<th>August 10 and 13, 2020</th>
<th>August 19, 2020</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>MRaw200716 (MUSCL oil)</td>
<td>MRaw200814 (MUSCL oil)</td>
</tr>
<tr>
<td>Extraction method</td>
<td>Soxhlet</td>
<td>sCO₂</td>
</tr>
<tr>
<td></td>
<td>Soxhlet 1</td>
<td>Soxhlet 2</td>
</tr>
<tr>
<td>Loaded amount (g)</td>
<td>11 g</td>
<td>17 g</td>
</tr>
<tr>
<td></td>
<td>20.4 g</td>
<td>19.8 g</td>
</tr>
<tr>
<td>Benzene soluble fraction (%)</td>
<td>49%</td>
<td>52%</td>
</tr>
<tr>
<td></td>
<td>62%</td>
<td>59%</td>
</tr>
<tr>
<td>Pyridine soluble fraction (%)</td>
<td>13%</td>
<td>12%</td>
</tr>
<tr>
<td></td>
<td>7%</td>
<td>9%</td>
</tr>
<tr>
<td>Residue (%)</td>
<td>25%</td>
<td>26%</td>
</tr>
<tr>
<td></td>
<td>22%</td>
<td>23%</td>
</tr>
<tr>
<td>Mass loss (%)</td>
<td>13%</td>
<td>10%</td>
</tr>
<tr>
<td></td>
<td>9%</td>
<td>9%</td>
</tr>
</tbody>
</table>
Upgrading the Benzene Soluble Fraction of the Product

- Ramaco will analyze and further process the benzene soluble portion of the experimental results and samples:
  - Obtain mass balance and material balances.
  - Process and upgrade the low softening point pitch and analyze for elemental composition, softening points, and degree of anisotropy.
  - Determine the mechanism which supercritical CO$_2$ reacts with the coal molecules that differs from standard coal conversion methods.

- The molecular weight of the benzene soluble fraction will be increased through distillation to the point it can be analyzed for softening point and able to be loaded into the Haake. The liquid portion will also be collected and analyzed.

- The material will then be upgraded using different conditions in the Haake and analyzed.
Quinoline Solubility and Separation

- Quinoline extraction performed on the benzene insoluble portion.
- Insoluble material removed by vacuum filtration.
- Quinoline solvent evaporated and recovered through distillation.
Supercritical CO$_2$ separation of MuSCL-oil with sequential co-solvents

Mesophase Conversion Using the Haake MiniLab

- Twin conical screw feeder circulate the pitch through the system at temperature.
- Product did not extrude from the Haake MiniLab and was removed as a solid.
- No dropping point was able to be obtained from this material.
- No mesophase regions or domains were observed under polarized light.
Objectives

- Obtain asphaltic pitch from Benzene Soluble pitch (BSP) as a potential precursor for mesophase pitch development.
  - BSP fraction account for 90 - 94 % of MuSCL-produced pitch (~2kg)
  - Determine and quantify fractions of saturates, aromatics, resins, and asphaltenes (SARA).
  - Characterize resins and asphaltenes using GC/MS, TGA, DSC and CHNS.

- Purify Benzene Insoluble Pitch (BIP).
  - The presence of aliphatic hydrocarbon and low MW fractions in the pitch could play an inhibiting role in producing mesophase pitch with enhancing carbonization.
  - Determine and quantify fractions of saturates, aromatics, resins, and asphaltenes (SARA).
  - Remove saturates, aromatics and resins.
GC/MS analysis of Benzene Soluble and Insoluble pitches

Search 57m/z for aliphatic hydrocarbons in BSP and BIP
Solvent Fractionation

Experimental Set up-1. Soxhlet extraction (BIP)

- **Sample**
  - Benzene Insoluble Pitch (10g)
- **Solvents**
  - n-Hexane (polarity index 0.1)
  - Toluene (2.4)
  - Dichloromethane (3.1)
  - Methanol (polarity 5.1) or Pyridine (5.3)

- **Soxhlet extraction**
  - Hexane (Saturate)
  - 30% Toluene + Hexane (Aromatics)
  - 30% DCM + Hexane (Resins)
  - Pyridine (Asphaltenes)

Loaded BIP:10.02g

1. Soxhlet extraction
2. Hexane (Saturates)
3. 30% Toluene in Hexane (Aromatics)
4. 30% Dichloromethane in Hexane (Resins)
5. Pyridine (Asphaltenes)
6. Quinoline soluble fraction + Solid
Solvent Fractionation

Result-1. Benzene Insoluble Pitch

Benzene Insoluble Pitch (BIP)

Hexane Soluble
Toluene + Hexane Soluble
DCM + Hexane Soluble
Pyridine Soluble

*Quinoline fraction was calculated by the difference

Asphaltene yield: 57.8%
Experimental Set up-2. Chromatographic column separation: BSP

- Sample
  - Benzene Soluble Pitch (Total ~ 2kg)
- Solvents
  - n-Hexane (polarity index 0.1)
  - Toluene (2.4)
  - Dichloromethane (3.1)
  - Methanol (polarity 5.1) or Pyridine (5.3)
- Column chromatography
  - Silica gel 62 and Silica gel 926
  - Neutral alumina
Result-2. Benzene Soluble Pitch

Benzene soluble Pitch (BSP)

Asphaltene yield: ~ 53%

*Quinoline fraction was calculated by the difference
Solvent Fractionation

Experimental set up

Soxhlet extraction

26.85g BSP loaded

Saturates (Paraffines) 27.4%

30% Toluene in Hexane

Aromatics 16.5%

Pyridine

Resins 9.7%

Solvent Fractionation

30% Dichloromethane in Hexane

Asphaltenes 42.4%

Pyridine

Solid 0.5%

Chromatographic Column

100% Hexane
Solvent Fractionation

- Asphaltene from Soxhlet: 15.6%
- Asphaltene from Chromatographic: 26.8%
### Simplified Solvent fractionation for BSP

The process involves:

1. **Soxhlet extraction**
2. **BSP loaded**
3. **Chromatographic Column**
4. **Solid**
5. **Resins Aromatics Saturates**

#### Solvent Fractionation

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight %</th>
<th>Molar Element ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C (H/C)</td>
<td>N (H/C)</td>
</tr>
<tr>
<td>Asphaltene BSP-Soxh_A</td>
<td>73.71 (1.31)</td>
<td>7.71 (0.49)</td>
</tr>
<tr>
<td>Asphaltene BSP_Soxh&amp;Chroma_B</td>
<td>75.42 (1.24)</td>
<td>8.84 (0.80)</td>
</tr>
</tbody>
</table>
Solvent Fractionation

Solvent fractionation for BIP

<table>
<thead>
<tr>
<th>Solvent Fractionation</th>
<th>Weight %</th>
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</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>Pyridine_BIP</td>
<td>59.07 (0.6)</td>
<td>7.7 (0.1)</td>
</tr>
<tr>
<td>Asphaltene_BIP</td>
<td>55.60 (0.10)</td>
<td>7.07 (0.77)</td>
</tr>
</tbody>
</table>
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Spinning of Fiber by Ramaco

- Fiber Spinning Initiated 3/26/21
  - Established Baseline and Verified Equipment
  - Achieved Stable Spinning AR24 Synthetic Mesophase
  - HAAKE extruder with 500micron orifice
  - Fiber Diameters from 40 micron to 70 micron
Coal to Carbon Fiber – Novel Supercritical CO2 Solvated Process (MUSCL)

Spinning of Fiber by Ramaco

Establishing Baseline with Synthetic Mesophase

AR24 Fibers Spun at 325°C AVG DIA 48um Observed Orientation of Mesogens
Coal to Carbon Fiber – Novel Supercritical CO2 Solvated Process (MUSCL)

Commercialization and Economic Analysis

Diagram showing the process flow from coal to carbon fiber, including stages such as gasification, activation, upgrading, and production of various products like mesophase pitch, carbon fiber, and heat & electricity.

Feedstock → MuScL process → MuScL System → Process → Intermediate product → Market

- Coal → MuScL process
- Medium oil, Heavy oil, Extra heavy oil → Condensers
- Gas (CO₂, H₂, CH₄, C₂ – C₆) → Char
- Gasification
- Activation
- Saturates, aromatics → Upgrading process (refomer, cracking, alkylation)
- Pitch → Mesophase Pitch
- Carbon fiber: Carbon gel
- Syngas (H₂) → Heat & electricity
- Activated carbon → Air, water purification

Products:
- Naphtha: Gasoline, Kerosene, Diesel, Heavy Oil
### Coal to Carbon Fiber – Novel Supercritical CO₂ Solvated Process (MUSCL)

**COVID-19 Impacts March-May 2020, Equipment Delivery Delays Revised Schedule for Task 4 Extended to July 31**
Conclusions

• First ever pyrolysis of coal under supercritical CO$_2$ conditions to produce pitch products.
• Observed low yields at initial set of conditions.
  • Investigation of further process conditions could increase yield.
• Fractionation of pitch with partial solvents in supercritical CO$_2$ performs similarly to conventional Soxlet extractions.
• Chemical analysis of pitch fractions in work.
• Will combine pitch fractions and thermally treat to perform conversion to mesophase.
• Fiber spinning baseline established.
• Supercritical CO$_2$ Fractionation provides more ecological alternative to conventional methods and utilizes available CO$_2$. 
Thank You

www.ramacocarbon.com

Acknowledgements

RAMACO:
Randall Atkins
Charlie Atkins
Grant Hazle
Luke Adsit

Terrapower:
Francesco Deleo
Josh Walter
Pyoungchung Kim

DOE PM: Jessica Mullen