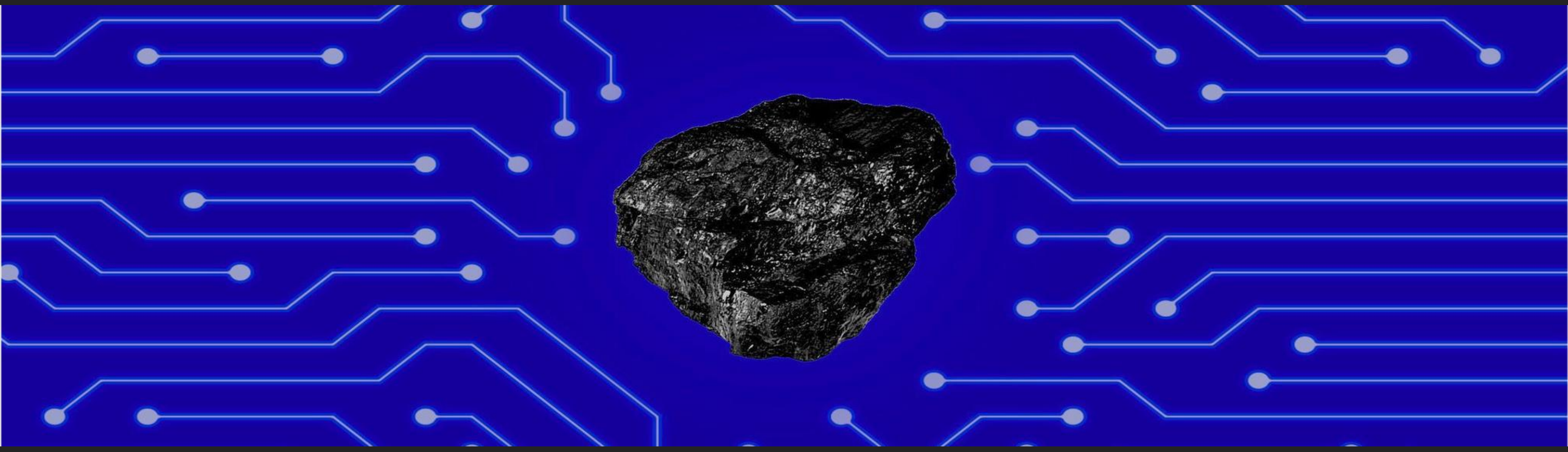
Carbon Fiber Precursor Pitch from Low-Cost Powder River Basin Coal



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

Prepared for the 2020 NETL Annual Coal Processing Project Review Meeting

Who We Are

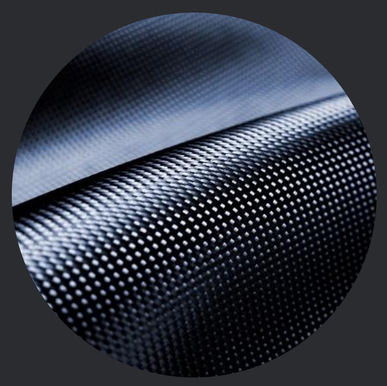
Ramaco Coal, founded in 2011, is a coal-based conglomerate with operations in five states. It consists of two main operating companies:

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

Carbon Fiber Precursor Pitch From PRB Coal

Evaluating Two Processes:
May Use Either or Both Commercially to Generate CF Precursor Pitch

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

LSDCL Low-Severity Direct Coal Liquefaction

- 50-years of Experience with Similar H-Coal Process
- Less Severe Conditions Than Traditional DCL (Much Lower Cost)
  - Lower Temperatures
  - Lower Pressures
  - No Catalyst Required

Two Funding Awards: Carbon Fiber Precursor Pitch Extraction Process Development

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Coal to Carbon Fiber – Novel Supercritical CO2 Solvated Process (MUSCL)

DE-FE-0031800

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

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

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

Coal to Carbon Fiber – Novel Supercritical CO2 Solvated Process

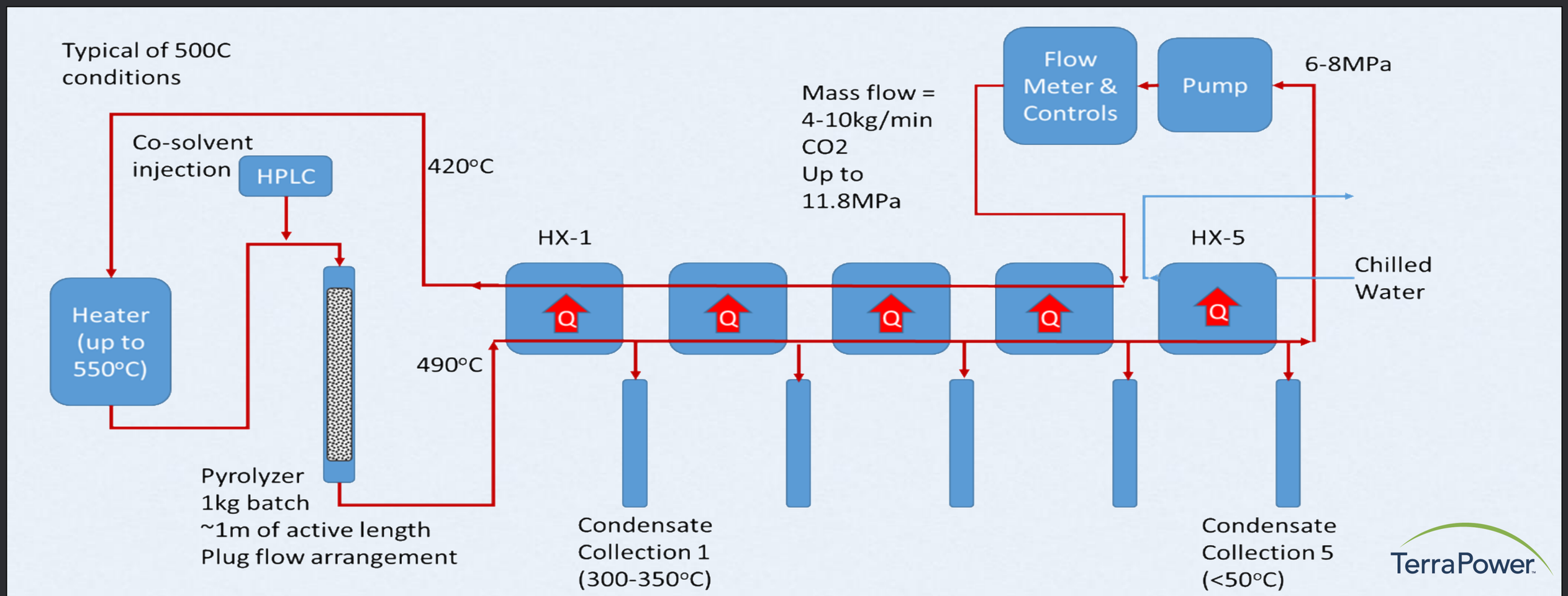
- Develop a vertically integrated continuous manufacturing process.
- Transform raw coal feedstocks into pitch and carbon fibers.
- Closed-system approach to processing environmentally hazardous intermediates like polycyclic aromatic compounds.

Carbon Fiber Precursor Pitch from Low-Cost Powder River Basin Coal

Pyrolysis Test Loop — MUSCL®

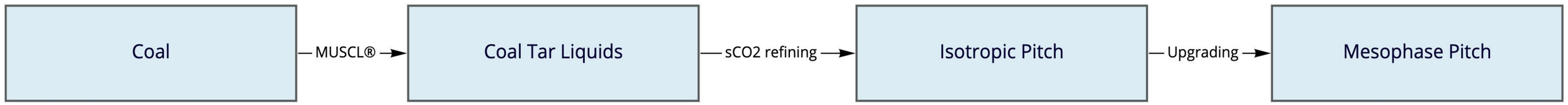
- TerraPower's pyrolysis test loop utilizes supercritical CO_2 in a closed loop.
- CO_2 is heated up to 550°C, and acts as the heating fluid for the feedstock to reach pyrolysis temperatures and serves as a pyrolysis product solvent.
- Kg batches of feedstock can be processed for testing various feedstock.
- Pyrolysis energy recovered using efficient 'reverse' distillation process.

Pyrolysis Product Sample is Recovered in Condensate Collection 2 and 3- "**MuSCL oil**"

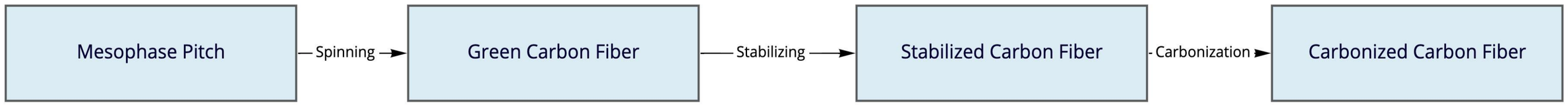


Pyrolysis Test Loop — MUSCL®

Budget Period 1



Budget Period 2



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.

Coal to Carbon Fiber – Novel Supercritical CO2 Solvated Process

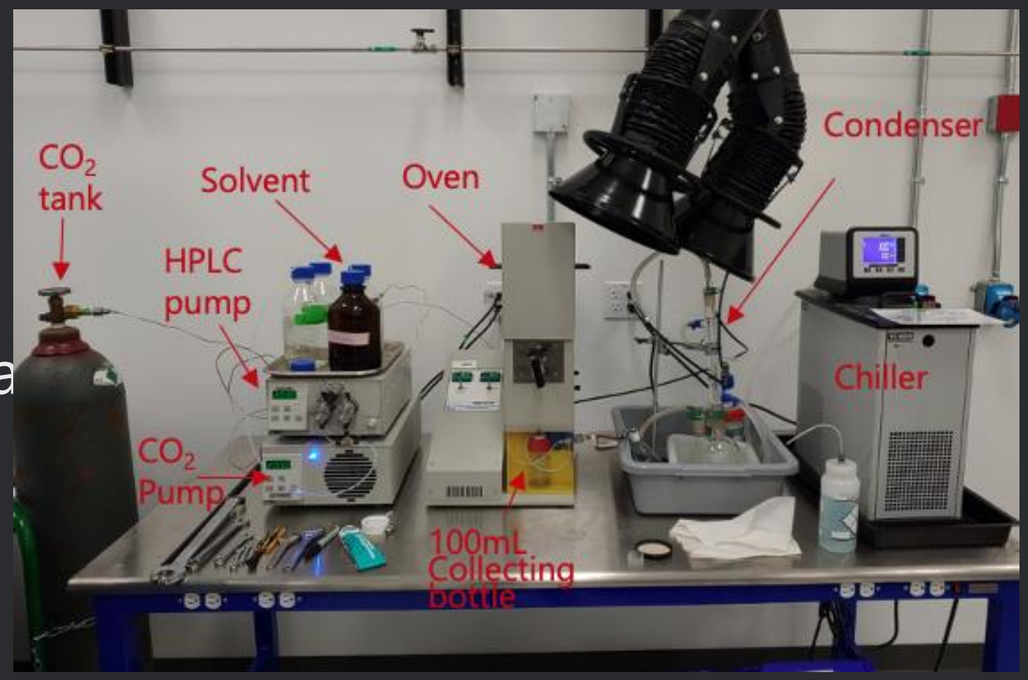
Current Progress: MUSCL® process successfully produced pyrolysis oils using the following system conditions.

Systems	Heater Output/Pyrolyzer Input	HX-1 to HX-4 Temperature Range	HX-5 Out (ES)	CO_2 Mass Flow	Pump Outlet Pressure
Target Values	450-500 °C	<450°C to >35 °C	<35 °C	5-10 kg/min	8-11 MPa
Achieved Values	485 °C	485 °C to 15 °C	15 °C	5 kg/min	6-11.5 MPa

Coal to Carbon Fiber – Novel Supercritical CO2 Solvated Process

Supercritical CO_2 separation of MuSCL-oil with sequential co-solvents

- **Sample:** MuSCL oil produced in July 16, 2020
- **Extraction method:**
  - SCO_2 extraction at 50 – 80 ºC and 20 – 30 MPa
  - Sample loading: SCO_2 (17 g), Soxhlet (10 g)
- **Solvent:** Benzene and Pyridine

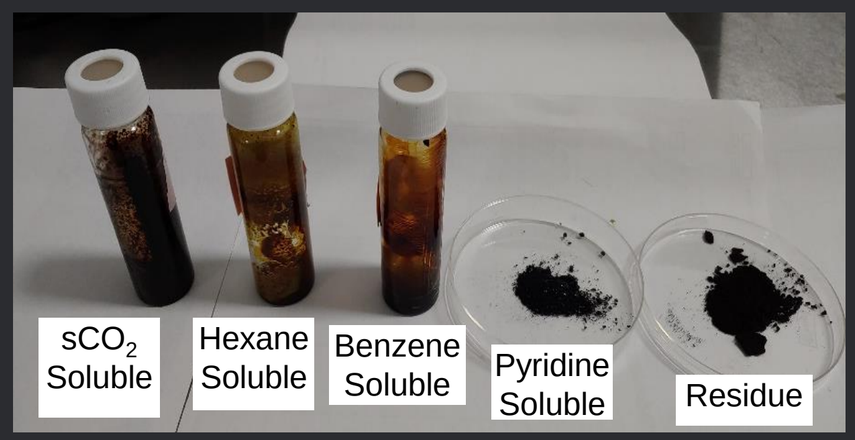


sCO_2 extraction system

MuSCL samples

0716-2020 0814-2020

100 mL sCO_2 vessel

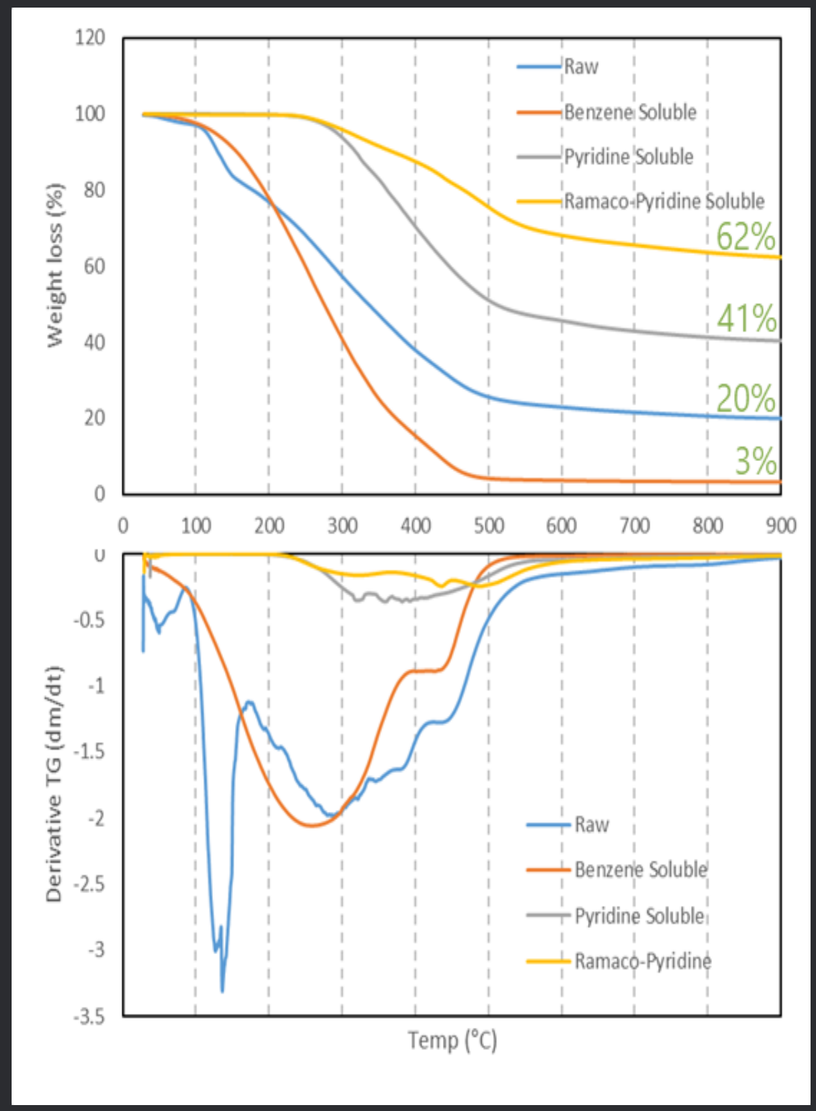


Sample Fractions

Coal to Carbon Fiber – Novel Supercritical CO2 Solvated Process

Supercritical CO_2 separation of MuSCL-oil with sequential co-solvents

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



	Soxhlet extraction	sCO2 extraction
Sample	MuSCL (July 16, 20)	MuSCL (July 16, 20)
Loaded amount (g)	11 g	17 g
Benzene soluble fraction (%)	49%	52%
Pyridine soluble fraction (%)	13%	12%
Residue (%)	25%	26%
Mass loss (%)	13%	10%

Coal to Carbon Fiber – Novel Supercritical CO2 Solvated Process

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Coal to Carbon Fiber - Novel Supercritical CO2 Solvated Process	Q3	Q4 / 2019			Q1 / 2020			Q2 / 2020			Q3 / 2020			Q4 / 2020			Q1 / 2021			Q2 / 2021			Q3 / 2021			Q4 / 2021		
	9	10	11	12	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3	4	5	6	7	8	9	10	11	12
▼ **Task 1 Project Management**																												
Finalize Teaming Agreement between Ramaco and Sub-Recipient																												
Update Project Management Plan																												
Quarterly Reports																												
Final Report																												
▼ **Task 2 Generation of Pyrolysis Coal Tar Pitch**																												
Subtask 2.1 Pyrolysis System Set-up																												
Subtask 2.2 Pyrolysis System Operation																												
Subtask 2.3 Coal Tar Pitch Analysis																												
Milestone 2 Completion of Pyrolysis Pitch Analysis																												
▼ **Task 3 sCO2/Co-Solvent Fractionization Pyrolysis Pitch**																												
Subtask 3.1 Solvent Fractionization Testing Preparation																												
Subtask 3.2 Performance of Supercritical Solvent Fractionizatio																												
Subtask 3.3 Analysis of Fractionated Coal Pitch Samples																												
Subtask 3.4 Sample Heat Treatment																												
Milestone 3 Completion of Solvent Fractionization																												
▼ **Task 4 Carbon Fiber Formation Testing**																												
Subtask 4.1 Carbon Fiber Spinning Preparations																												
Subtask 4.2 Set-up of Mesophase to Fiber Forming Equipment																												
Subtask 4.3 Carbon Fiber Formation Testing																												
Milestone 4 Complete Carbon Fiber Formation Testing																												
▼ **Task 5 Commercial Feasibility Assessment**																												
Subtask 5.1 Determination of Pyrolysis to Fiber Process Yields																												
Subtask 5.2 Integrated System Capital Cost Estimation																												
Milestone 5 Completion of Feasibility Assessment																												

COVID-19 Impacts March-May 2020, Project Recovered

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®.

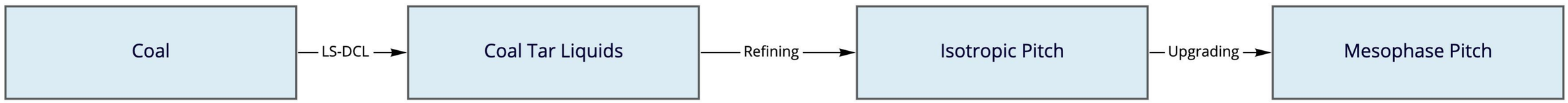
- Pilot plant development started in 1960's.

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

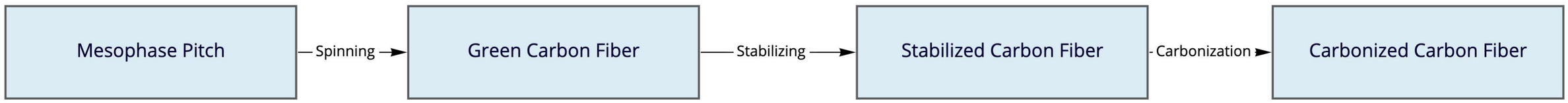
- License/Basic engineering design and provided start-up support for Shenhua Direct Coal Liquefaction Plant, a successful start-up in 2008.

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-CoalTM/H-OilTM, **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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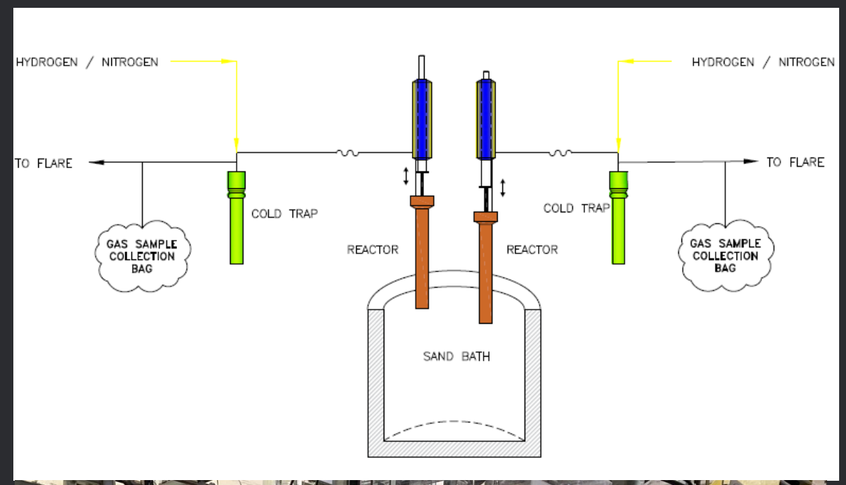
Micro-autoclave (Unit 223) Coal Reactivity Testing
To Determine Conditions for Pilot Operations

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

hti

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

RAMACO CARBON

Micro-autoclave (Unit 223) Coal Reactivity Testing Results pt.1

223-28		6	6	7	7	8	8	9	9	10	10
Reactor		K-1	K-2	K-1	K-2	K-1	K-2	K-1	K-2	K-1	K-2
Conditions											
Pressure	**Mpa**	6.9	3.5	6.9	3.5	6.9	3.5	6.9	3.5	6.9	6.9
Temperature	**C**	400	400	400	400	413	413	413	413	407	407/418
Time	**minutes**	60	60	90	90	45	45	60	60	30	30/30
Mass Balance											
Coal	**g**	4.00	4.00	4.01	4.00	4.00	4.01	4.00	4.01	4.00	4.01
MF Coal	**g**	3.40	3.40	3.40	3.40	3.40	3.40	3.40	3.40	3.40	3.40
Solvent	**g**	16.01	16.02	16.02	16.02	16.01	16.01	16.01	16.01	16.01	16.01
Total	**g**	19.41	19.42	19.42	19.42	19.41	19.41	19.41	19.41	19.41	19.41
Filter Solids	**g**	0.73	0.96	0.63	0.83	0.62	0.85	0.62	0.85	0.99	0.49
Filter Liquid	**g**	19.47	19.26	18.67	18.78	18.86	19.09	18.86	19.09	18.65	18.97
Total	**g**	20.20	20.22	19.30	19.61	19.48	19.94	19.48	19.94	19.64	19.46
Material Balance	**%**	104.09	104.10	99.34	100.99	100.37	102.73	100.37	102.73	101.12	100.25
Ash Balance	**%**	74.93	91.83	99.31	103.21	105.93	107.80	105.93	107.80	111.01	106.15

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

RAMACO CARBON

Micro-autoclave (Unit 223) Coal Reactivity Testing Results pt. 2

223-28		6	6	7	7	8	8	9	9	10	10
Reactor		K-1	K-2	K-1	K-2	K-1	K-2	K-1	K-2	K-1	K-2
Conditions											
Pressure	Mpa	6.9	3.5	6.9	3.5	6.9	3.5	6.9	3.5	6.9	6.9
Temperature	C	400	400	400	400	413	413	413	413	407	407/418
Time	minutes	60	60	90	90	45	45	60	60	30	30/30
Conversion											
Coal	%	75.00	73.02	85.84	80.36	87.15	80.85	89.80	83.25	77.76	91.02
Toluene Ins	%	71.41	71.14	84.33	78.40	83.19	77.62	86.16	79.08	72.42	87.14
CHX	%	57.64	55.32	71.12	69.06	69.89	65.40	67.77	69.70	62.49	74.94
MCR	%	55.07	54.35	64.55	62.65	66.39	62.57	67.12	64.20	57.38	67.78
410 C+	%	30.65	36.92	44.59	42.13	38.97	42.90	42.20	35.54	30.65	39.22
525 C+	%	44.61	50.88	58.10	57.31	53.66	56.87	55.41	49.15	46.14	56.29
525+ Yield	W% MAF	30.39	22.14	27.74	23.05	33.49	23.98	34.39	34.10	31.61	34.73
525 C+ MCR	%	65.58	84.32	76.75	76.80	62.00	76.20	65.94	55.86	64.45	66.91
525+ TI	%	11.84	8.48	5.45	8.51	11.84	13.46	10.56	12.22	16.88	11.15
525+Asphaltene	%	45.29	71.47	47.60	40.53	39.71	50.96	53.50	27.51	31.41	35.14
MCR/Asphaltene		1.45	1.18	1.61	1.90	1.56	1.50	1.23	2.03	2.05	1.90
410+ Yield	W% MAF	44.36	36.10	41.25	38.23	48.18	37.95	47.60	47.71	47.10	51.80
410 C+ MCR	%	44.94	51.72	51.61	46.31	43.09	48.16	47.64	39.93	43.26	44.86
410+ TI	%	8.11	5.20	3.67	5.13	8.23	8.51	7.63	8.74	11.33	7.48
410+Asphaltene	%	31.03	43.84	32.01	24.44	27.60	32.21	38.65	19.66	21.08	23.56
MCR/Asphaltene		1.45	1.18	1.61	1.90	1.56	1.50	1.23	2.03	2.05	1.90

hti

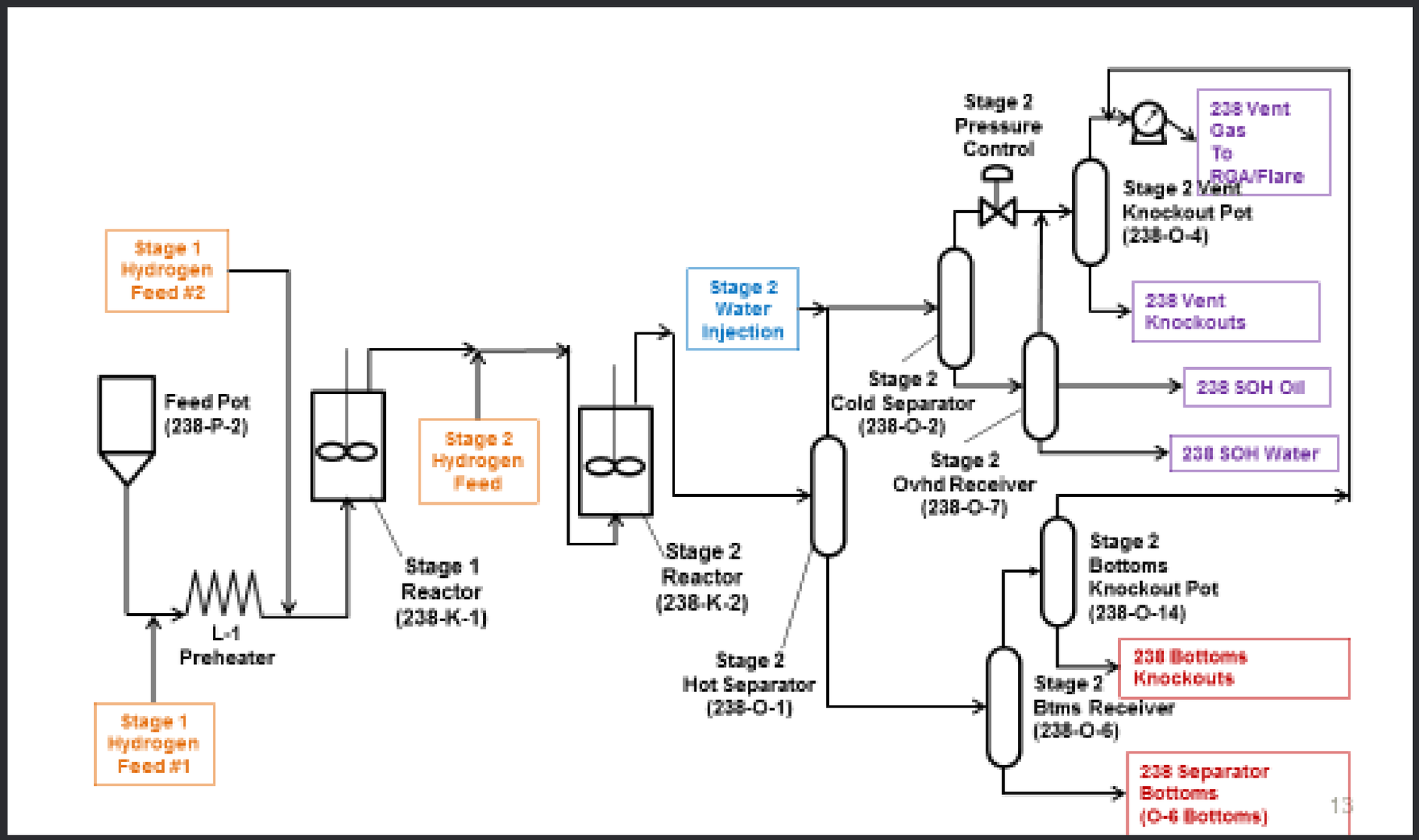
High-Yield Pitch Synthesis Process for Producing Carbon Fiber from Coal

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

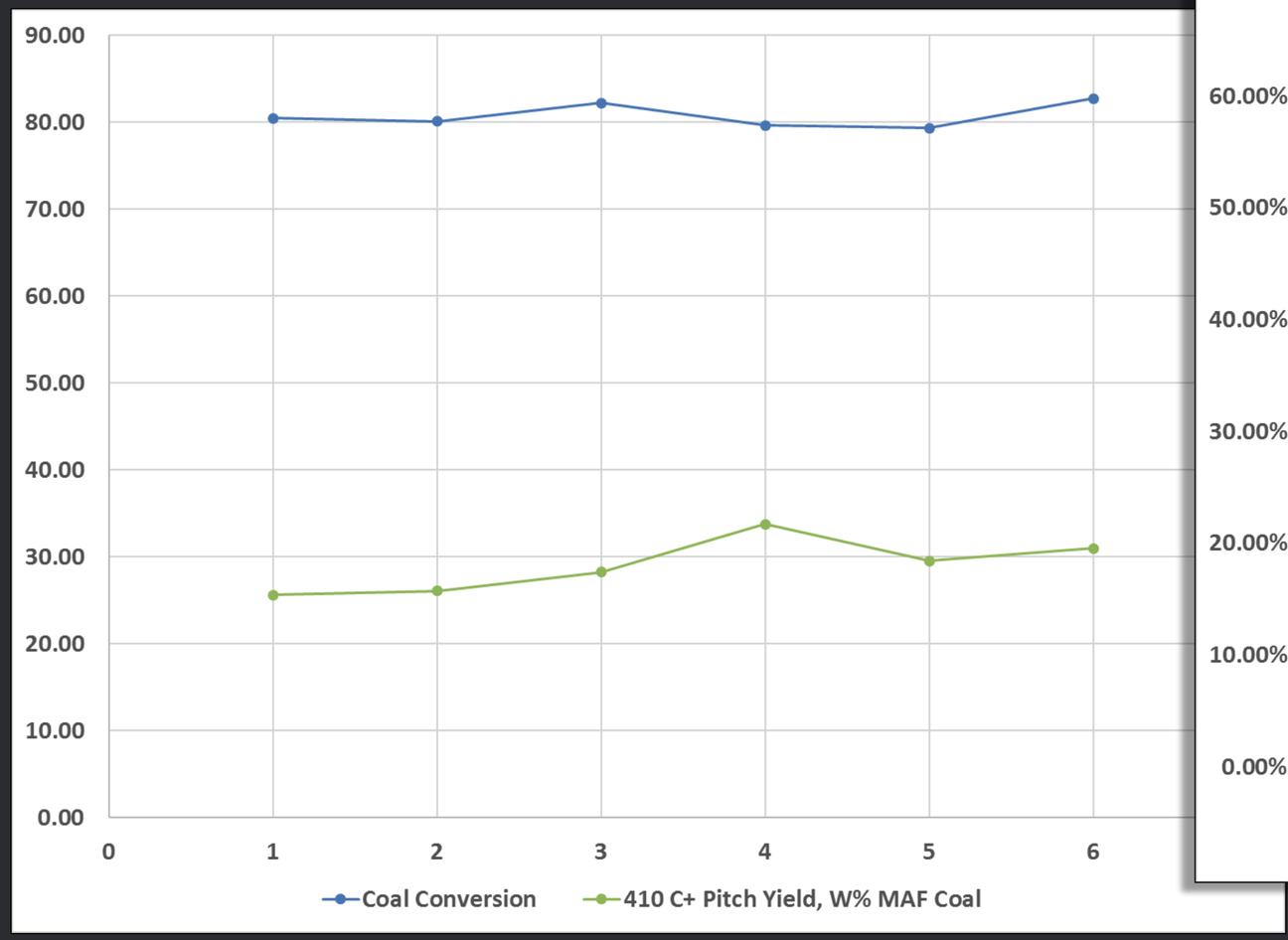
Pilot Operations (Unit 245) Processing



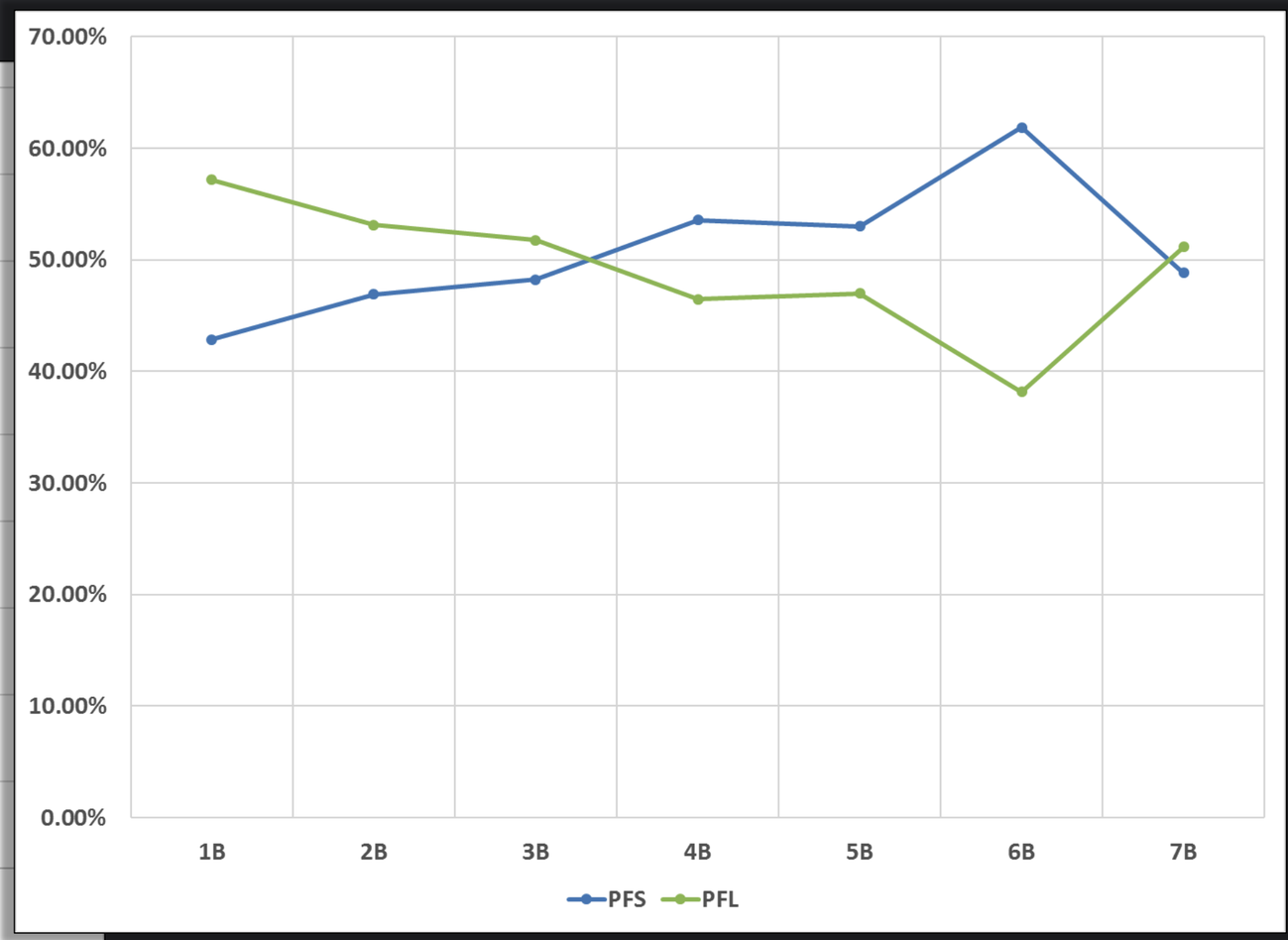
High-Yield Pitch Synthesis Process for Producing Carbon Fiber from Coal

Pilot Operations (Unit 245) Processing

Coal Conversion & Pitch Yield (%)



Lab Pressure Filter Recovery



Per 7 days of operation

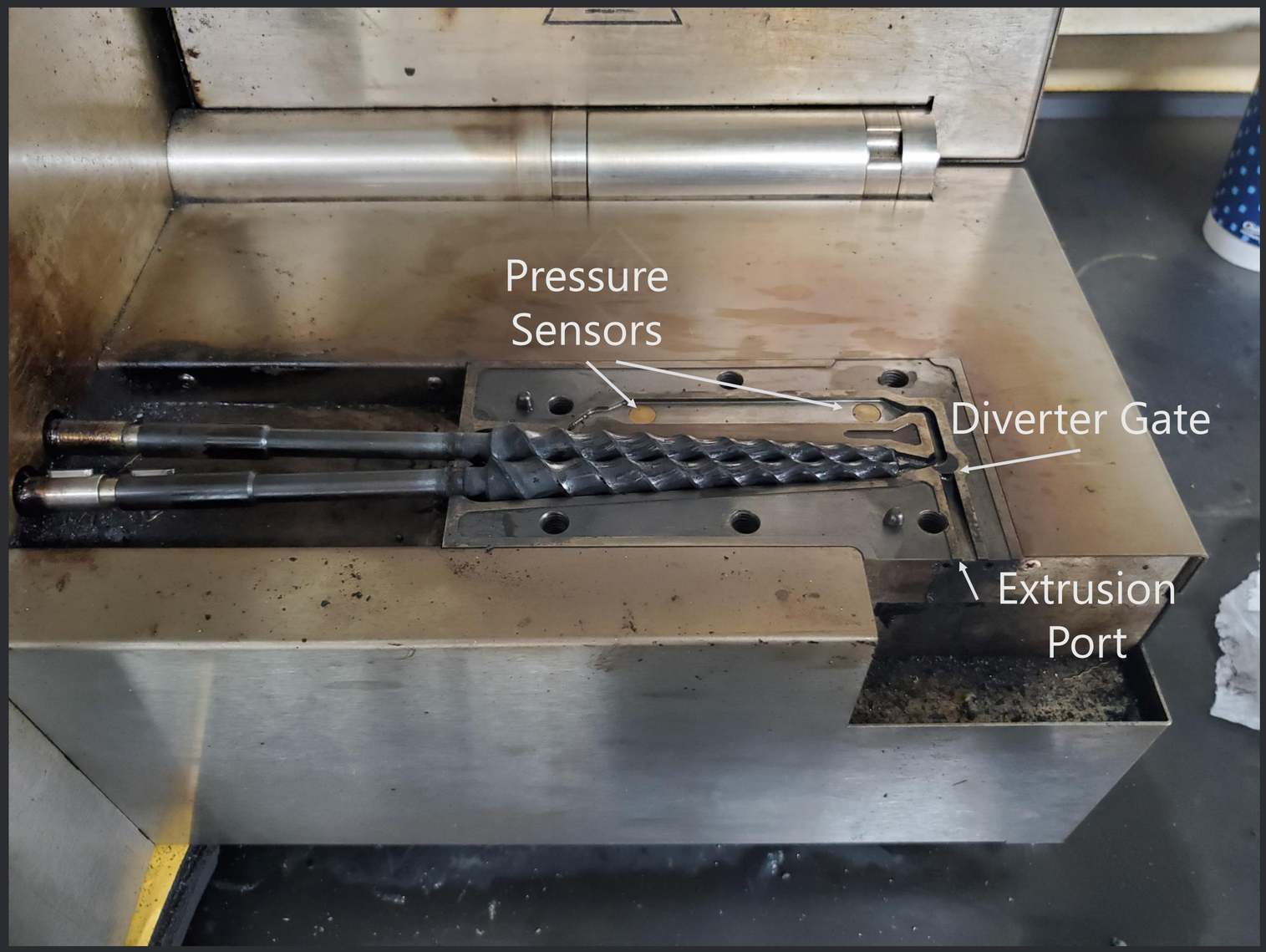
High-Yield Pitch Synthesis Process for Producing Carbon Fiber from Coal

Conversion of Pitch to Mesophase by Ramaco

HAAKE Minilab 3 Conical Twin Screw Extruder

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

Conversion of Pitch to Mesophase by Ramaco



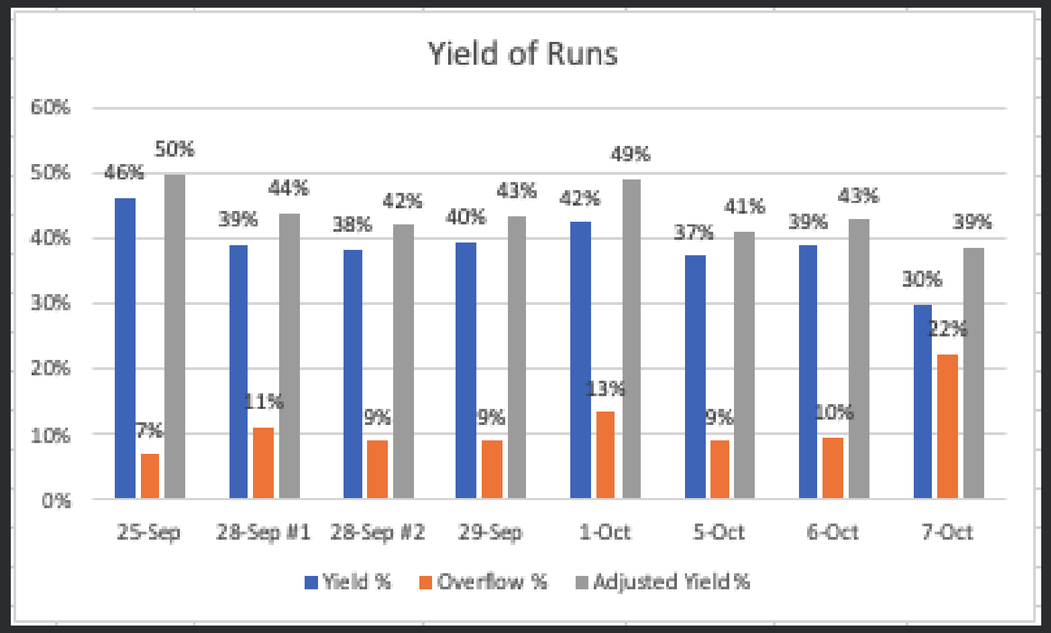
Pitch recirculates during thermal treatment and is extruded after completion

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

RAMACO CARBON

Conversion of Pitch to Mesophase by Ramaco

Date	Time	Temperature	Atmosphere	Droppin	Yield %	Overflow %	Adjusted Yield %
25-Sep	120	380° C	N2 Continuous	191.6° C	46%	7%	50%
28-Sep #1	60	400° C	N2 Continuous	174.7° C	39%	11%	44%
28-Sep #2	60	400° C	N2 Continuous	208.6° C	38%	9%	42%
29-Sep	90	400° C	N2 Continuous	No Drop	40%	9%	43%
1-Oct	90	400° C	N2 Continuous	259.2° C	42%	13%	49%
5-Oct	60	400° C	N2 Box	256.0° C	37%	9%	41%
6-Oct	60	400° C	N2 Box	200.5° C	39%	10%	43%
7-Oct	90	400° C	N2 Box	No Drop	30%	22%	39%

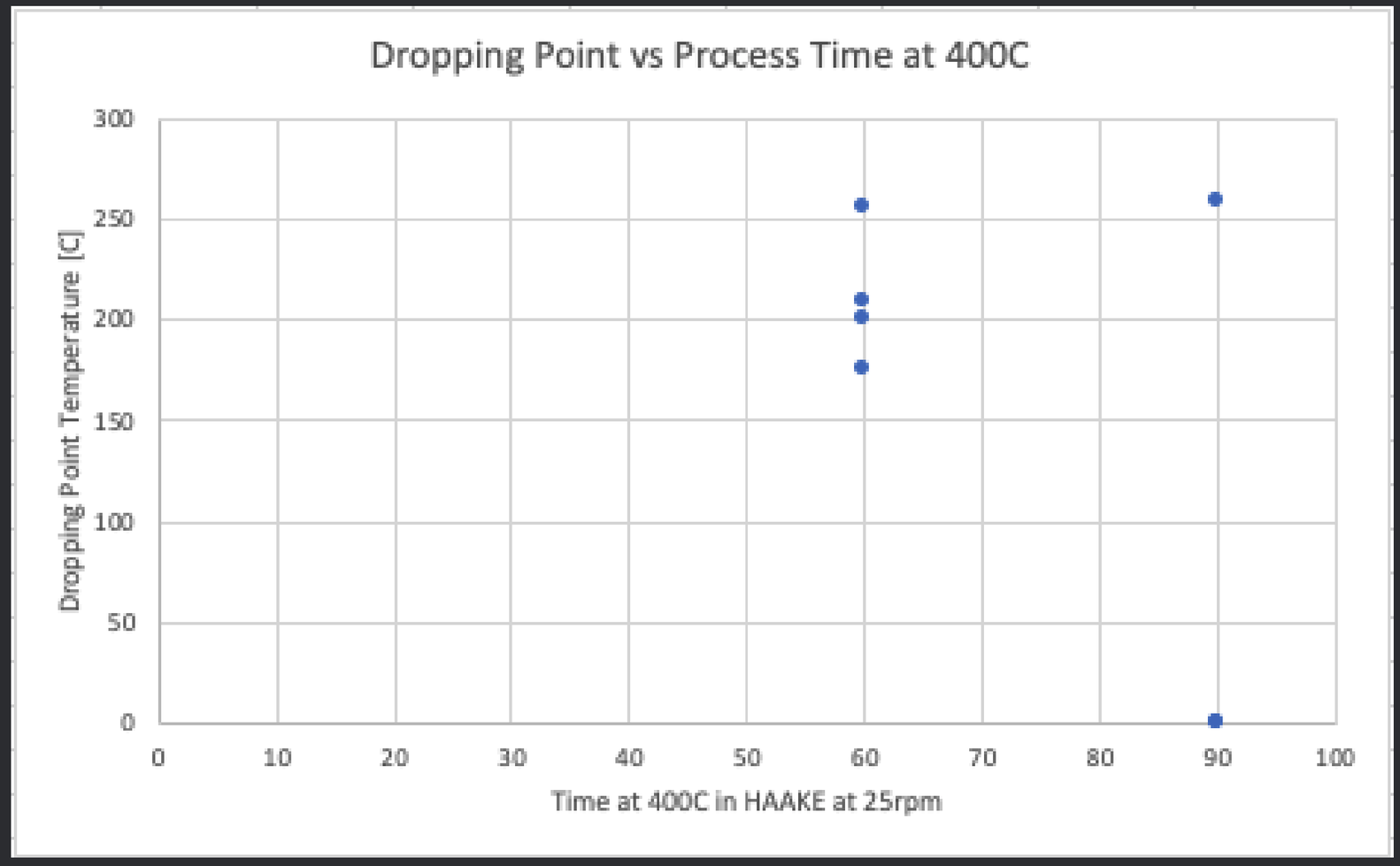


High-Yield Pitch Synthesis Process for Producing Carbon Fiber from Coal

RAMACO CARBON

Conversion of Pitch to Mesophase by Ramaco

Mettler DP70

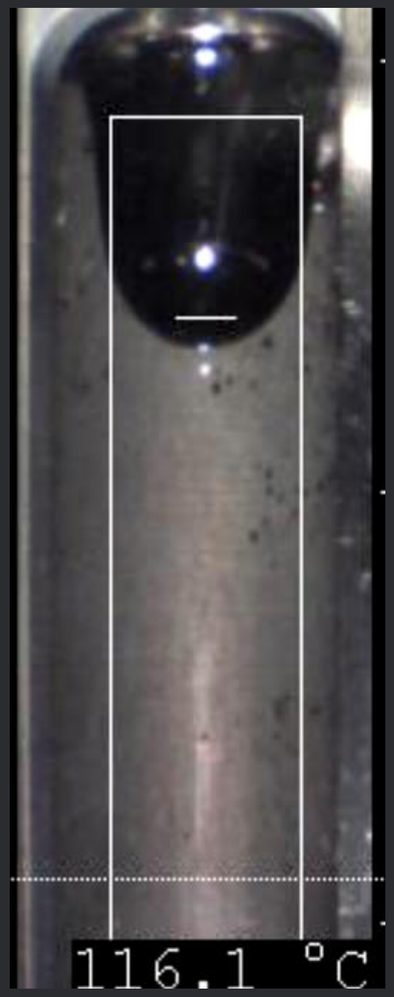


- Large Variability in Dropping Point
- Observed Oxidation at Extrusion Port
- Added Cover and Nitrogen Purge on Exit Port

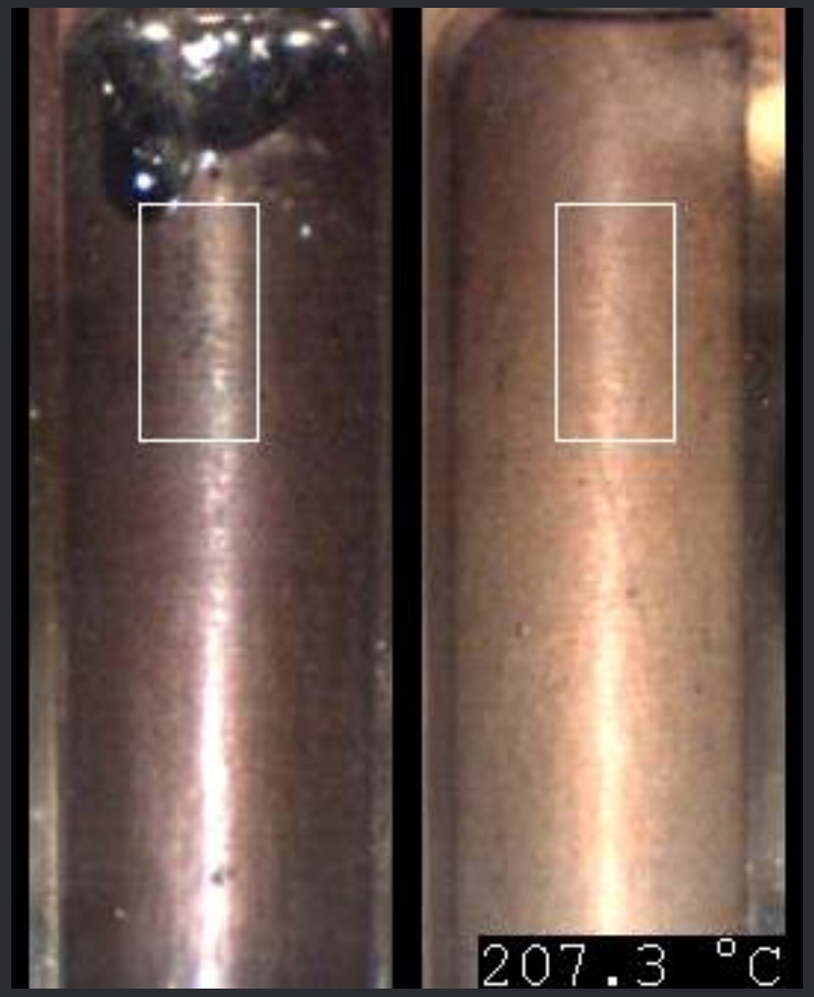
High-Yield Pitch Synthesis Process for Producing Carbon Fiber from Coal

RAMACO CARBON

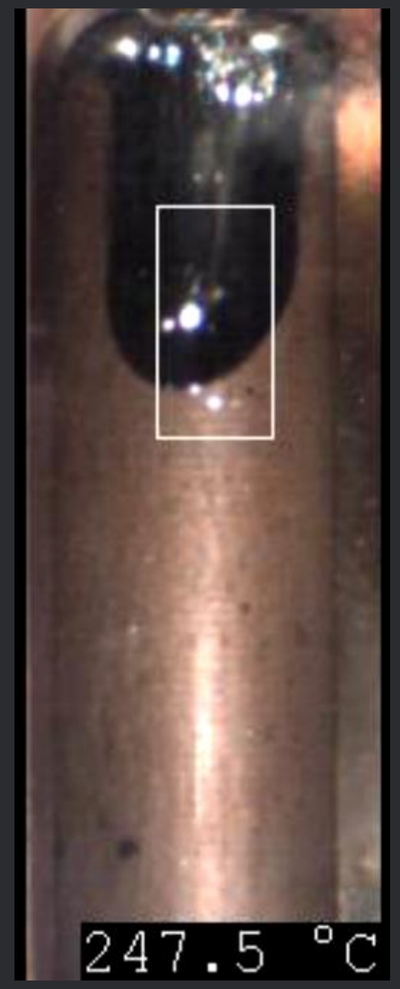
Conversion of Pitch to Mesophase by Ramaco



As-Received
Isotropic Pitch



90 mins at 400C
Sept. 29, 2020
Two-phase Behavior

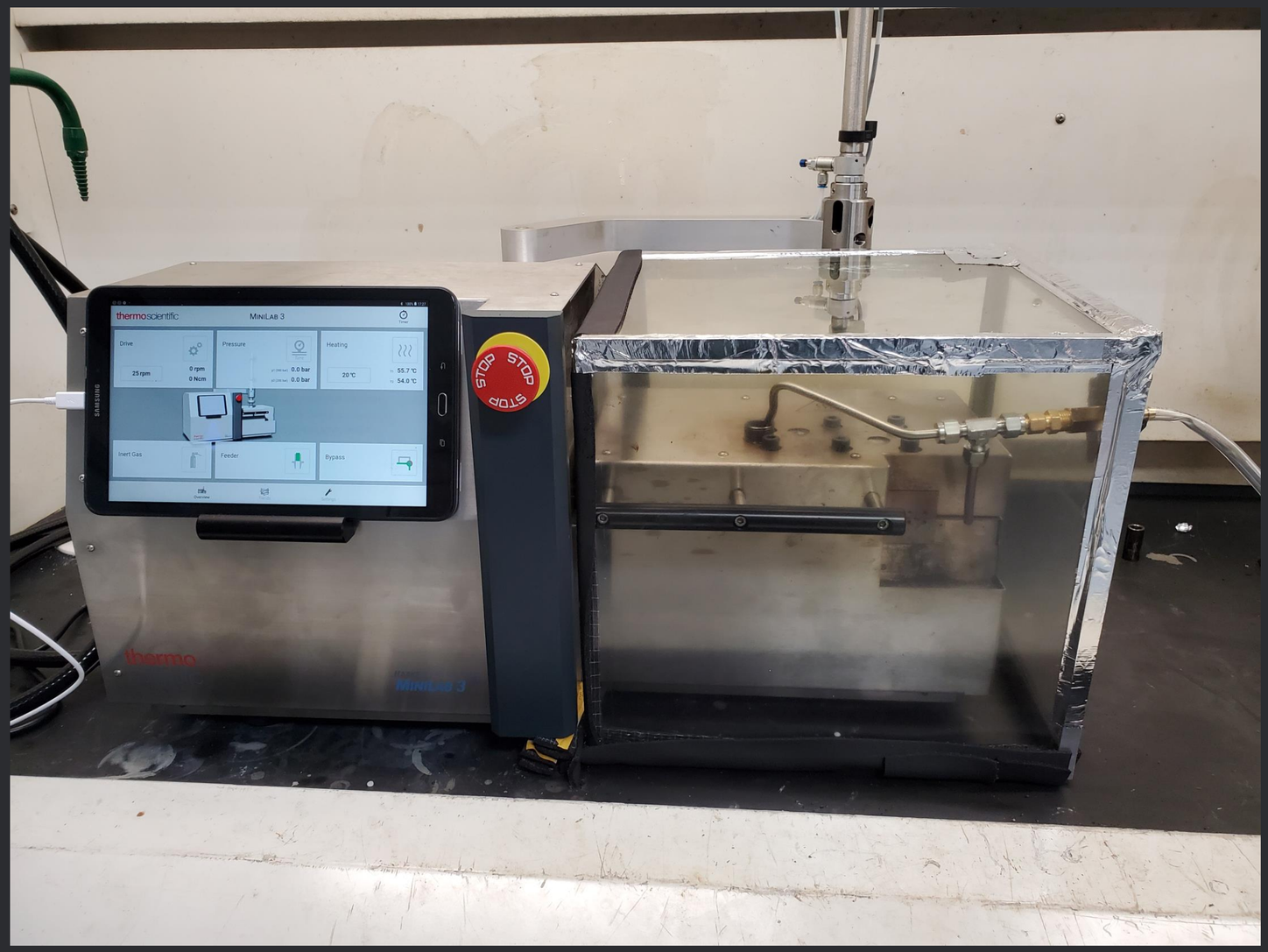


90 mins at 400C
Oct. 1, 2020

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

RAMACO CARBON

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

RAMACO CARBON

Title	Q	Q4 / 2019			Q1 / 2020			Q2 / 2020			Q3 / 2020			Q4 / 2020			Q1 / 2021			Q2 / 2021			Q3 / 2021			Q4 / 2021			Q
	9	10	11	12	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3	4	5	6	7	8	9	10	11	12	1
Task 1 Project Management																													
Finalize Teaming Agreement between Ramaco and Sub-Recipient																													
Update Project Management Plan																													
Quarterly Reports																													
Topical Reports																													
Briefings/Technical Presentations																													
Final Report																													
Task 2 Coal/Conversion Screening																													
Subtask 2.1 Extraction/Shipping/Recieving of Coal																													
Subtask 2.2 Preparation of Coal																													
Milestone 2 Completion of Task 2																													
Task 2 > Task 3 Decision Planning Point																													
Task 3 Feedstock Production																													
Subtask 3.1 LSDCL Processing																													
Subtask 3.2 Liquid Distillation to Isotropic Pitch																													
Subtask 3.3 Delivery of Pitch to Ramaco																													
Subtask 3.4 Conversion of Isotropic Pitch to Mesophase																													
Milestone 3 Completion of Feedstock Production																													
Task 3 > Task 4 Decision Planning Point																													
Task 4 Carbon Fiber Production																													
Subtask 4.1 Carbon Fiber Spinning Preparations																													
Subtask 4.2 Set-up of Mesophase to Fiber Forming Equipment																													
Subtask 4.3 Carbon Fiber Formation Testing																													
Milestone 4 Complete Carbon Fiber Formation Testing																													
Task 5 Commercialization Plan																													
Subtask 5.1 Determination of Overall Process Yields																													
Subtask 5.2 Integrated System Capital Cost Estimation																													
Milestone 5 Completion of Feasibility Assessment																													

COVID-19 Impacts March-May 2020, Project Back on Track

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

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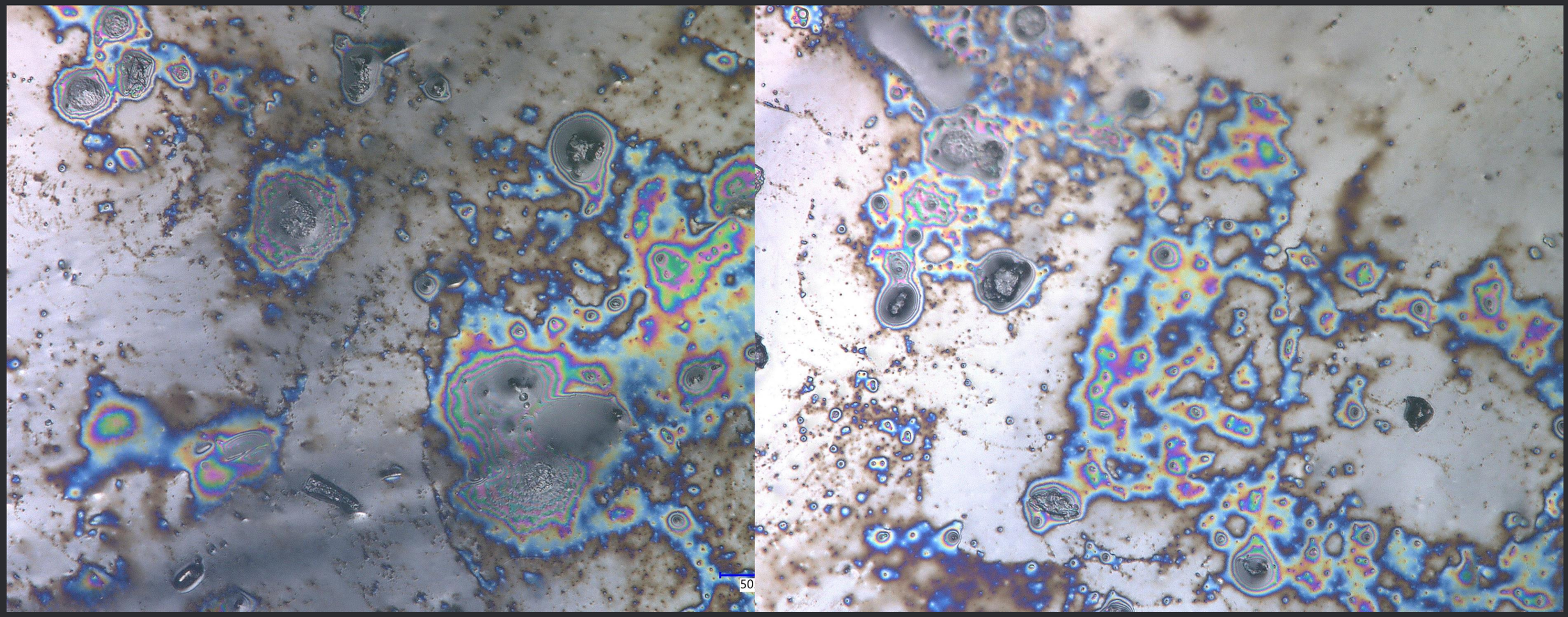

Coalescing Mesophase Domains Observed after 60mins at 400C
(Microscopy of Un-polished Pitch Surface)

Thank You

RAMACO CARBON

www.ramacocarbon.com

Acknowledgements

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