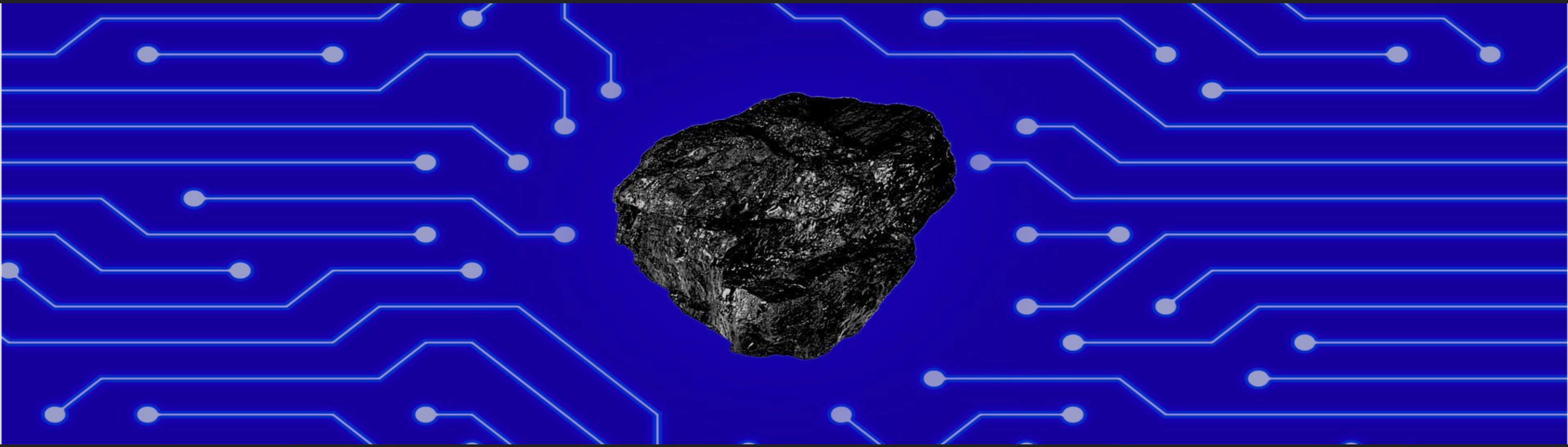
Coal to Carbon Fiber – Novel Supercritical CO_2 Solvated Process (MUSCL)



By **Charles Hill** and **Chris Yurchick** —
Co-PIs @ Ramaco Carbon
DE-FE0031800

Prepared for the 2021 NETL Annual Coal Processing Project Review Meeting

Who We Are

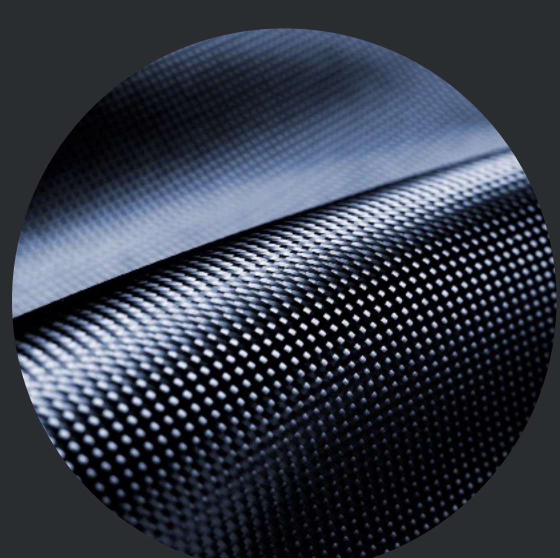
Ramaco Coal, founded in 2011, is a coal-based conglomerate with operations in five states. It consists of two main operating companies:

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



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

Coal to Carbon Fiber – Novel Supercritical CO_2 Solvated Process (MUSCL) DE-FE0031800

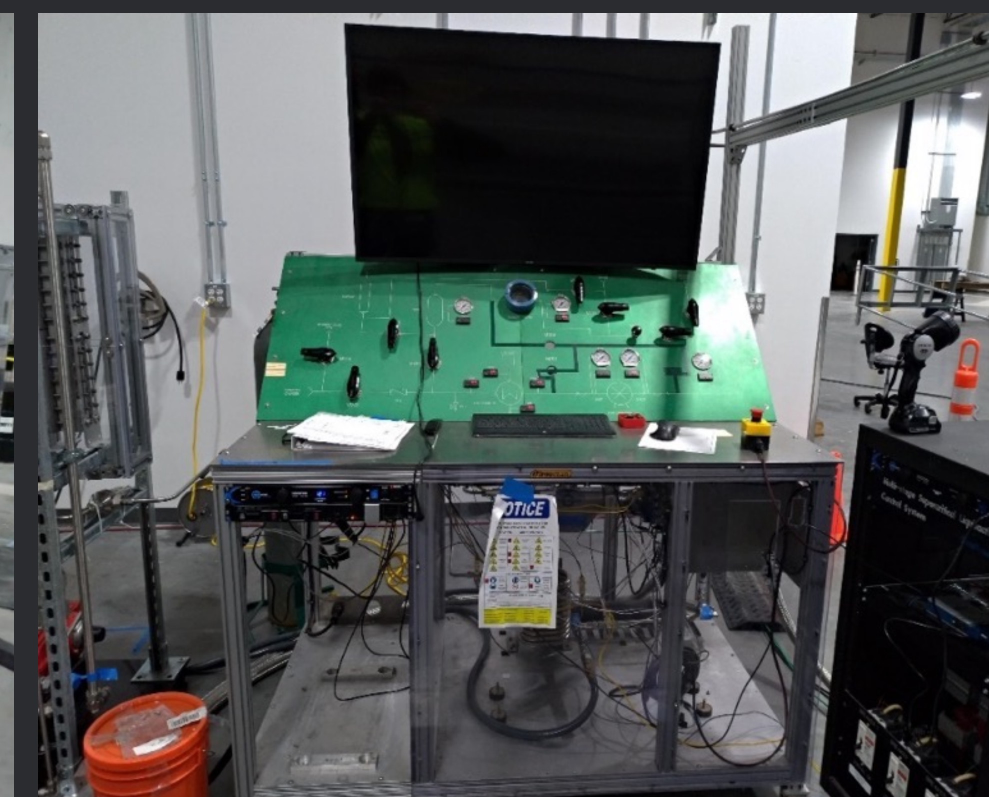
DOE Funding: $733,299
Cost Share: $323,500
Total Value: $1,056,799

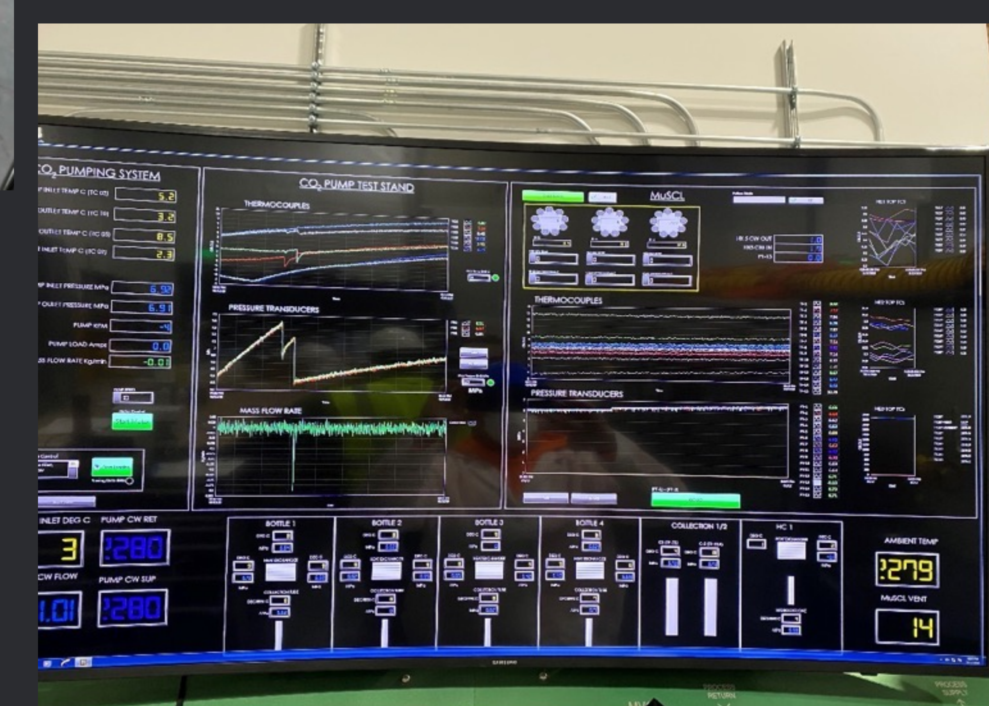
Budget Period 1: 14 months
Budget Period 2: 10 months

MUSCL Multi-Ultra Supercritical Coal Liquefaction

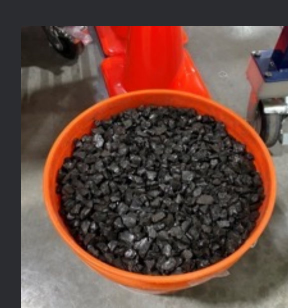
- Brand New Process Never Attempted Before
- Closed Loop System > No Emissions
- Lower Cost > No Hydrogen Required
- Selective Extractions > Ideal for Upgrading to Mesophase
- More Ecologically Sound Than Traditional Processes (Greener)

Coal to Carbon Fiber – Novel Supercritical CO_2 Solvated Process





View of test space for sCO_2 pyrolysis loop.



Place coal here!

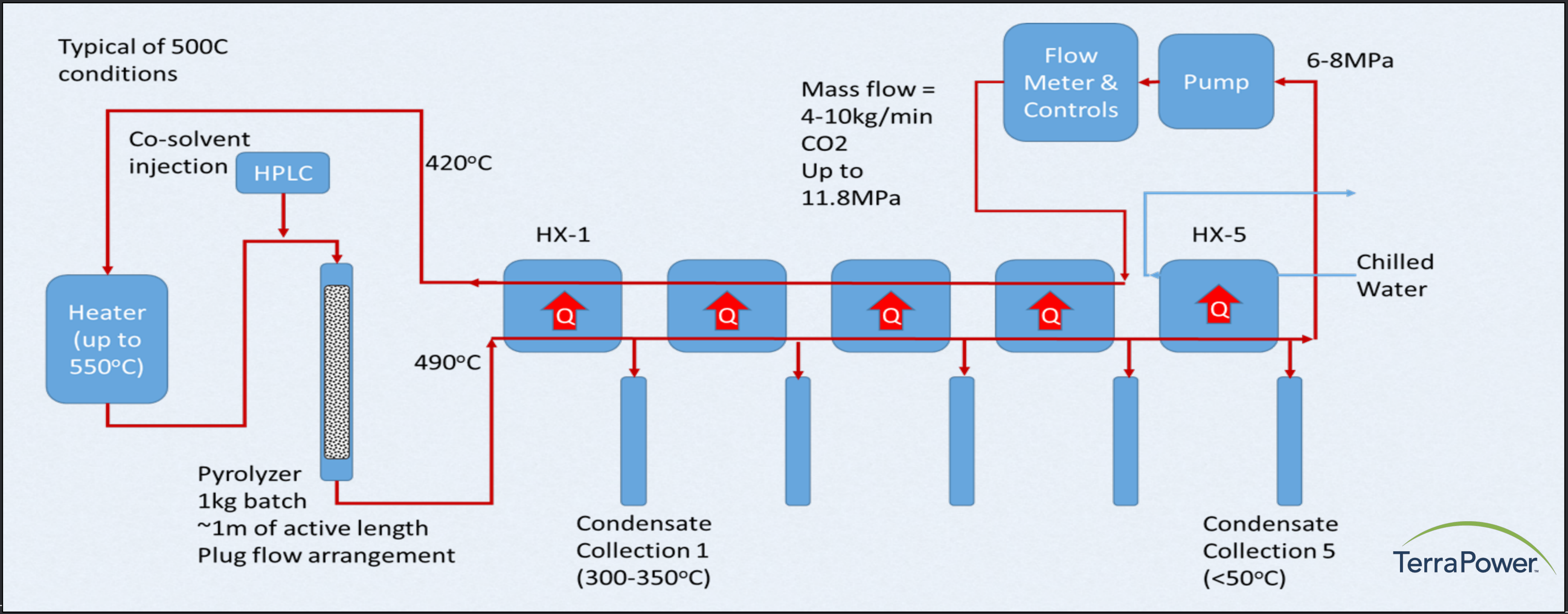
Supercritical CO2 (sCO_2) test loop.

Test loop control station.

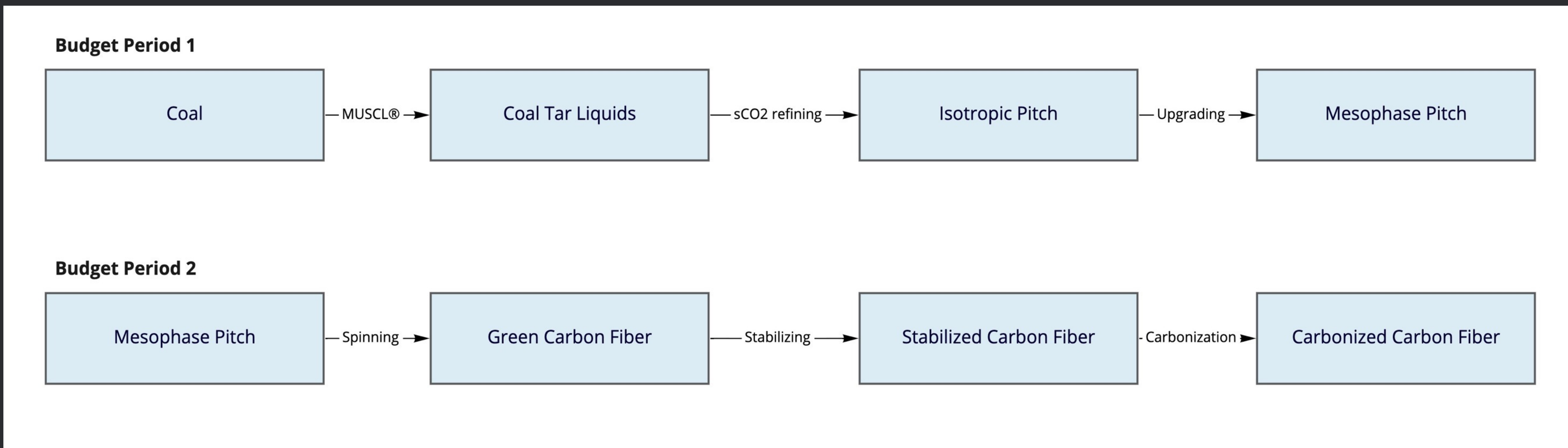
Pyrolysis Test Loop — MUSCL

- TerraPower's pyrolysis test loop utilizes supercritical CO_2 in a closed loop.
- CO_2 is heated up to 550ºC, 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



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_2 separation of MUSCL-oil with sequential co-solvents

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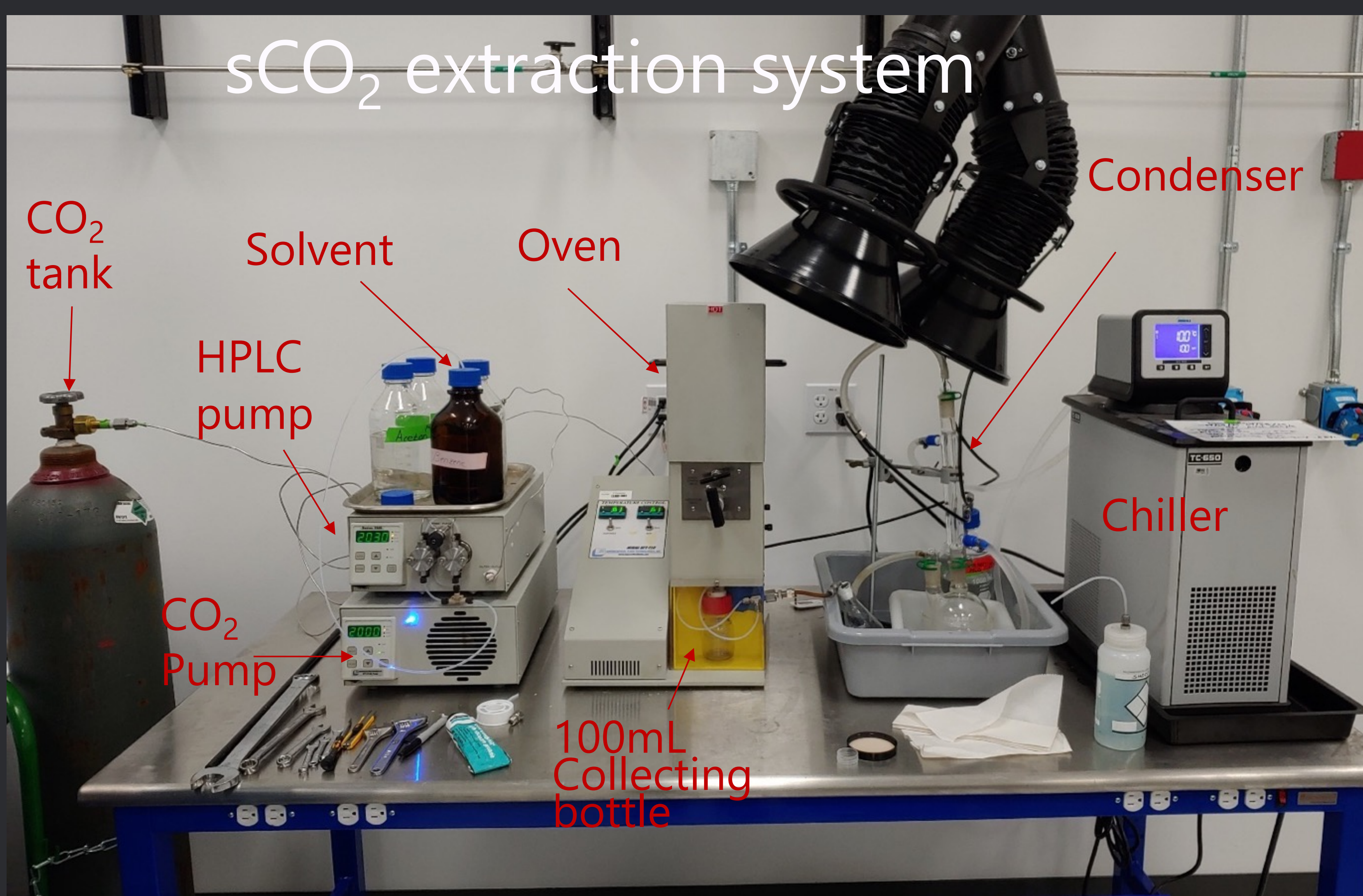
Modified Supercritical CO_2 extraction system (August 10, 2020)

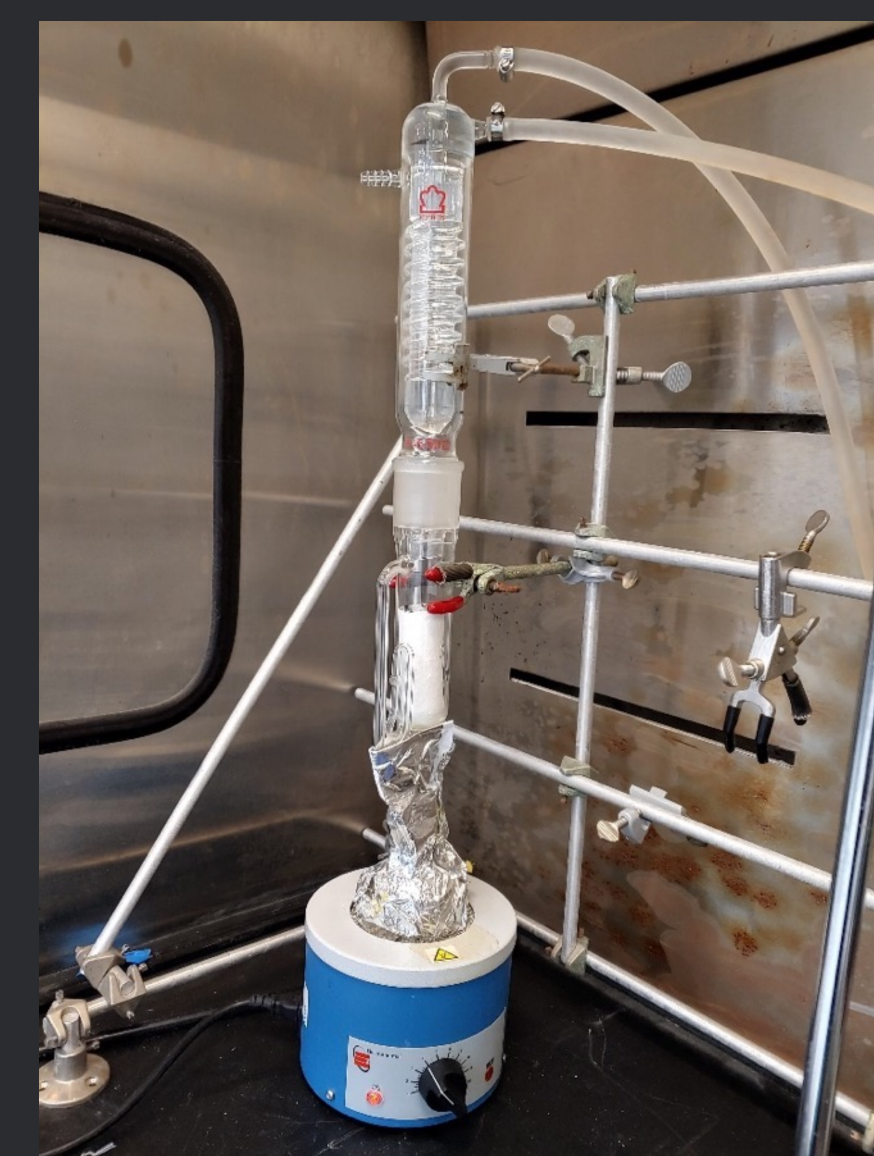
- Reaction vessel : 100 mL
- 5 um stainless steel bag
- Sample loading: 17 g

- 50 ° C and 20 MPa for Benzene Soluble fraction
- 70 ° C and 30 MPa for Pyridine Soluble fraction



100 mL sCO_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

	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%

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

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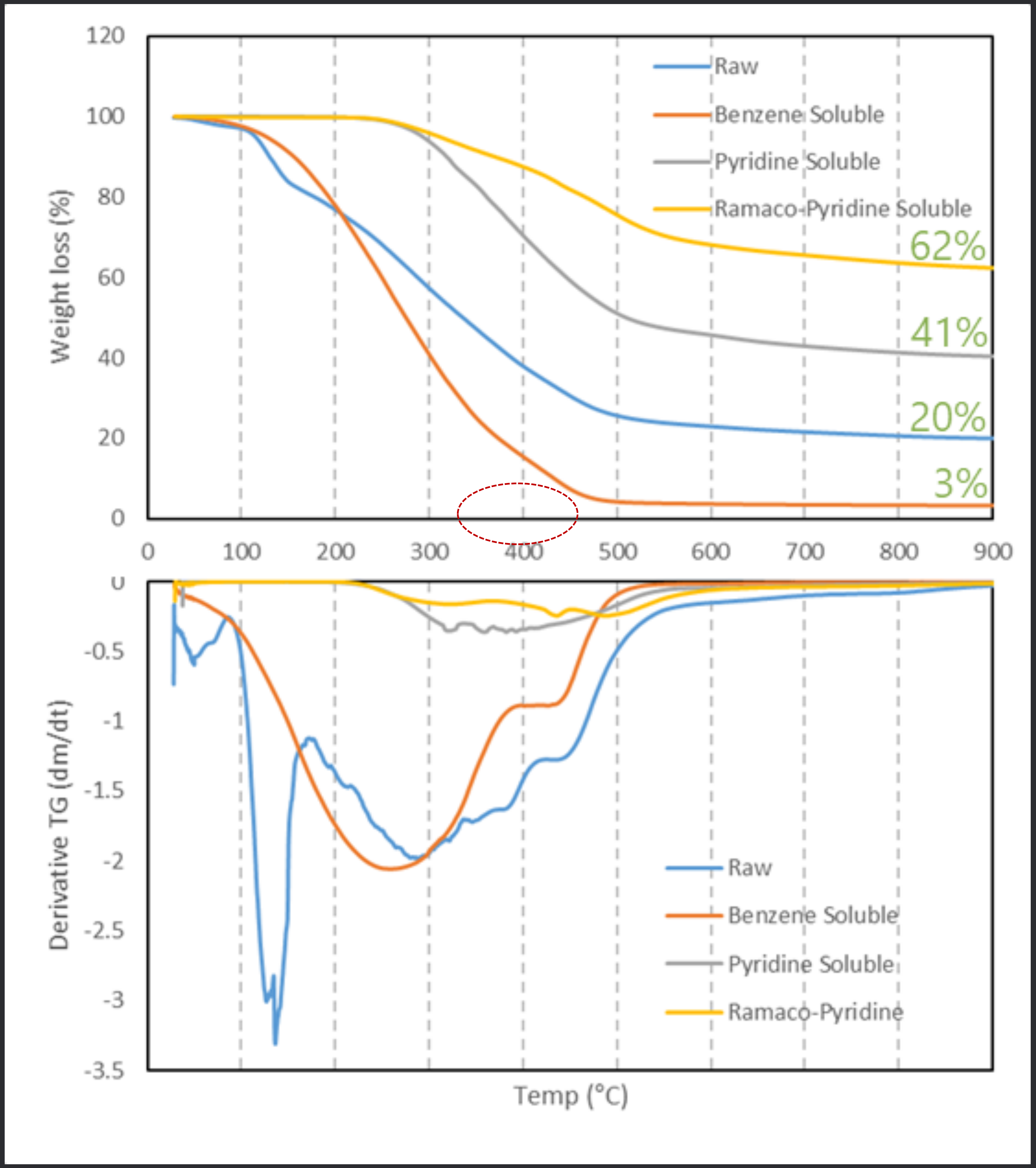
Results 2 – Thermogravimetric analysis (TGA)

- 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.



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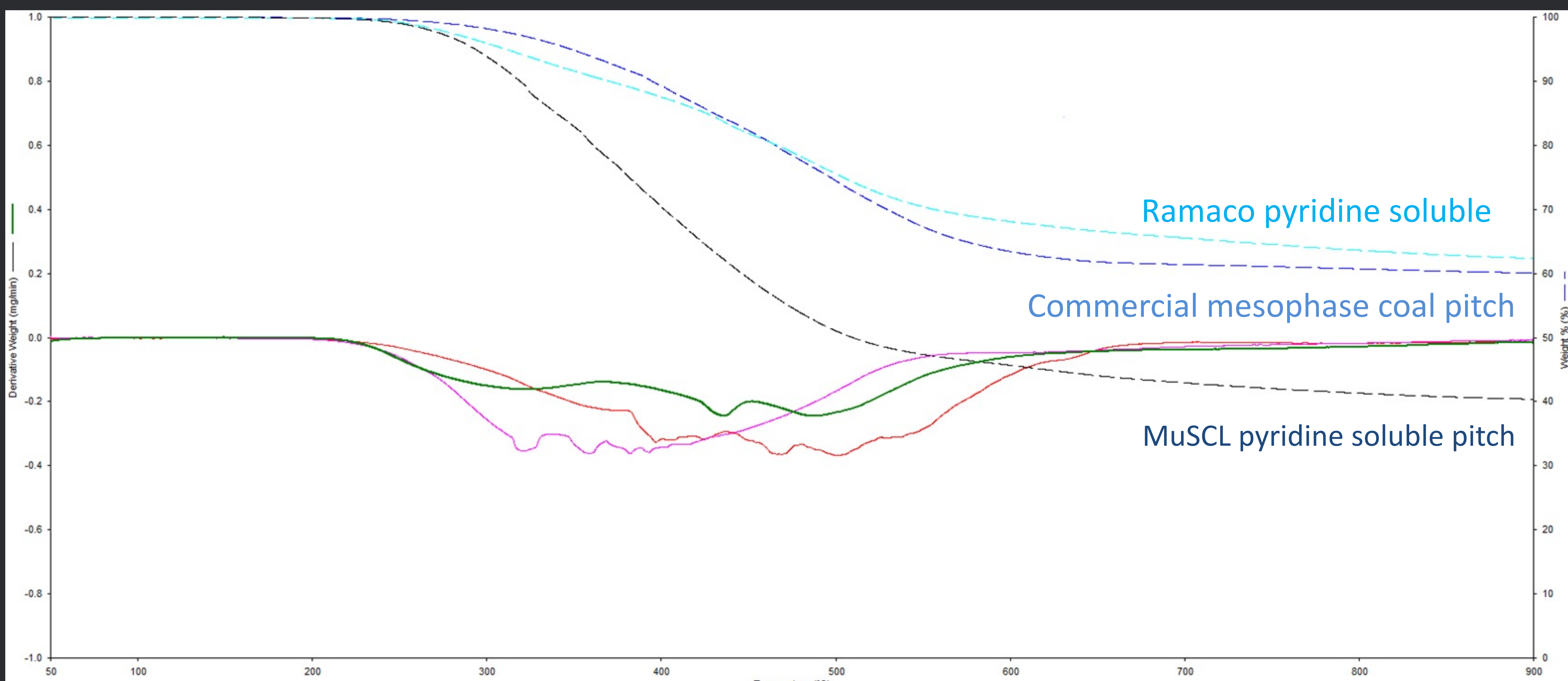
Supercritical CO_2 separation of MUSCL-oil with sequential co-solvents

Results 3 – Comparison with commercial mesophase coal pitch



62%

60%

40%

MUSCL Samples

0716-2020 0814-2020

- 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

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

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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.

Experiment date	August 10 and 13, 2020		August 19, 2020	
Sample	MRaw200716 (MUSCL oil)		MRaw200814 (MUSCL oil)	
Extraction method	Soxhlet	sCO_2	Soxhlet 1	Soxhlet 2
Loaded amount (g)	11 g	17 g	20.4 g	19.8 g
Benzene soluble fraction (%)	49%	52%	62%	59%
Pyridine soluble fraction (%)	13%	12%	7%	9%
Residue (%)	25%	26%	22%	23%
Mass loss (%)	13%	10%	9%	9%

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

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.

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

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

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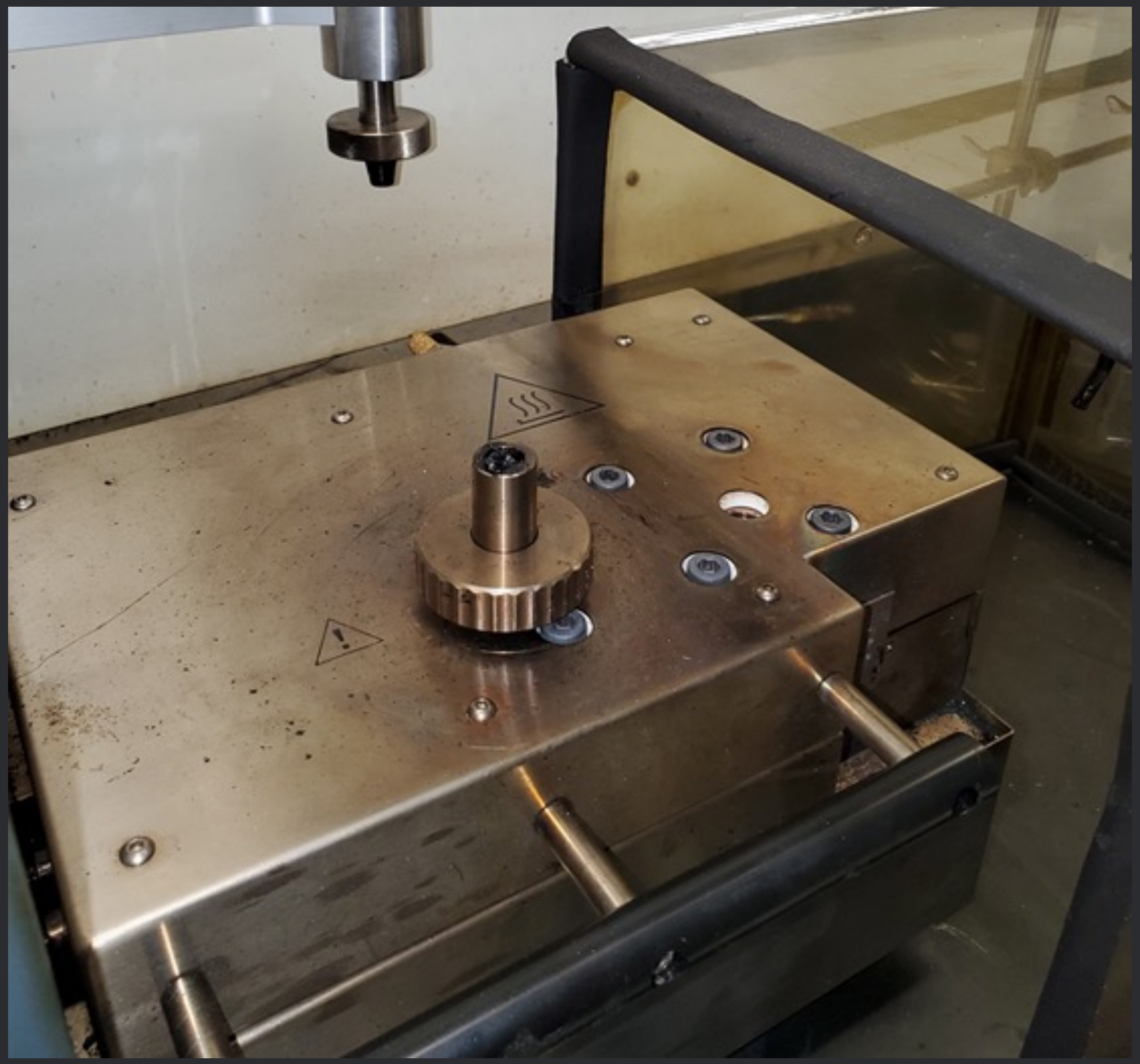
Mesophase Conversion Using the Haake MiniLab

- 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



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Solvent Fractionation

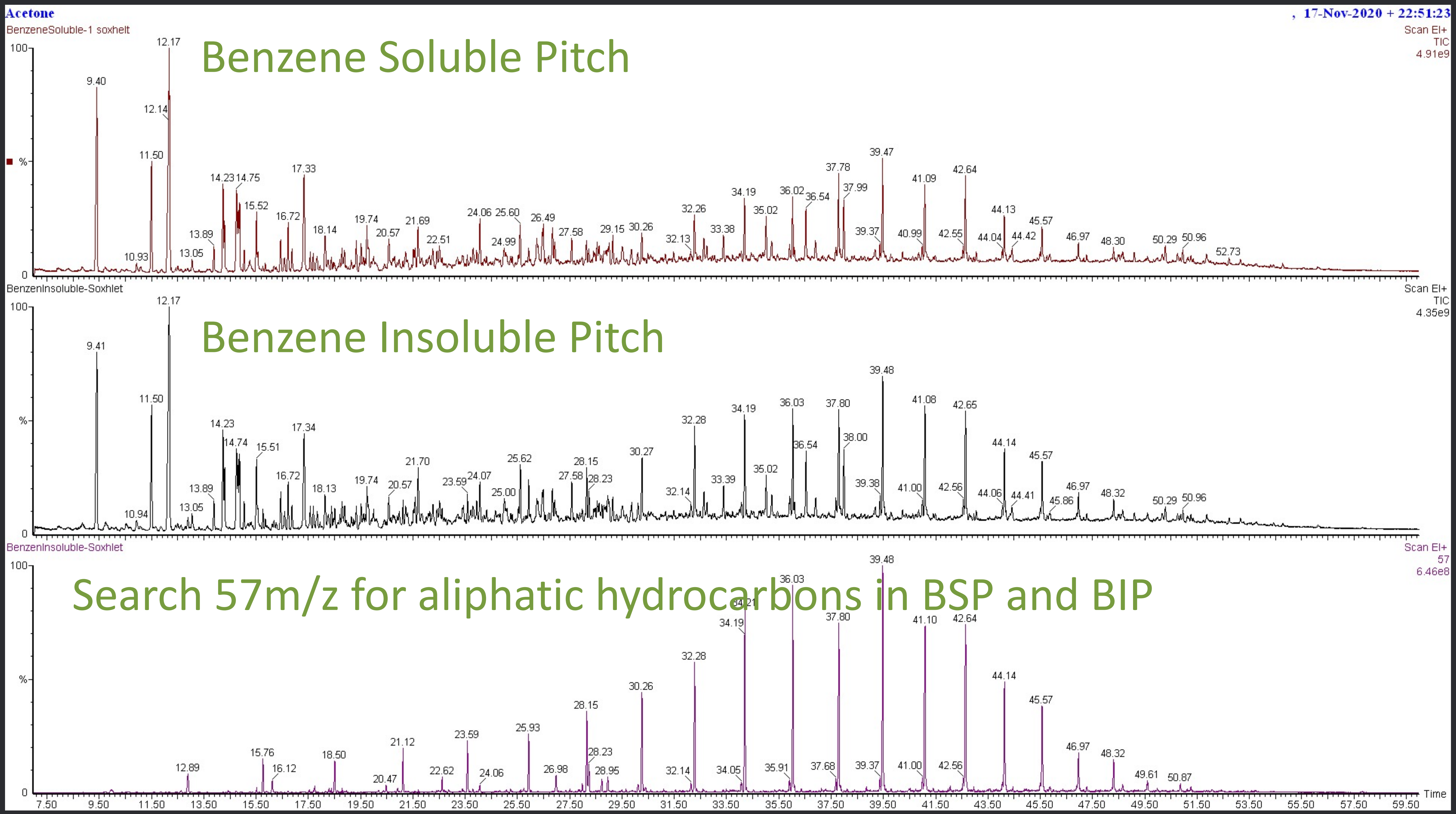
Objectives

- **Obtain asphaltenic 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.

Solvent Fractionation

GC/MS analysis of Benzene Soluble and Insoluble pitches



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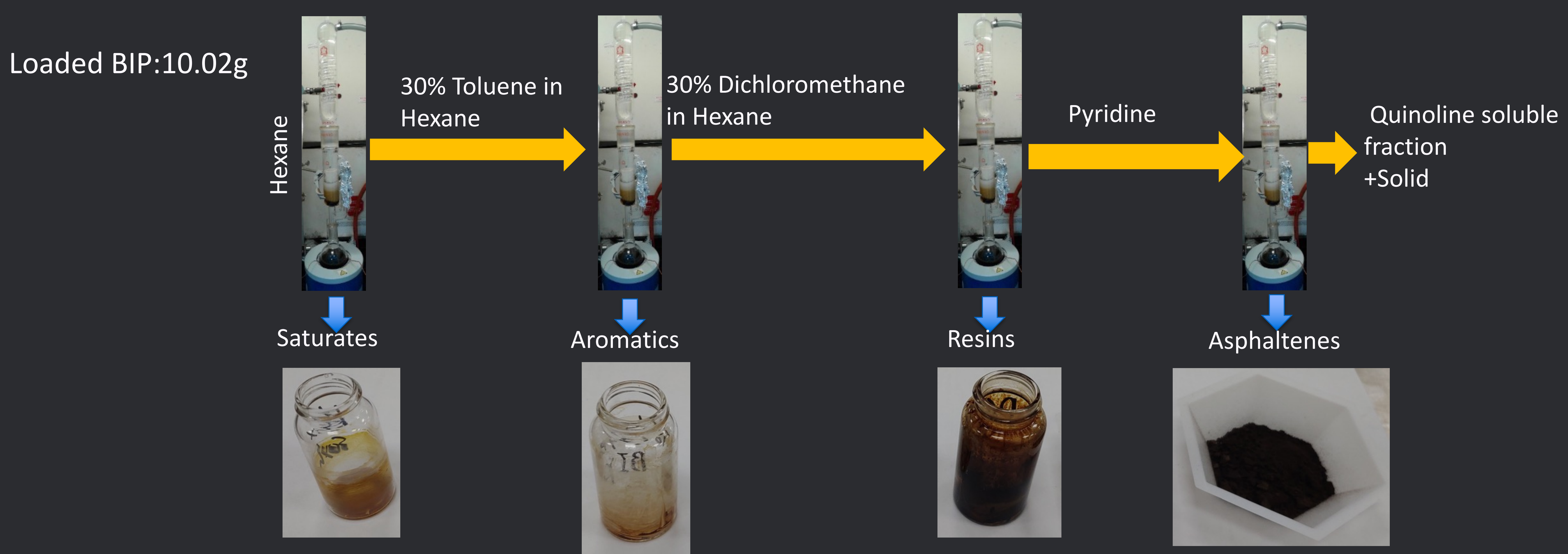
Experimental Set up-1. Soxhlet extraction (BIP)

- 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)



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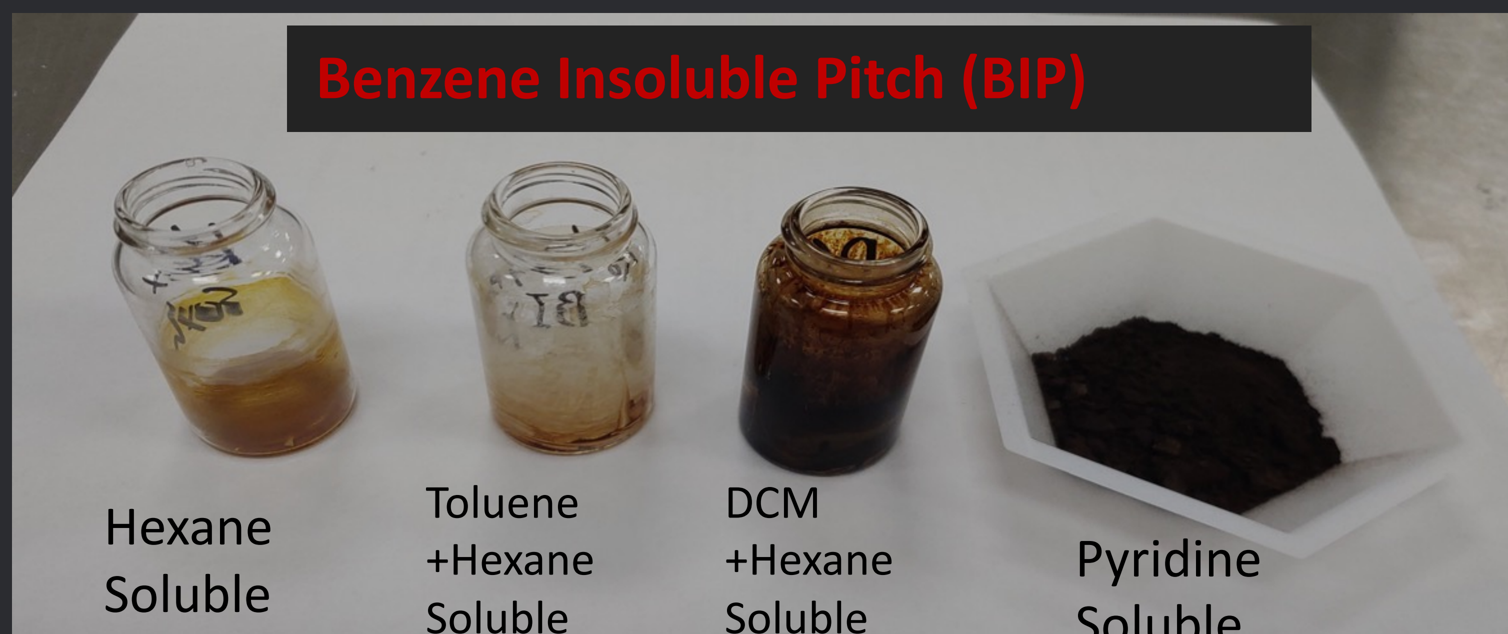
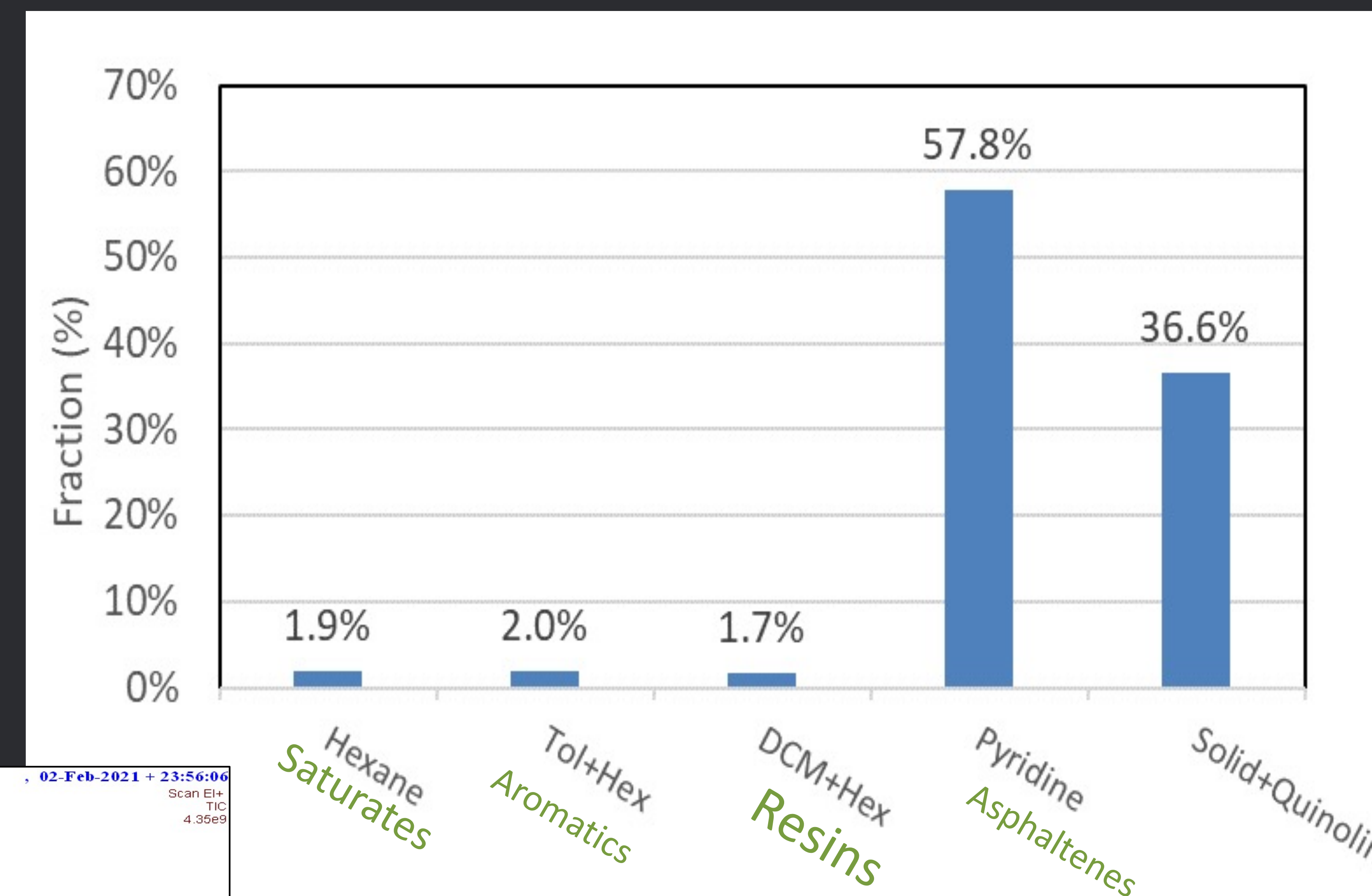
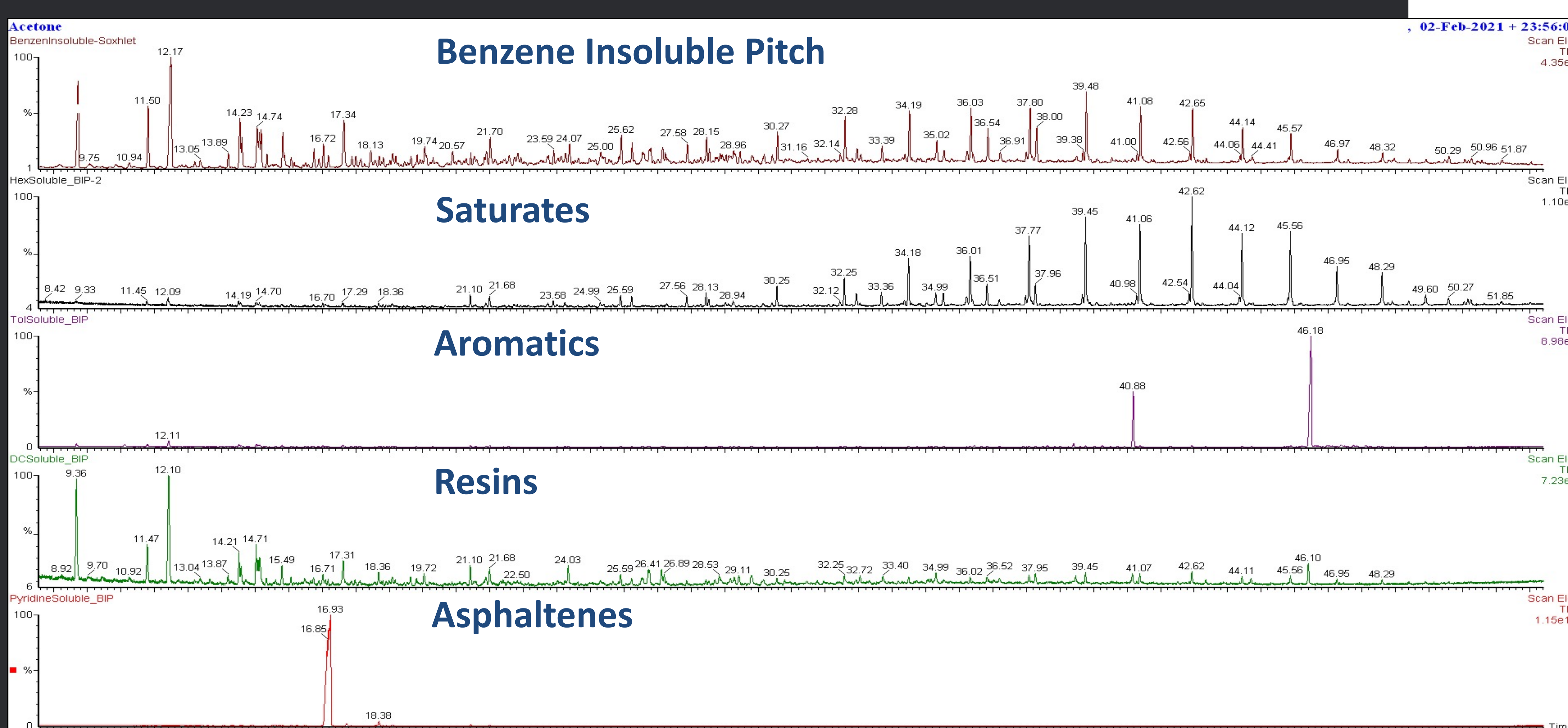
Solvent Fractionation

Result-1. Benzene Insoluble Pitch





+Quinoline fraction was calculated by the difference

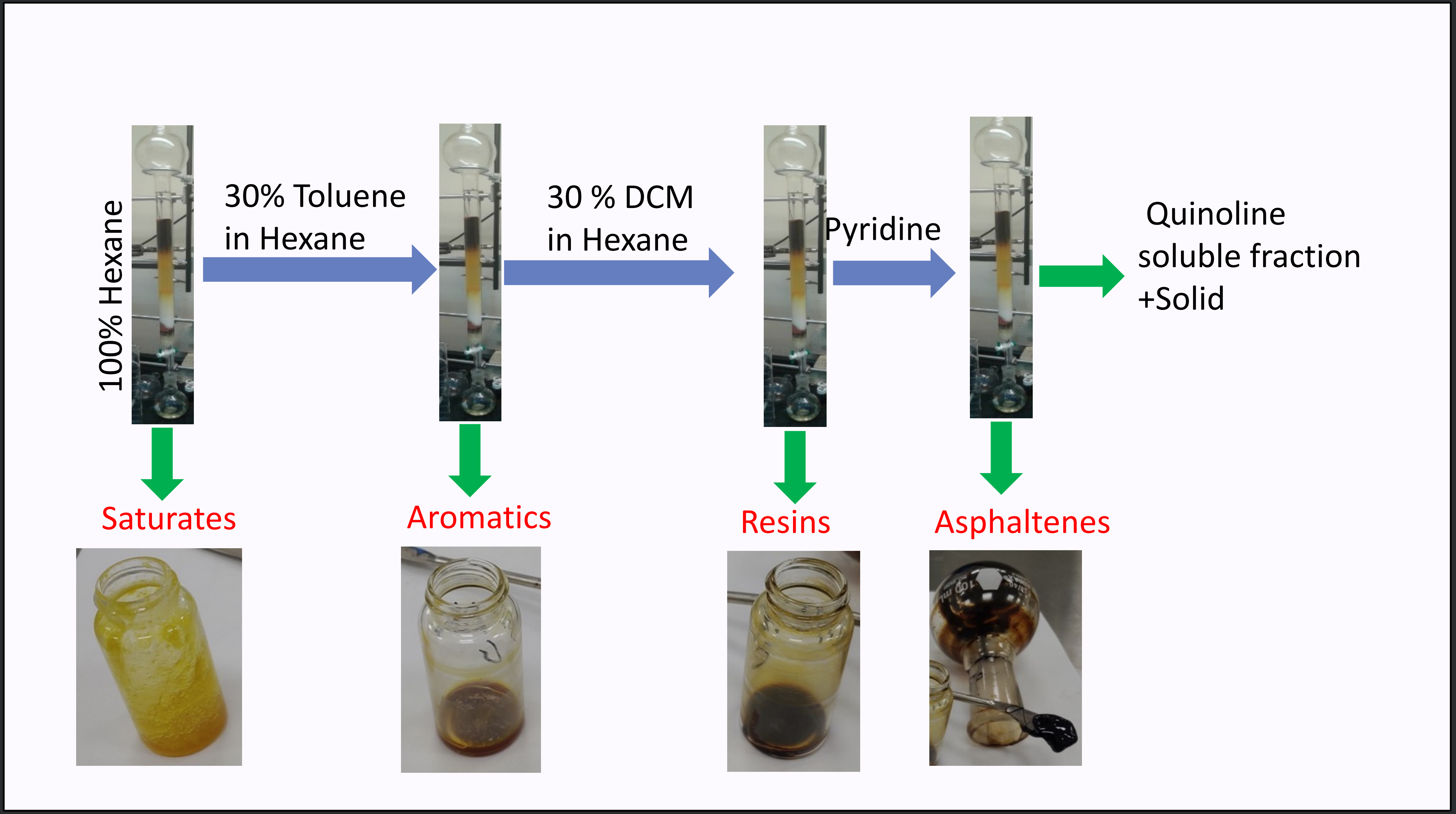


Asphaltene yield: 57.8%

Solvent Fractionation

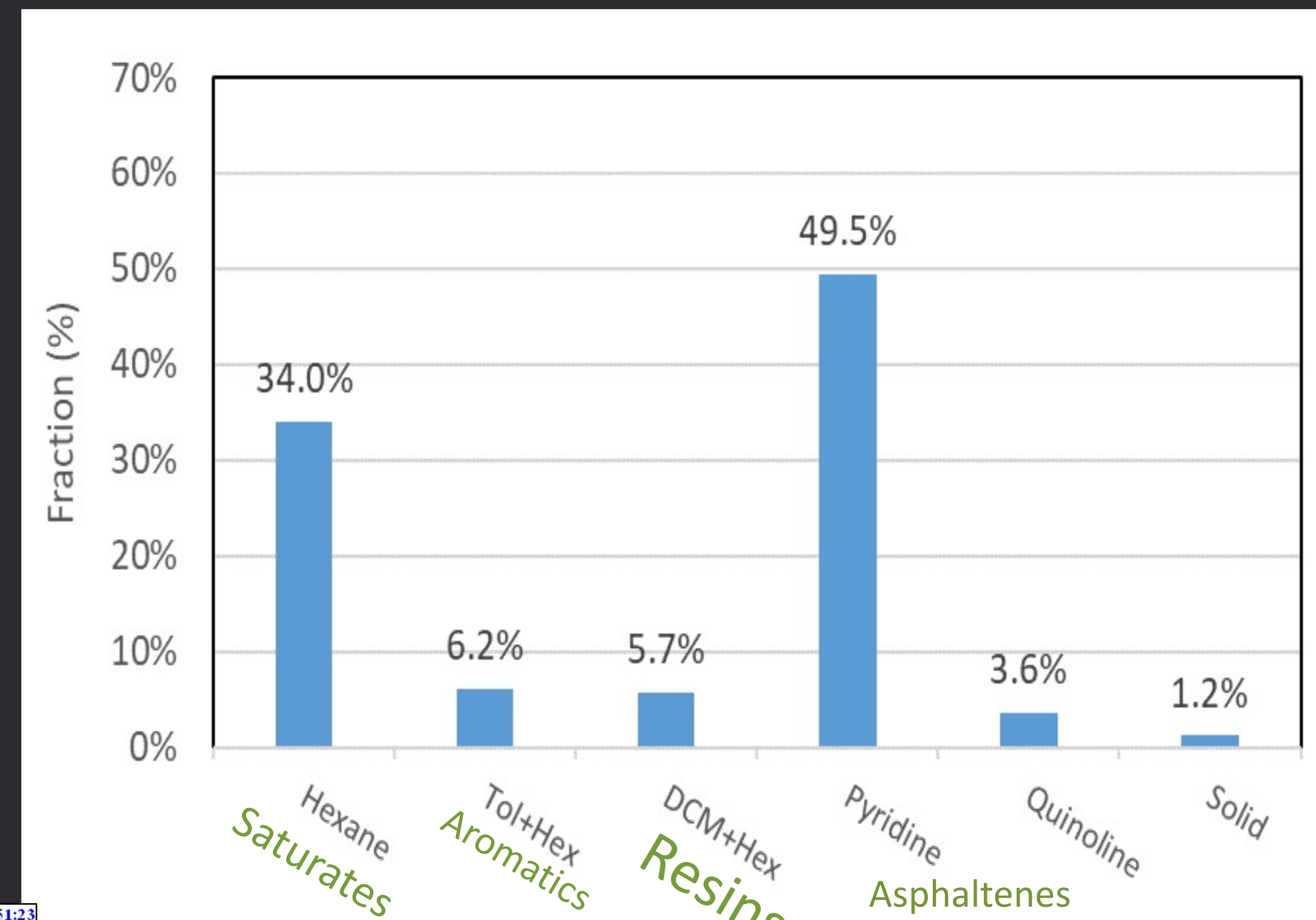
Experimental Set up-2. Chromatographic column separation: BSP

- 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

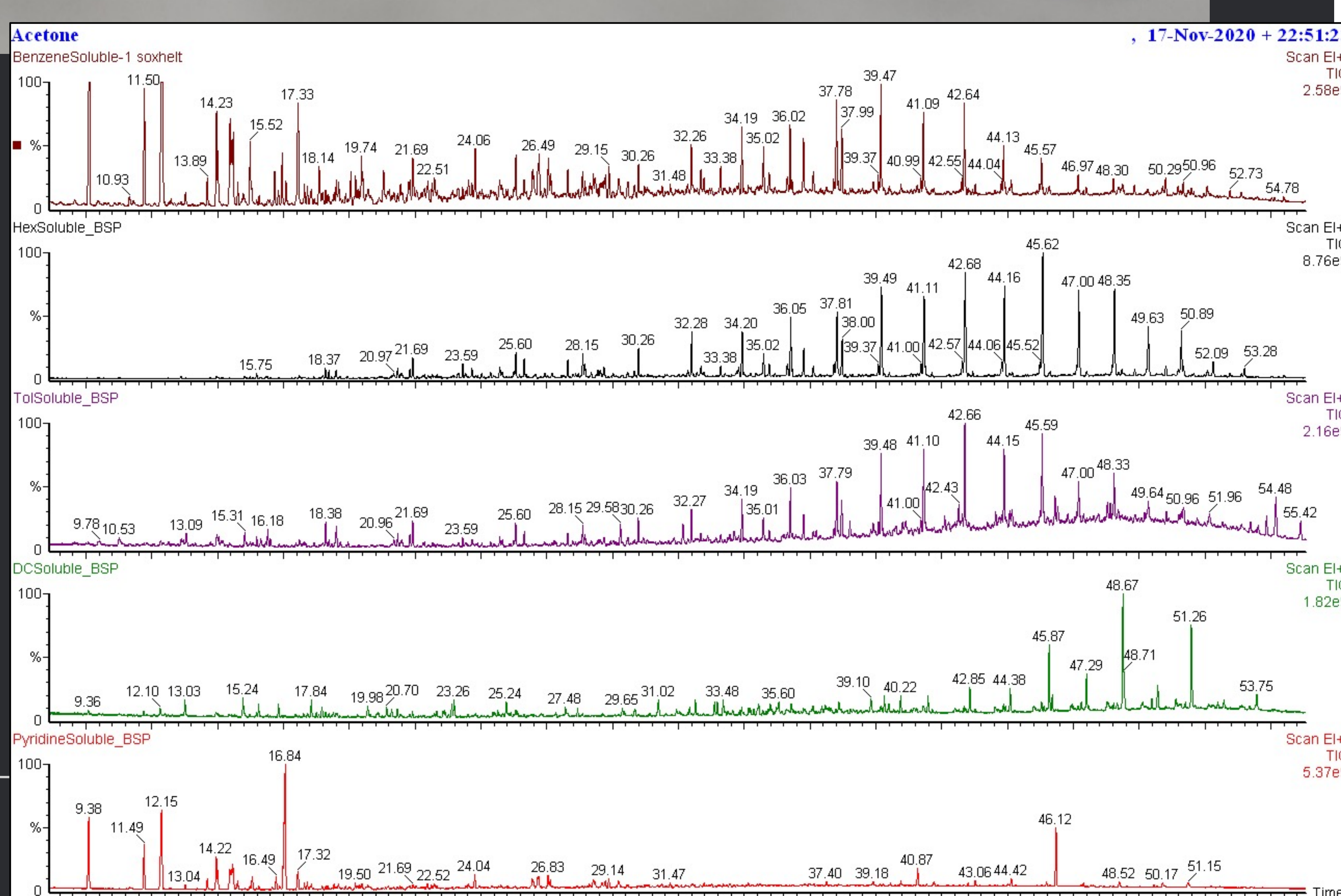


Solvent Fractionation

Result-2. Benzene Soluble Pitch



*Quinoline fraction was calculated by the difference

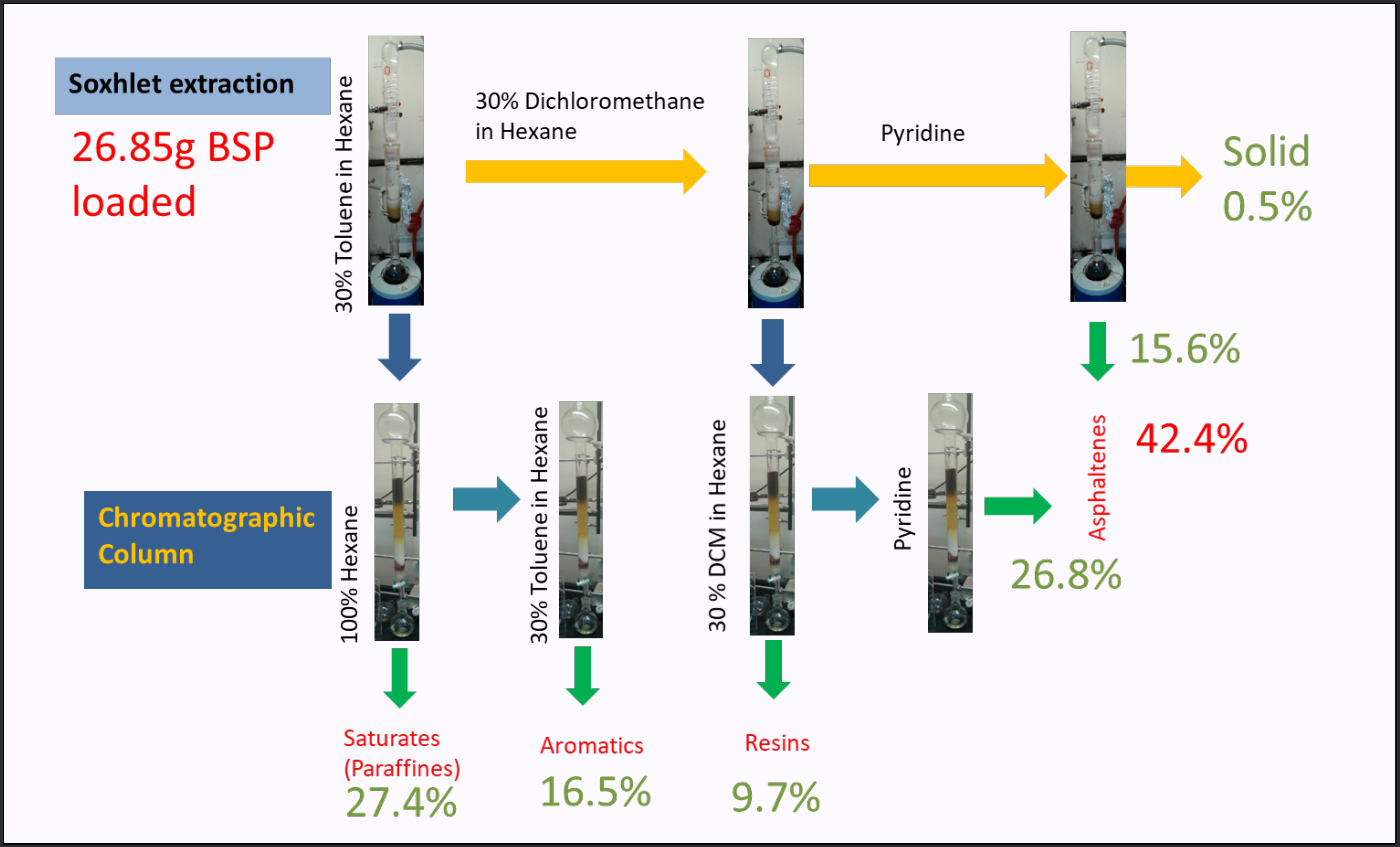


<u>Asphaltene yield: ~ 53%</u>

Solvent Fractionation

Results

Experimental set up



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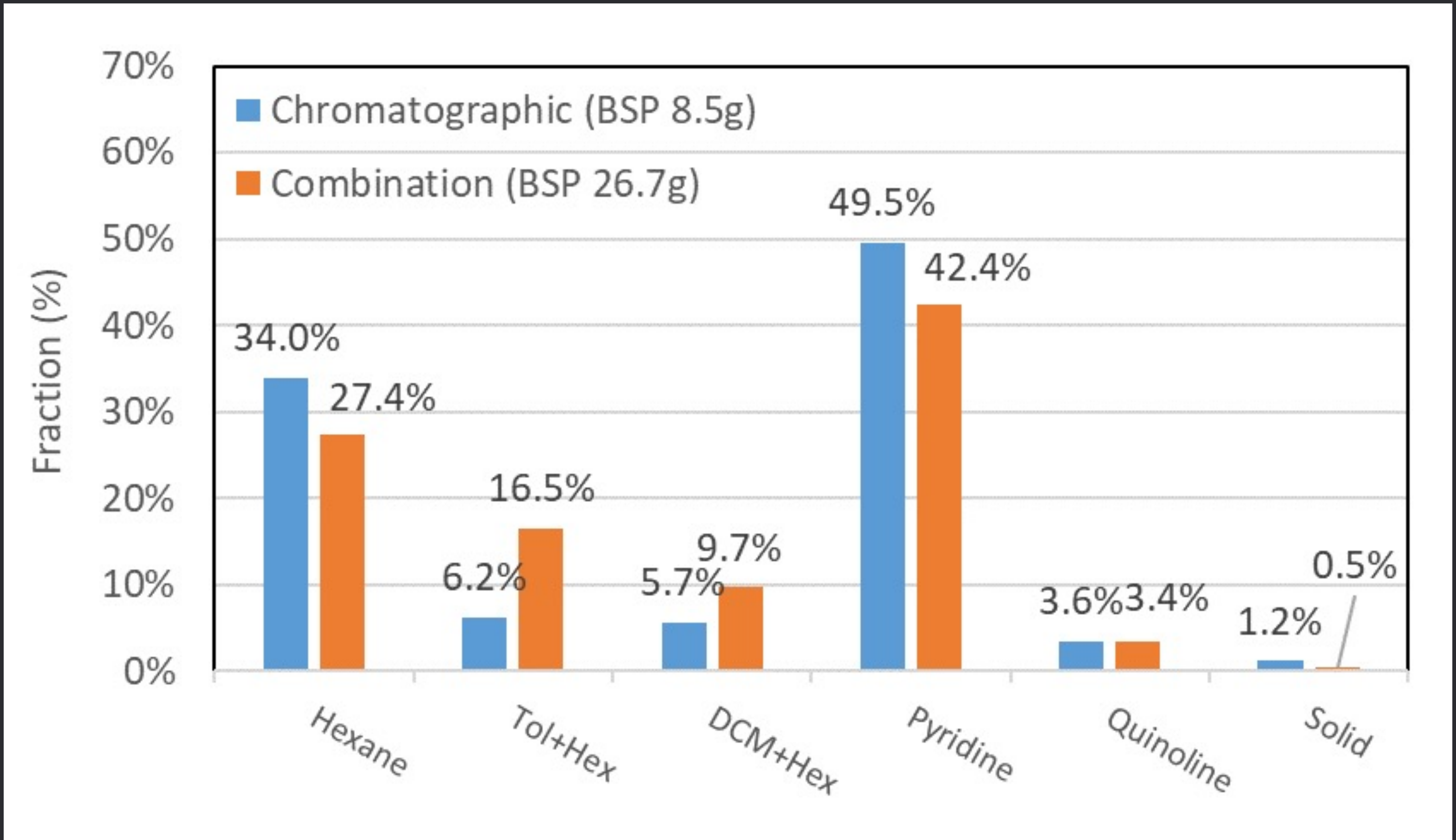
Solvent Fractionation

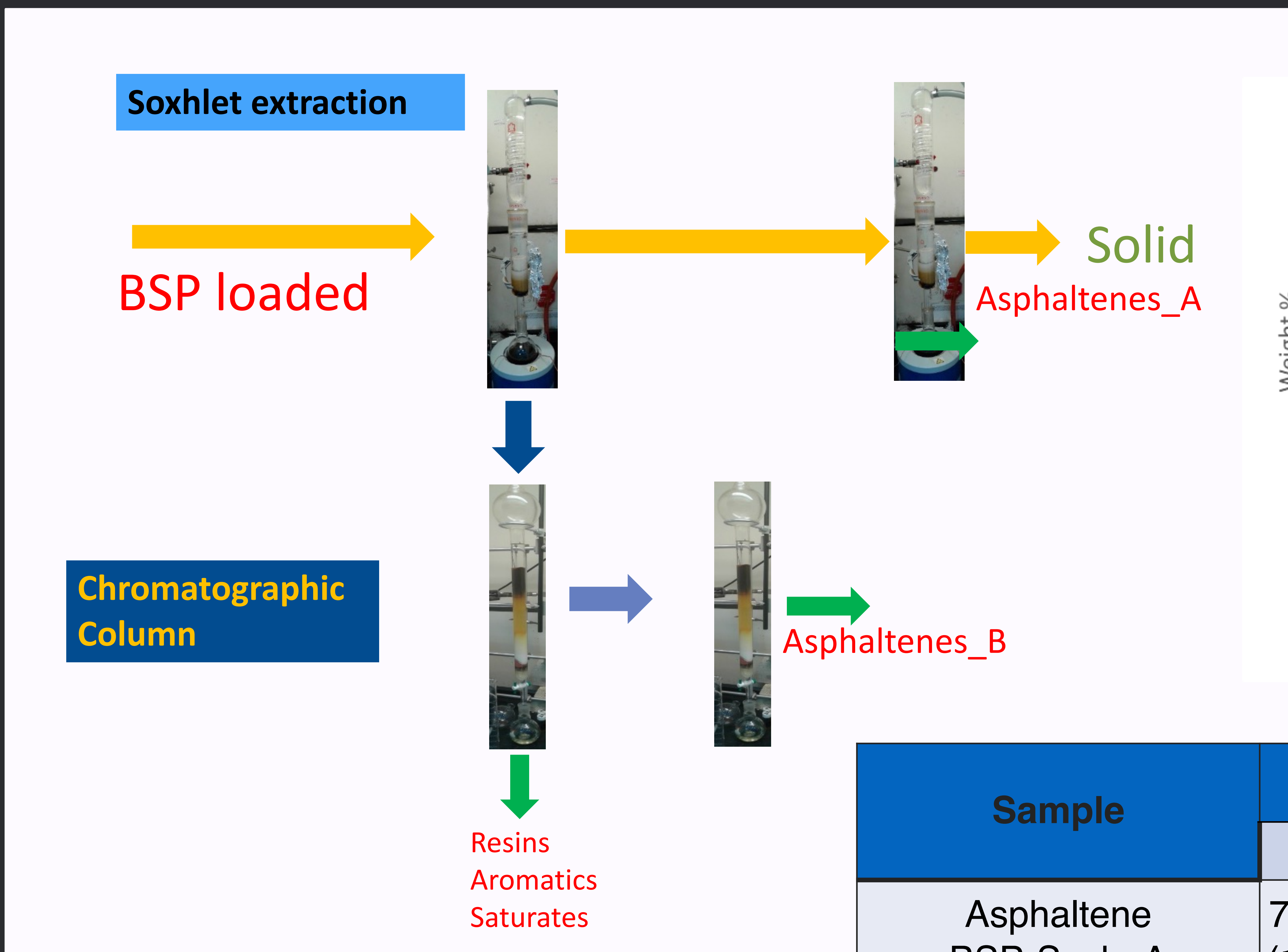
Results

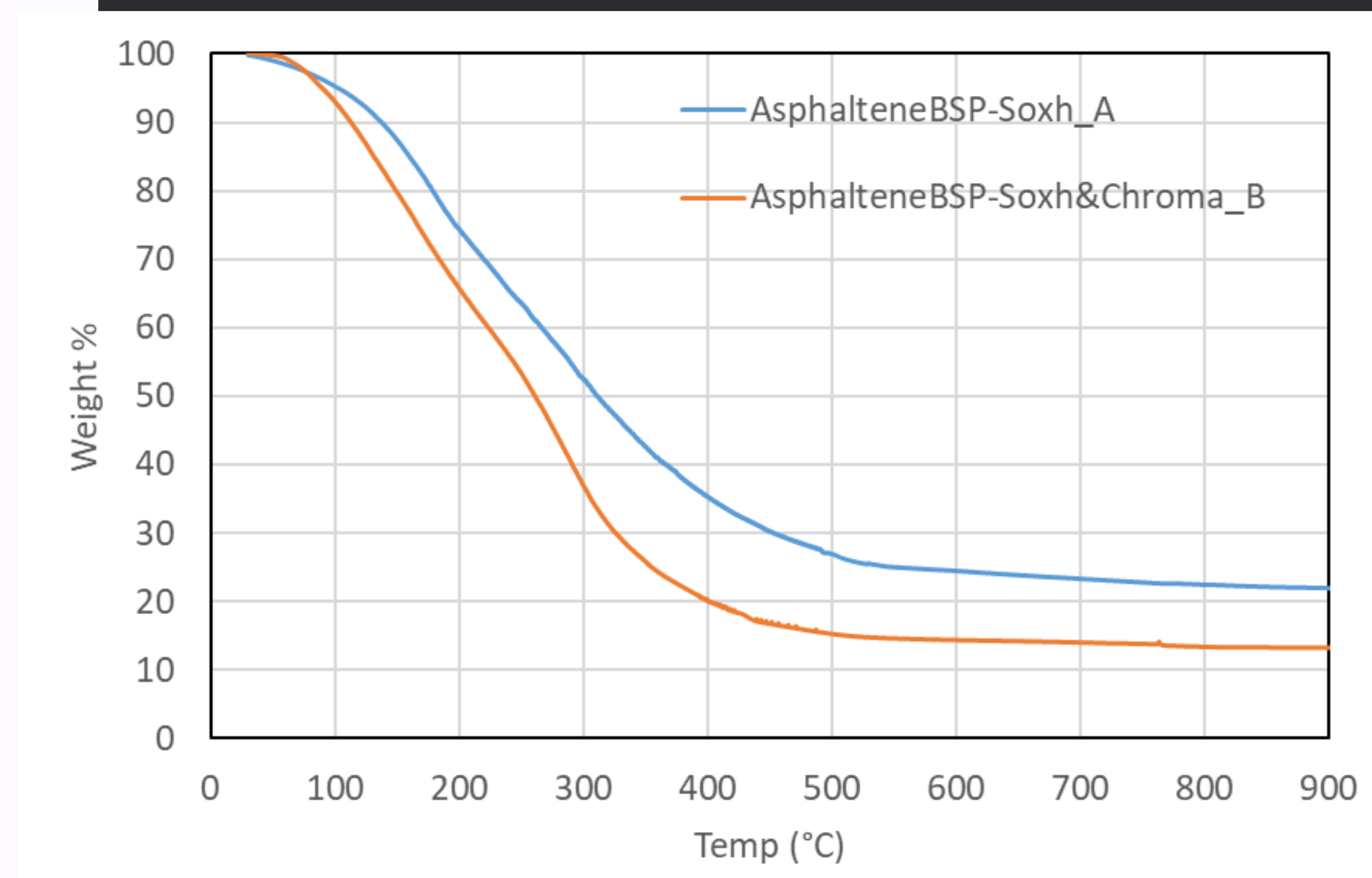
- Asphaltene from Soxhlet: 15.6%
- Asphaltene from Chromatographic: 26.8%



Solvent Fractionation

Simplified Solvent fractionation for BSP



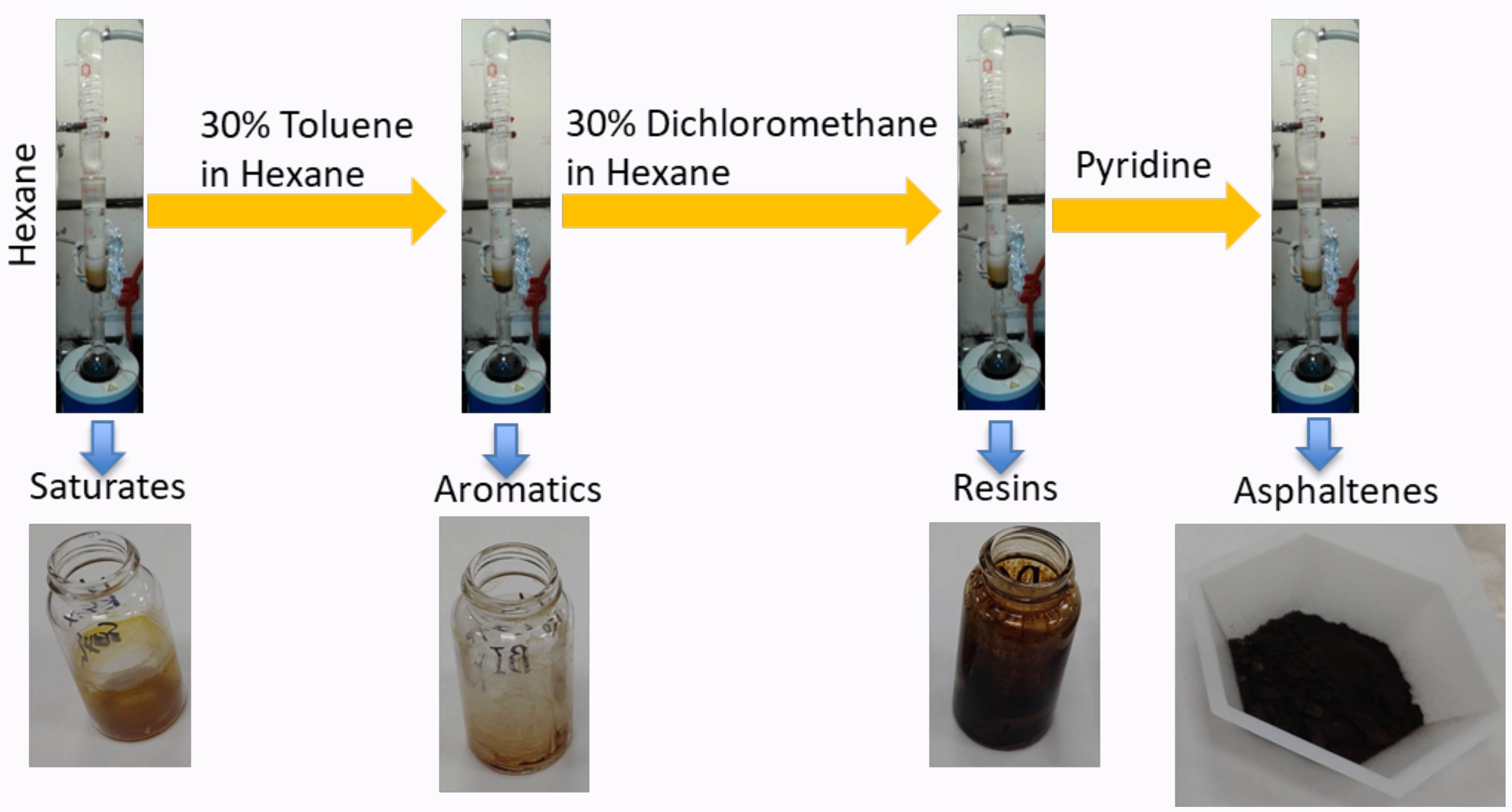


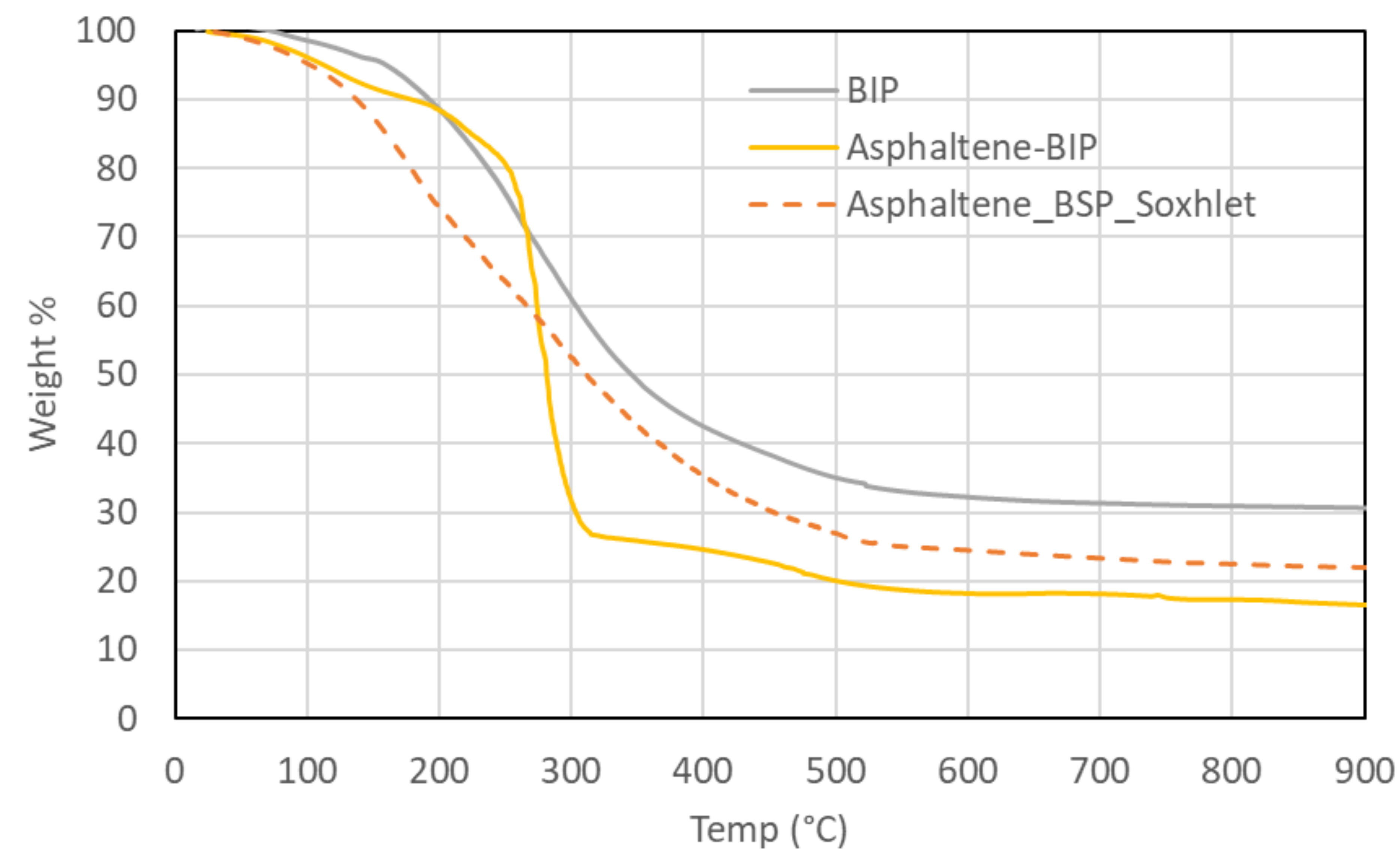
Sample	Weight %					Molar Element ratio	
	C	H	N	S	Sum	H/C	N/C
Asphaltene BSP-Soxh_A	73.71 (1.31)	7.71 (0.49)	6.15 (0.13)	1.15 (0.32)	90.88 (2.03)	1.25 (0.06)	0.07 (0.00)
Asphaltene BSP_Soxh&Chroma-B	75.42 (1.24)	8.84 (0.80)	5.65 (0.16)	0.98 (0.57)	88.71 (1.75)	1.40 (0.12)	0.06 (0.00)

Solvent Fractionation

Solvent fractionation for BIP

Loaded BIP:10.02g



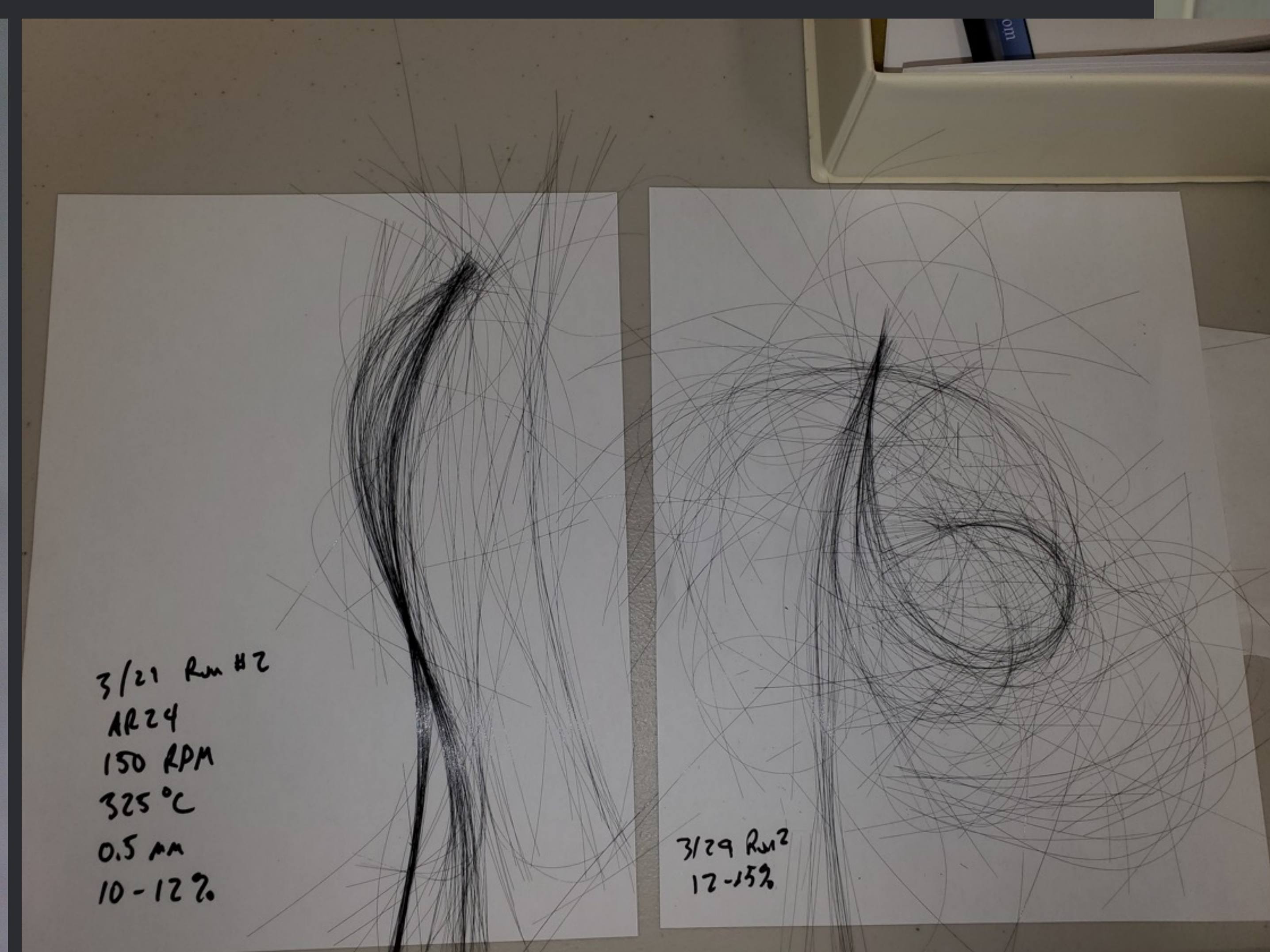


	Weight %						Molar Element ratio	
	C	H	N	S	Sum		H/C	N/C
Pyridine_BIP	59.07 (0.6)	7.7 (0.1)	1.71 (0.0)	1.30 (0.1)	70.4		1.54	0.02
Asphaltene_BIP	55.60 (0.10)	7.07 (0.77)	9.25 (9.25)	0.74 (0.00)	72.17 (1.14)		1.51 (0.17)	0.14 (0.00)

Coal to Carbon Fiber – Novel Supercritical CO_2 Solvated Process (MUSCL)

Spinning of Fiber by Ramaco

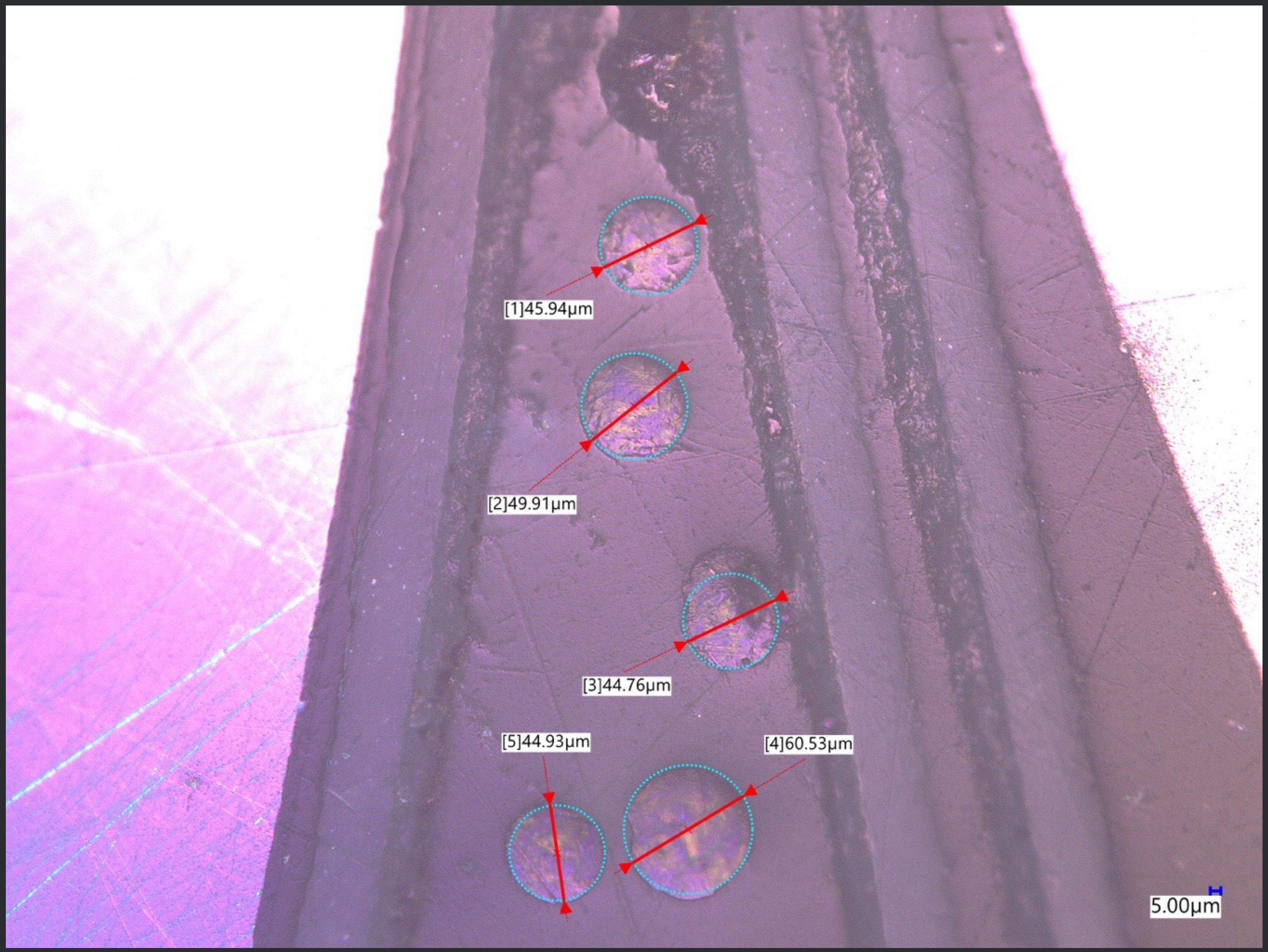
- Fiber Spinning Initiated 3/26/21
  - Established Baseline and Verified Equipment
  - Achieved Stable Spinning AR24 Synthetic Mesophase
  - HAAKE extruder with 500micron orifice
  - Fiber Diameters from 40 micron to 70 micron

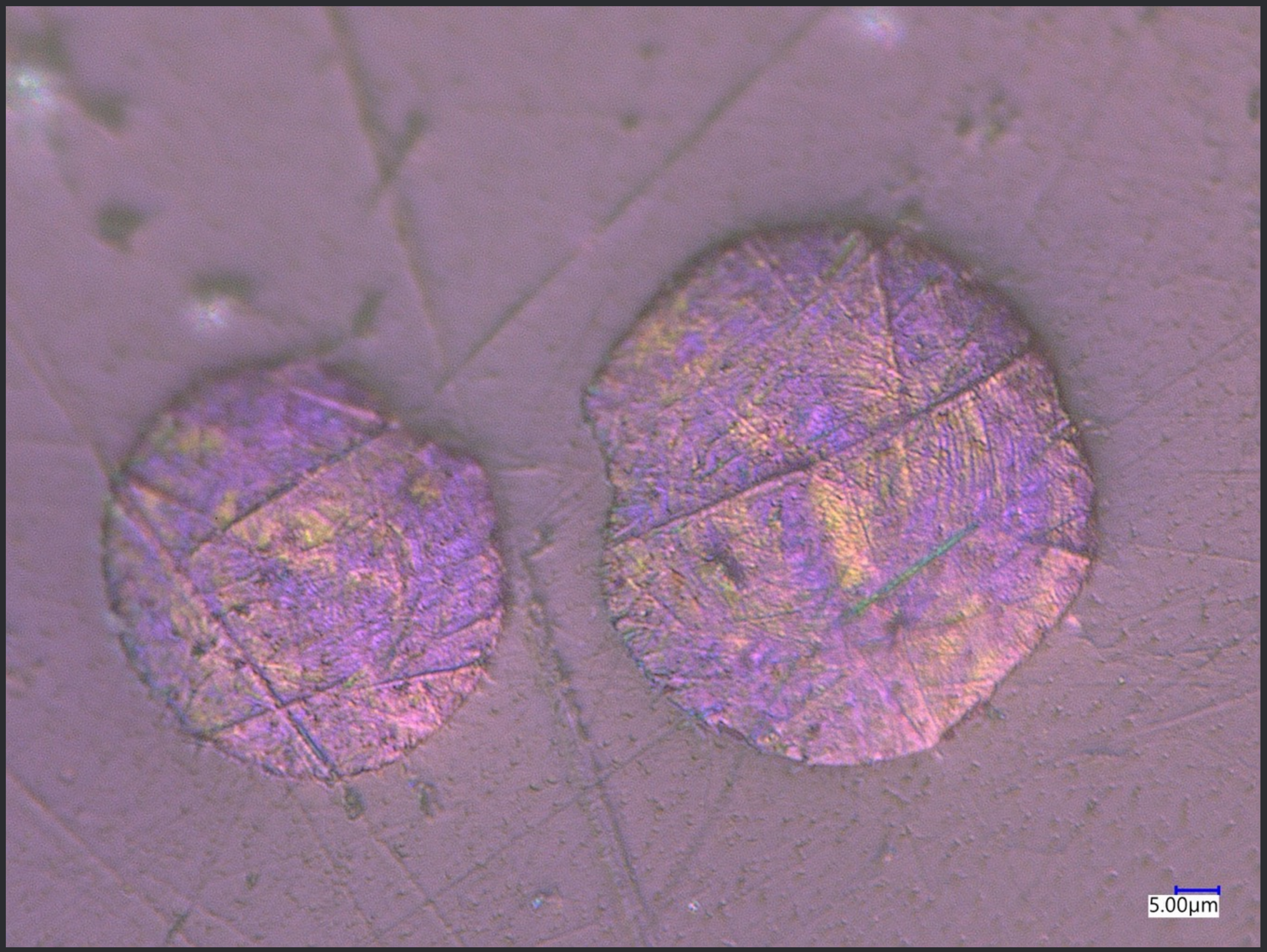


Coal to Carbon Fiber – Novel Supercritical CO2 Solvated Process (MUSCL)

Spinning of Fiber by Ramaco

Establishing Baseline with Synthetic Mesophase

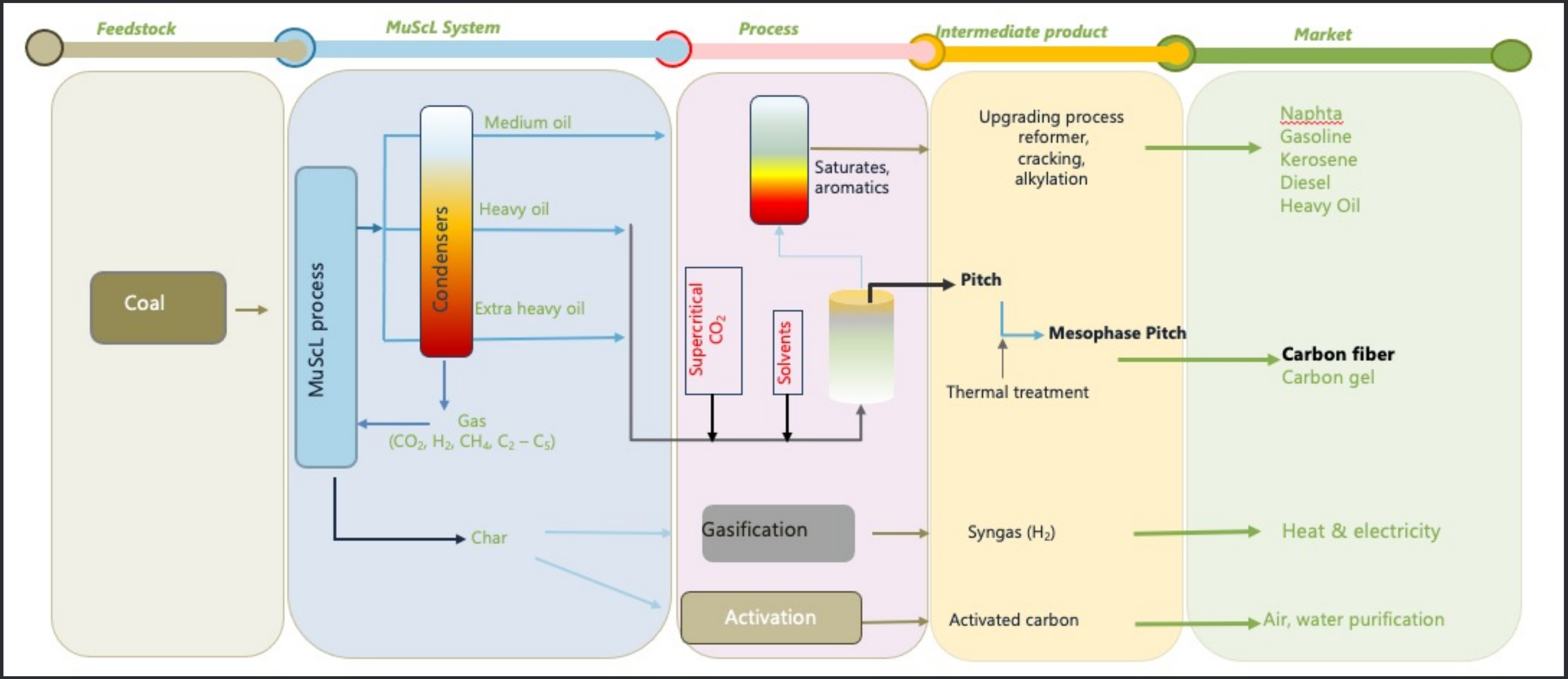




AR24 Fibers Spun at 325C AVG DIA 48um Observed Orientation of Mesogens

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

Commercialization and Economic Analysis



Coal to Carbon Fiber – Novel Supercritical CO_2 Solvated Process (MUSCL)

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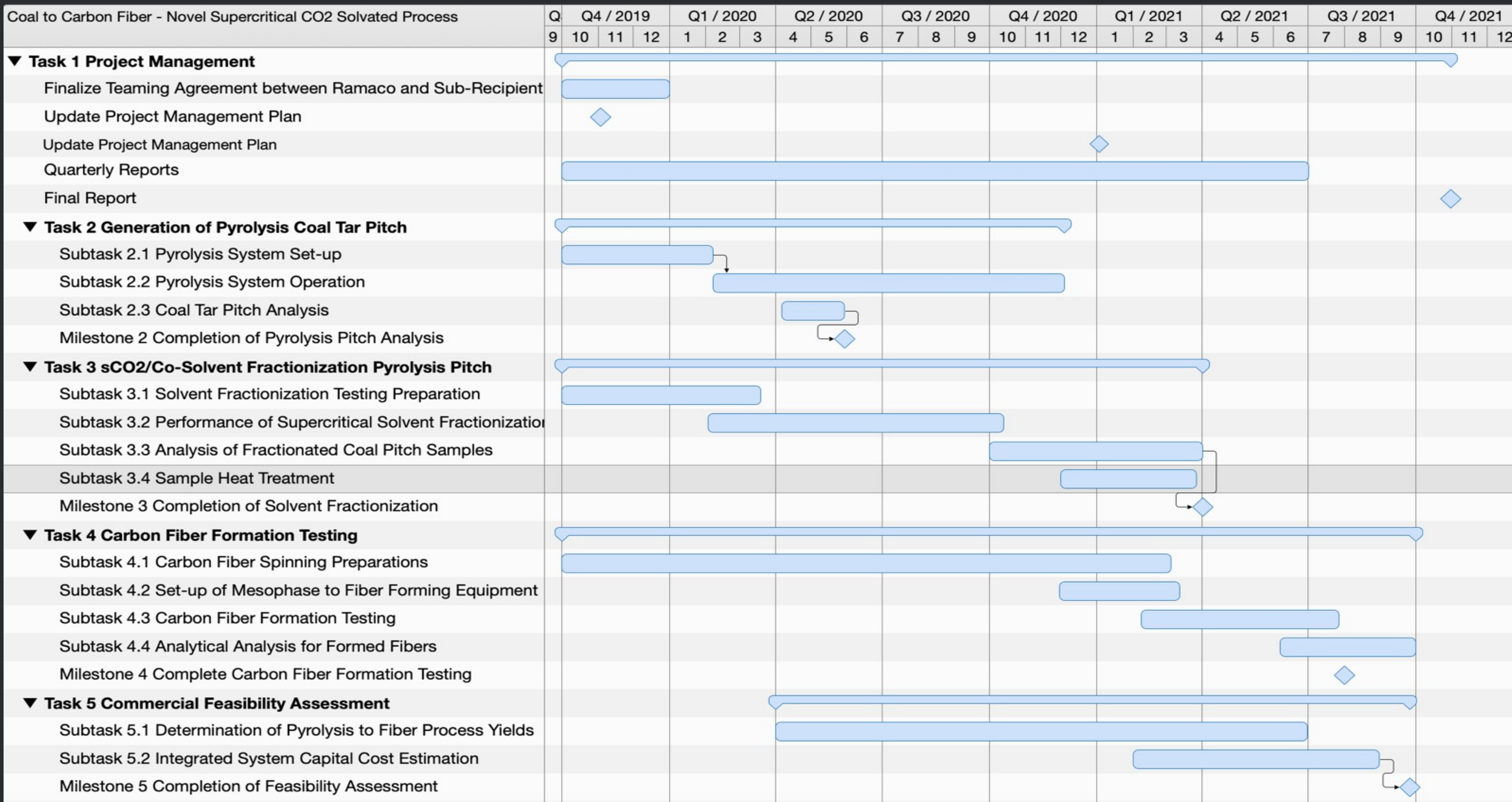

COVID-19 Impacts March-May 2020, Equipment Delivery Delays
Revised Schedule for Task 4 Extended to July 31

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Coal to Carbon Fiber – Novel Supercritical CO_2 Solvated Process (MUSCL)

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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.

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Thank You

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www.ramacocarbon.com

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