Coal to Carbon Fiber (C2CF)

Continuous Processing for High Value Composites

DE-FE0031796

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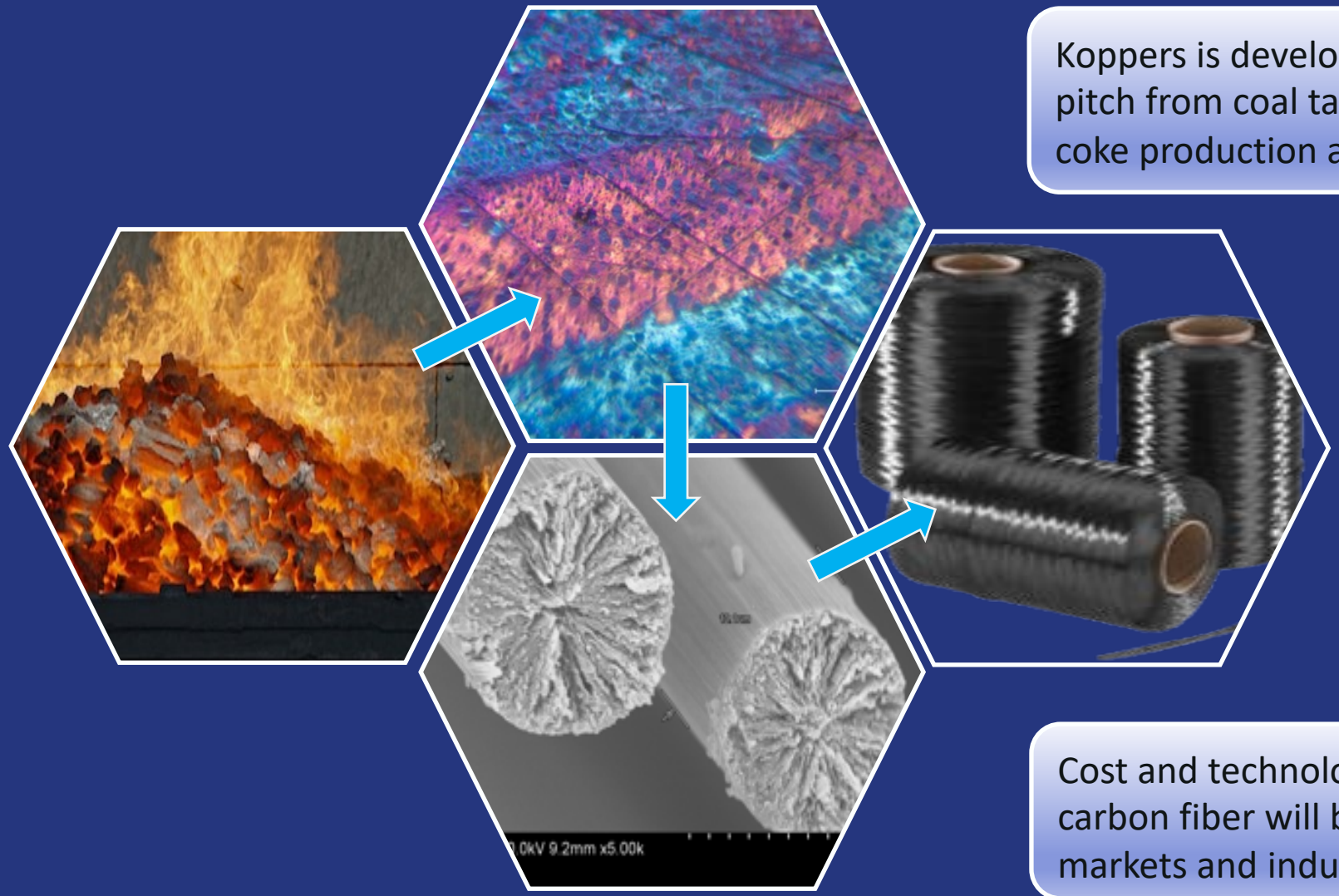
Center for Applied Energy Research

C2CF Coal to Carbon Fiber:

Continuous Processing for High Value Composites



Koppers is developing a spinnable mesophase pitch from coal tar recovered from metallurgical coke production at integrated steel mills.

UK is developing stable multifilament melt spinning and continuous thermal conversion

Prototype composite parts will be demonstrated with the carbon fiber.

Cost and technology gap analyses for the carbon fiber will be evaluated, for new markets and industries for US coal.

Overview

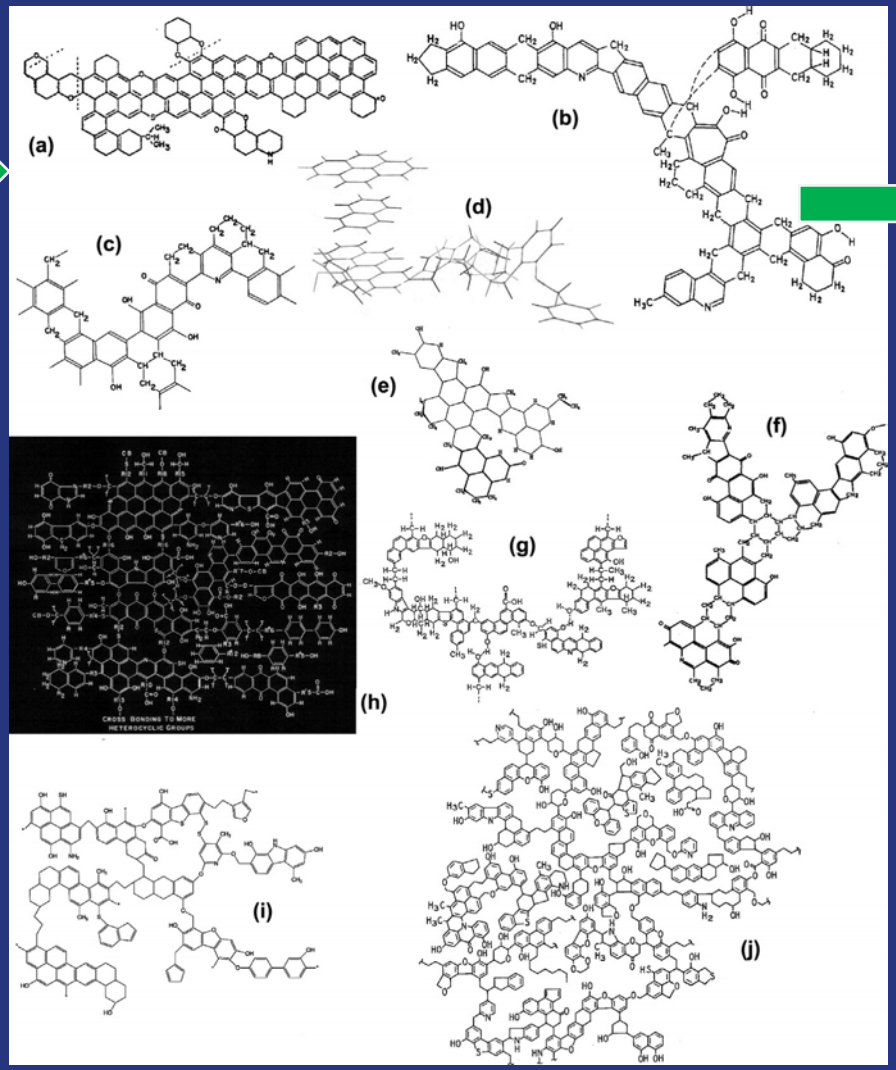
- Project rationale and goals

- Task Updates: Successes & Challenges
  1. Coal Tar to Mesophase Pitch
  2. Melt Spinning & Tensile Properties

- Future Direction & Challenges
- Concluding Remarks

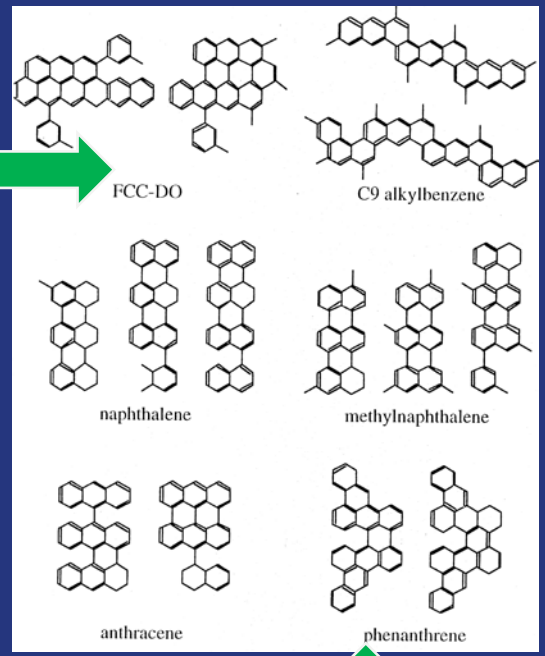
Rationale: Source Compounds in Coal

https://www.worldcoal.org/coal/what-coal

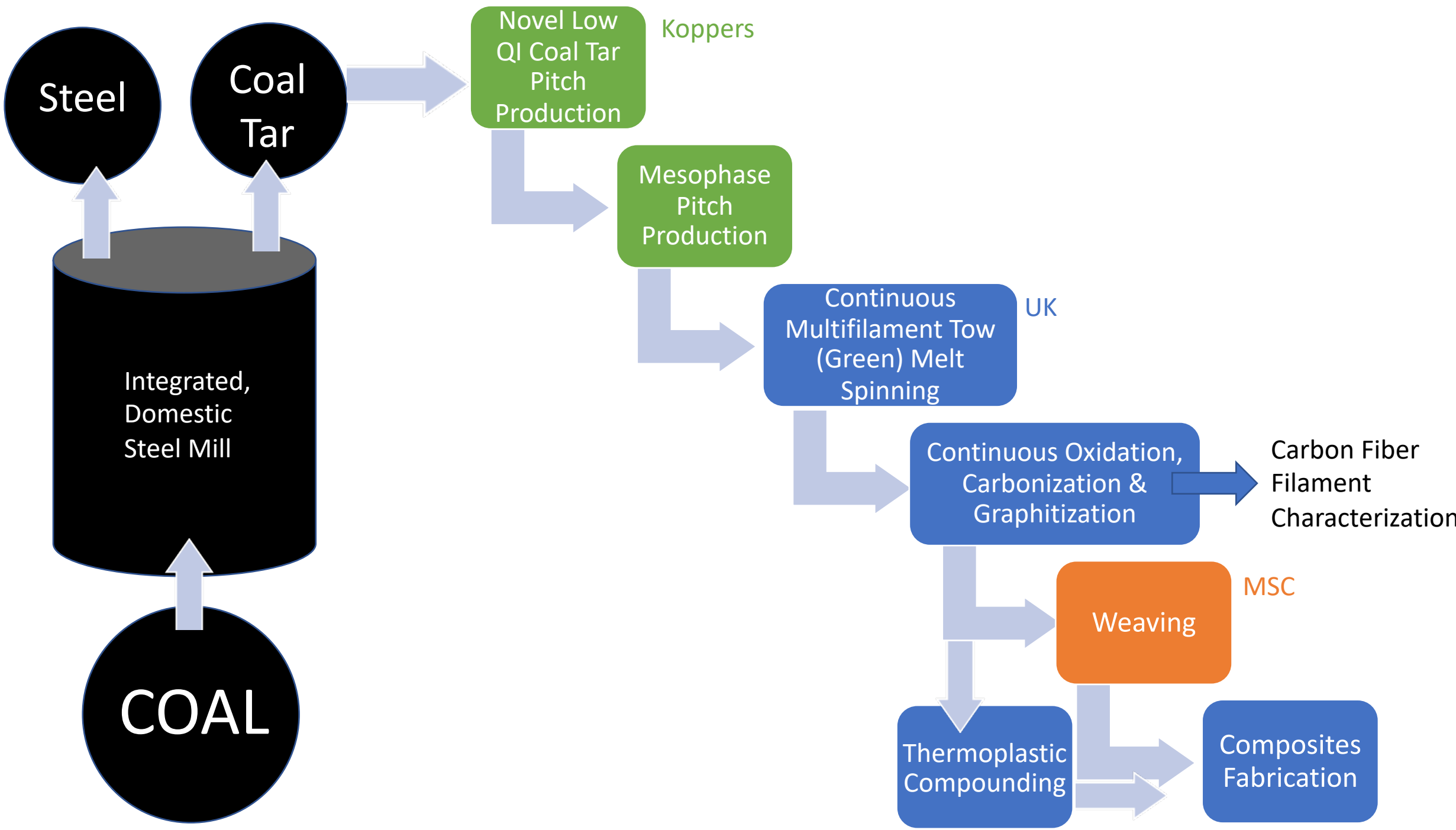


J.P. Mathews, A.L. Chaffee / Fuel 96 (2012) 1–14

I. Mochida et al. / Carbon 38 (2000) 305 –328

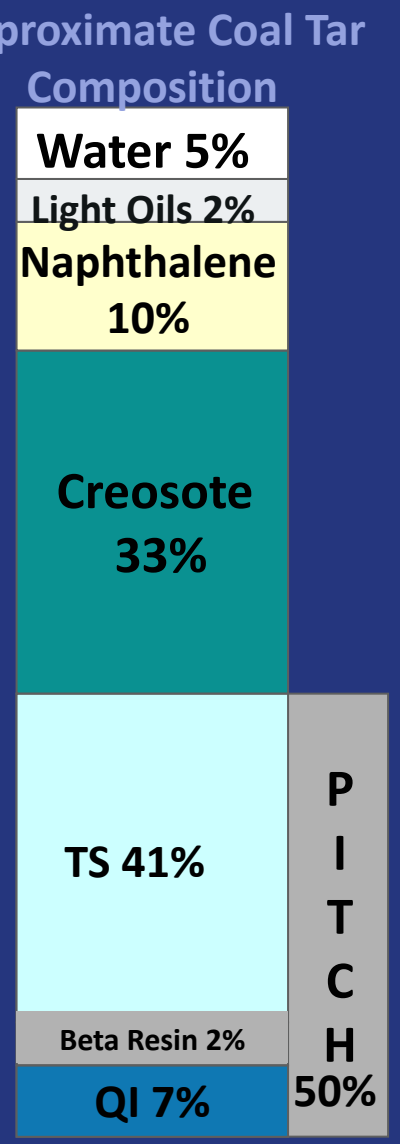


mesophase


Steel
Coal Tar
COAL
Integrated, Domestic Steel Mill
Novel Low QI Coal Tar Pitch Production
Koppers
Mesophase Pitch Production
Continuous Multifilament Tow (Green) Melt Spinning
UK
Continuous Oxidation, Carbonization & Graphitization
Carbon Fiber Filament Characterization
Weaving
MSC
Thermoplastic Compounding
Composites Fabrication

Initial Economics: Coal Products Conclusions

- 1570 kt coal – from single site
- 80 kt coal tar (450 kt/yr US production of coal tar)
  - 16 kt of chemical oil, including valuable naphthalene
  - 24 kt of distillates creosote (for railroad tie production) and carbon black precursor (essential for tire production).
- 40 kt isotropic coal tar pitch ($800/t)
  - $32M, for binder pitch for electrodes
- 20 kt mesophase pitch
- 16 kt carbon fiber (180 kt/yr CF market)
  - $1.76B, for even-higher value composites ($50/lb CF)
- Value add relative to the isotropic CTP
  - 55x ($50/lb)
  - 5.5x ($5/lb)



Project Goals: ... To maximize the coal value chain

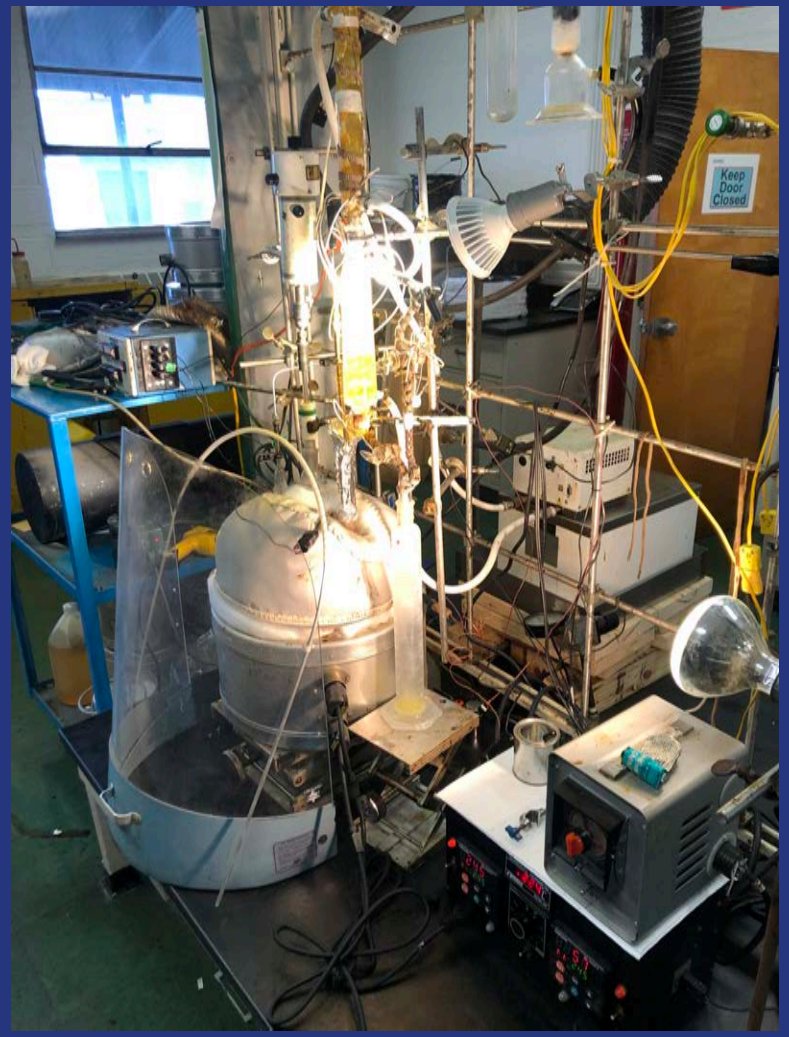
- Develop and scale efficient processing technology for ultra-low quinoline insolubles (QI) coal tar pitch and subsequent mesophase pitch
- Clarify and simplify tedious continuous multifilament spinning and thermal conversion
  - Efficient production of high performance carbon fiber products (woven carbon fiber preforms, continuous, and chopped tow)
- Demonstrate and characterize representative composite parts
- Economic & Technological Gap Analyses

Tasks Updates

Task 2: Coal Tar to Mesophase

Low QI coal tar pitch production

Small-scale mesophase production

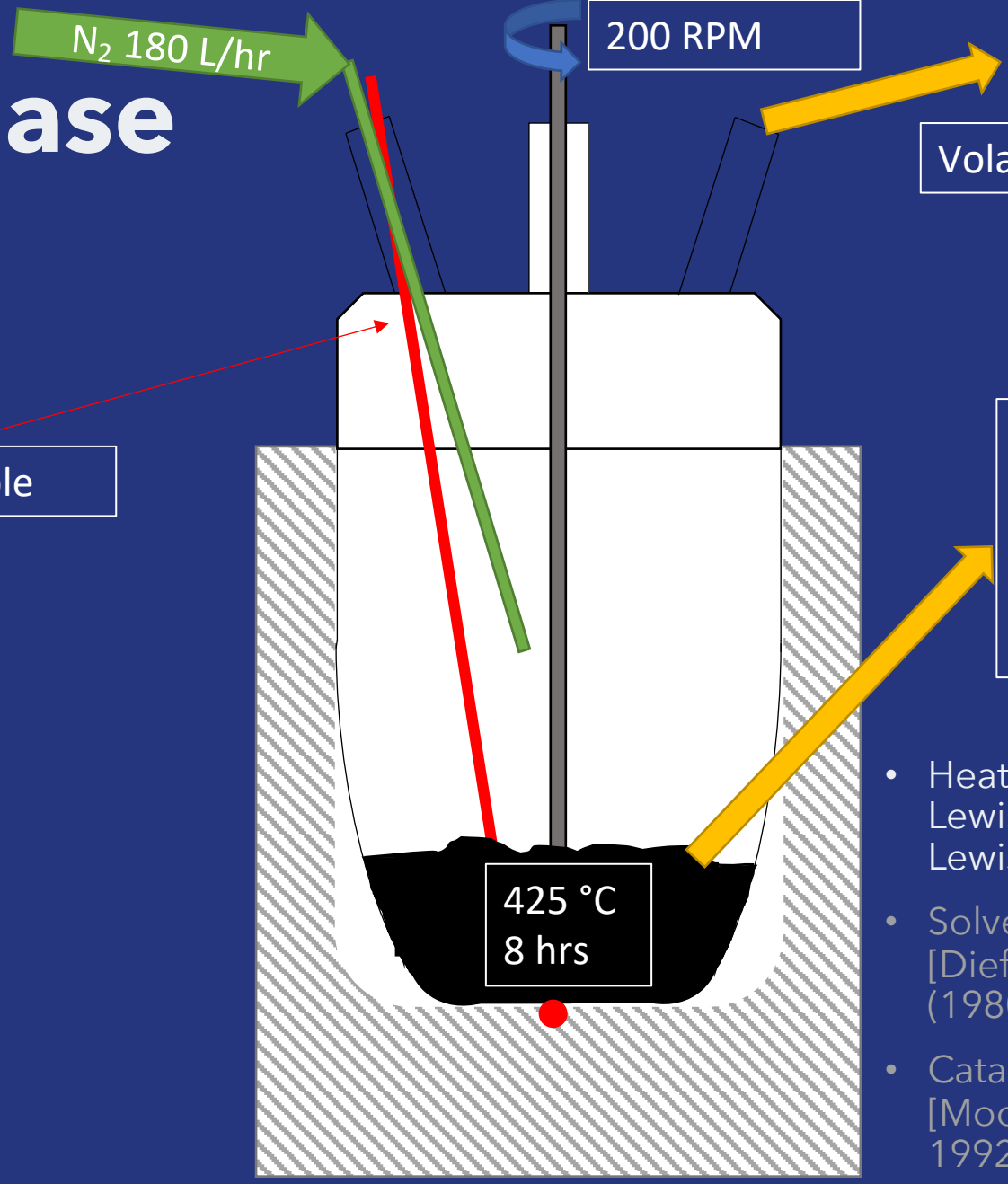


Coal tar derived mesophase pitch

Making Mesophase *Example*

START: Coal Iso Pitch:
Tsp ~ 100 °C
C/H = 18.62 wt.%
QI = 0.36 wt.%
TI = 19.83 wt.%
THFI = 11.61 wt.%

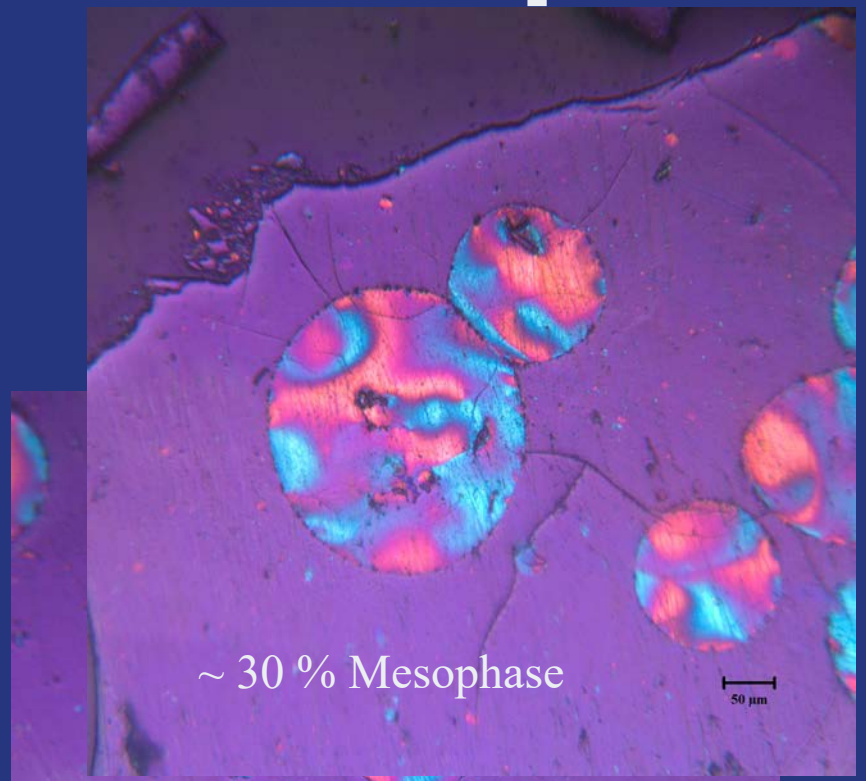
FINAL: Mesophase
~ 51 wt.% yield
~ 60 vol% mesophase
Tsp ~ 300 °C
C/H = 26.42 wt.%
QI = ~ 45 wt.%



Post processing:
Vacuum distillation
< 1 Torr
340 C 5 min
~ 3 wt.% volatiles

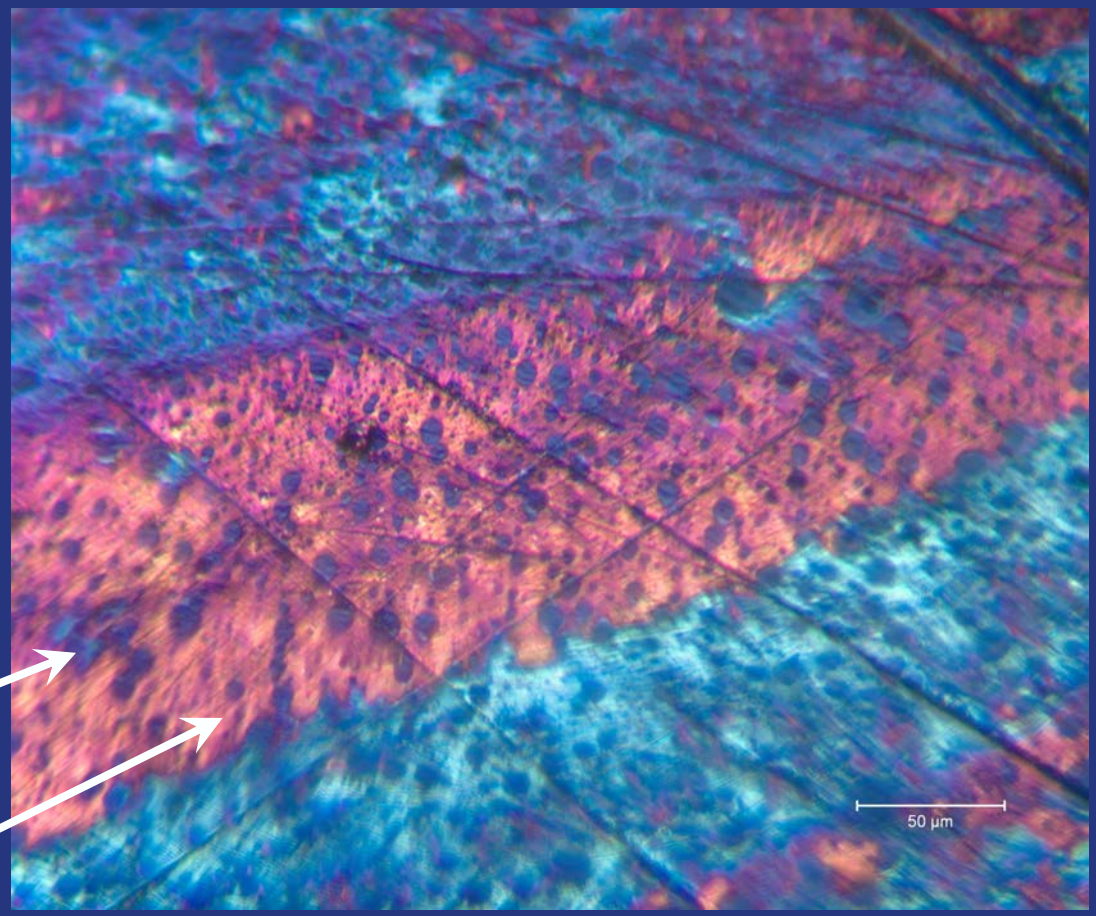
- Heat soaking [Singer(1977), Lewis (1977). Chwastiak and Lewis (1978)]
- Solvent-extraction [Diefendorf and Riggs (1980)]
- Catalytic polymerization [Mochida et al. (1988, 1990, 1992)]

Development of Mesophase



Isotropic

Mesophase

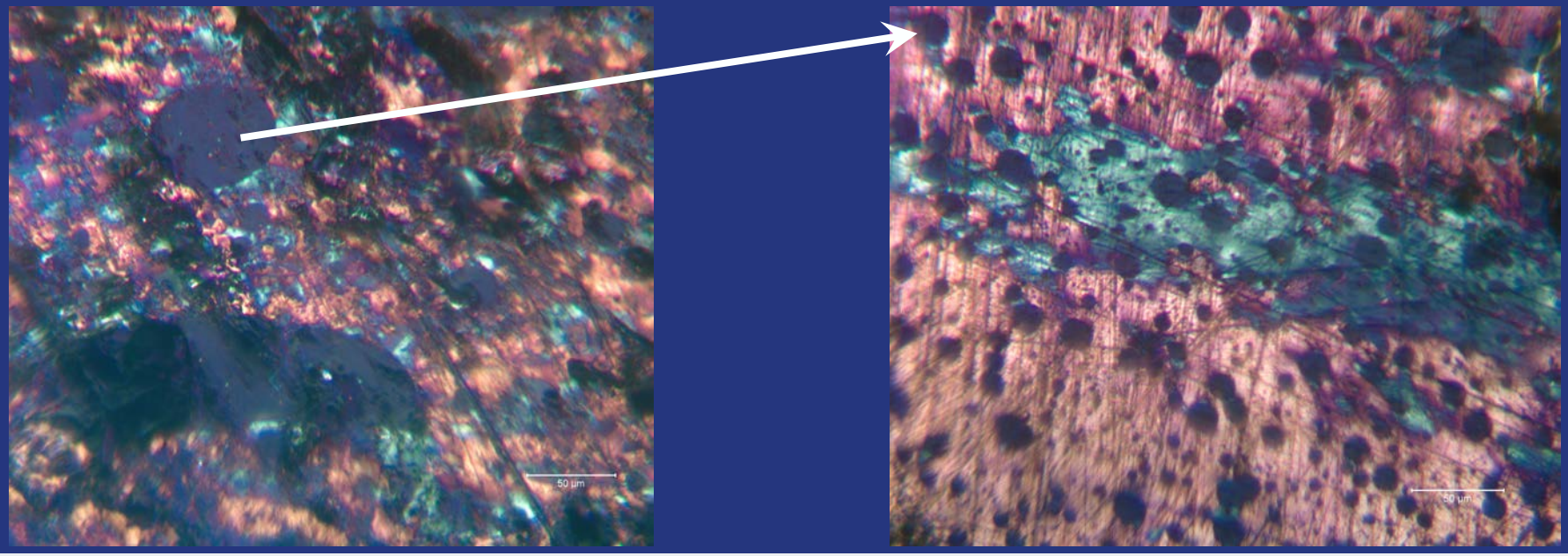


~ 60 % Mesophase

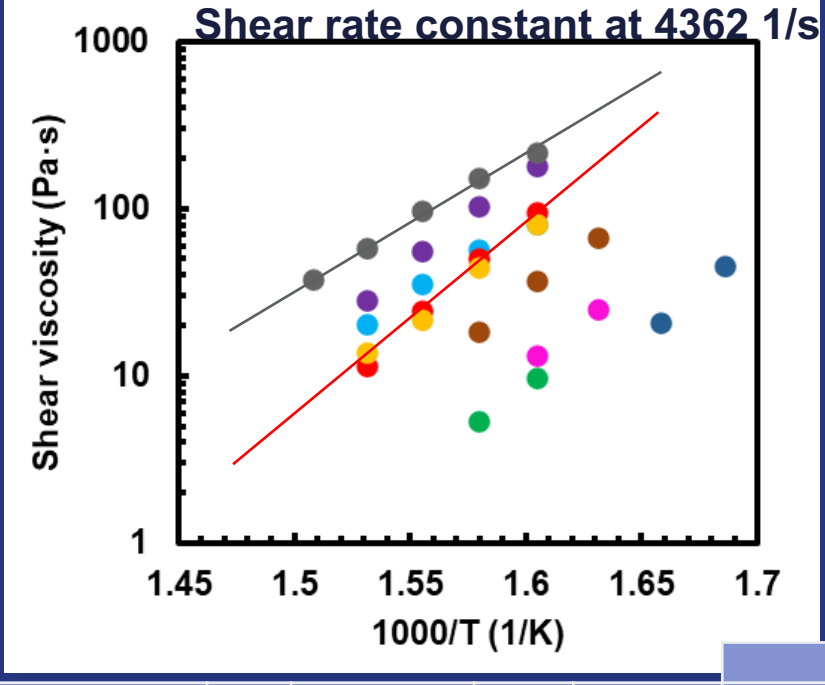
ASTM D4616-95.

Updates

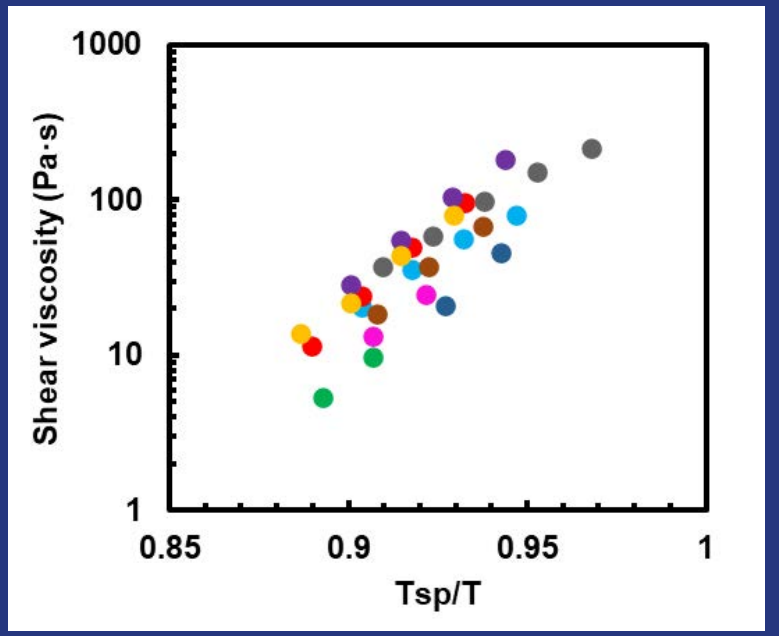
- Isotropic binder inclusions promote spinnability
  - 100% mesophase is difficult to spin (will not flow) and Tsp too high (> 350 °C)
  - Up to ~ 40% binder inclusions spins well
    - Should be homogeneously dispersed and small (~ 10 micron)
    - Tsp ~ 305 °C



Capillary Rheology

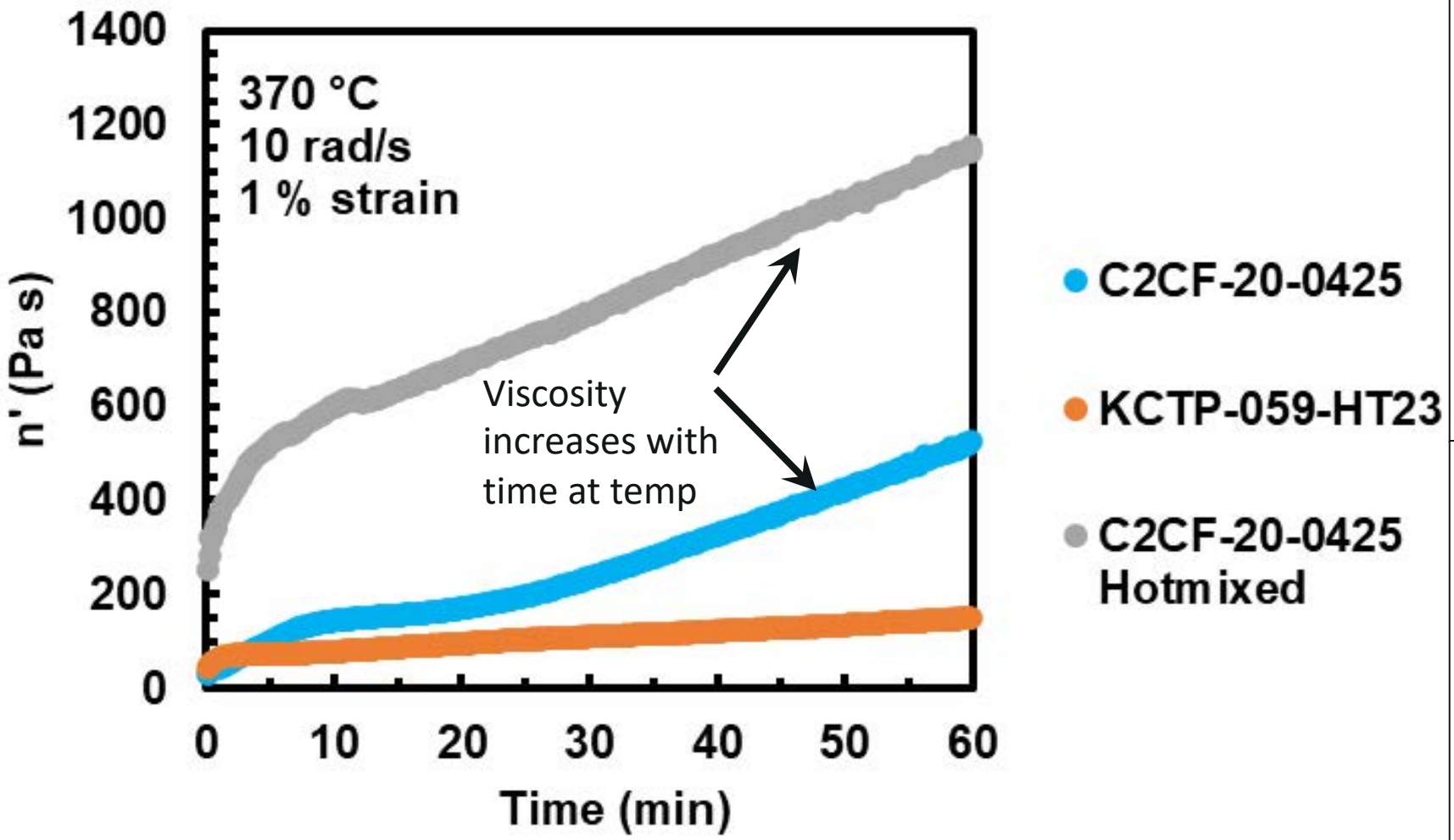


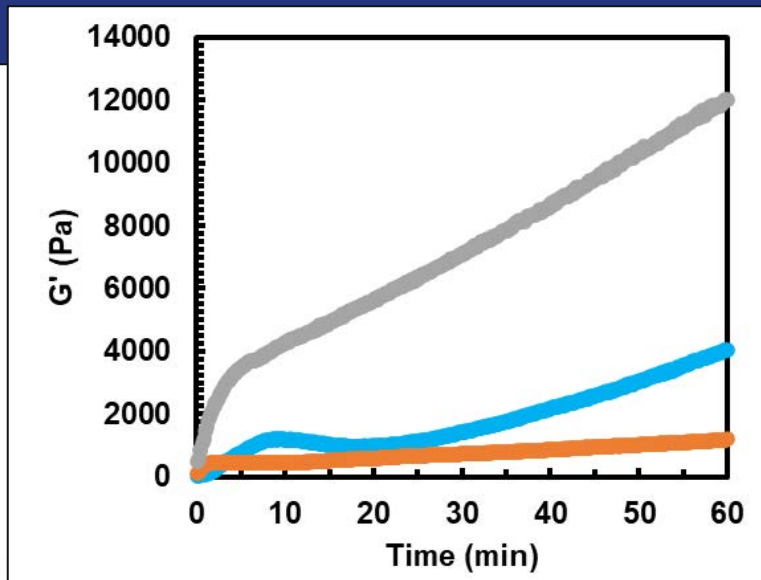
$$\eta = \eta_0 e^{\frac{E_a}{RT}}$$

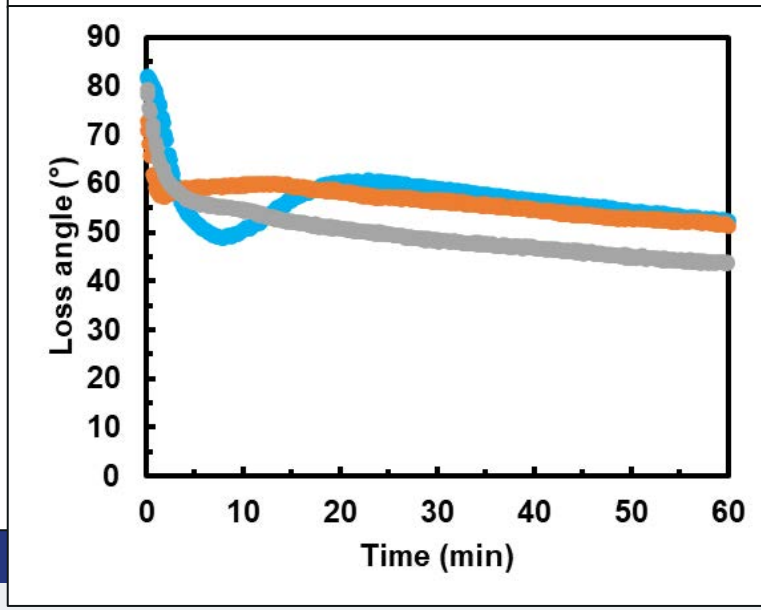


					Pressure spinning info				
Sample	QI (%)	% Mesophase	Tsp (C)	Ea (kJ/mol)	Pitch T (C)	Spool speed	Duration (min)	Comments	Estimated viscosity at pressure spinning T (Pa s)
C2CF-20-0425	58.84	72.83	317	154.1	360-386	0.4	3.17	can only be taken up very slowly	20 to 60
C2CF-20-0425 HM	TBD	55.5	330	153.5	398	2.6	1		~27
KCTP-038-HT7	55.86	90.05	308	235	~355	1.5-3.5	6.5 cont.	spins/spools well	~70
KCTP-051-HT7	52.97	57.72	286	232.4	~360	2-3.2	30 s	jet spins well but difficulty maintaining continuous tow	~2
KCTP-052-HT6	60.87	59.42	292	194.1	340-344	0.5-1.0	8 cont.	spins very well	~20
KCTP-053-HT21	66.8	77.5	315	208.5	365-370	0.4-0.7	6 cont.	spins very well	~64
KCTP-058-HT21	47.47	60.3	292	197.6	362-367	2.5-3.5	9 cont.	spins very well	~5
KCTP-059-HT23	55.45	62.59	306	203.1	365-371	1.2-2.0	10+ cont.	spins very well	~26

Time stability of pitches (Oscillatory rheology)







What is a "spinnable" coal tar mesophase?

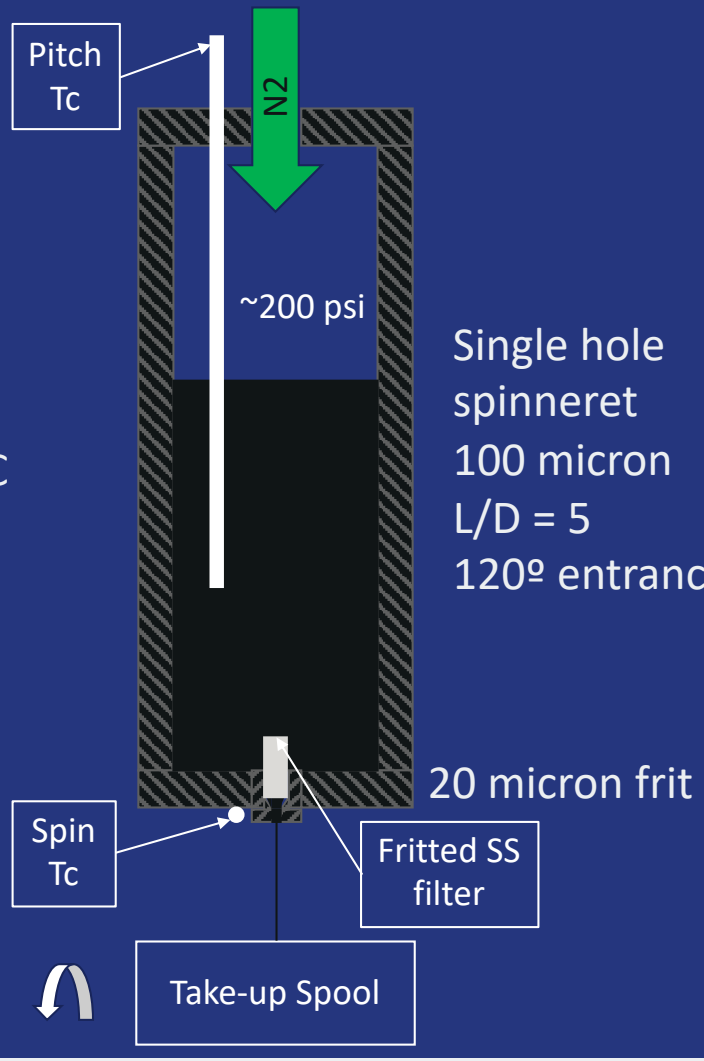
Initial target of 10 min of uninterrupted melt spinning

- Mesophase content
  - ~ 60 to 80 vol%
  - Well-dispersed, small (~10 micron) isotropic binder inclusions
- Softening point temperature
  - ~ 305 °C, < 350 °C
- Capillary rheology
  - Activation energy of flow of ~ 190 – 230 kJ/mol
- Viscosity stable with time at temperature
  - 10s of min

- Issues for further investigation
  - Spinnability association with chemistry of mesophase
    - aromaticity, Mw distribution, etc.

Subtask 3.1 – Melt Spinning Pressure Spinning

Spinning
Temperature = 370 C

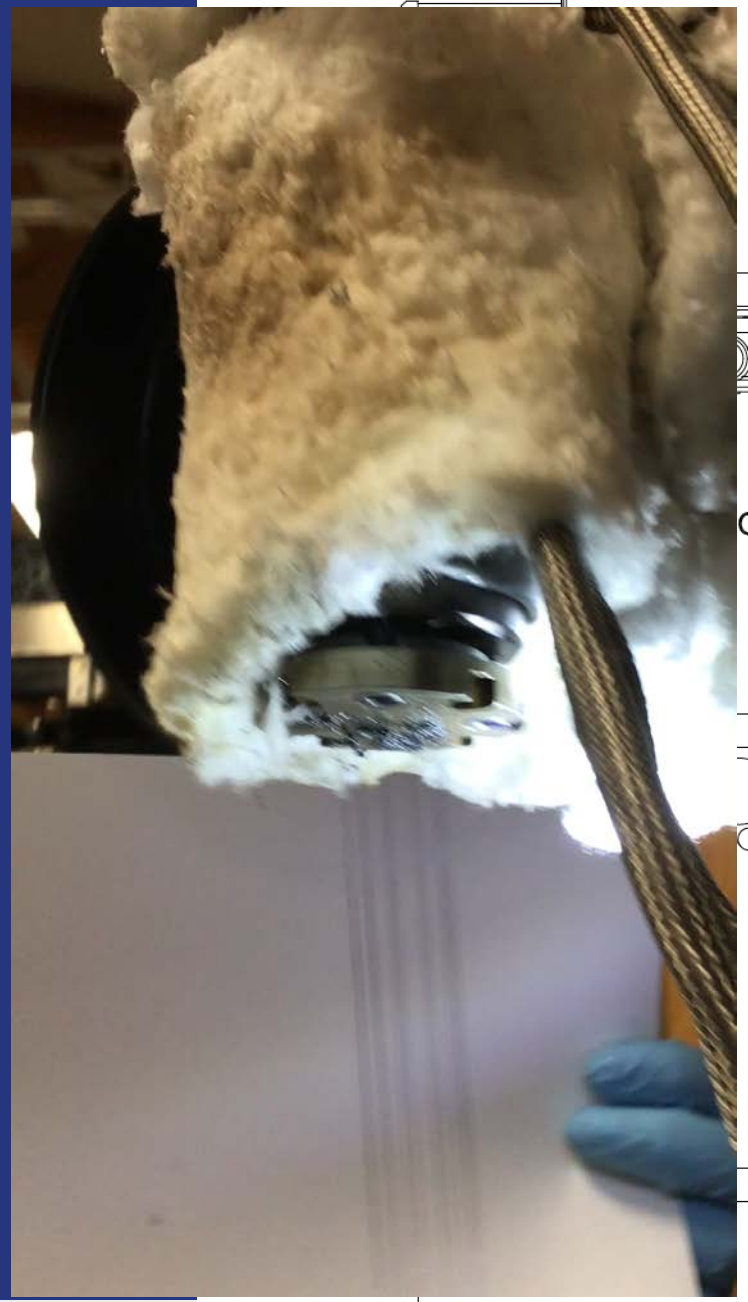


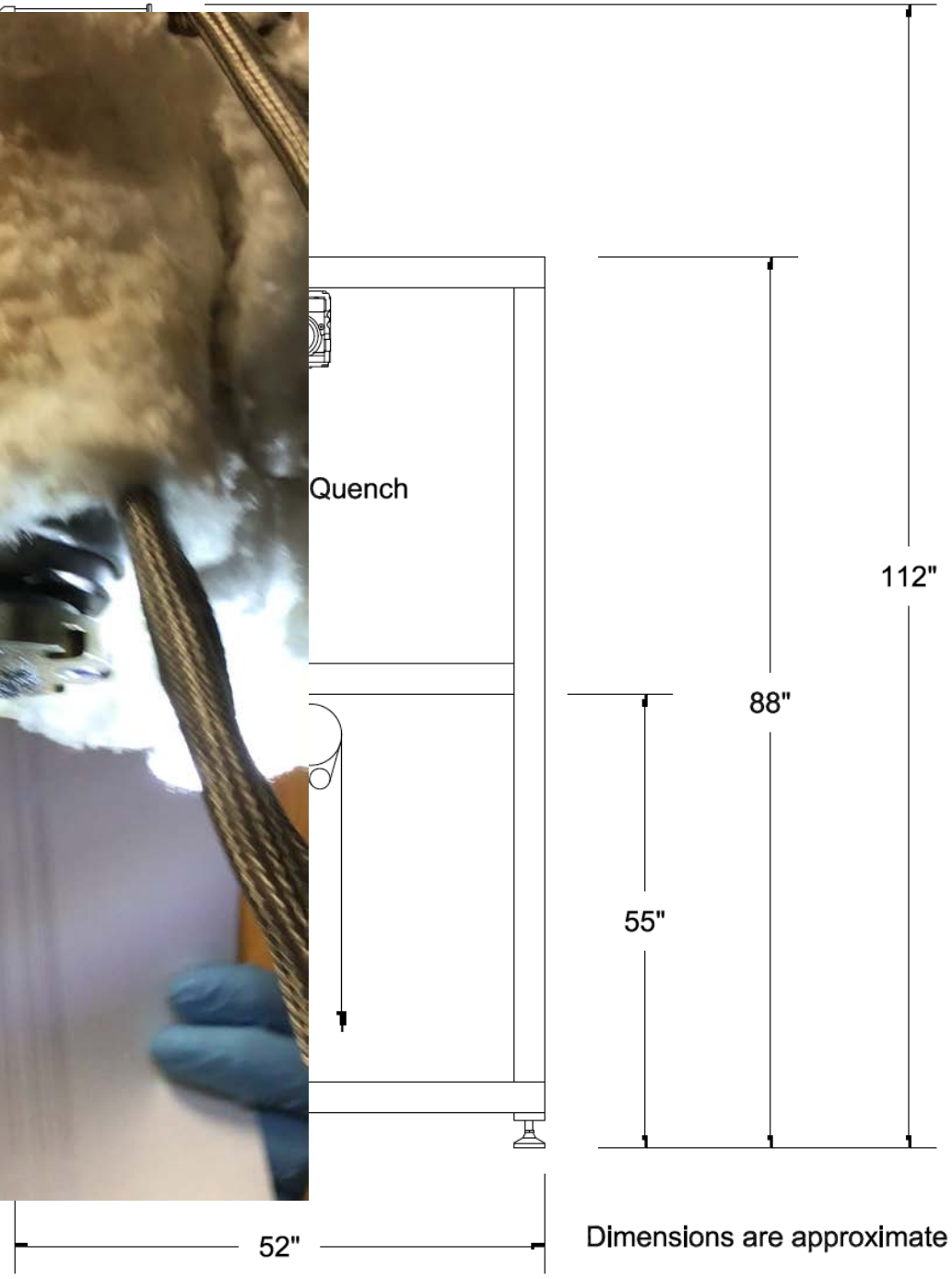
Single hole
spinneret
100 micron
L/D = 5
120º entrance

20 micron frit

Multifilament Spinning

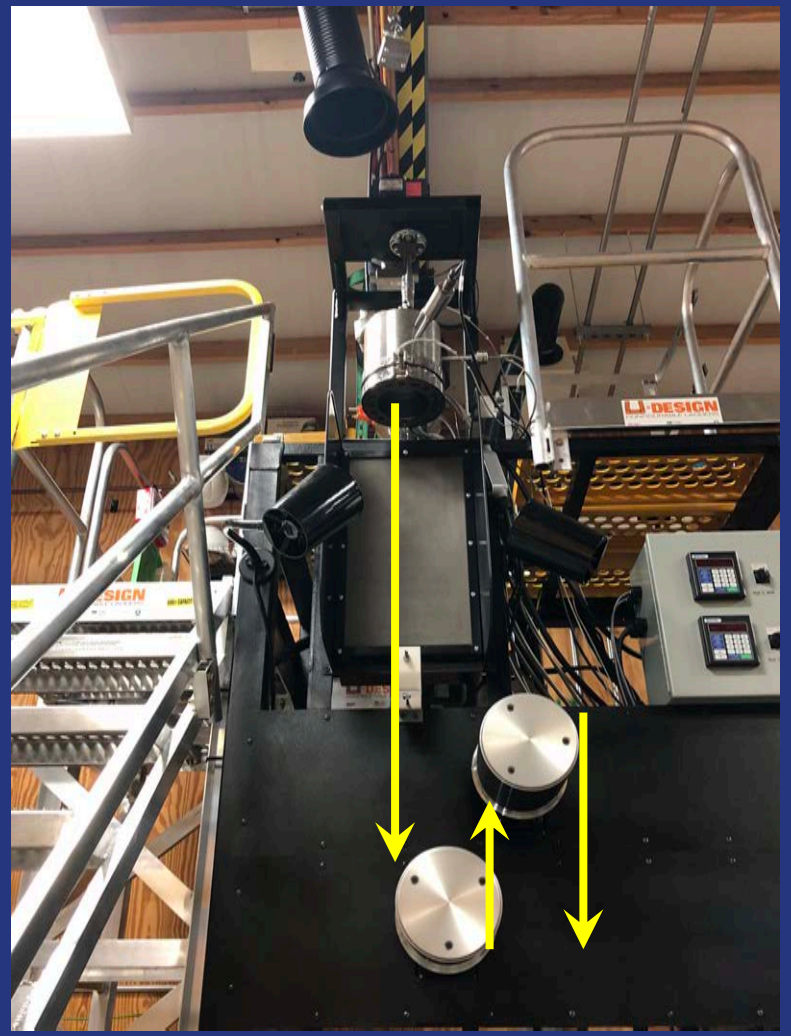
- Spooled
- Continuous, hooped green fiber tow on porous carbon screen trays
- Key Challenges:
  - Green fiber fragility
  - Start Up
  - High T ~370 °C



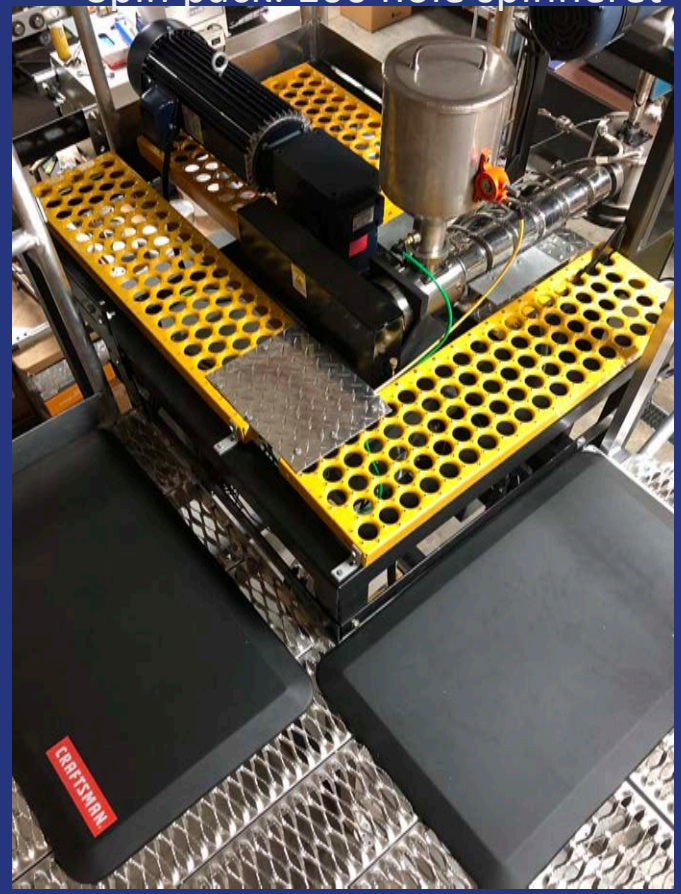


AJ Extruder System

Set up on-site Oct 2020



1” Extruder
Metering pump
Spin pack: 100 hole spinneret



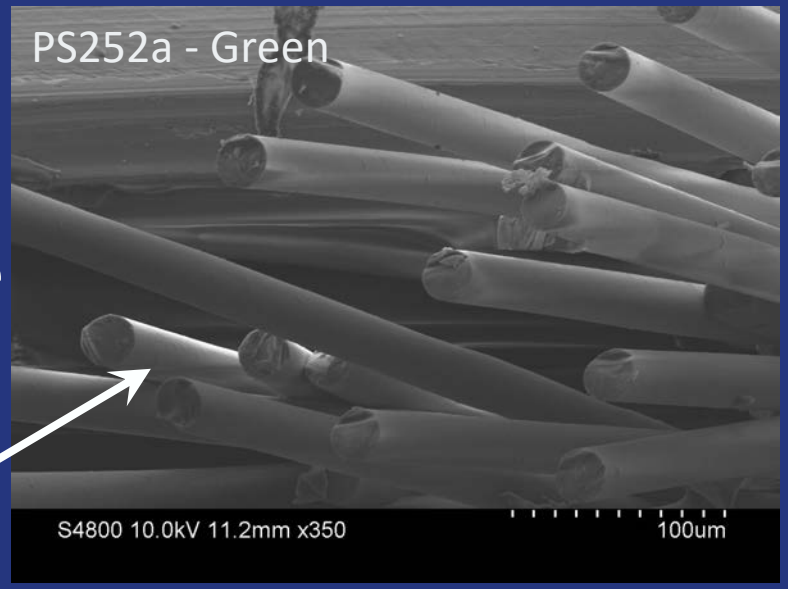
Carbon Fibers – effect of % mesophase

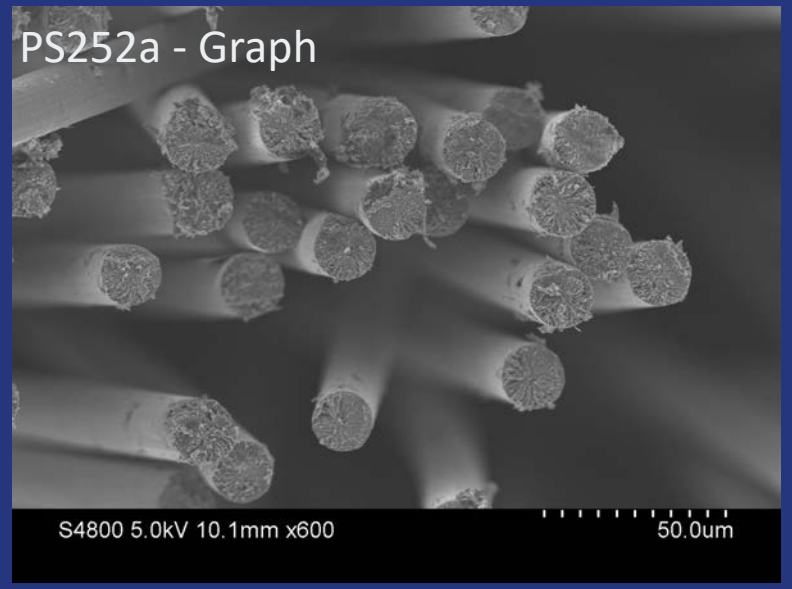
Batch oxidation, carbonization & graphitization
Single filament tensile testing.

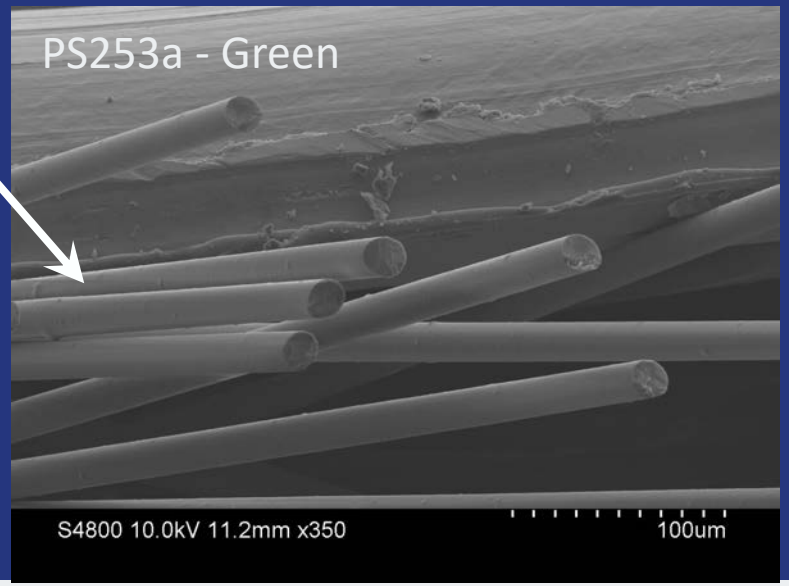
59.4 %
Mesophase

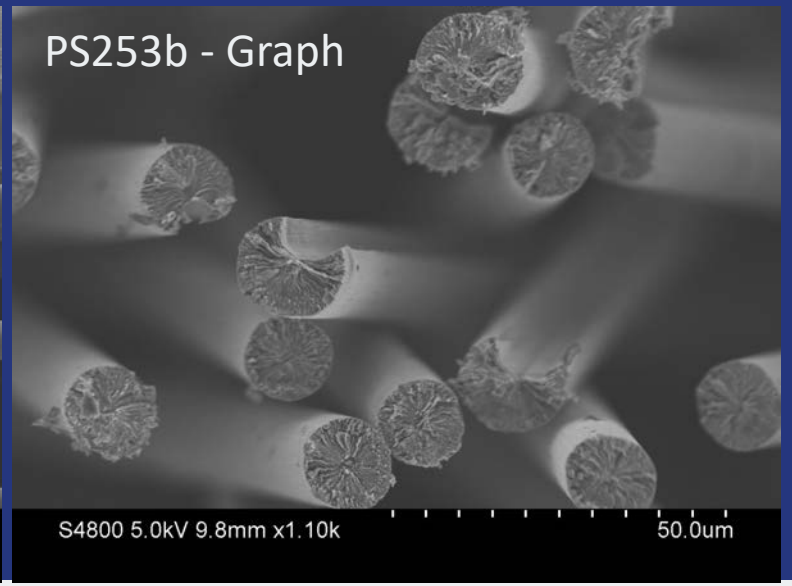
Mesophase sample	Tsp (ºC)	QI (%)	% Mesophase
052	292	60.9	59.4
053	315	66.8	77.5

77.5 %
Mesophase

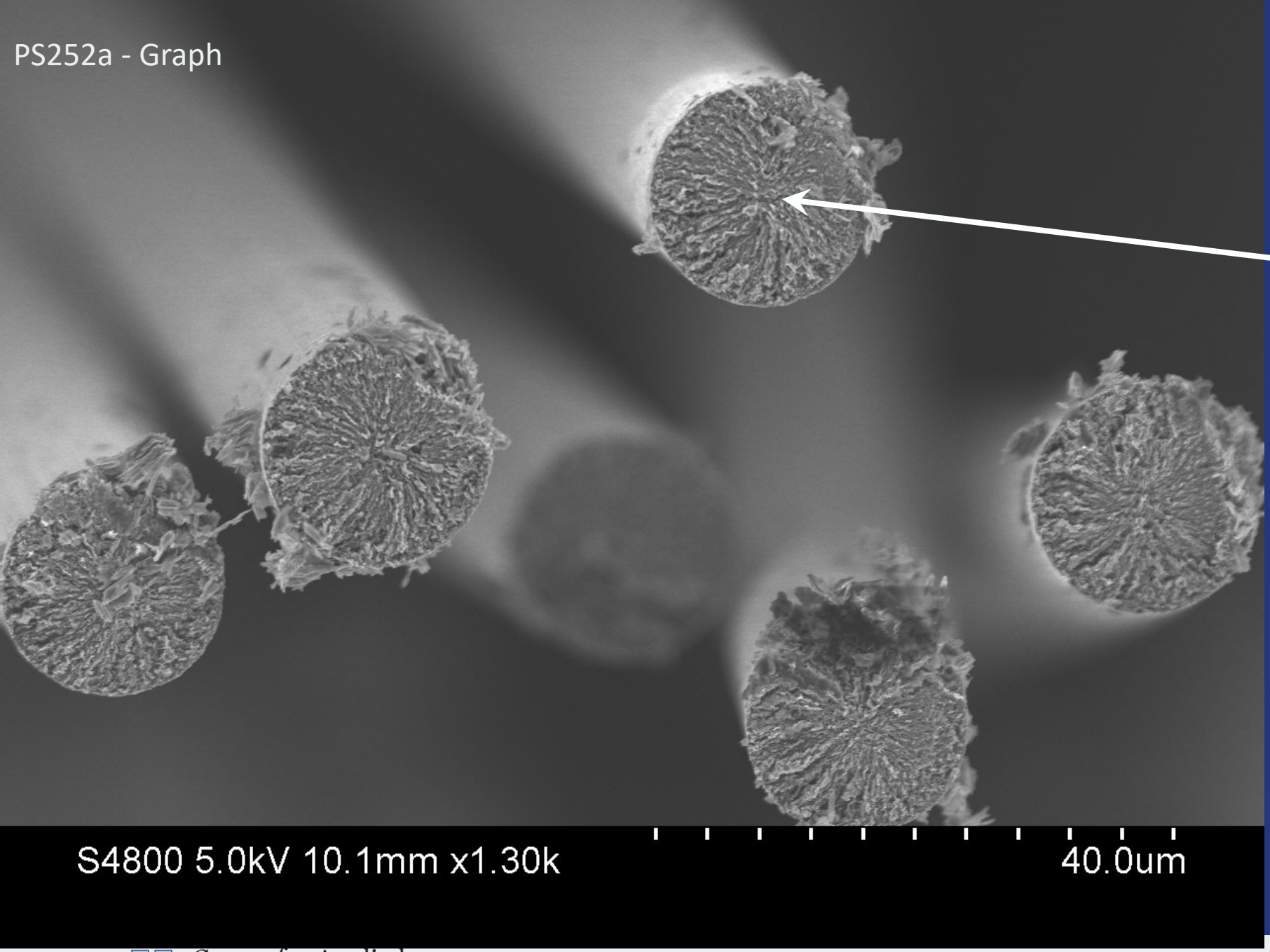








PS252a - Graph



Radial texture of graphitized fibers

Tensile properties

% Mesophase	Fiber	Diameter (um)	Stdev (um)	Stress At Break (MPa)	Stdev (MPa)	Modulus (GPa)	Stdev (GPa)	Strain at Break (%)	Stdev (%)	Strain Energy Density (MJ/m3)	Stdev (MJ/m3)	N	CY %
59.4 %	PS252a-052-GF671	17.70	0.75	1061.0	296.7	623.6	42.4	0.17%	0.05%	0.97	0.51	40	79.23%
	PS252b-052-GF671	17.62	0.95	1022.4	378.6	592.2	66.6	0.17%	0.06%	0.84	0.69	40	79.20%
77.5 %	PS253a-053-GF671	15.18	2.21	881.8	201.3	609.2	40.1	0.14%	0.03%	0.59	0.32	40	71.93%
	PS253b-053-GF671	15.18	2.21	901.8	279.5	613.4	60.8	0.15%	0.05%	0.57	0.38	40	80.20%

- % Mesophase did not govern CF properties or yield
  - Both had moduli ~ 600 GPa (87 MSI)
  - Lower % mesophase showed ~ 17% increase in strength

Review of Progress

- Coal tar derived mesophase production at 1s kg scale
  - Progress defining a ‘spinnable’ mesophase
    - Mesophase and binder content
    - Softening point temperature
    - Rheology and stability

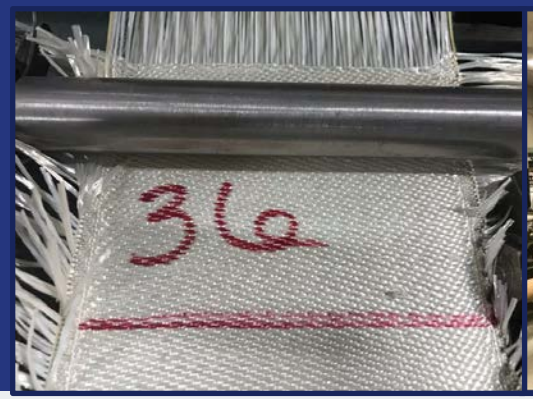
- Single filament tensile properties measured
  - Moduli up to 600 GPa (87 MSI)
  - Strength still low at ~ 1 GPa (145 ksi) – strain to failure low at 0.15%
  - Results not very sensitive to mesophase content between 59 and 78%

Future

- Multifilament melt spinning
  - Challenges:
    - Start up
    - Stability
- Quantitative and qualitative defining of SPINNABLE coal tar mesophase – measurable properties
  - Physical: Tsp, % mesophase, QI
  - Rheology: viscosity, activation energy of flow, stability with time, extensional
  - Chemistry: aromaticity index, Mw distribution
- 1s to 10s of kg of coal tar mesophase processing
  - Challenges
    - Reproducible processing of SPINNABLE mesophase
- Tasks 3.2 – 3.4 requiring continuous multifilament tow

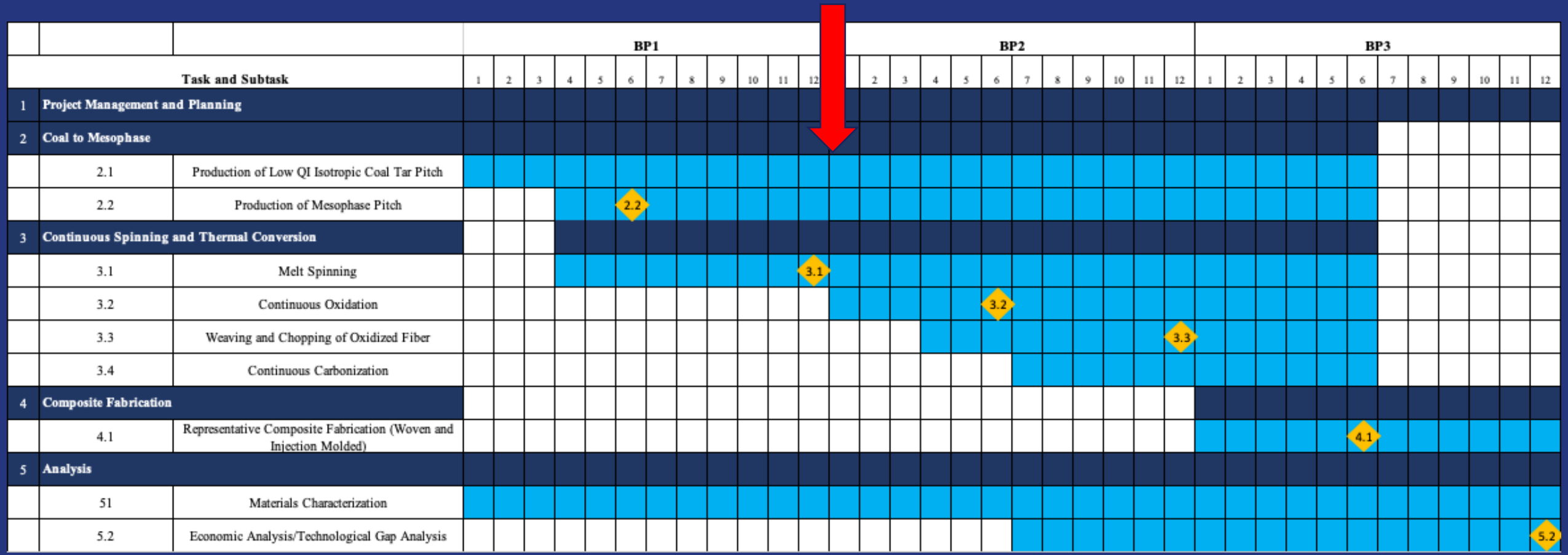
Subtask 3.2 – Continuous Oxidation
Subtask 3.3 – Weaving
Subtask 3.4 – Continuous Carbonization
Task 4.0 – Composite Fabrication

- The green fiber is extremely fragile
- No tension required!
- 11 – 1 ft temperature zones
- Down to 0.5 inch/min
- Air or N_2
- Spooled after oxidation for subsequent weaving processing into fabric



Gantt Chart

We are here: Oct 2020



		Task and Subtask	BP1												BP2												BP3											
			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	2	3	4	5	6	7	8	9	10	11	12
1	**Project Management and Planning**																																					
2	**Coal to Mesophase**																																					
	2.1	Production of Low QI Isotropic Coal Tar Pitch																																				
	2.2	Production of Mesophase Pitch						2.2																														
3	**Continuous Spinning and Thermal Conversion**																																					
	3.1	Melt Spinning												3.1																									
	3.2	Continuous Oxidation																		3.2																			
	3.3	Weaving and Chopping of Oxidized Fiber																								3.3													
	3.4	Continuous Carbonization																																					
4	**Composite Fabrication**																																					
	4.1	Representative Composite Fabrication (Woven and Injection Molded)																														4.1						
5	**Analysis**																																					
	51	Materials Characterization																																				
	5.2	Economic Analysis/Technological Gap Analysis																																				5.2

Milestone Chart

Task/ Subtask	Milestone Title/Description	Planned Completion Date	Actual Completion Date	Verification method
2.2	Production of ≥ 1 kg pitch containing ~~≥ 90%~~ mesophase and a softening point ≥ 300 °C	03/31/2020		Topical Report
3.1	Continuous melt spinning of ~~≥ 90%~~ mesophase pitch, with ≥ 100 filaments, for ≥ 10 minutes	09/30/2020		Quarterly Report
3.2	Production of non-fused oxidized mesophase pitch fiber with high strain-to-failure	03/31/2021		Quarterly Report
3.3	Production of a plain weave sample from oxidized mesophase pitch fiber with ≥ 100 warp ends and produce ≥ 100 g of chopped oxidized mesophase pitch fiber	09/30/2021		Quarterly Report
4.1	Production of continuous fiber composite using mesophase pitch derived carbon fiber through resin infusion and curing, as well as a ≥ 10 wt.% thermoplastic and injection molded sample, and report thermal and mechanical properties for both	03/31/2022		Quarterly Report
5.2	Final Report for project	09/30/2022		Final Report

Concluding Remarks

- Immediate future: Multifilament spinning
  - High modulus carbon fiber has been demonstrated
  - Stable & robust multifilament tow processing demonstration is key
- Scale up spinnable coal tar mesophase production
  - 10s of kg up to tonnes scale processing
- Sharpen the value prospect for future scale up
  - Cost of coal tar mesophase & carbon fiber processing
  - Market for fiber (continuous, chopped)
    - Final value add relative to coal tar binder pitch
- The CF market is approximately 180 kt/yr (with ~10% CAGR)
    - Opportunity for pitch to take some PAN market share (pitch currently at ~ 5%)
    - Only 3 major producers of pitch-based structural carbon fiber
      - Mitsubishi Chemical "Dialead" - JAPAN
      - Nippon Graphite Fiber "Granoc" – JAPAN
      - Solvay Composite Materials "Thornel" - USA

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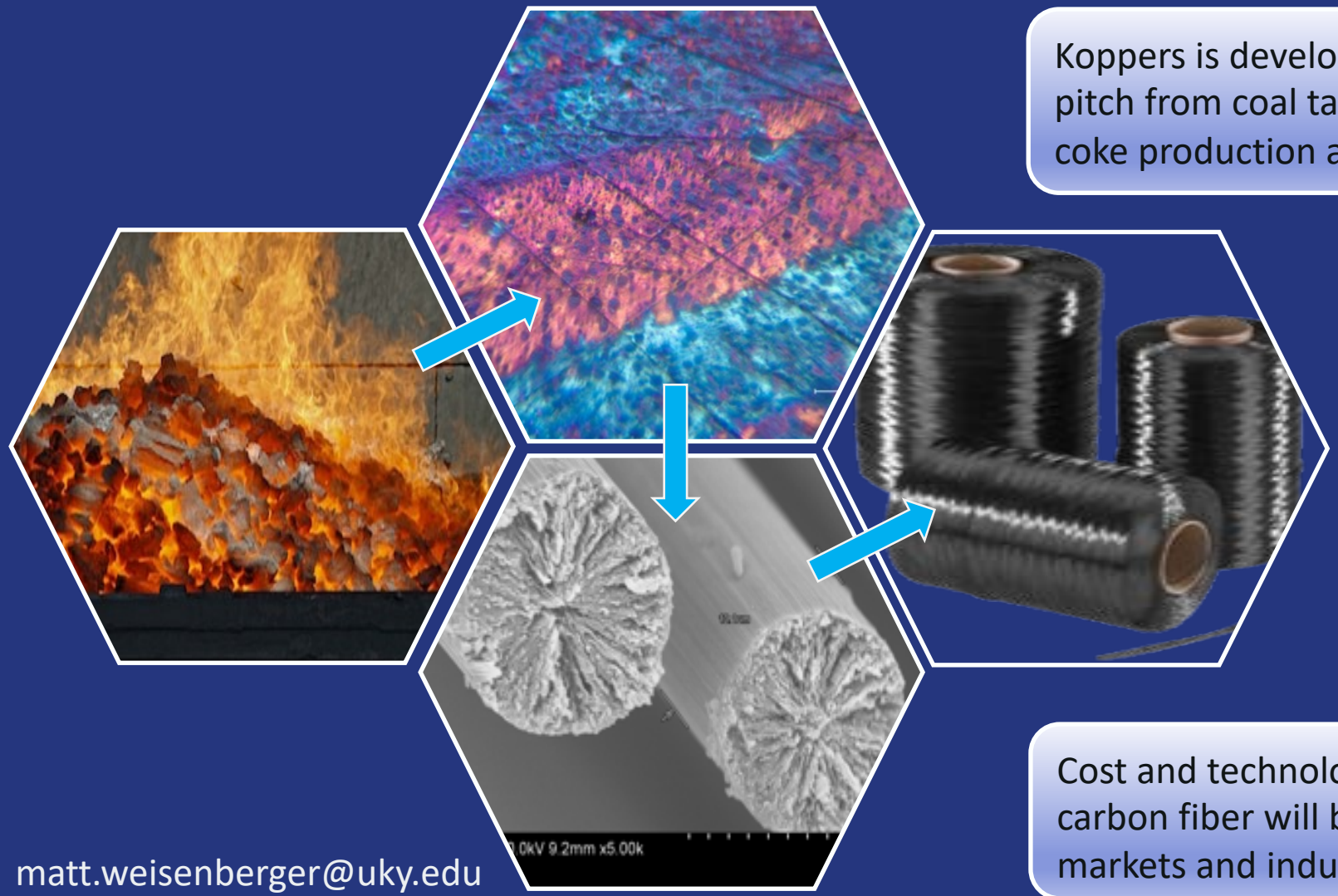

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