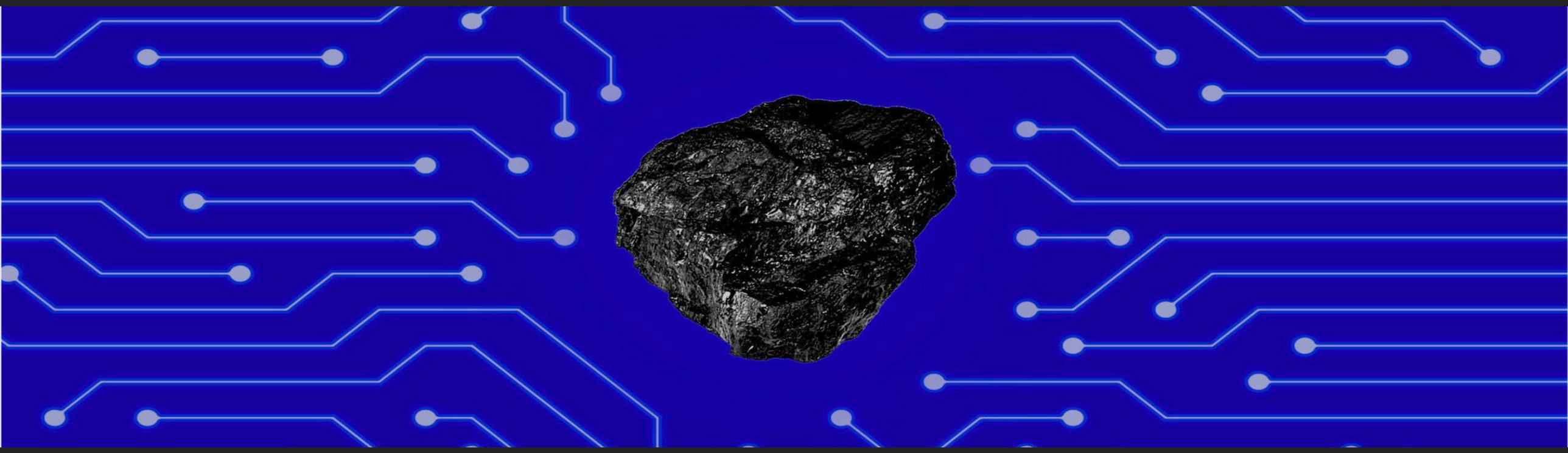
Experimental Validation & Continuous Testing of an On-Purpose High-Yield Pitch Synthesis Process for Producing Carbon Fiber from Coal (LSDCL)



By **Charles Hill** and **Chris Yurchick** —
Co-PIs @ Ramaco Carbon

Prepared for the 2020 NETL Annual Coal Processing Project Review Meeting

Who We Are

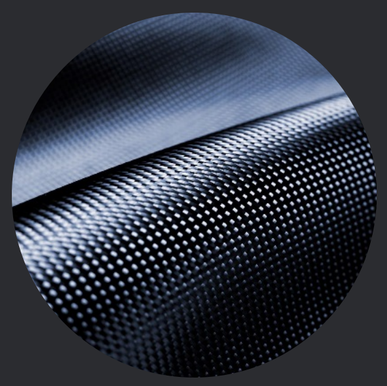
Ramaco Coal, founded in 2011, is a coal-based conglomerate with operations in five states. It consists of two main operating companies:

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



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

Experimental Validation & Continuous Testing of an On-Purpose High-Yield Pitch Synthesis Process for Producing Carbon Fiber from Coal (LSDCL)

DE-FE-00310801

DOE Funding: $883,365
Cost Share: $220,842
Total Value: $1,104,207

Budget Period 1: 1-12 months
Budget Period 2: 2-12 months

- Produced over 100kg of high-quality isotropic pitch.
- Much lower cost than PAN and more ecologically sound (greener)
- Demonstrated mesophase conversion at acceptable yields.
- Demonstrated initial fiber production with good draw down ratios.

High-Yield Pitch Synthesis Process for Producing Carbon Fiber from Coal

- Develop a process to create high-quality carbon fiber precursor material from U.S. coal using **low-severity direct coal liquefaction (LS-DCL)** techniques in the synthesis of coal tar pitch.
- Project could lead to **cost reductions** to take advantage of a secure, plentiful domestic coal feedstock, and may significantly expand the market for pitch-based carbon fiber.

High-Yield Pitch Synthesis Process for Producing Carbon Fiber from Coal

Direct Coal Liquefaction Technology – HTI H-Coal® Development History:

- Same development path/pilot units as H-Oil®.

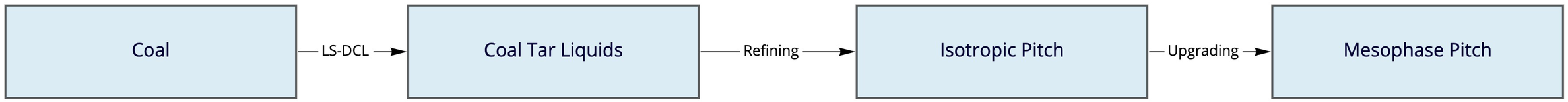
- Pilot plant development started in 1960's.

- DOE-supported scale-up to demonstration scale (200 TPD) in 1980s. This Catlettsburg, KY facility is pictured on the right.

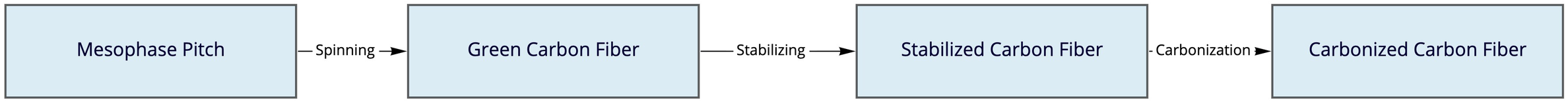
- License/Basic engineering design and provided start-up support for Shenhua Direct Coal Liquefaction Plant, a successful start-up in 2008 with a capacity of 6000 tons per day of coal.

High-Yield Pitch Synthesis Process for Producing Carbon Fiber from Coal

Budget Period 1



Budget Period 2



- Main technical focus area is on the **LS-DCL step**
- LS-DCL is derived from long established process technologies, H-Coal™/H-Oil™, **originally commercialized for liquid transportations fuels**
- LS-DCL constitutes an incremental, lower severity, change in process conditions to produce **on-purpose isotropic pitch** and valuable co-products
- Other processing steps are to be practiced by conventional means

High-Yield Pitch Synthesis Process for Producing Carbon Fiber from Coal

Project Objectives & Success Criteria

1. Demonstrate that coal tar pitch-based isotropic pitch can be made in **high yield >35%** in a low severity DCL process.

2. Illustrate techno-economic viability of producing **mesophase pitch at $1.50/lb.**

3. Validate that the resulting **mesophase** pitch is a suitable carbon fiber precursor, satisfying the most basic physical property criteria, such as:

- Softening point (300°C –375°C).
- Sufficiently high mesophase content (35% -90%).
- Sufficiently low QI content.
- Ability to spin continuous monofilament fiber.

High-Yield Pitch Synthesis Process for Producing Carbon Fiber from Coal

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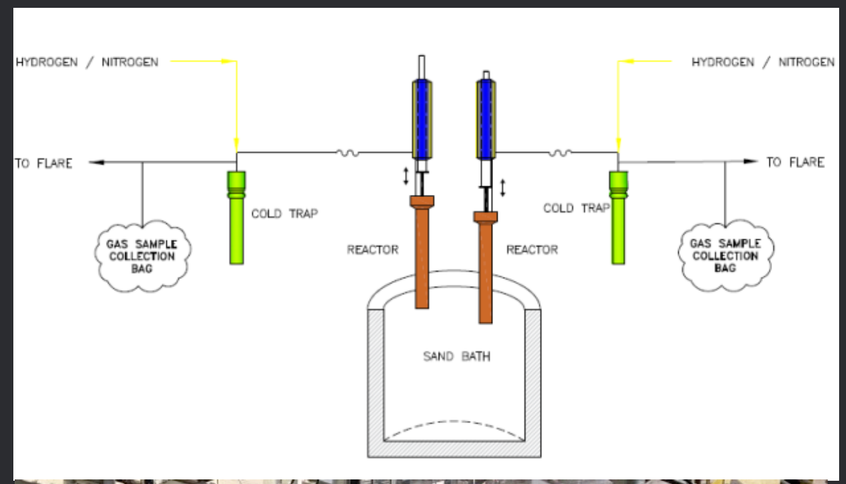
Micro-autoclave (Unit 223) Coal Reactivity Testing

To Determine Conditions for Pilot Operations

Unit 223 has side-by-side reactors to allow parallel testing. The reactors were charged with coal (4 g) and solvent (16 g) and were threaded onto the shaker arm assembly. The reactors were pressurized to the desired test pressure with hydrogen, nitrogen, or other gas via 3-mm tubing that was welded into the reactor cap.



Run# 223-28-	Reactor #	Time @Temperature Minutes	Temperature deg C	Starting Pressure	Coal g	Solvent g
6	K-1	60	400	6.90 MPa/H2	4.00	16.00
6	K-2	60	400	3.45 MPa/H2	4.00	16.00
7	K-1	90	400	6.90 MPa/H2	4.00	16.00
7	K-2	90	400	3.45 MPa/H2	4.00	16.00
8	K-1	45	413	6.90 MPa/H2	4.00	16.00
8	K-2	45	413	3.45 MPa/H2	4.00	16.00
9	K-1	60	413	6.90 MPa/H2	4.00	16.00
9	K-2	60	413	3.45 MPa/H2	4.00	16.00
10	K-1	30	407	6.90 MPa/H2	4.00	16.00
10	K-2	30/30	407/418	6.90 MPa/H2	4.00	16.00

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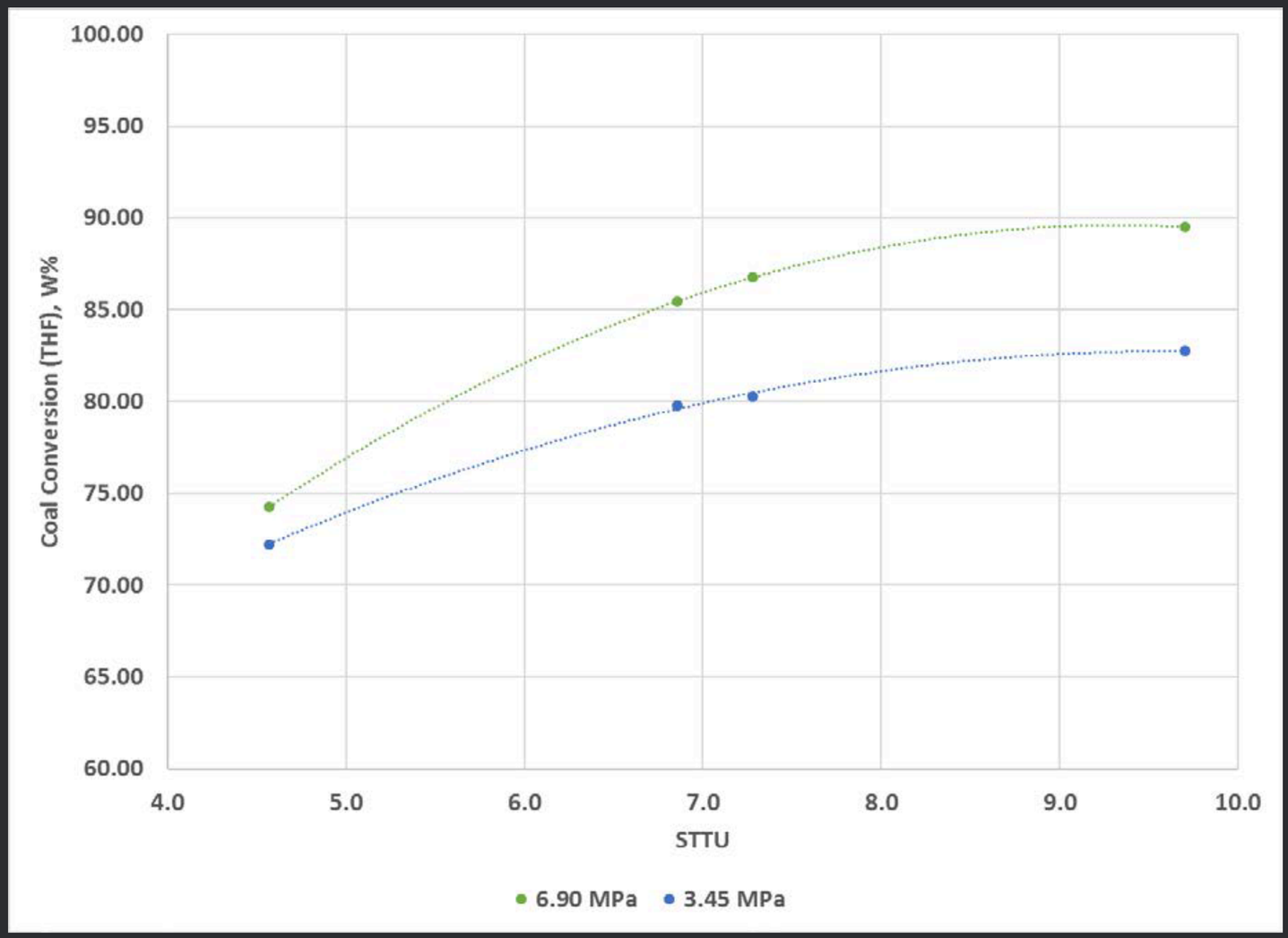
High-Yield Pitch Synthesis Process for Producing Carbon Fiber from Coal

Micro-autoclave (Unit 223) Coal Reactivity Testing Results

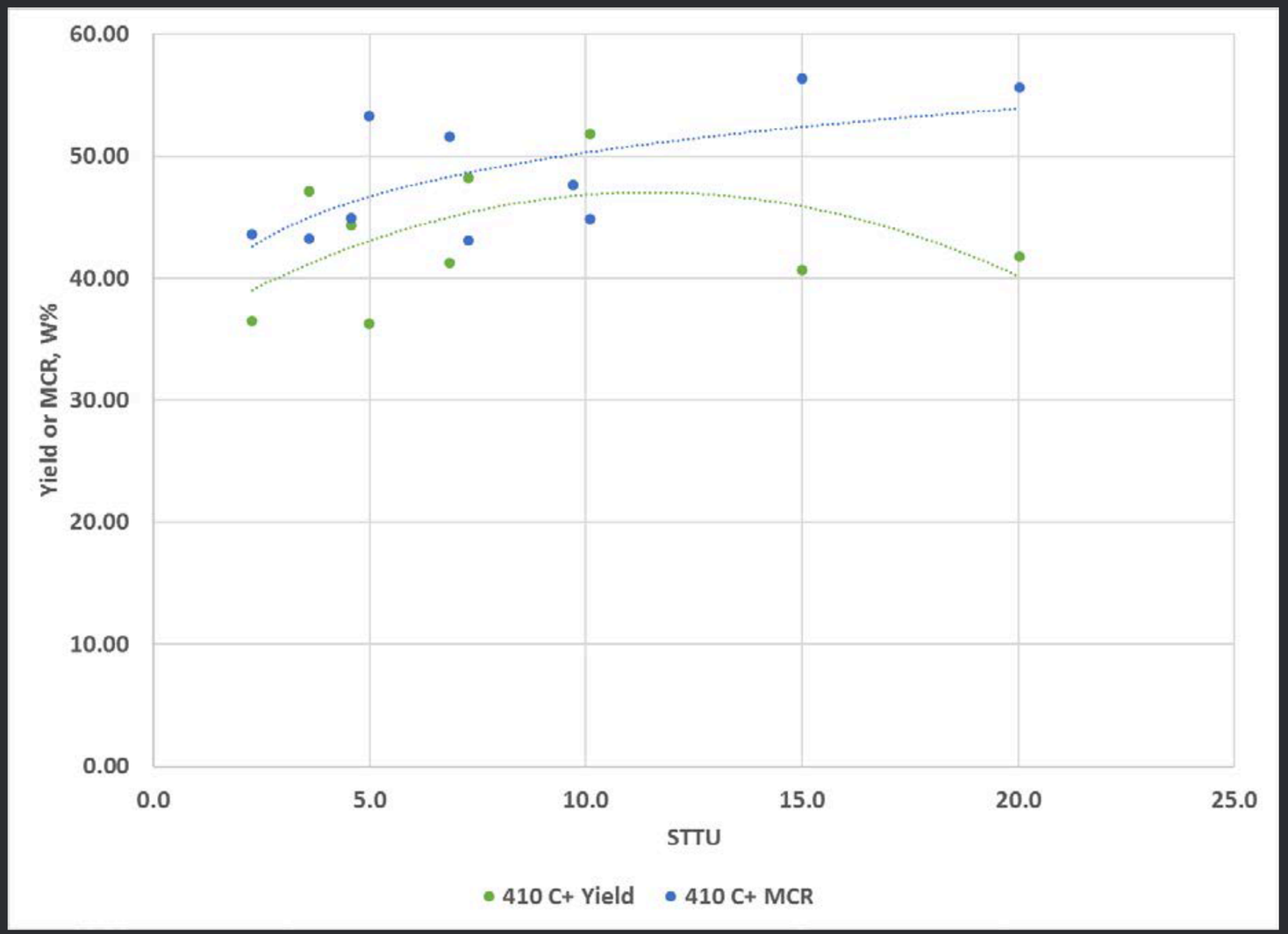
Coal Conversion H2 Pressure Effect



High-Yield Pitch Synthesis Process for Producing Carbon Fiber from Coal

Micro-autoclave (Unit 223) Coal Reactivity Testing Results

Pitch Yield and Quality at 6.9MPa



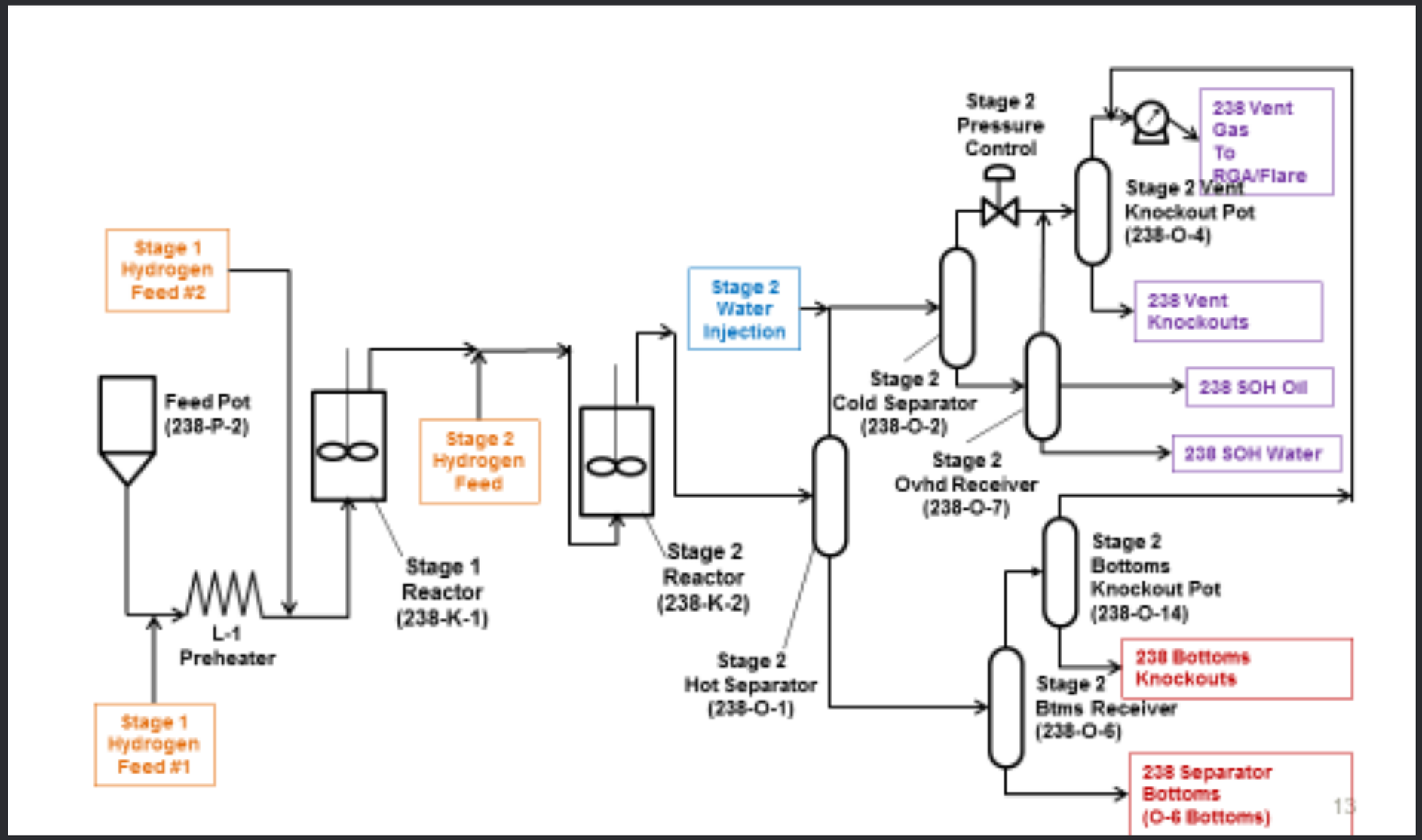
High-Yield Pitch Synthesis Process for Producing Carbon Fiber from Coal

Micro-autoclave (Unit 223) Coal Reactivity Testing

- The last test performed (Test 10) in K2 simulated a 2-stage operation
- Reaction time of 30 minutes in each stage
- Temperatures of 407°C and 418 °C respectively.
- Results from this last test are excellent with:
  - 90 % coal conversion,
  - 35 % 525 C+ pitch yield
  - MCR:Asphaltene ratio of 1.9
- These conditions were selected for continuous operation in the pilot (Unit 245).

High-Yield Pitch Synthesis Process for Producing Carbon Fiber from Coal

Pilot Operations (Unit 245) Processing



High-Yield Pitch Synthesis Process for Producing Carbon Fiber from Coal

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Pilot Operations (Unit 245) Processing

Coal Conversion & Pitch Yield (%)

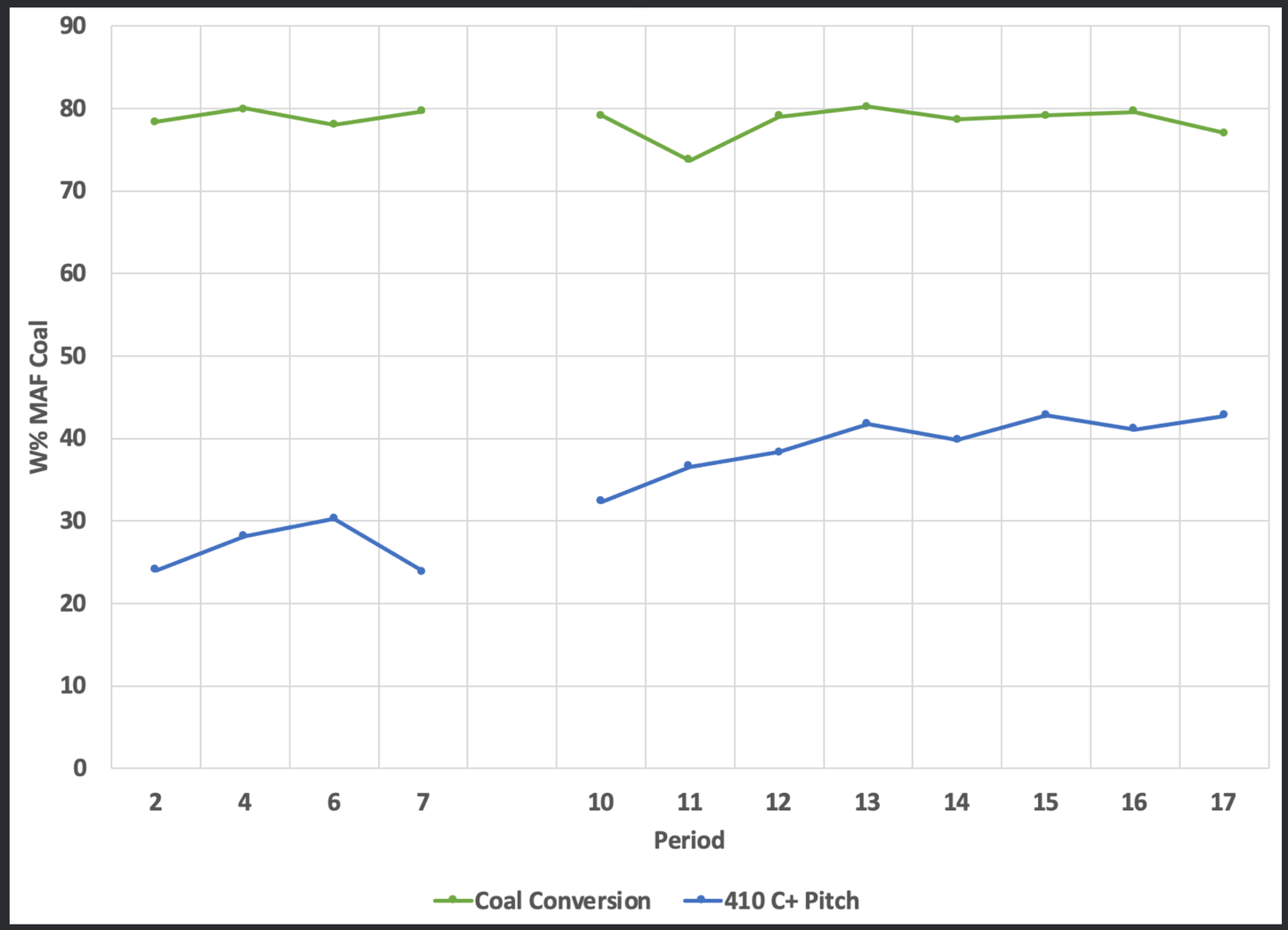

Table 1 – Average Performances

Periods	1-7	10-17
Periods Averaged	2,4,6,7	10-17
Coal Conversion, W% MAF Coal	79.0	78.9
410 °C+ Pitch Yield, W % MF Coal	25.2	37.3
410 °C+ Pitch, MCR	41.2	42.1

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High-Yield Pitch Synthesis Process for Producing Carbon Fiber from Coal

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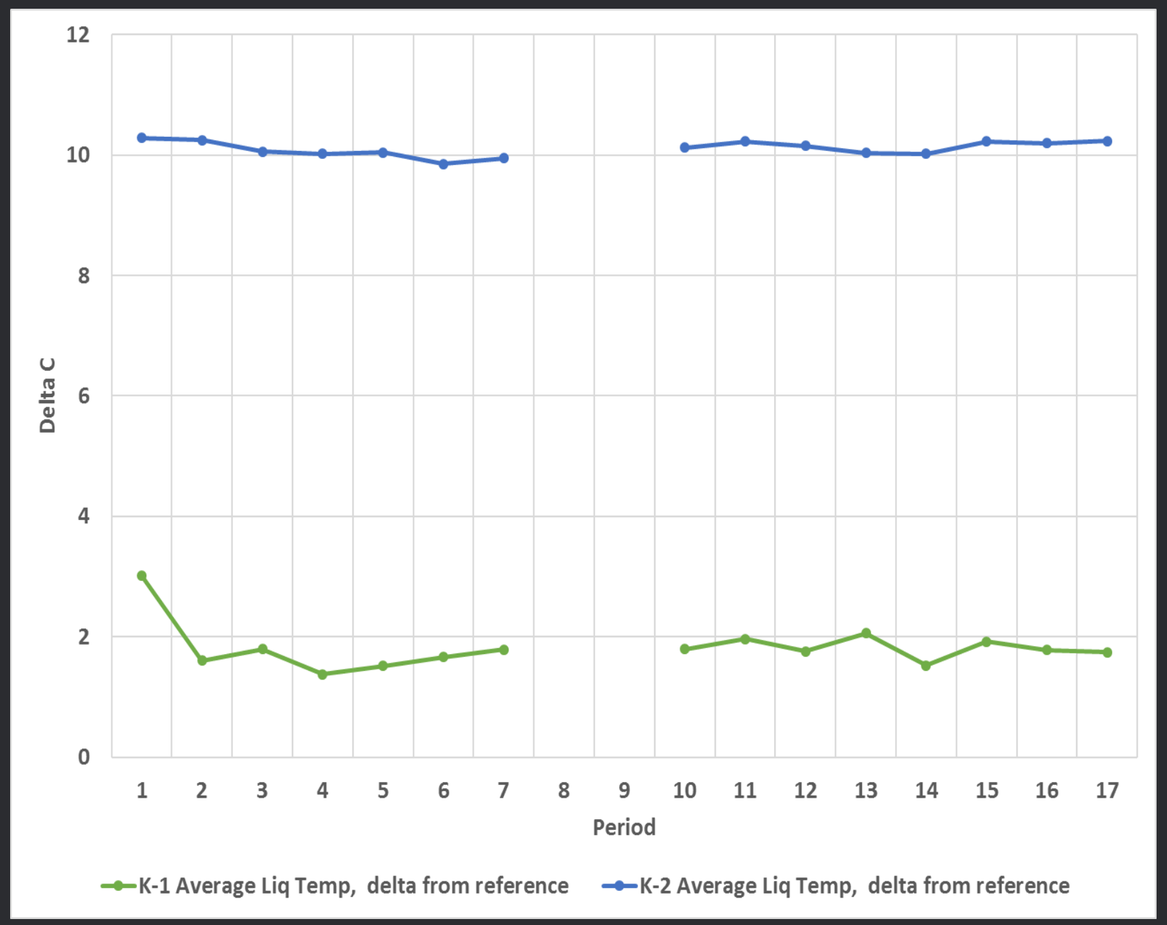
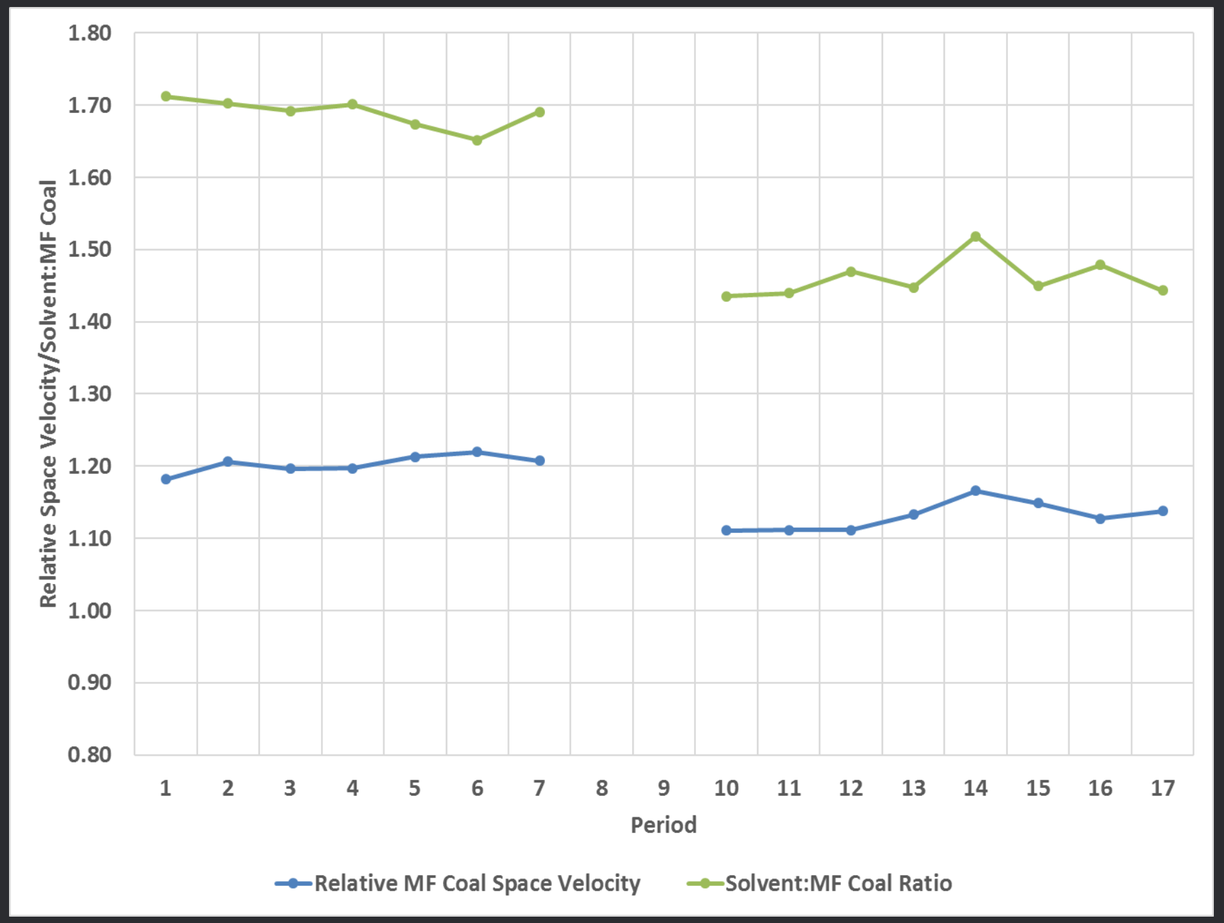
Pilot Operations (Unit 245) Processing

Reactor Temperatures



Reactor Space Velocity/Solvet:MF Coal Ratio



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High-Yield Pitch Synthesis Process for Producing Carbon Fiber from Coal

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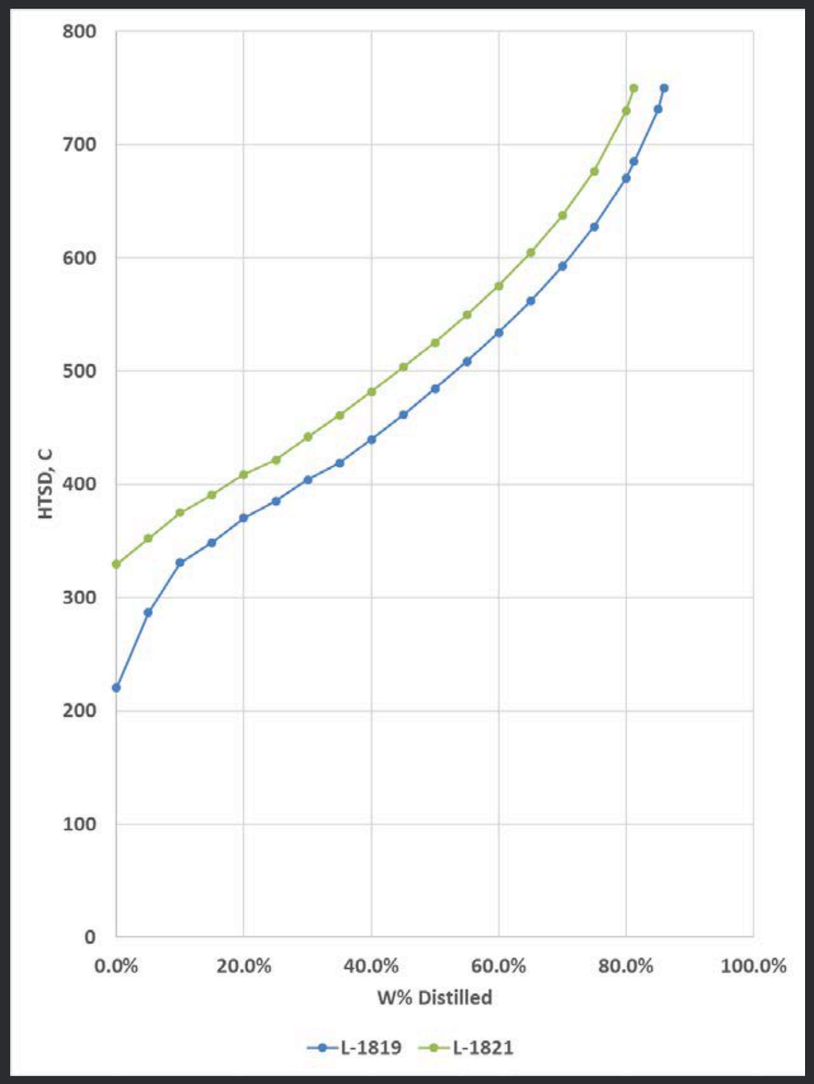
Batch Vacuum Distillation



hti

High-Yield Pitch Synthesis Process for Producing Carbon Fiber from Coal

Pressure Filter Solids (PFS)

Period	Filter Solids, g
1B	1843
2A	2948
2B	2258
3A	3428
3B	3297
4A	4142
4B	2216
5A	3713
5B	2602
6A	3686
6B	2593
7A	3799
7B	3899
Total	40424

Investigating Product Value for REE Extraction

High-Yield Pitch Synthesis Process for Producing Carbon Fiber from Coal

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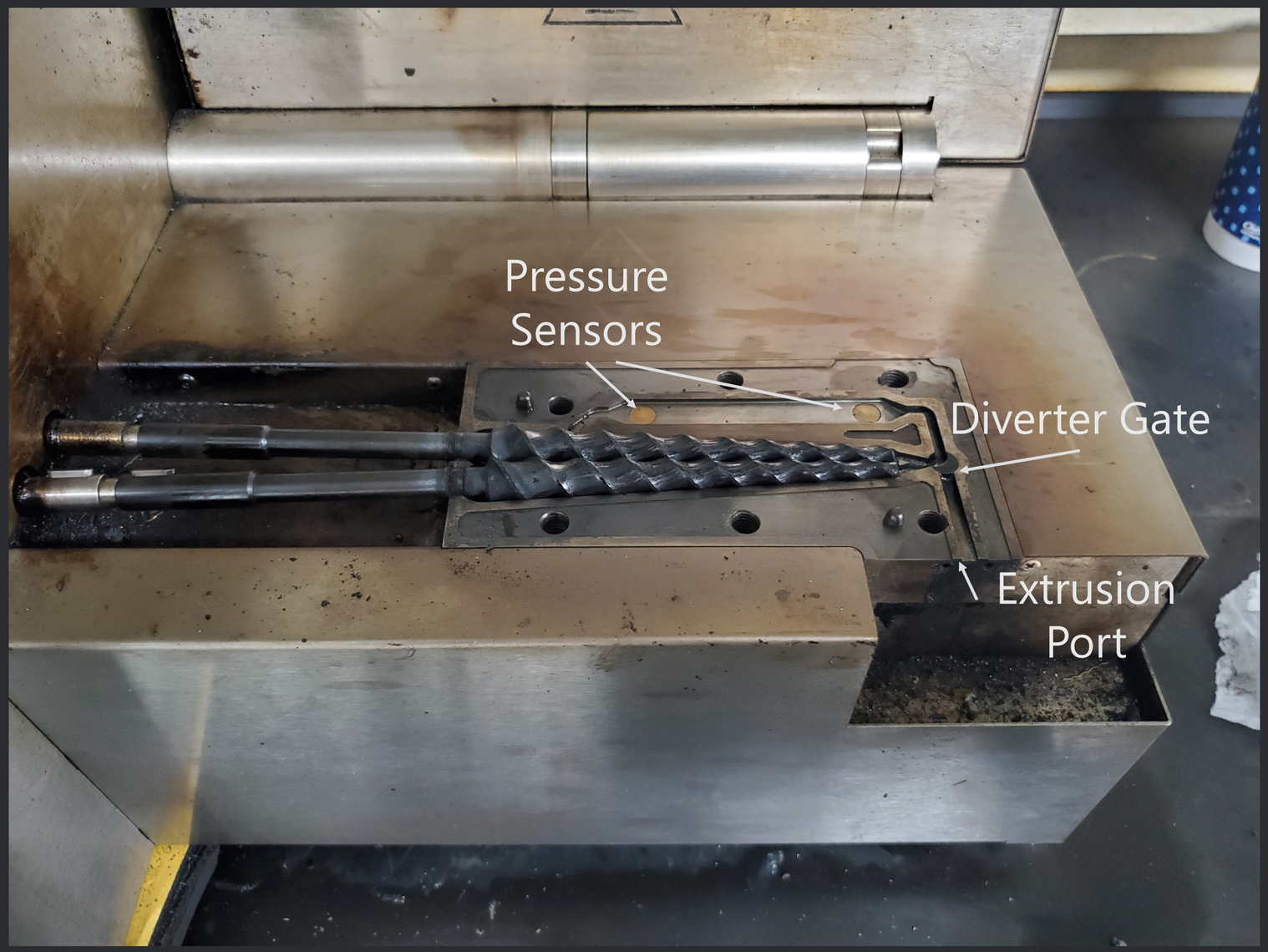
Conversion of Pitch to Mesophase by Ramaco



Pitch recirculates during thermal treatment and is extruded after completion

High-Yield Pitch Synthesis Process for Producing Carbon Fiber from Coal

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Conversion of Pitch to Mesophase by Ramaco

Added Box for Nitrogen Purge at Inlet and Exit Ports

High-Yield Pitch Synthesis Process for Producing Carbon Fiber from Coal

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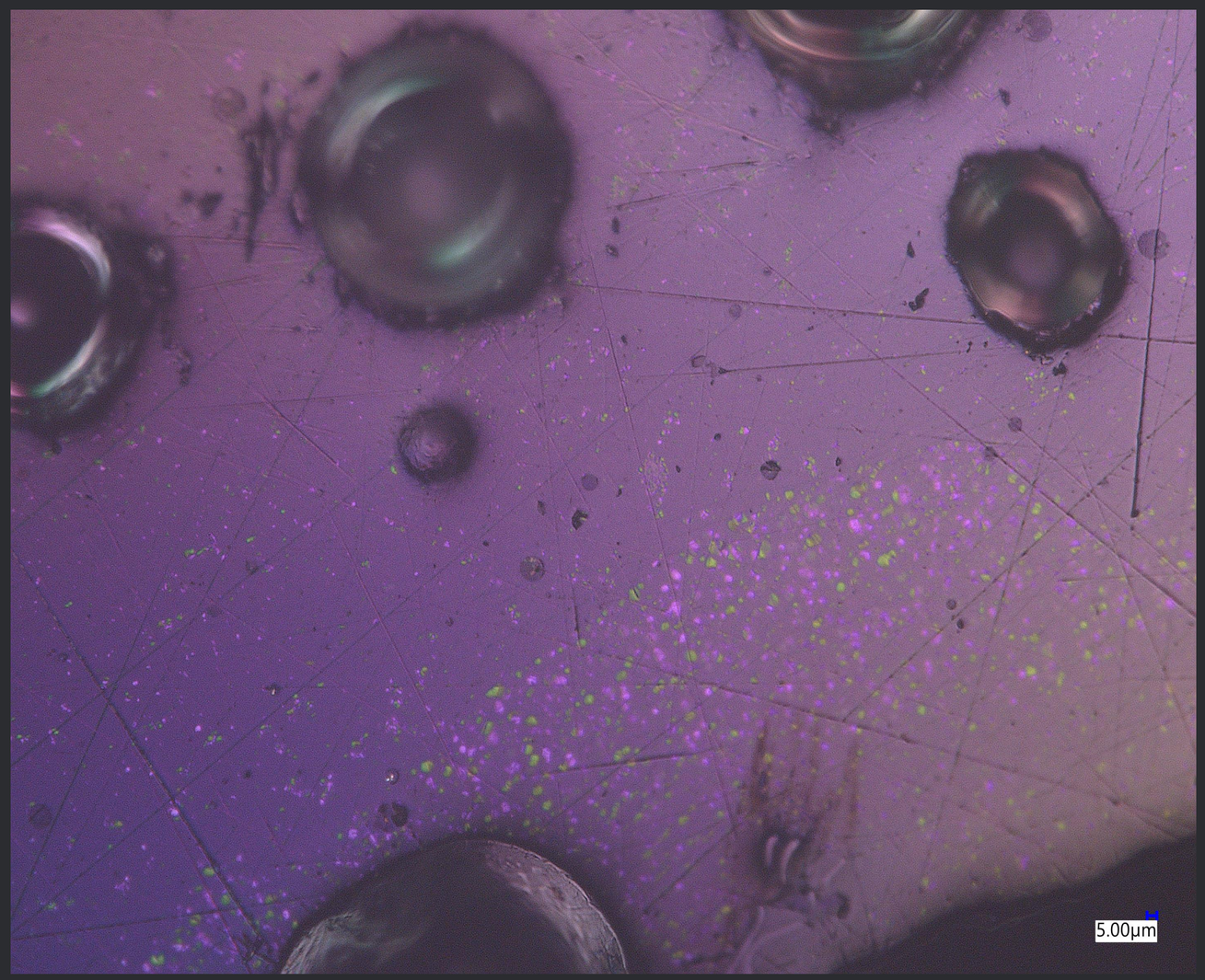
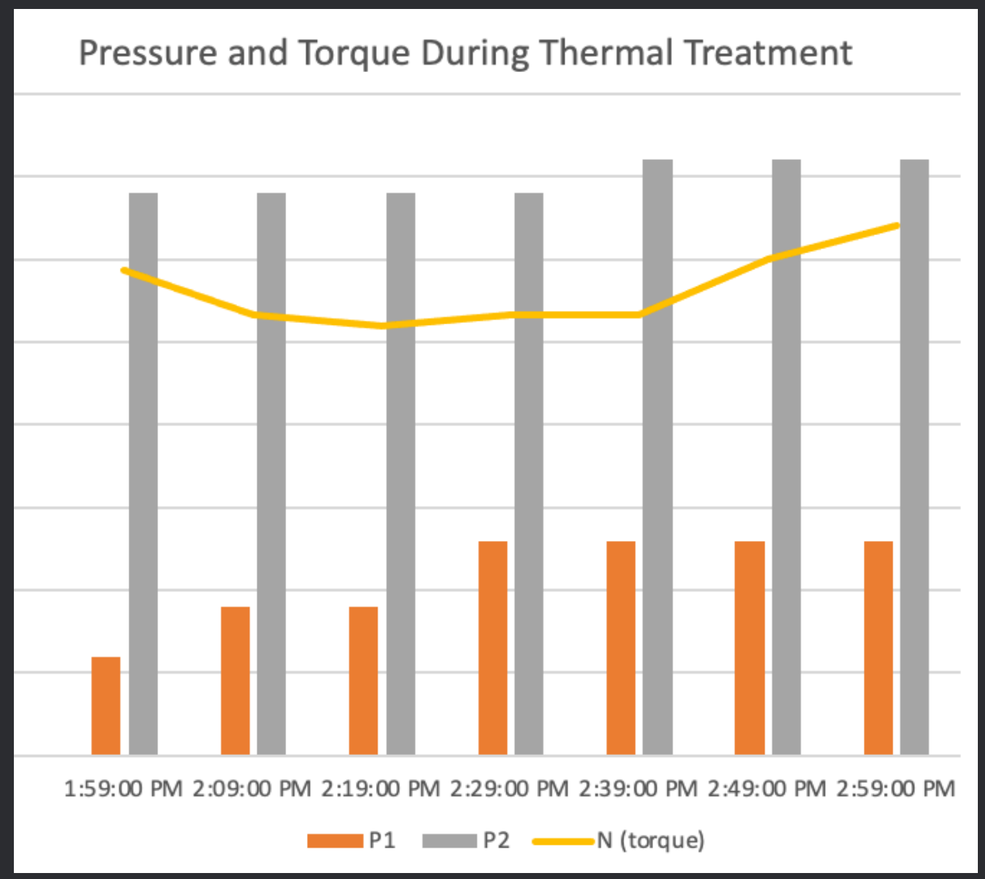
Conversion of Pitch to Mesophase by Ramaco



Mesophase Formation after 60m at 400C Image 500X

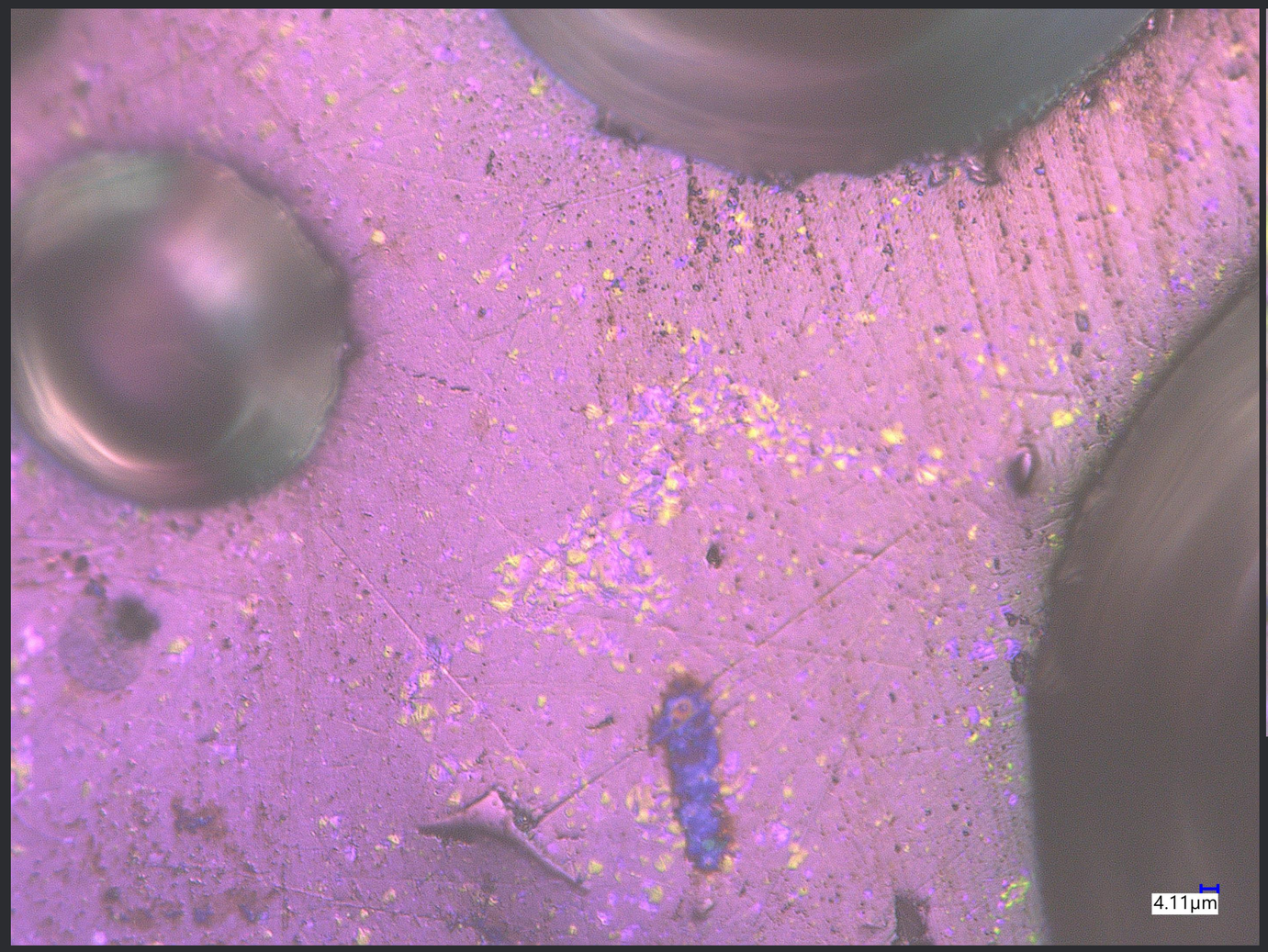


In-line flow pressures and torque recorded during conversion

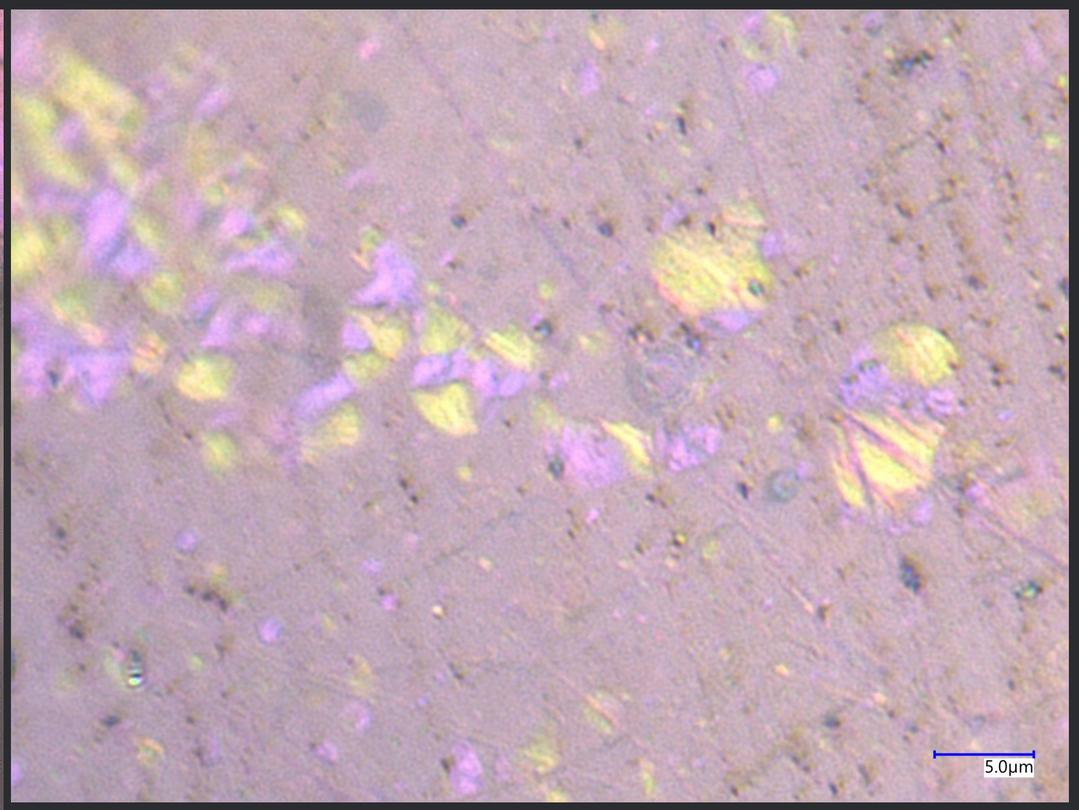
High-Yield Pitch Synthesis Process for Producing Carbon Fiber from Coal

RAMACO CARBON

Conversion of Pitch to Mesophase by Ramaco



Mesophase Formation after 75m at 400C Image 500X

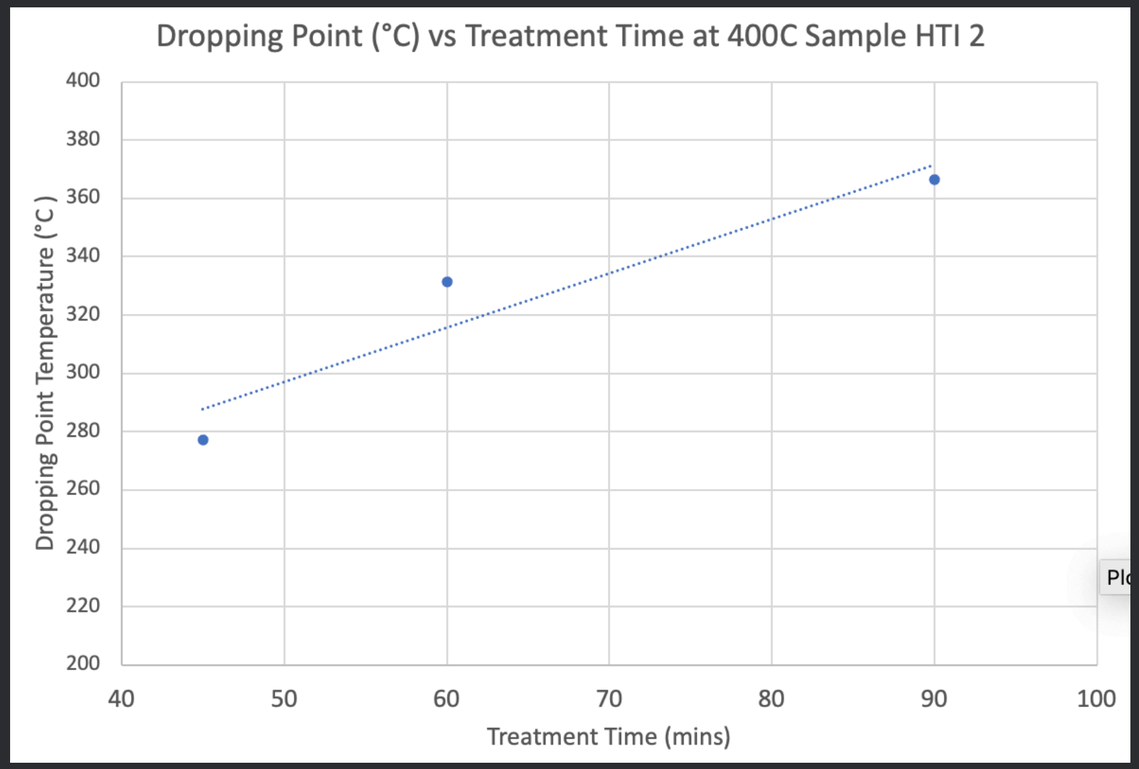


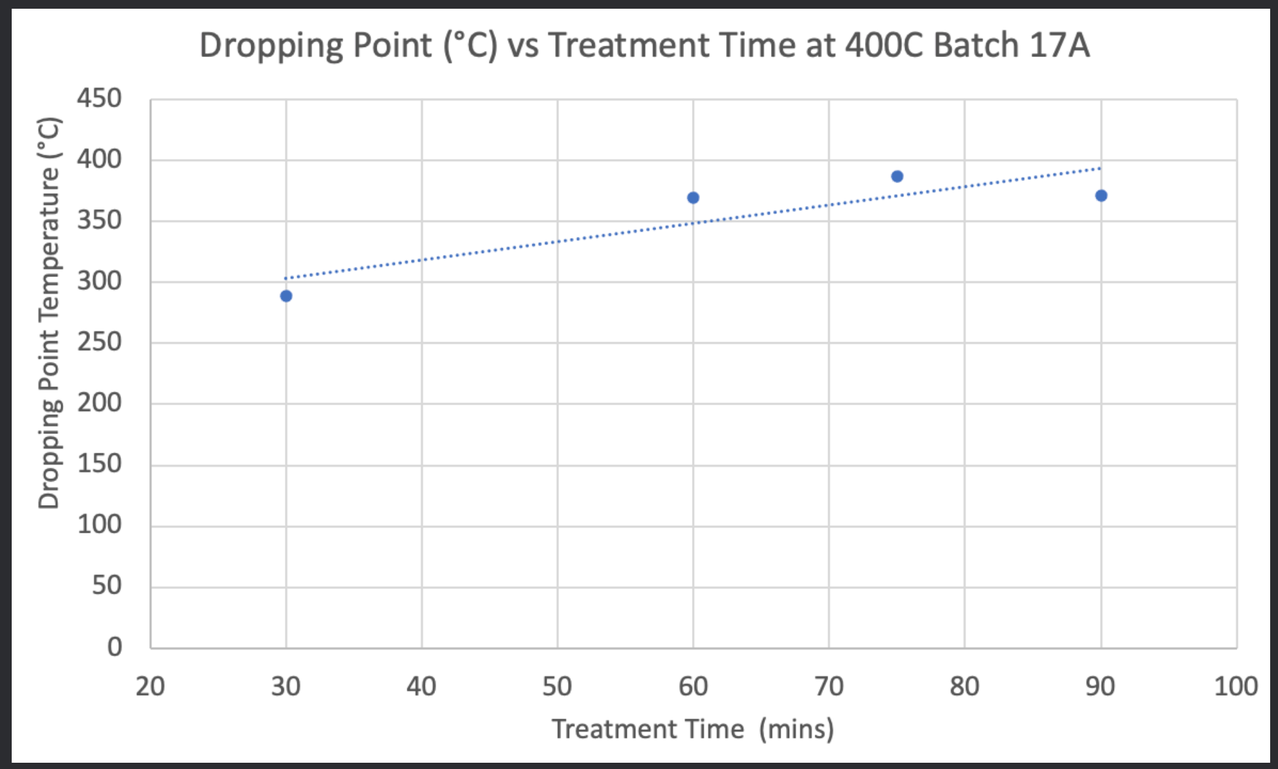
Mesophase Formation after 75m at 400C Image 6000X

High-Yield Pitch Synthesis Process for Producing Carbon Fiber from Coal

RAMACO CARBON

Conversion of Pitch to Mesophase by Ramaco





- Dropping Point of Starting Materials.
  - HTI 2 DP is 114.7°C
  - Batch 17A is 144.7°C

- Increasing Trends in Dropping Point Observations
- Large Variability and Two-Phase Behavior at Longer Treatment Times

High-Yield Pitch Synthesis Process for Producing Carbon Fiber from Coal

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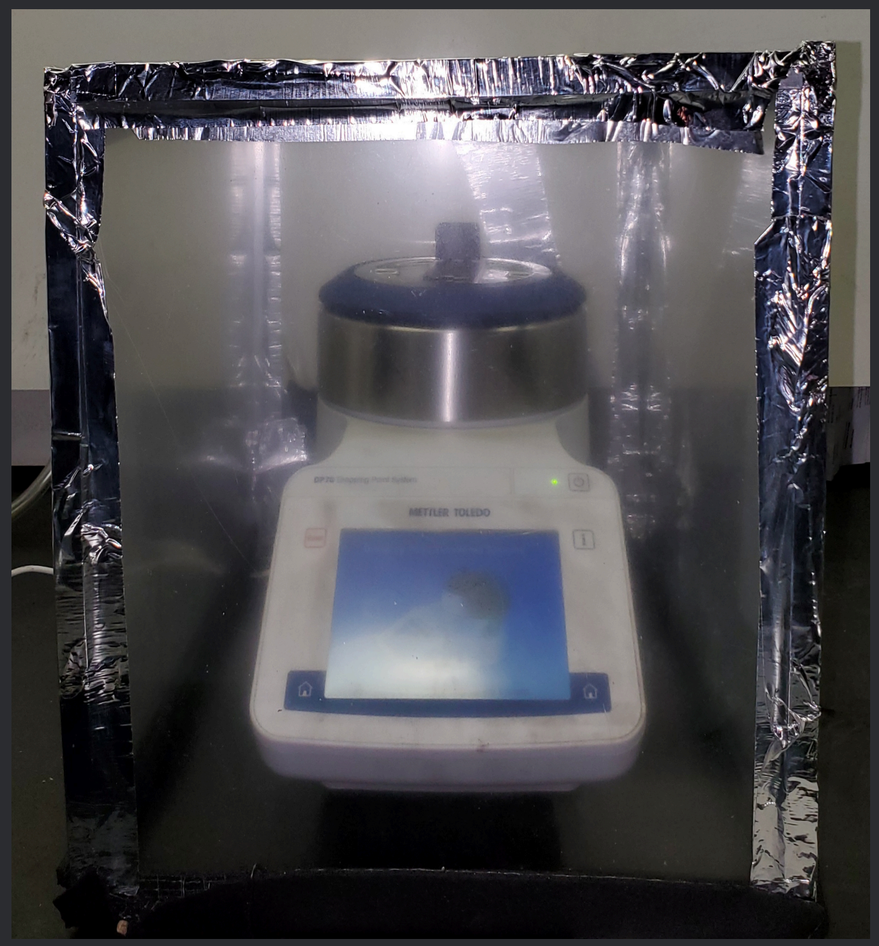
Conversion of Pitch to Mesophase by Ramaco



Mettler DP70

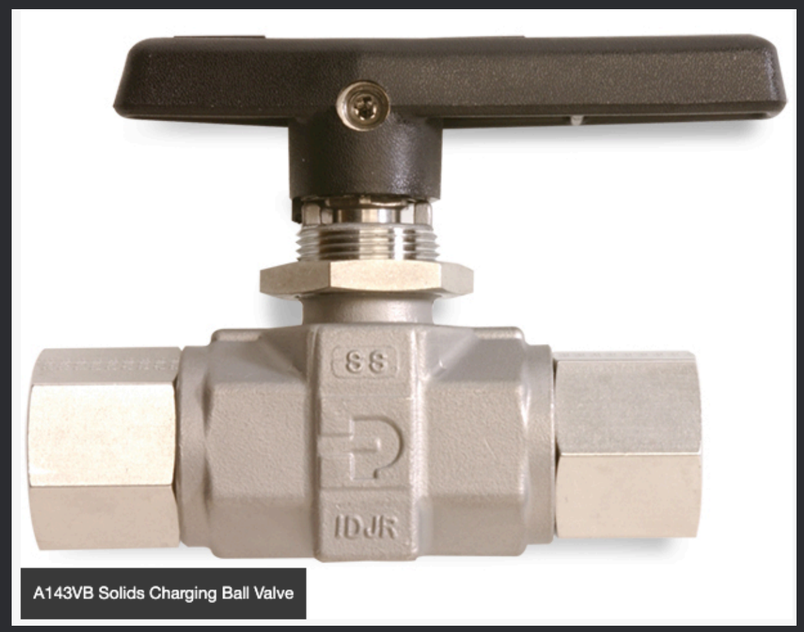
- Large Variability in Dropping Point
- Observed Oxidation of Pitch Surface
- Added Cover and Nitrogen Purge on Mettler DP70

High-Yield Pitch Synthesis Process for Producing Carbon Fiber from Coal

Conversion of Pitch to Mesophase by Ramaco

Scale to larger batches in traditional stirred/sparged reactor

- Produce quantities adequate for filtering and spinning
- Improve consistency and repeatability



A143VB Solids Charging Ball Valve

1L Parr Reactor, Gas Entrainment Impeller, and Solids Charging Port (expected delivery 4/30)

High-Yield Pitch Synthesis Process for Producing Carbon Fiber from Coal

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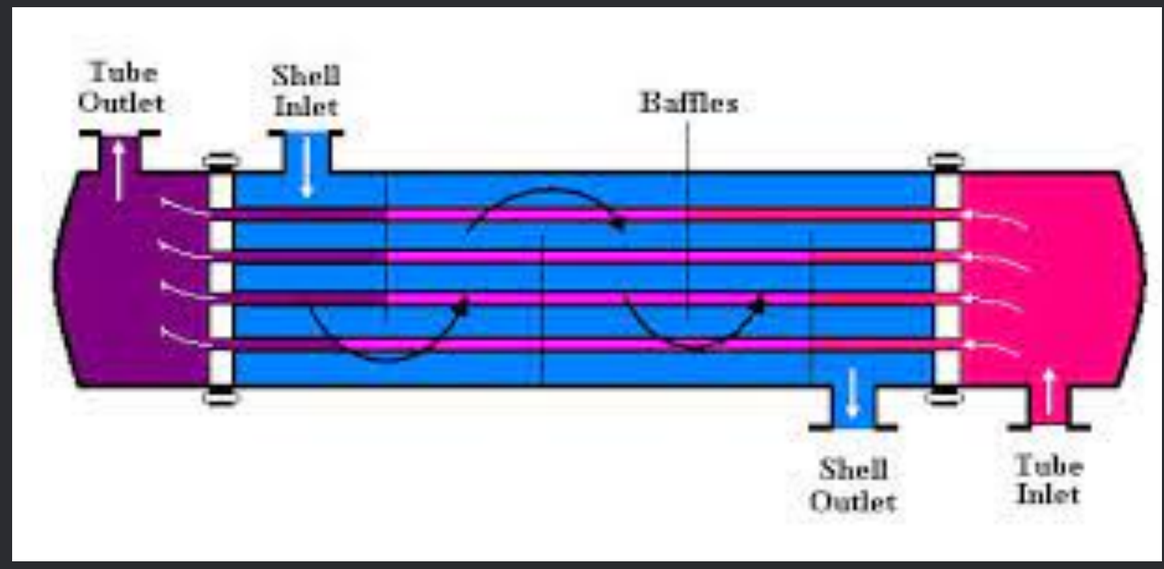
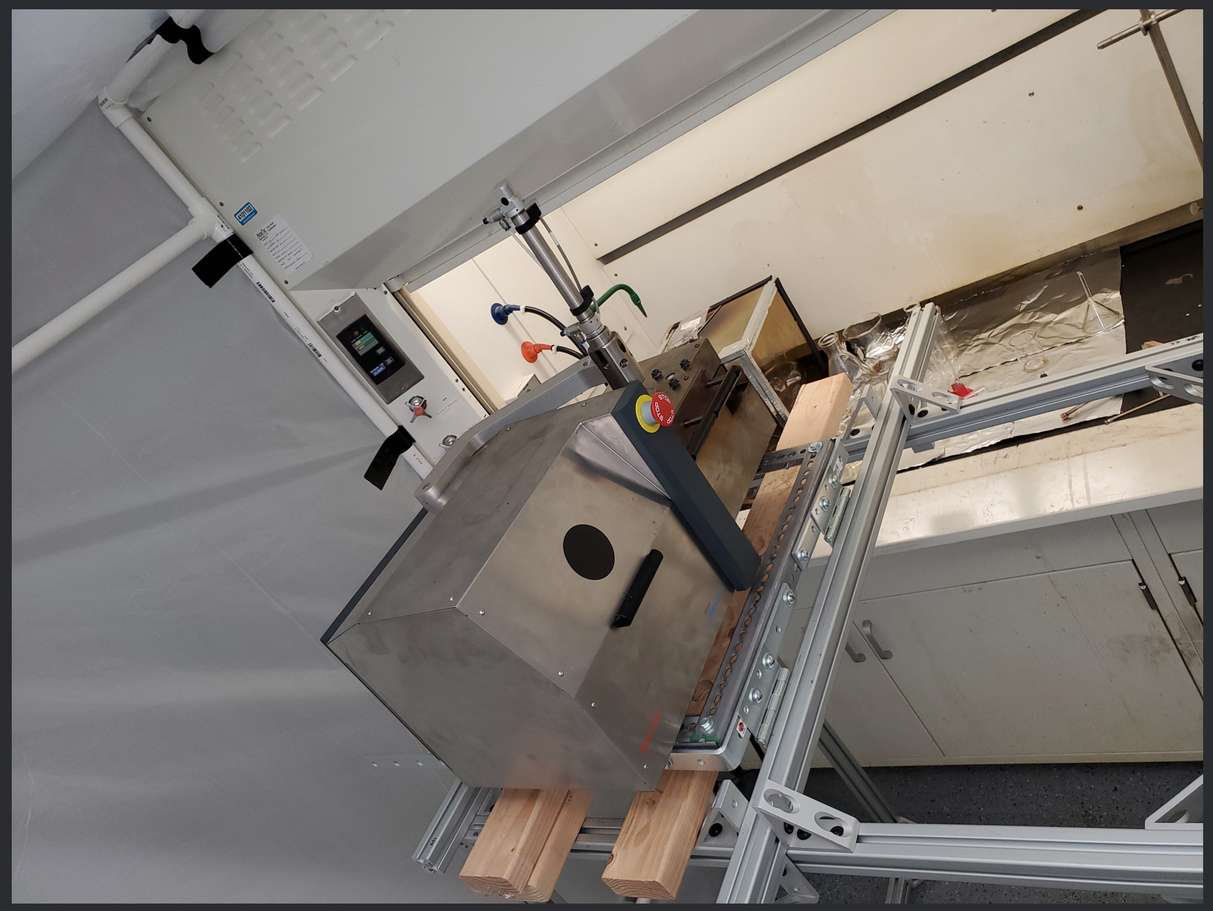
Recovery of Liquid Volatiles from Mesophase Reaction

- Various coal-derived volatile fractions are emitted in the vapor form from the mesophase reaction by controlling the pitch composition and process variables
- Volatile composition varies as the reaction progresses
- The volatile recovery system will condense and collect the volatiles and permit volatile fractions to be separated and analyzed at various points throughout the reaction.



High-Yield Pitch Synthesis Process for Producing Carbon Fiber from Coal

Spinning of Fiber by Ramaco



HAAKE on Hinged Rack Enables Spinning of 5g Samples

High-Yield Pitch Synthesis Process for Producing Carbon Fiber from Coal

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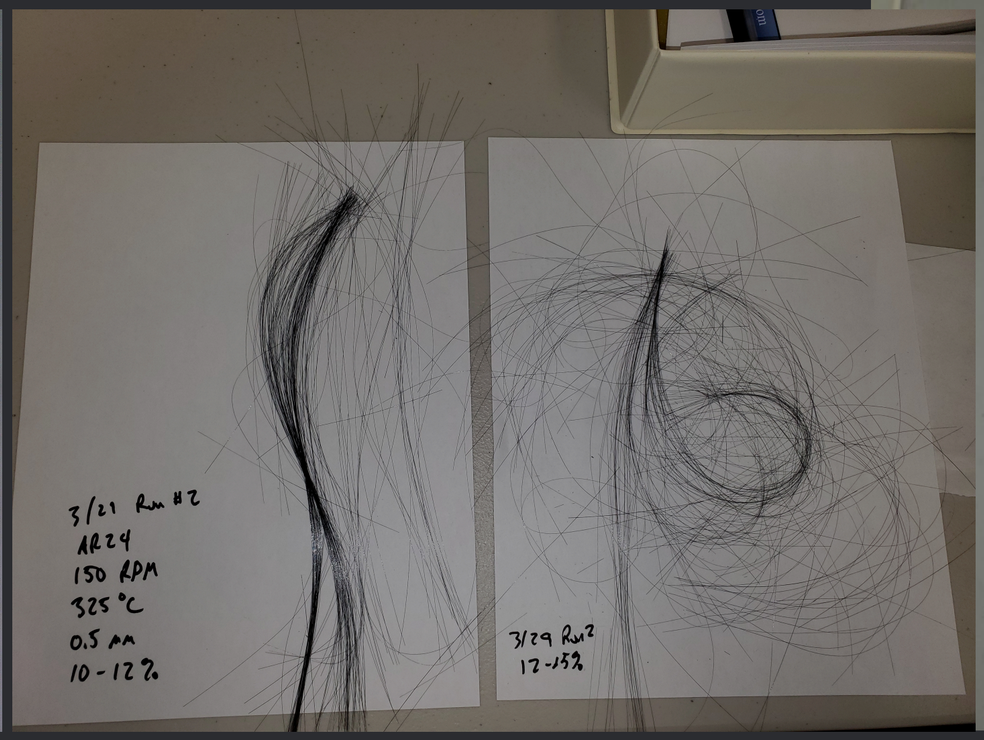
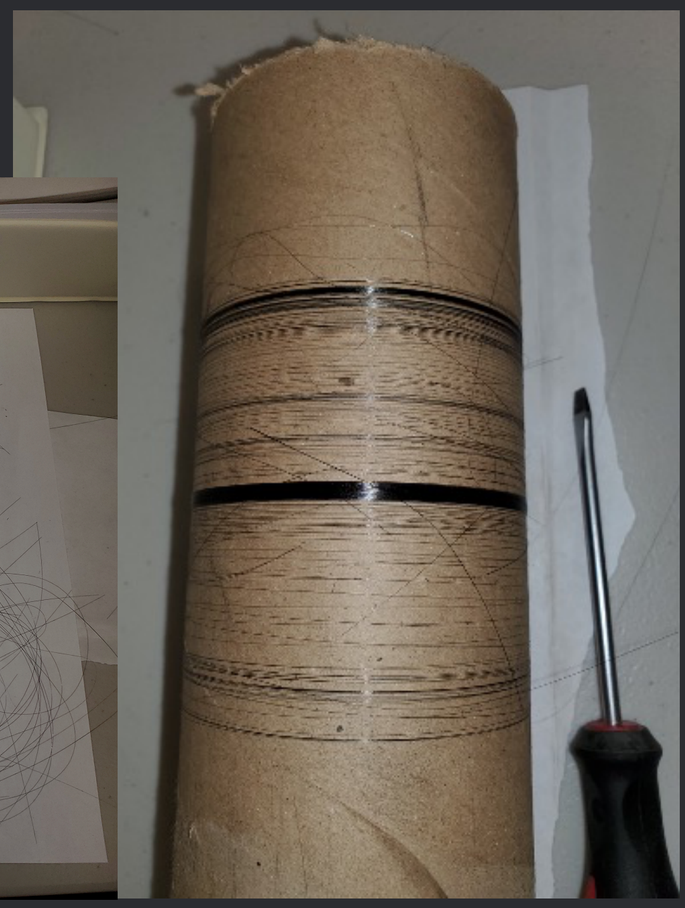
Spinning of Fiber by Ramaco

- Fiber Spinning Initiated 3/26
  - Establish Baseline and Verify Equipment
  - Achieved Stable Spinning AR24 Synthetic Mesophase
  - HAAKE extruder with 500micron orifice
  - Fiber Diameters from 40 micron to 70 micron





High-Yield Pitch Synthesis Process for Producing Carbon Fiber from Coal

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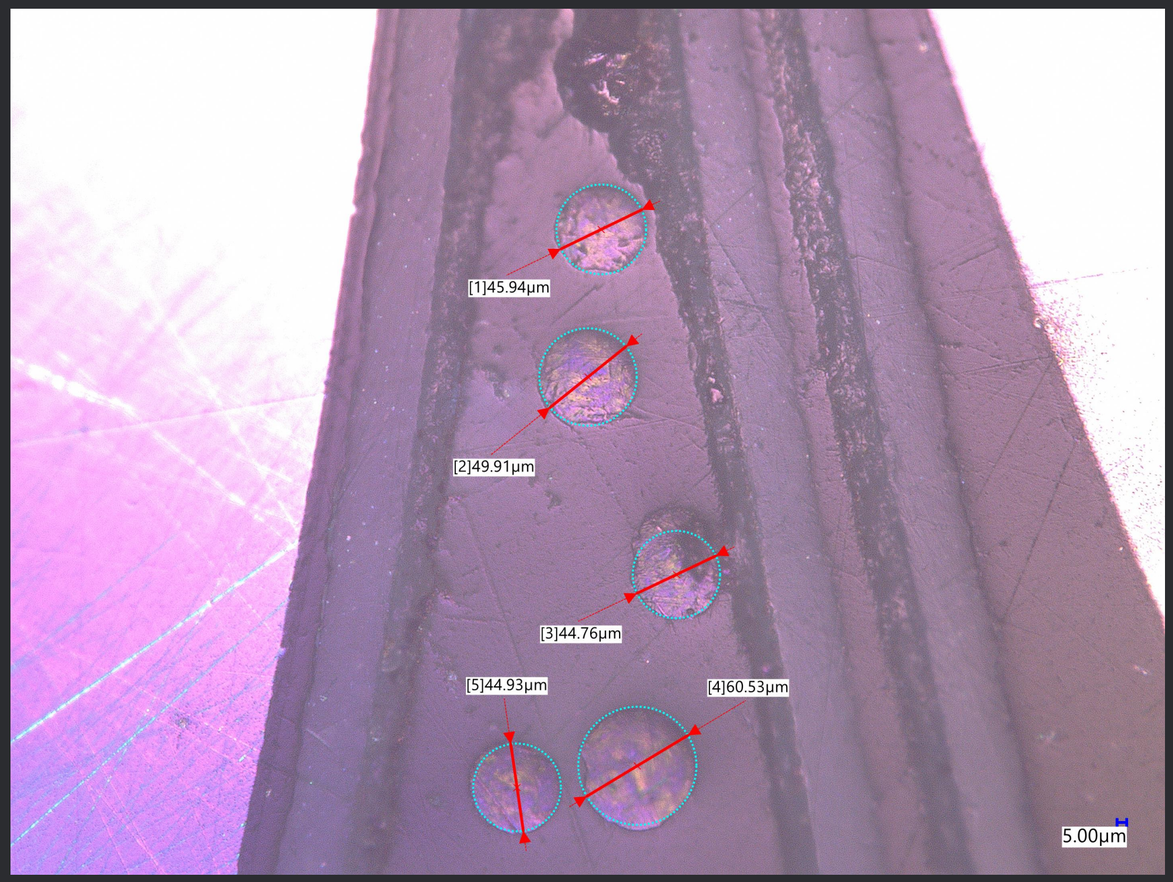
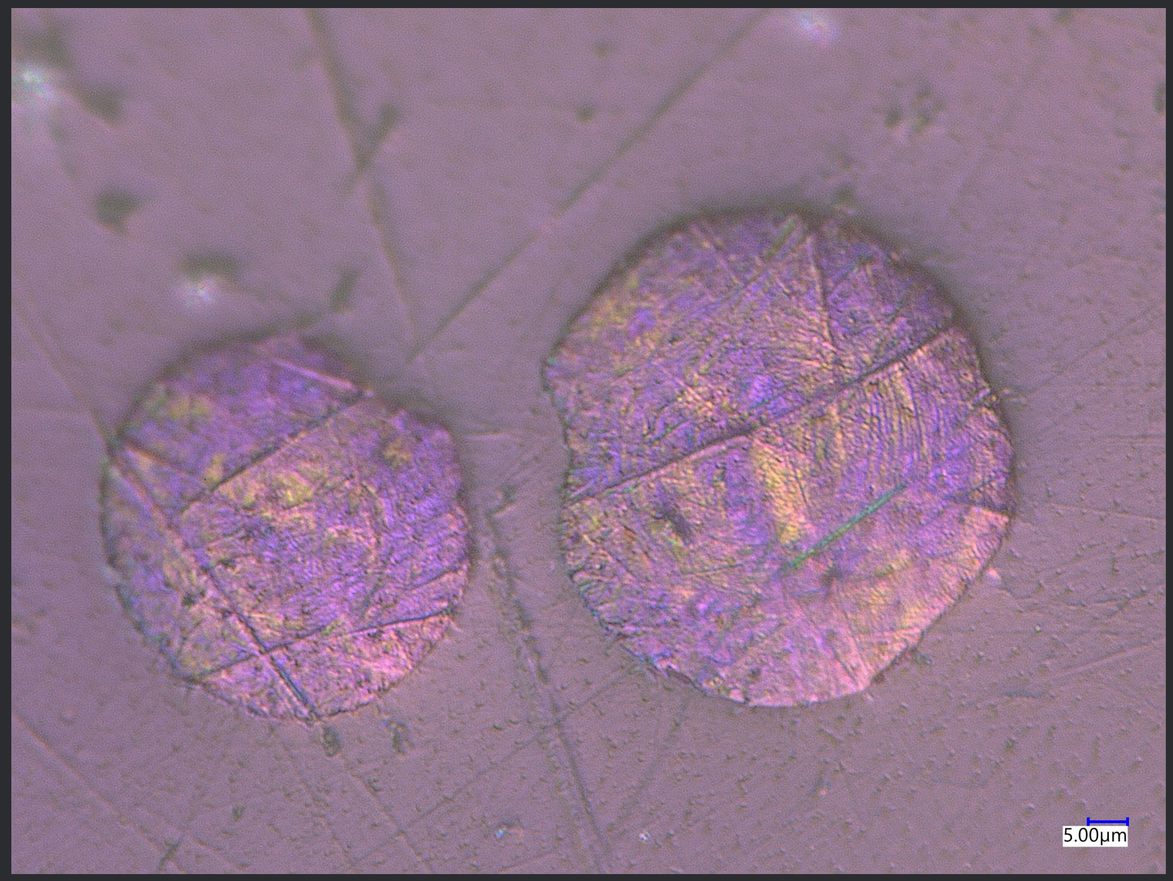
Spinning of Fiber by Ramaco

Establishing Baseline with Synthetic Mesophase





AR24 Fibers Spun at 325C AVG DIA 48um Observed Orientation of Mesogens

High-Yield Pitch Synthesis Process for Producing Carbon Fiber from Coal

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Spinning of Fiber by Ramaco

- Fiber Spinning HTI VSB As-Received Isotropic Pitch
  - Easy to Spin
  - HAAKE extruder with 500micron orifice
  - Fiber Diameters Observed
    - 77 micron at 50RPM
    - 22 micron at 150RPM

High-Yield Pitch Synthesis Process for Producing Carbon Fiber from Coal

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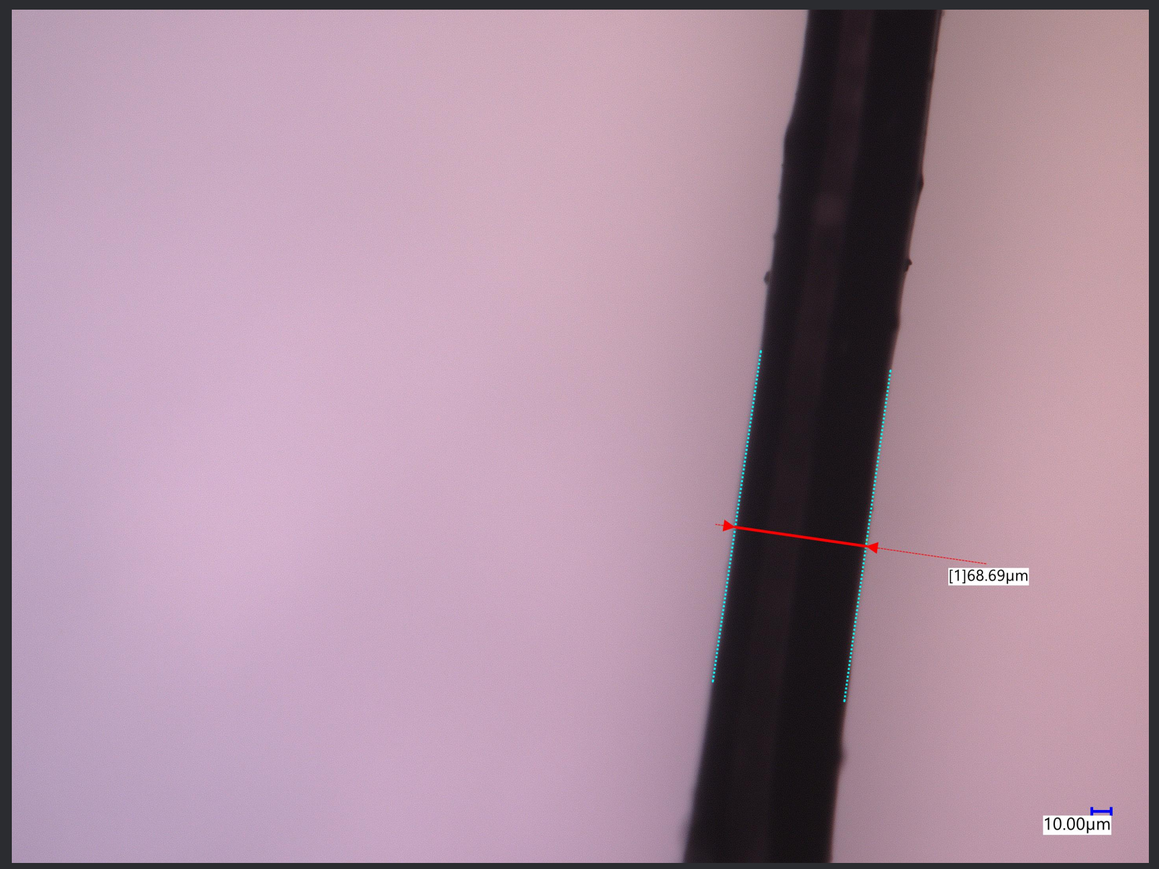
Spinning of Fiber by Ramaco

- Fiber Spinning Thermally Treated Pitch 60mins at 400C
  - Difficult to Spin due to Clogs
  - HAAKE extruder with 500micron orifice
  - Fiber Diameters Inconsistent Averaged 70microns



High-Yield Pitch Synthesis Process for Producing Carbon Fiber from Coal

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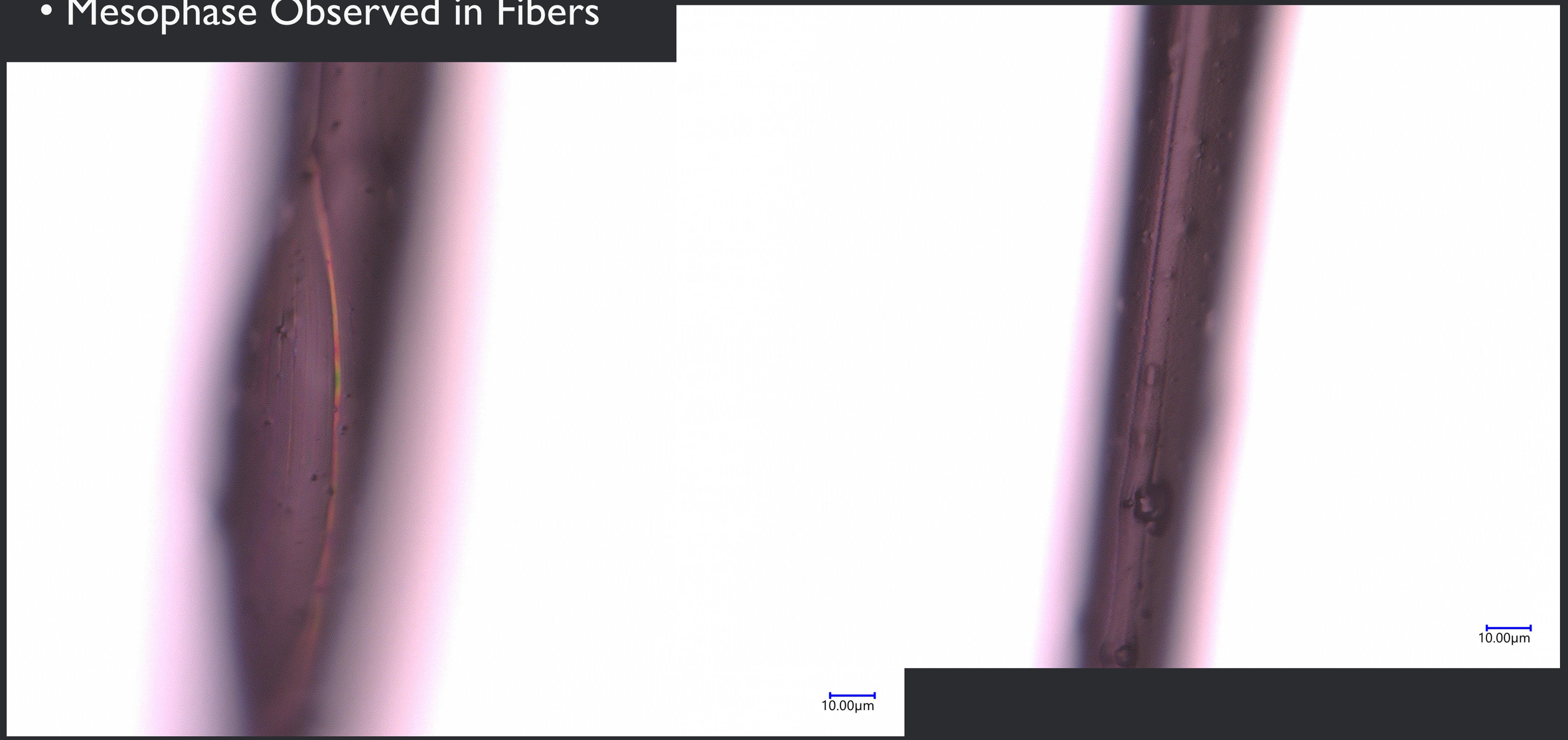
Spinning of Fiber by Ramaco

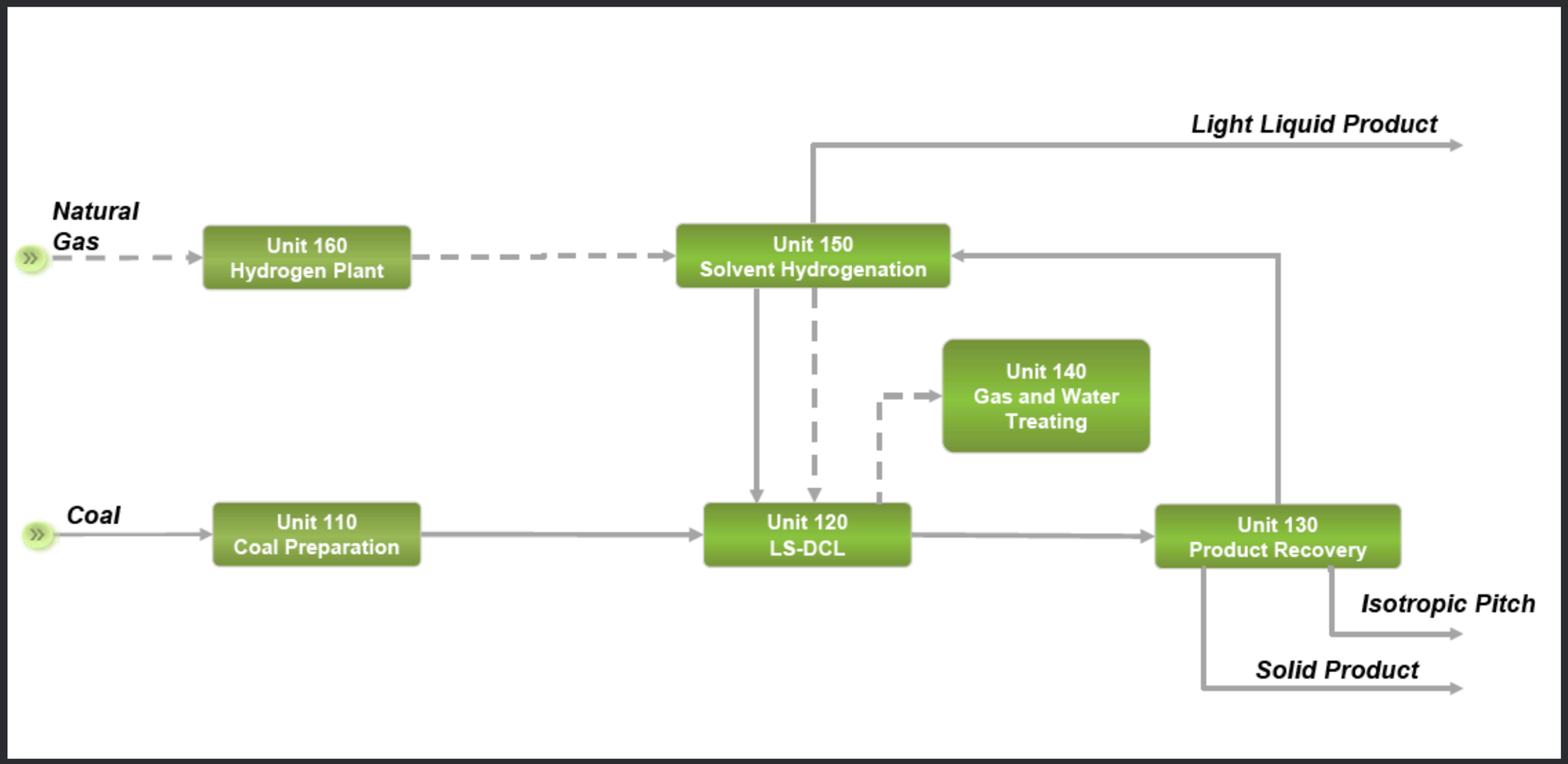
- Fiber Spinning Thermally Treated Pitch 60mins at 400C
  - Mesophase Observed in Fibers



High-Yield Pitch Synthesis Process for Producing Carbon Fiber from Coal

Commercialization and Economic Analysis

LS-DCL Simplified Block Flow Diagram



High-Yield Pitch Synthesis Process for Producing Carbon Fiber from Coal

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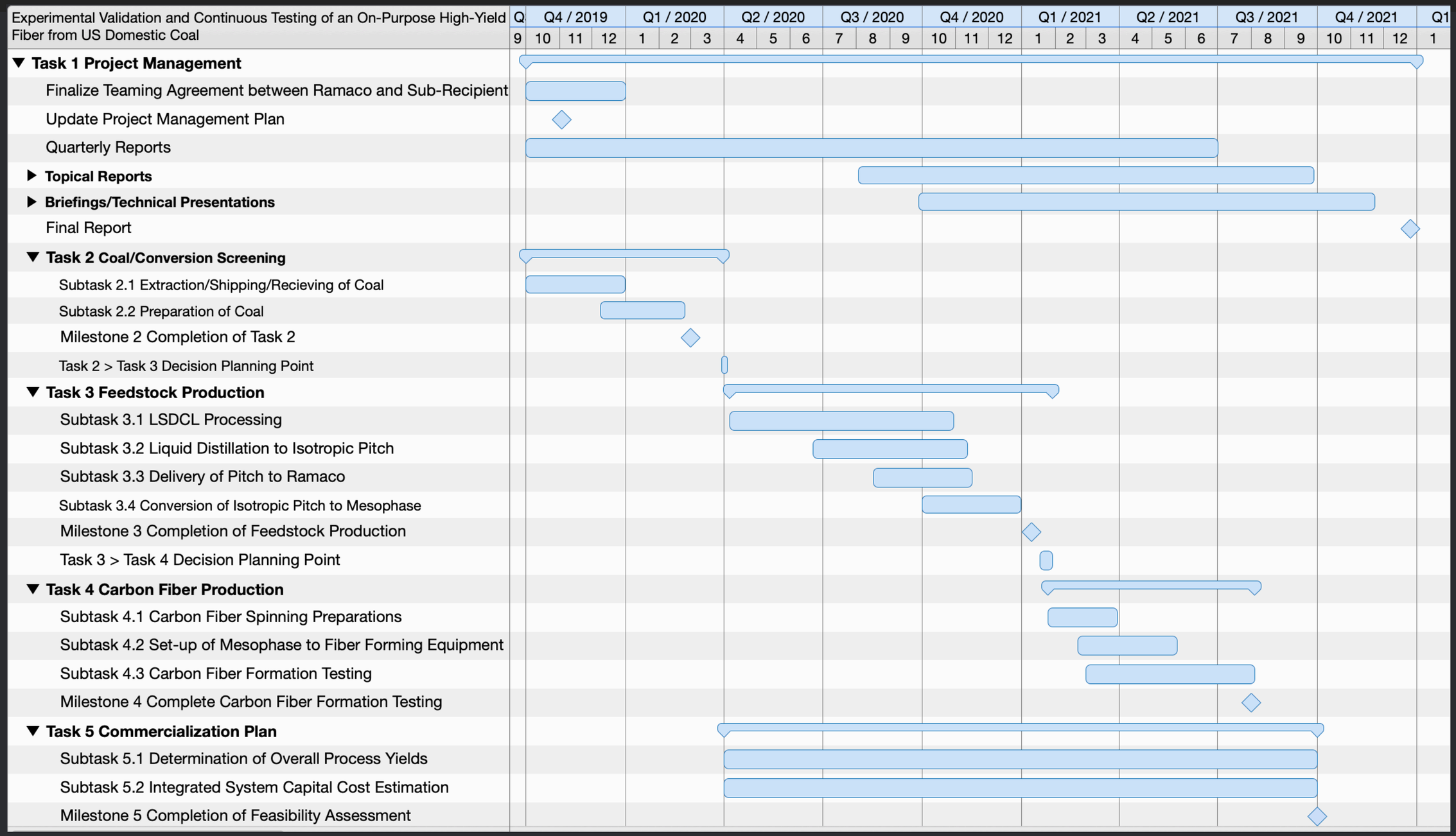

COVID-19 Impacts March-May 2020, Equipment Delivery Delays Revised Schedule for Task 4 Extended to July 31

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Conclusions

- Produced over 100kg of high-quality isotropic pitch.
- Much lower cost than PAN and more ecologically sound (greener)
- Demonstrated mesophase conversion at acceptable yields.
- Demonstrated initial fiber production with good draw down ratios.

Thank You

www.ramacocarbon.com

Acknowledgements

RAMACO:
Charlie Atkins
Grant Hazle
Luke Adsit

HTI:
John Duddy
Jeffery Gentler
Sukesh Parasher

DOE PM: Mike Fasouletos