Coal to Carbon Fiber (C2CF)
Continuous Processing for High Value Composites

DE-FE0031796

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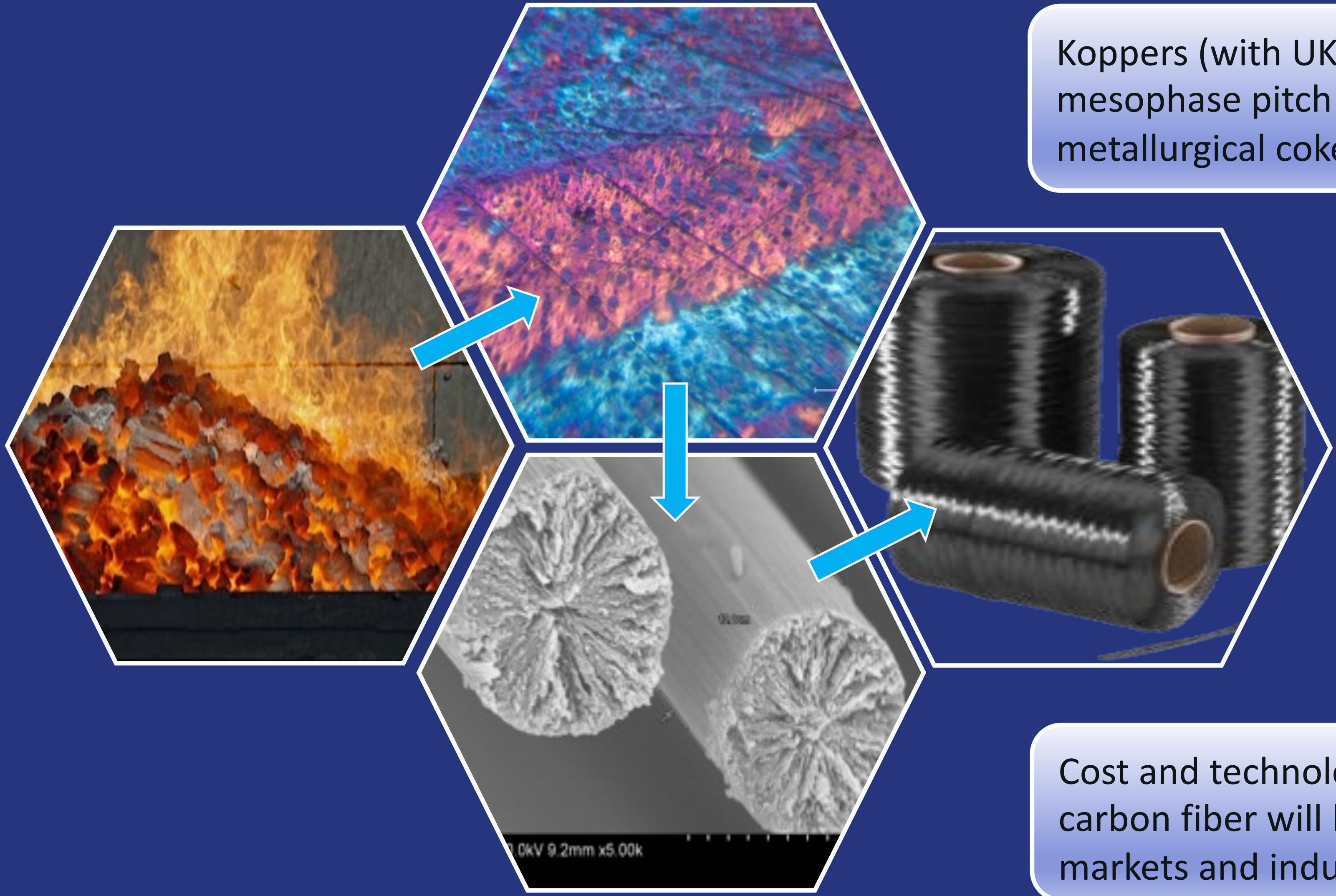
Center for Applied Energy Research

Disclaimer

- Acknowledgment: "This material is based upon work supported by the Department of Energy Award Number DE-FE0031796."

C2CF Coal to Carbon Fiber:

Continuous Processing for High Value Composites



Koppers (with UK) 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

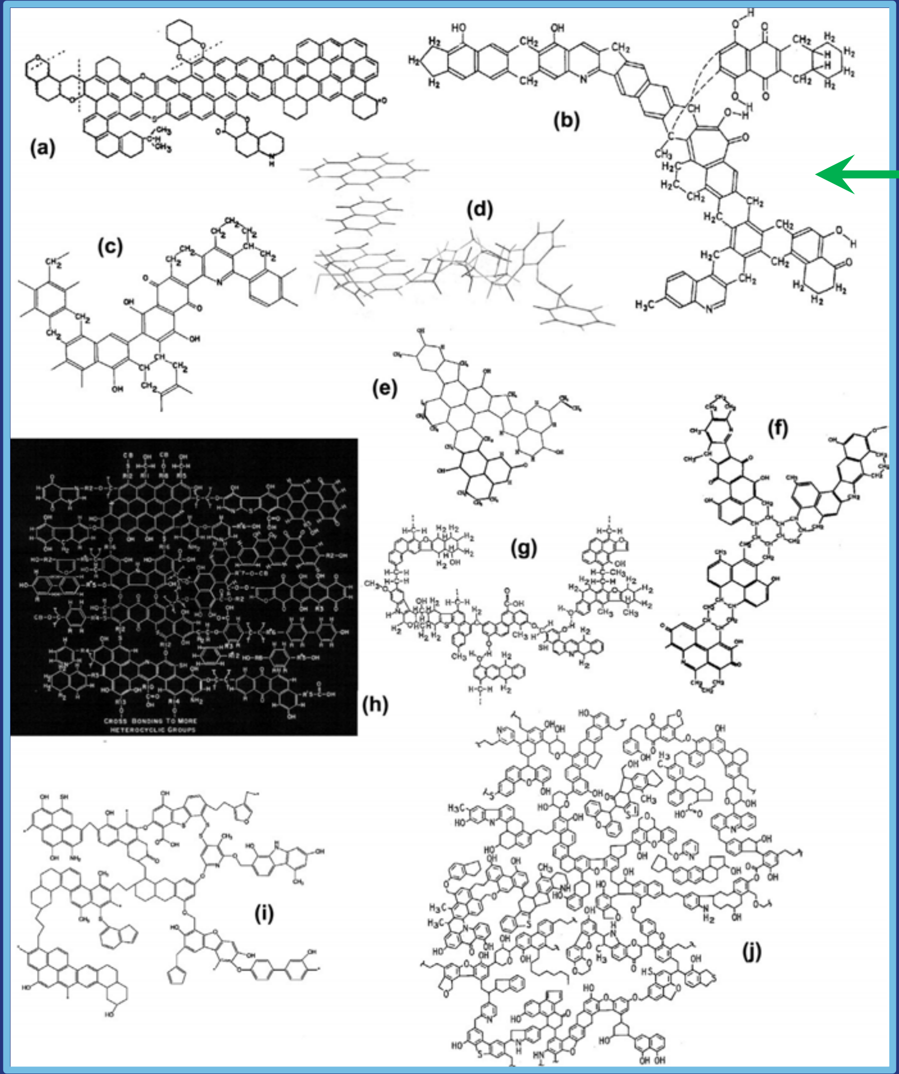
Prototype composite parts will be demonstrated with the carbon fiber.

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

Overview

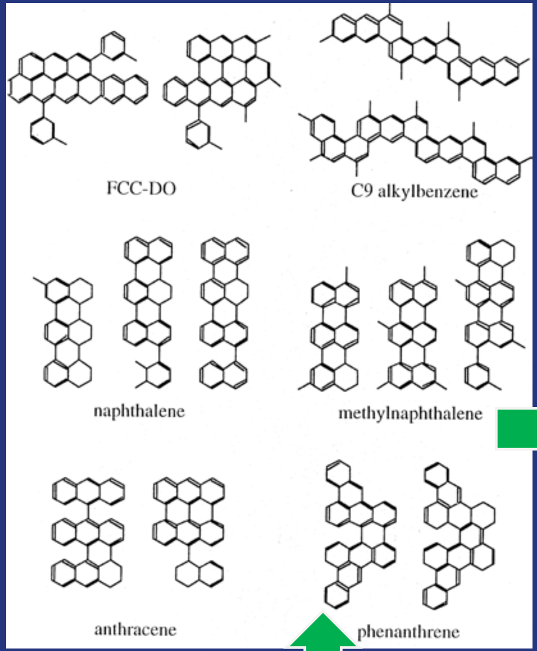
- Project rationale and goals
- Task Updates: Successes & Challenges
  1. Coal Tar to Mesophase Pitch
  2. Melt Spinning & Thermal Conversion (oxidation)
     - The "spinnability" problem: "the ease of stable filament formation"
  3. Tensile Properties
- Future Direction & Challenges

Rationale: Source Compounds in Coal



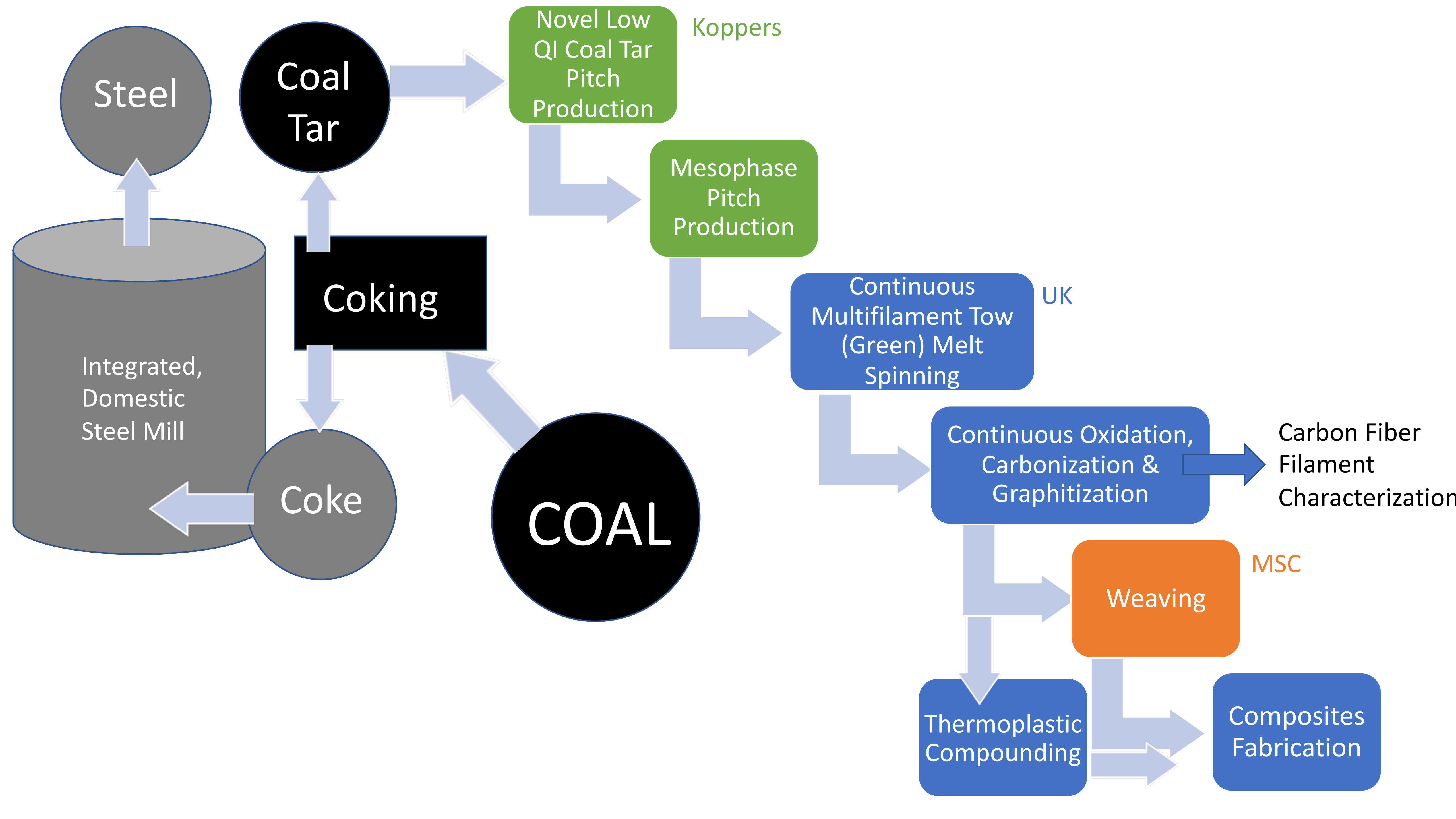
J.P. Mathews, A.L. Chaffee / Fuel 96 (2012) 1–14

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

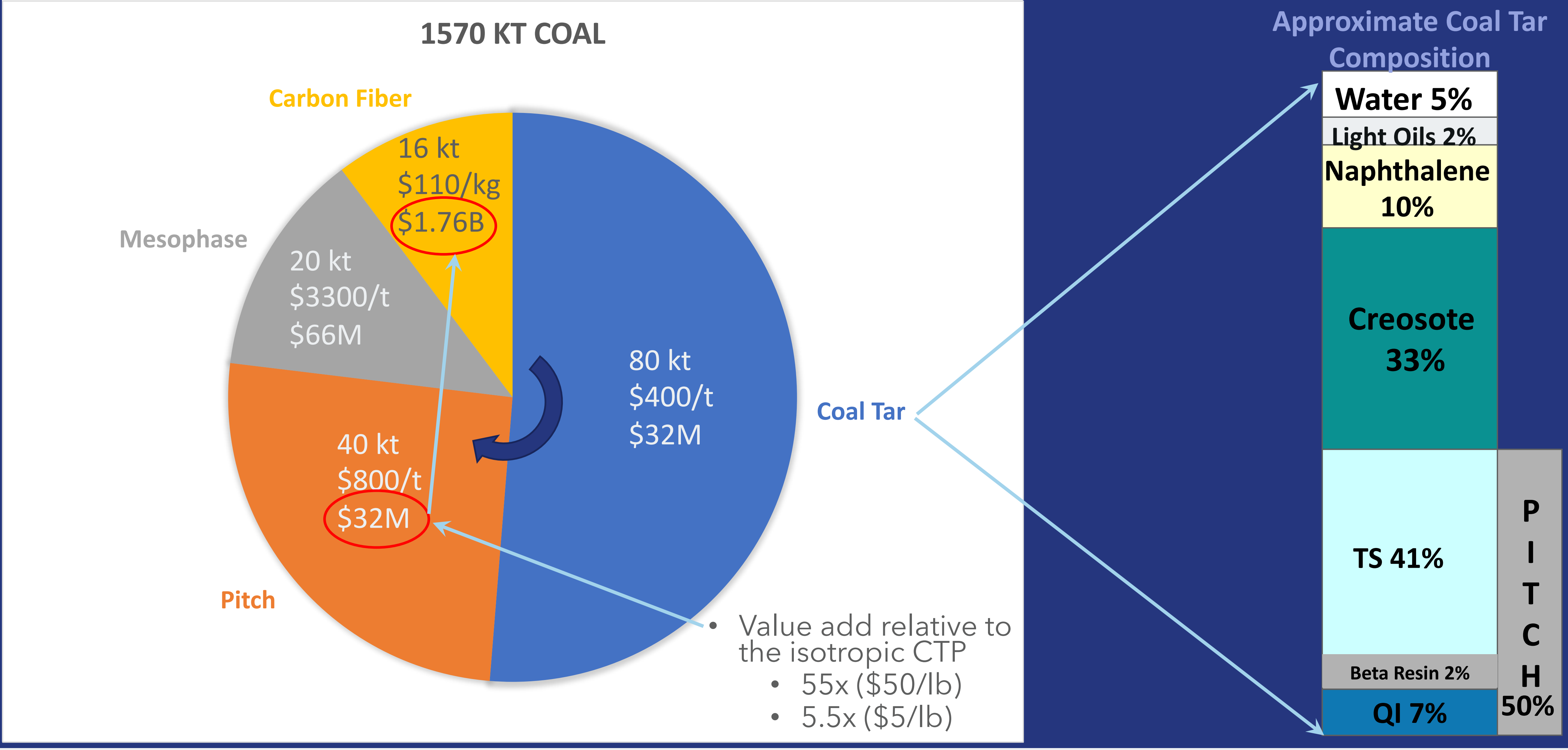


mesophase

Carbon fiber


Steel
Coal Tar
Coking
Integrated, Domestic Steel Mill
Coke
COAL
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: Case Study Value Add



- Value add relative to the isotropic CTP
  - 55x ($50/lb)
  - 5.5x ($5/lb)

Carbon Fiber Economics: Pitch is cheaper

- Pitch based CF
  - Could be:
    - 2-3x cheaper than PAN
- Why?
  - Cheaper precursor
  - 30% better yield
  - Melt, not solution spun
  - No tension during ox/carb
- 160 kt/yr capacity
  - Only ~ 5% is pitch based CF → 5 -10 kt/yr
    - Mitsubishi
    - Nippon
    - Solvay

DISCLAIMER: Approximate Costs

Precursor	Precursor cost ($/kg)	CF Yield (wt.%)	*Precursor CF cost ($/kg) (not price)
AN	2.25		
PAN[a]	4.00 – 9.17	50 %	8.00 - 18.34 (13.17)
Coal Tar	0.40		
Mesophase pitch	3.30 – 5.00	80 %	4.13 – 6.25 (5.19)

[a] Carbon 142 (2019) 610-649

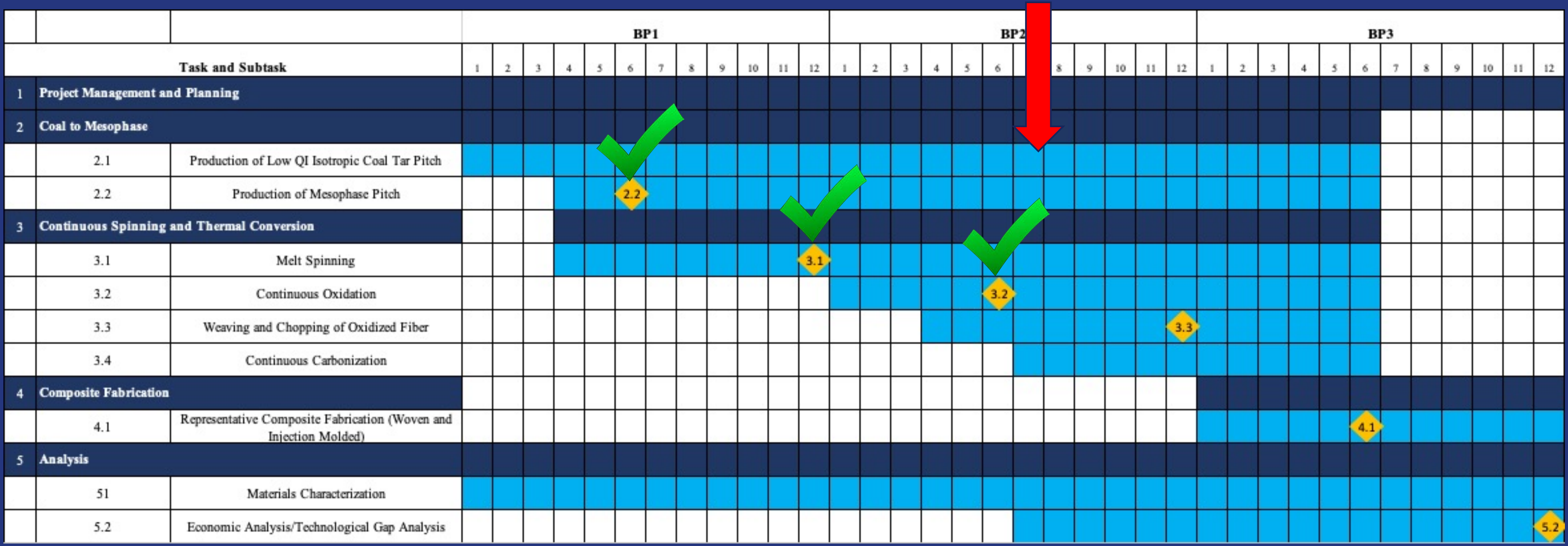
Fiber	$/lb per modulus
Glass Fiber:	$0.01/lb-GPa
SM PAN CF:	$0.03/lb-GPa
IM PAN CF:	$0.06/lb-GPa
HM Pitch CF:	$0.07/lb-GPa

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

- Develop and scale efficient processing technology to produce coal tar derived, spinnable, mesophase pitch
  - ultra-low quinoline insolubles (QI) precursor
- 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

Gantt Chart

We are here: April 2021



Milestone Chart

Task/ Subtask	Milestone Title/Description	Planned Completion Date	Actual Completion Date	Verification method
2.2	Production of ≥ 1 kg pitch containing ≥ ~~90%~~ (60 wt.%) mesophase and a softening point ~~≥ 300 °C~~ (≤ 315 °C)	03/31/2020	04/10/2020	Topical Report
3.1	Continuous melt spinning of ~~≥ 90%~~ mesophase pitch, with ≥ 100 filaments, for ≥ 10 minutes	09/30/2020	11/04/2020	Quarterly Report
3.2	Production of non-fused oxidized mesophase pitch fiber with high strain-to-failure	03/31/2021	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

Tasks Updates

Task 2: Coal Tar to Mesophase

Low QI coal tar pitch production

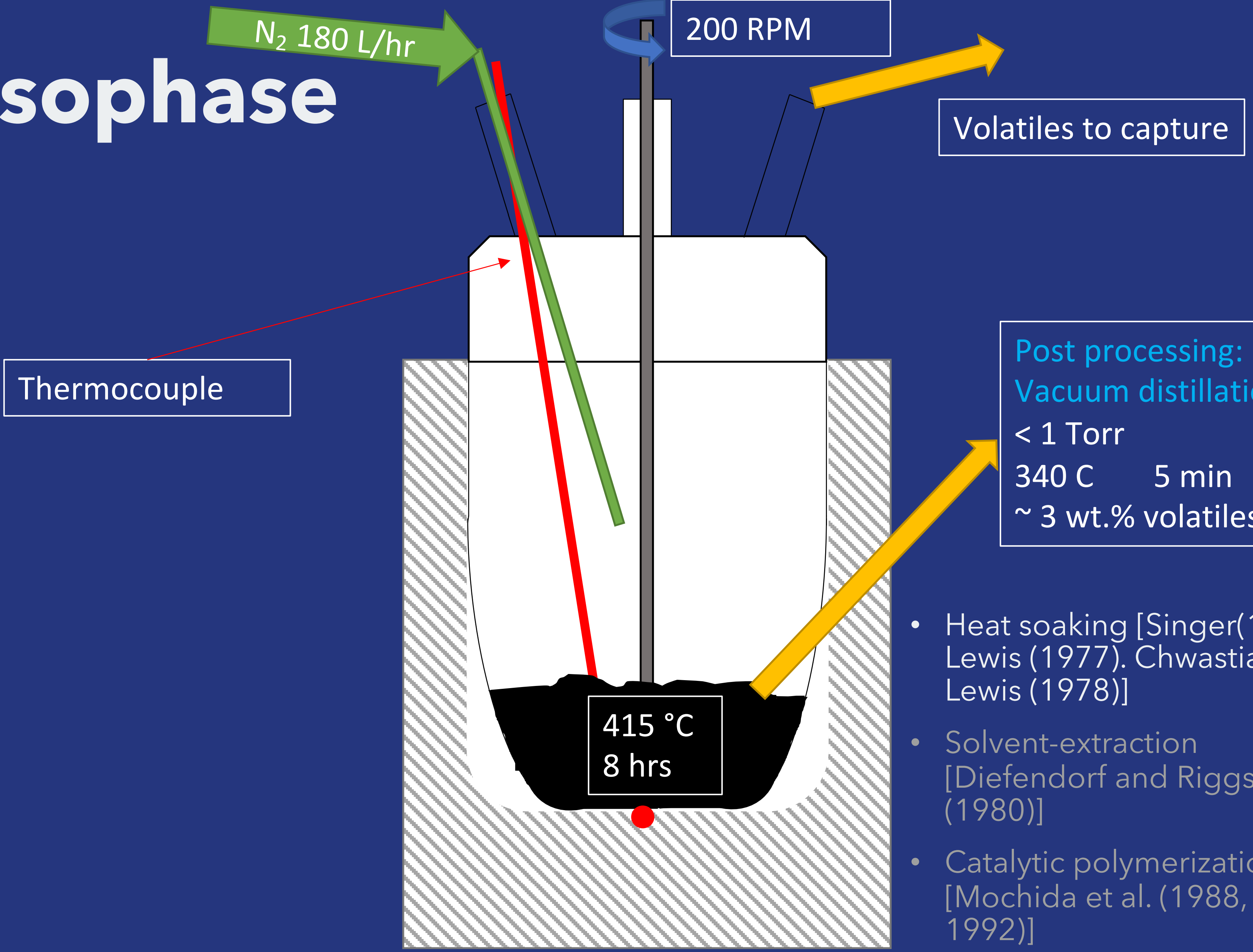
1 kg/batch mesophase production

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.%

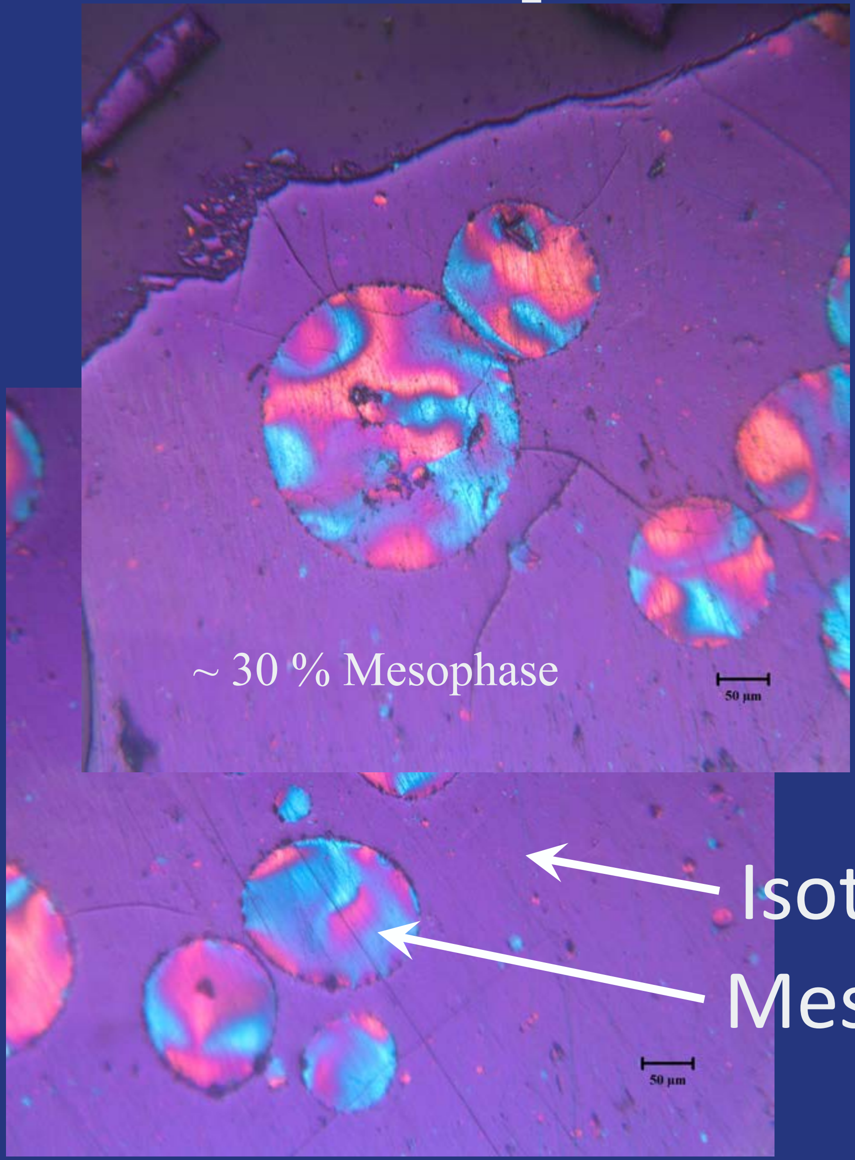
FINAL: Mesophase
~ 51 wt.% yield
~ 60 vol% mesophase
Tsp ~ 300 °C
C/H = 26 wt.%
QI = ~ 50 wt.%



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

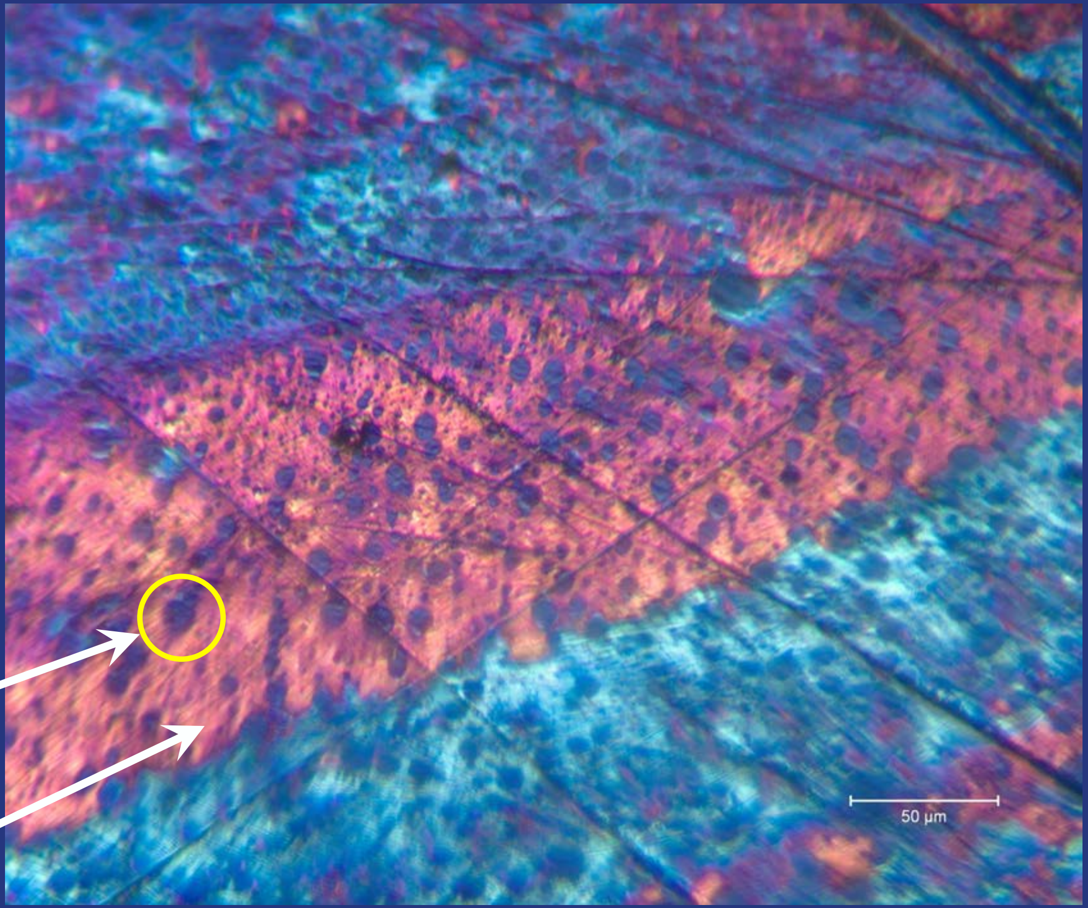
- Heat soaking [Singer(1977), Lewis (1977). Chwastiak and Lewis (1978)]
- Solvent-extraction [Diefendorf and Riggs (1980)]
- Catalytic polymerization [Mochida et al. (1988, 1990, 1992)]

Development of Mesophase



Isotropic

Mesophase

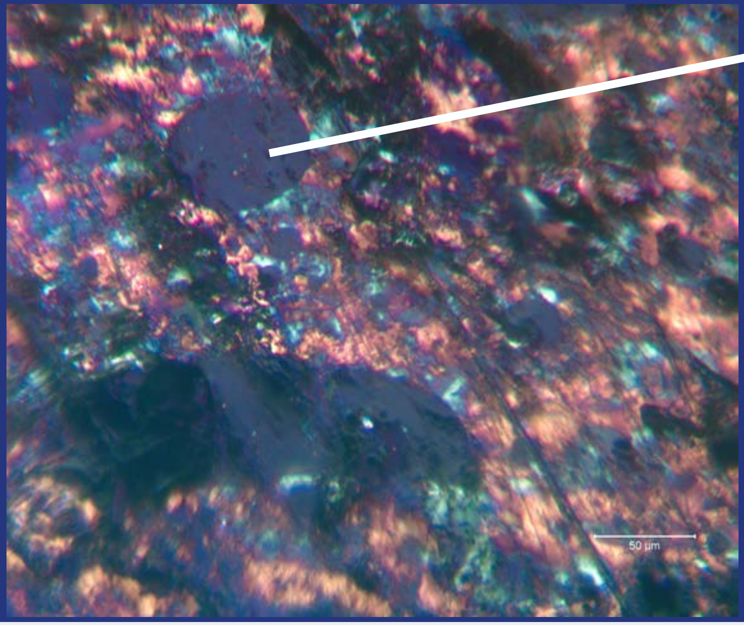


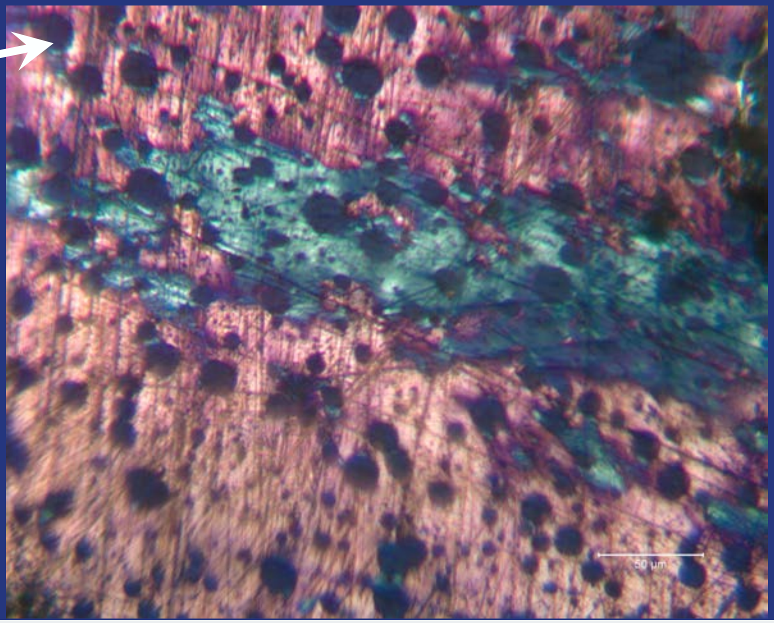
~ 60 % Mesophase

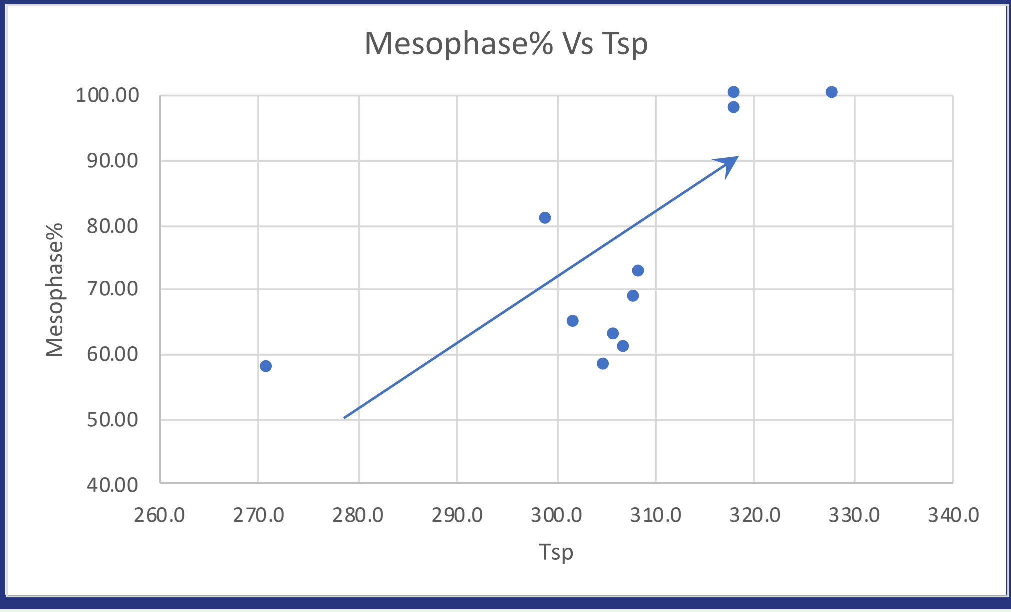
ASTM D4616-95.

Concentration of mesophase

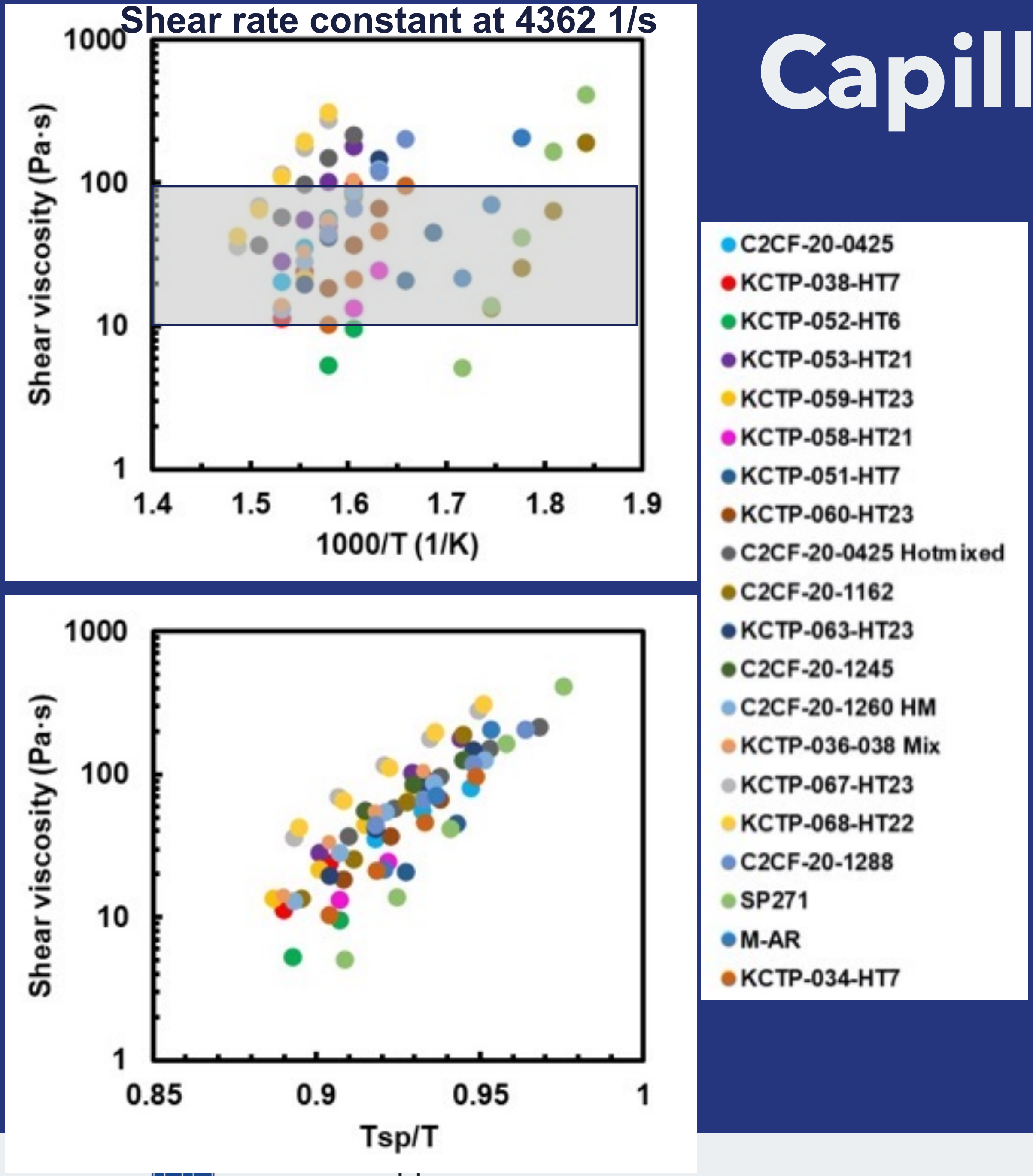
- Isotropic binder inclusions lower Tsp, which facilitates spinning
  - 100% mesophase from coal tar pitch is difficult to spin (will not flow) because the Tsp is too high (> 320 °C)
  - Up to ~ 40% binder inclusions of isotropic pitch spins well
    - Should be homogeneously dispersed and small (~ 10 micron)
    - Tsp ~ 305 °C





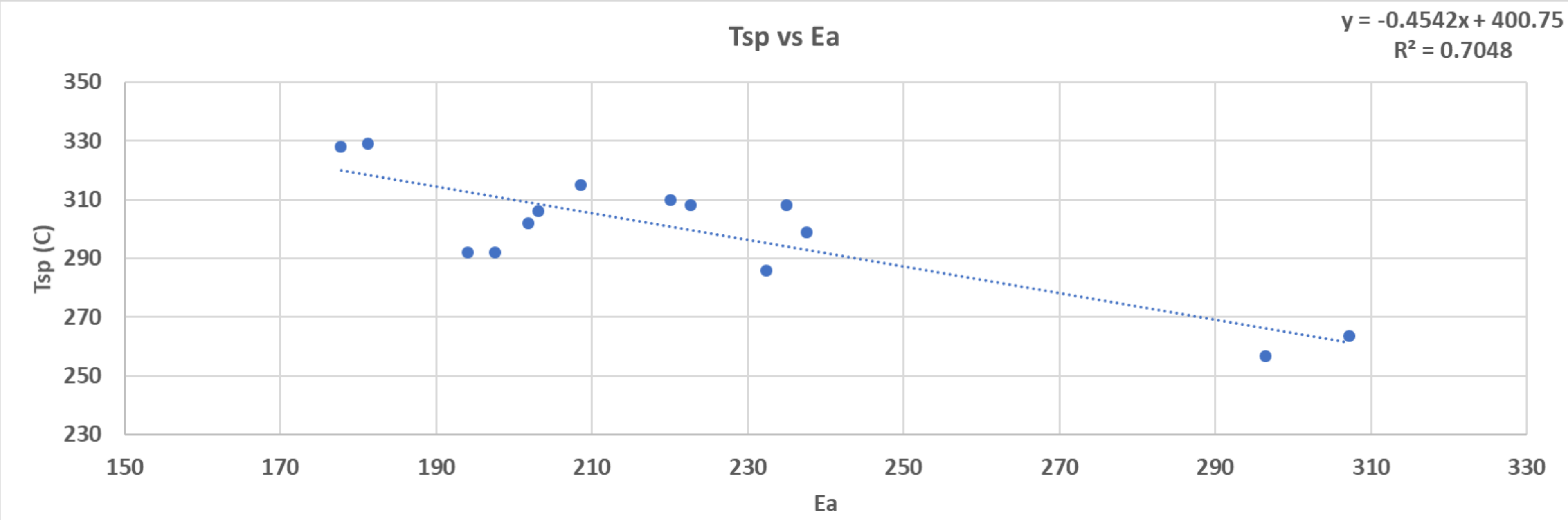


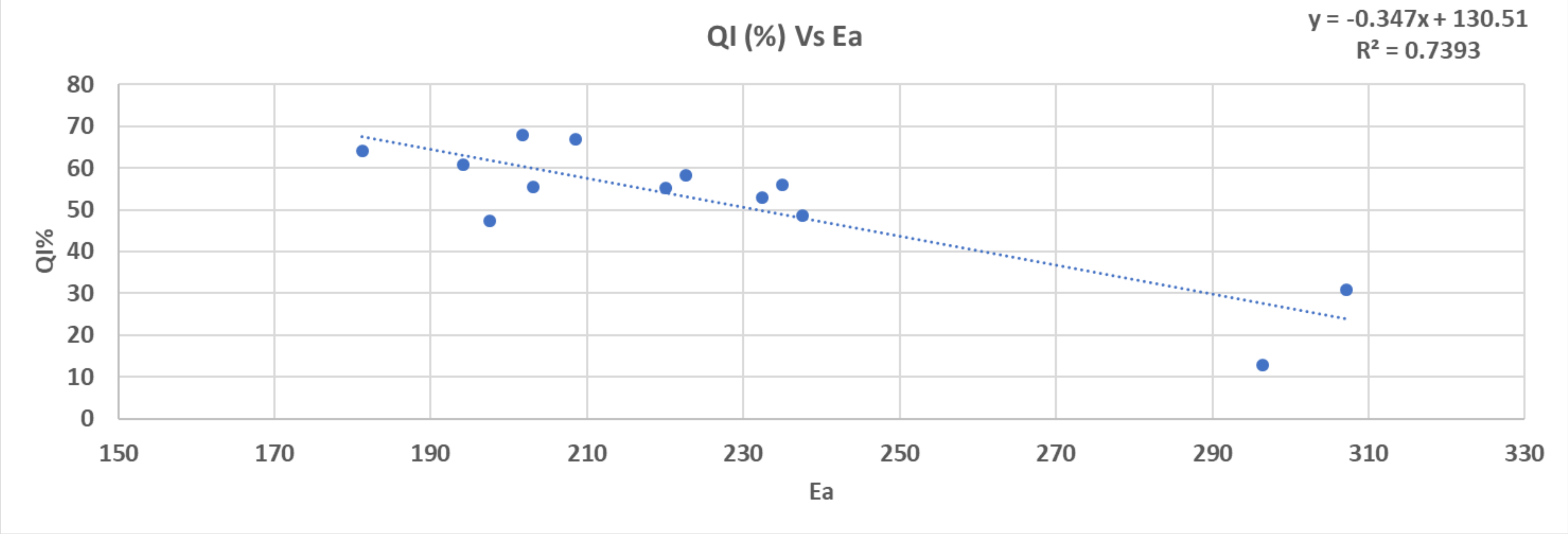
Capillary Rheology



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

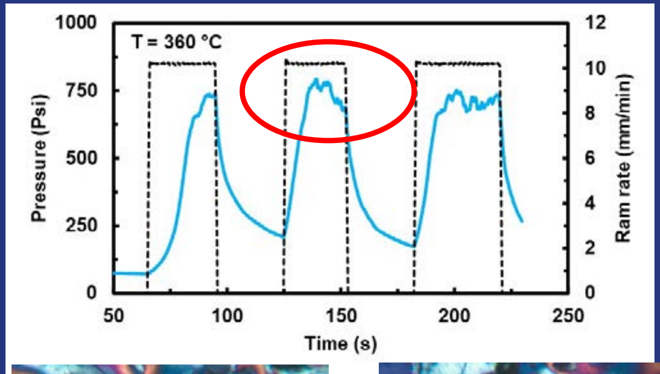
Sample	QI (%)	% Mesophase	Tsp (C)	Ea (kJ/mol)	Estimated viscosity at pressure spinning T (Pa
C2CF-20-0425	58.84	72.83	317	154.1	20 to 60
C2CF-20-0425 HM	58.4	55.5	330	153.5	~27
KCTP-038-HT7	55.86	90.05	308	235	~70
KCTP-051-HT7	52.97	57.72	286	232.4	~2
KCTP-052-HT6	60.87	59.42	292	194.1	~20
KCTP-053-HT21	66.8	77.5	315	208.5	~64
KCTP-058-HT21	47.47	60.3	292	197.6	~5
KCTP-059-HT23	55.45	62.59	306	203.1	~26
KCTP-060-HT23	67.93	64.65	302	201.8	~11
C2CF-20-1162	25.94	16.7	240	219.4	-
KCTP-063-HT23	-	68.4	308	222.6	-
C2CF-20-1245	47.16	62.1	306	132.5	-
C2CF-20-1260 HM	52.81	60.5	310	187.3	~31
KCTP-036-038 Mix	55.24	90	310	220.1	~73
KCTP-067-HT23	-	100	328	177.8	~83
KCTP-068-HT22	-	100	329	181.2	-
C2CF-20-1288	65.45	79.6	302	165.0	~30
SP271	12.93	100	256.72	296.4	~87
M-AR	30.85	100	263.65	307.2	~16
KCTP-034-HT7	48.5	80.56	299	237.5	~22



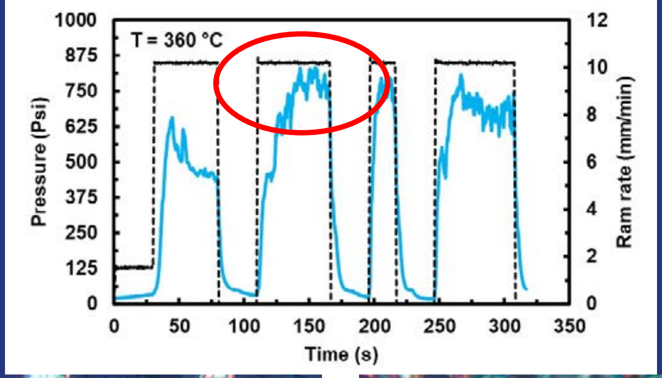


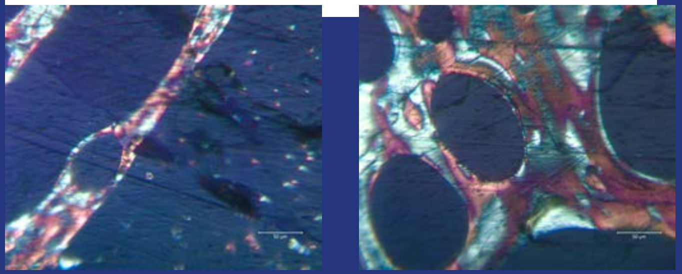
Tsp and QI decrease with increasing Ea

C2CF-20-0425 (58.84%)

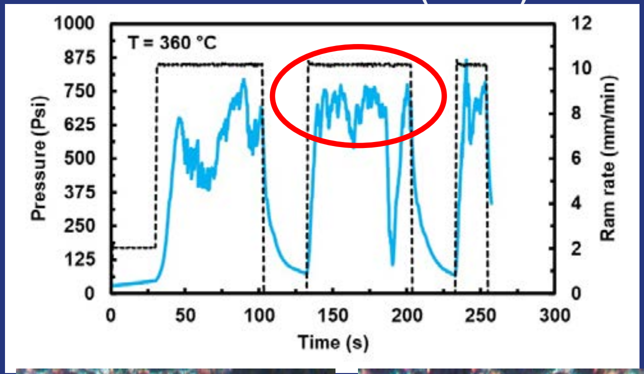


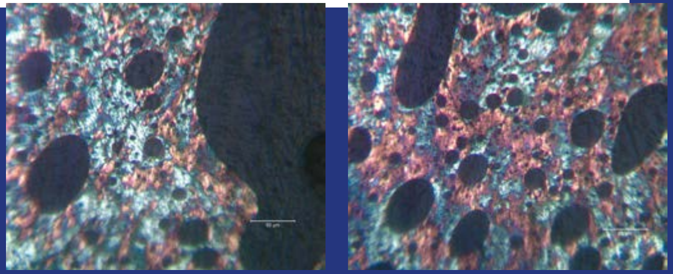
C2CF-20-1245 (62.1%)



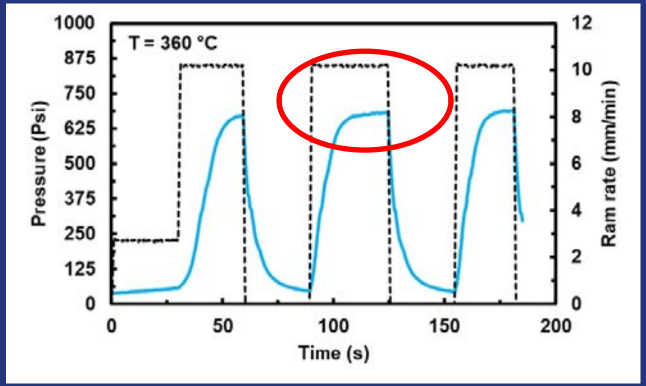


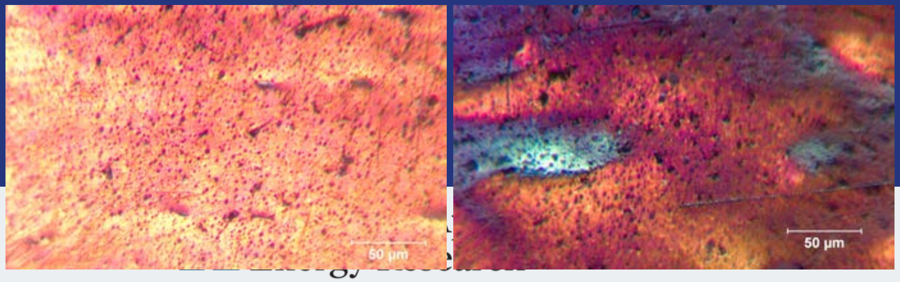
C2CF-20-1260 HM (60.5%)



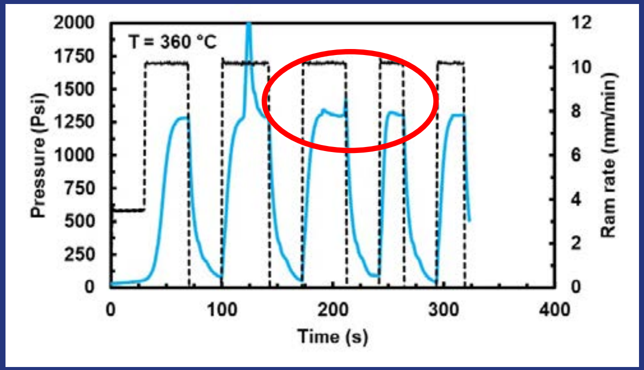


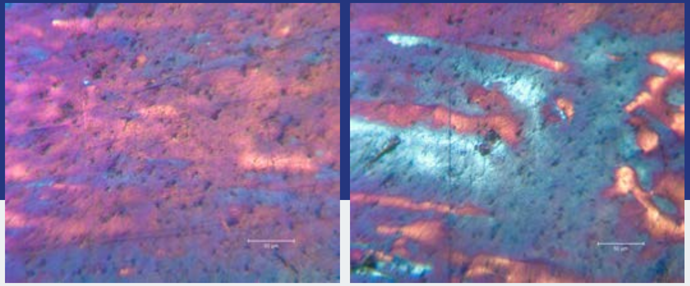
KCTP-036-038 Mix (90%)



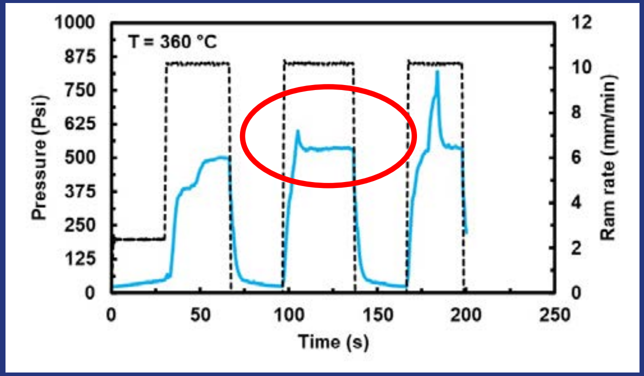


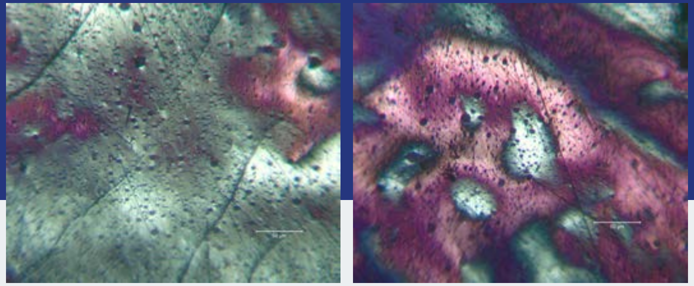
KCTP-053-HT21 (77.5%)





KCTP-063-HT23 (68.4%)





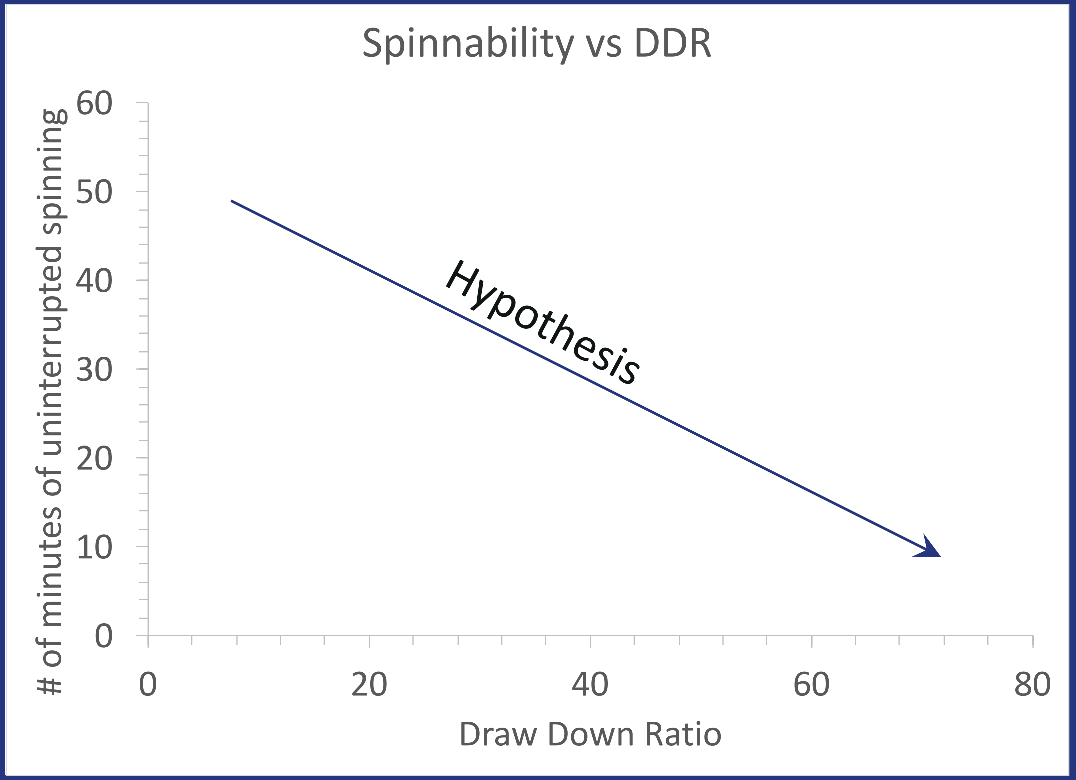
What is a "spinnable" coal tar mesophase?

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, or < 320 °C
- Capillary rheology
  - Activation energy of flow of ~ >190 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.

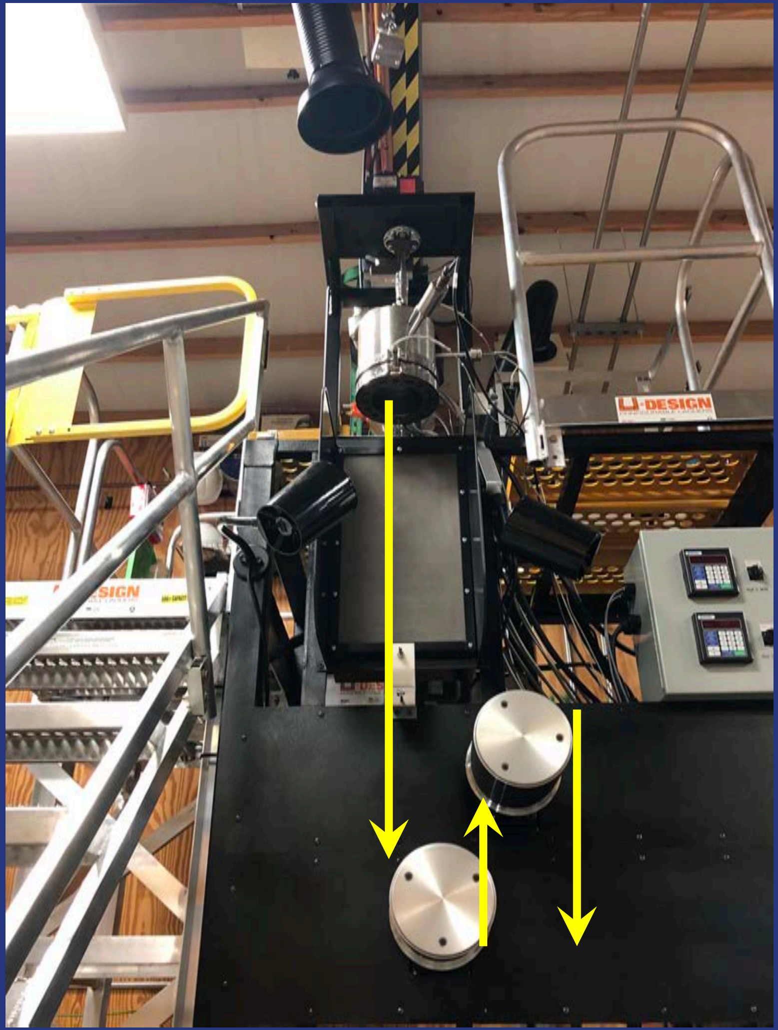
We are working to build charts like this



Subtask 3.1 – Melt Spinning

AJ Extruder System

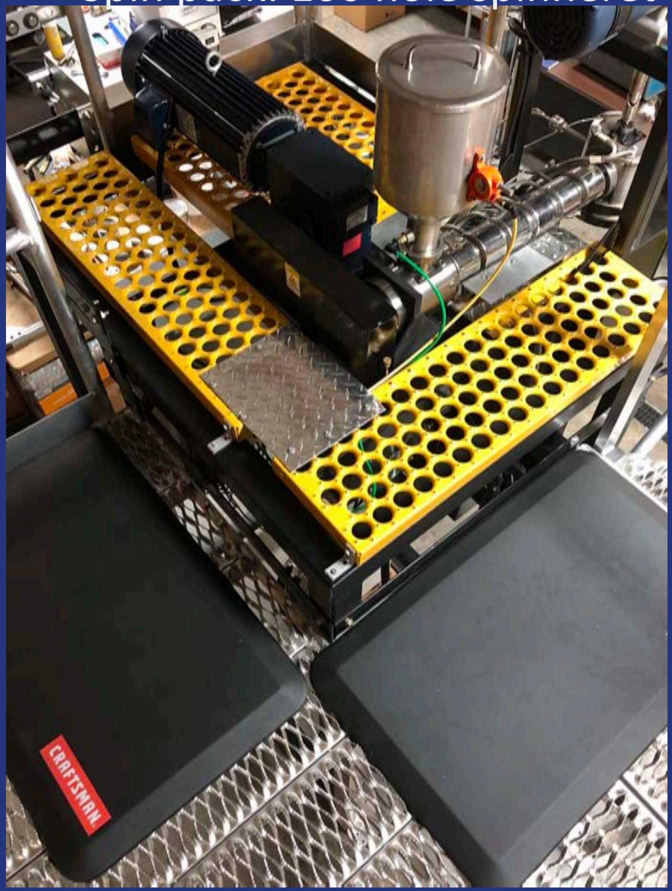
Operational Winter 2020 - 2021



1” Extruder

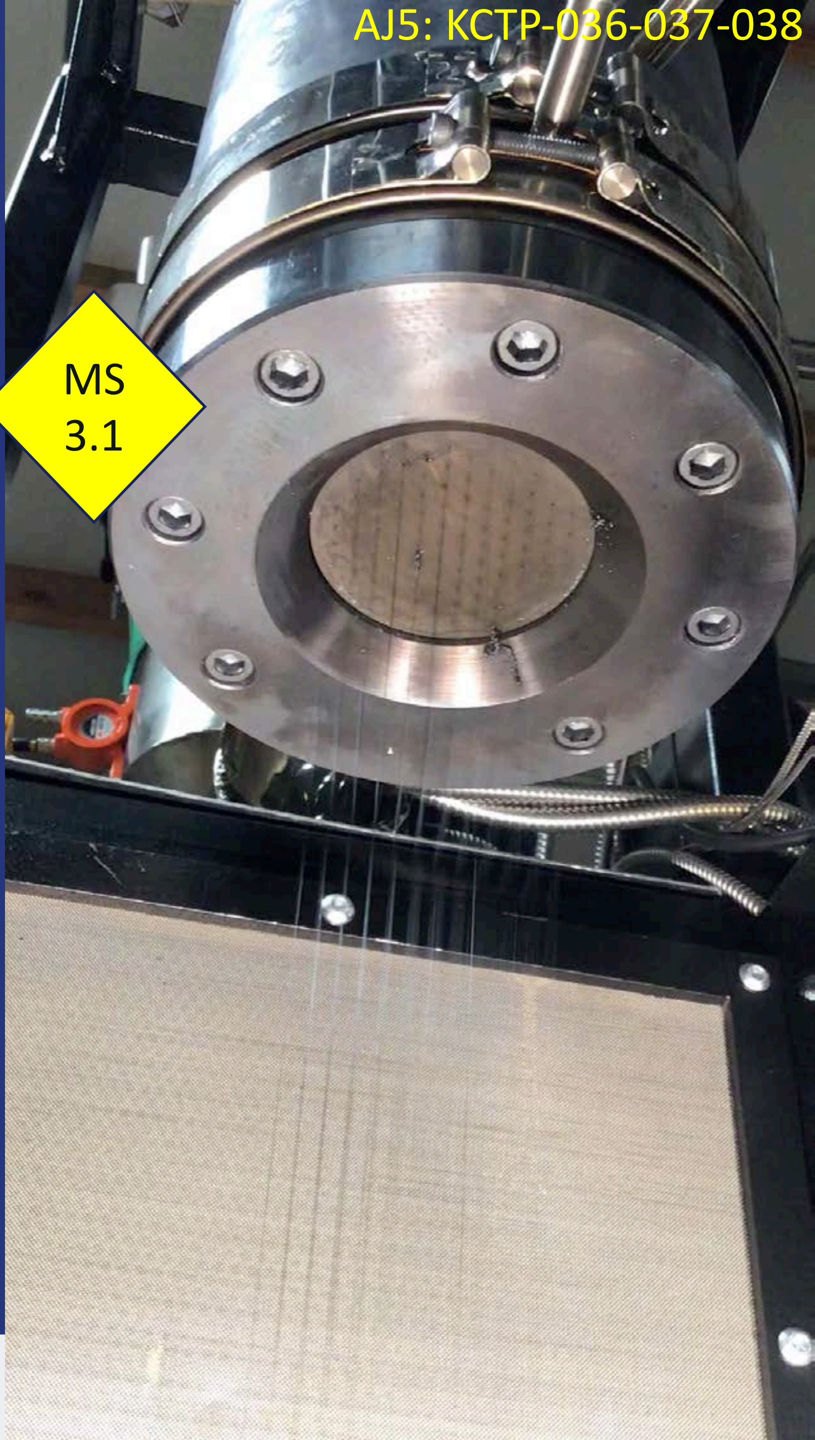
Metering pump

Spin pack: 100 hole spinneret

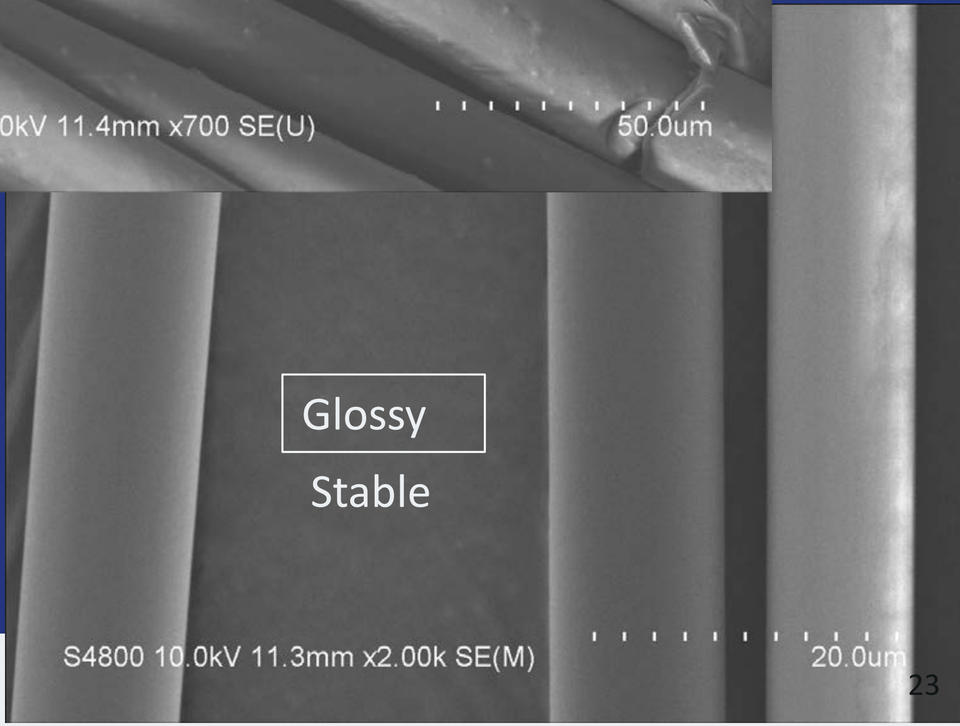


100 filament mesophase spinning

- Multifilament melt spinning is a major milestone of the project
- Spinnability:
  - Relative 'ease' of fiber formation
  - Complex interplay of temperature and rate dependent flow of mesophase pitch
  - Stability of the process to proceed for 10s of minutes to hours, uninterrupted
- Important measurable factors
  - Softening point temperature (QI)
  - Viscosity(T)
    - E_a of flow

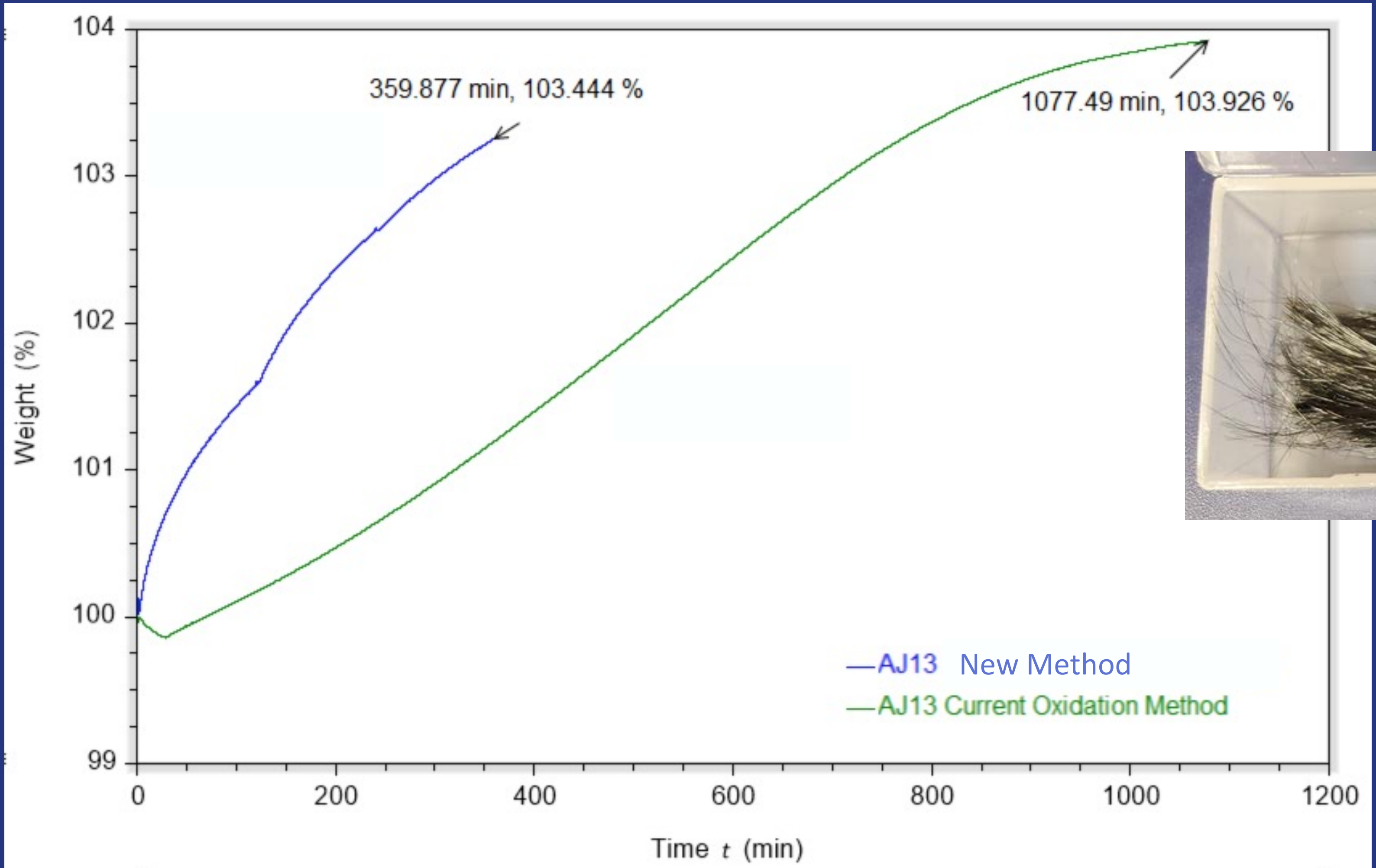


Spinning Stability: Green Fiber Luster



Oxidation Studies of AJ13 Pitch Fiber

Current oxidation method is designed for isotropic (not mesophase) pitch fiber, and requires extensive time at temperature



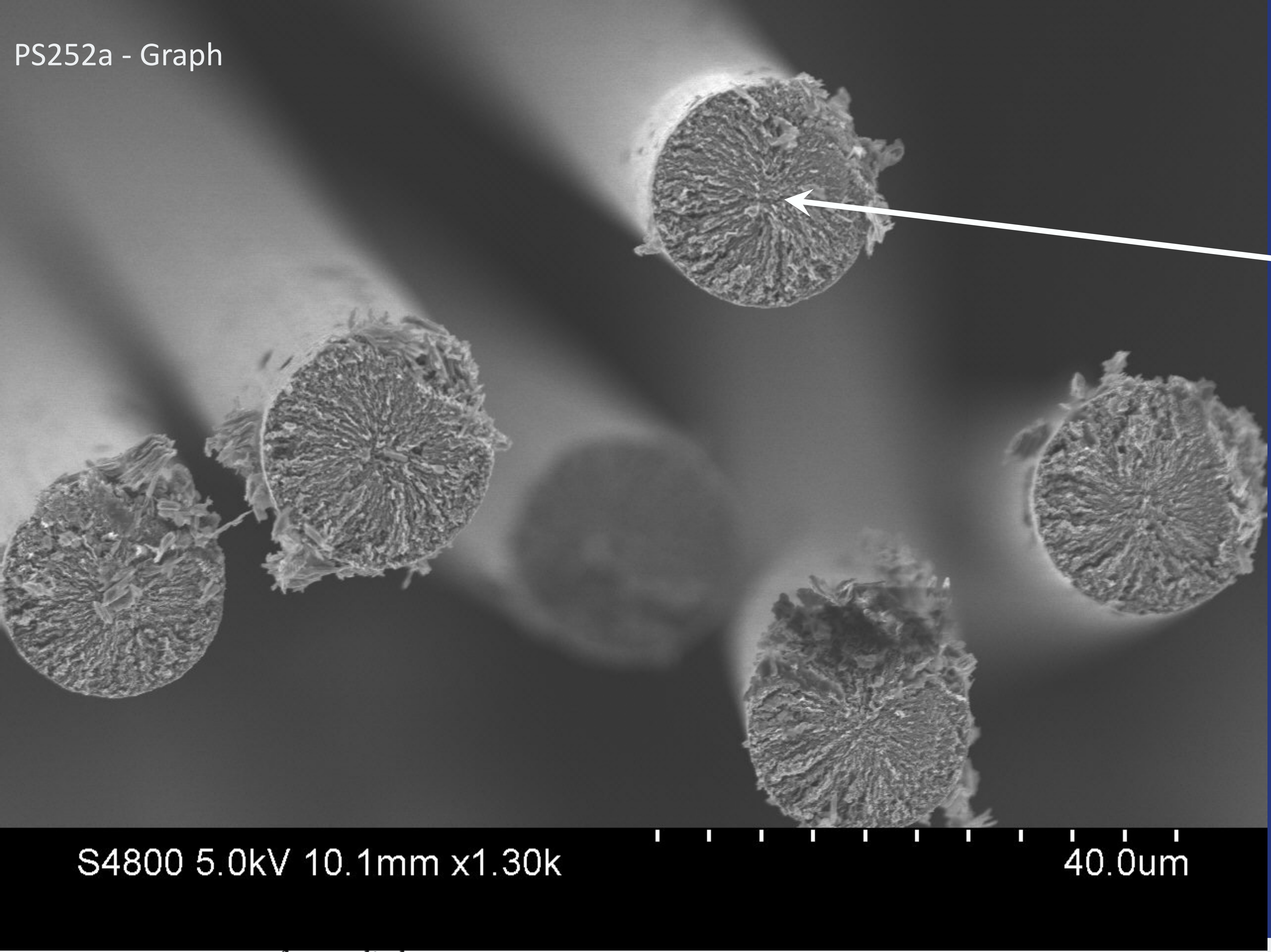
3X reduction in requisite oxidation time

Oxidized Pitch Fiber - Resilience

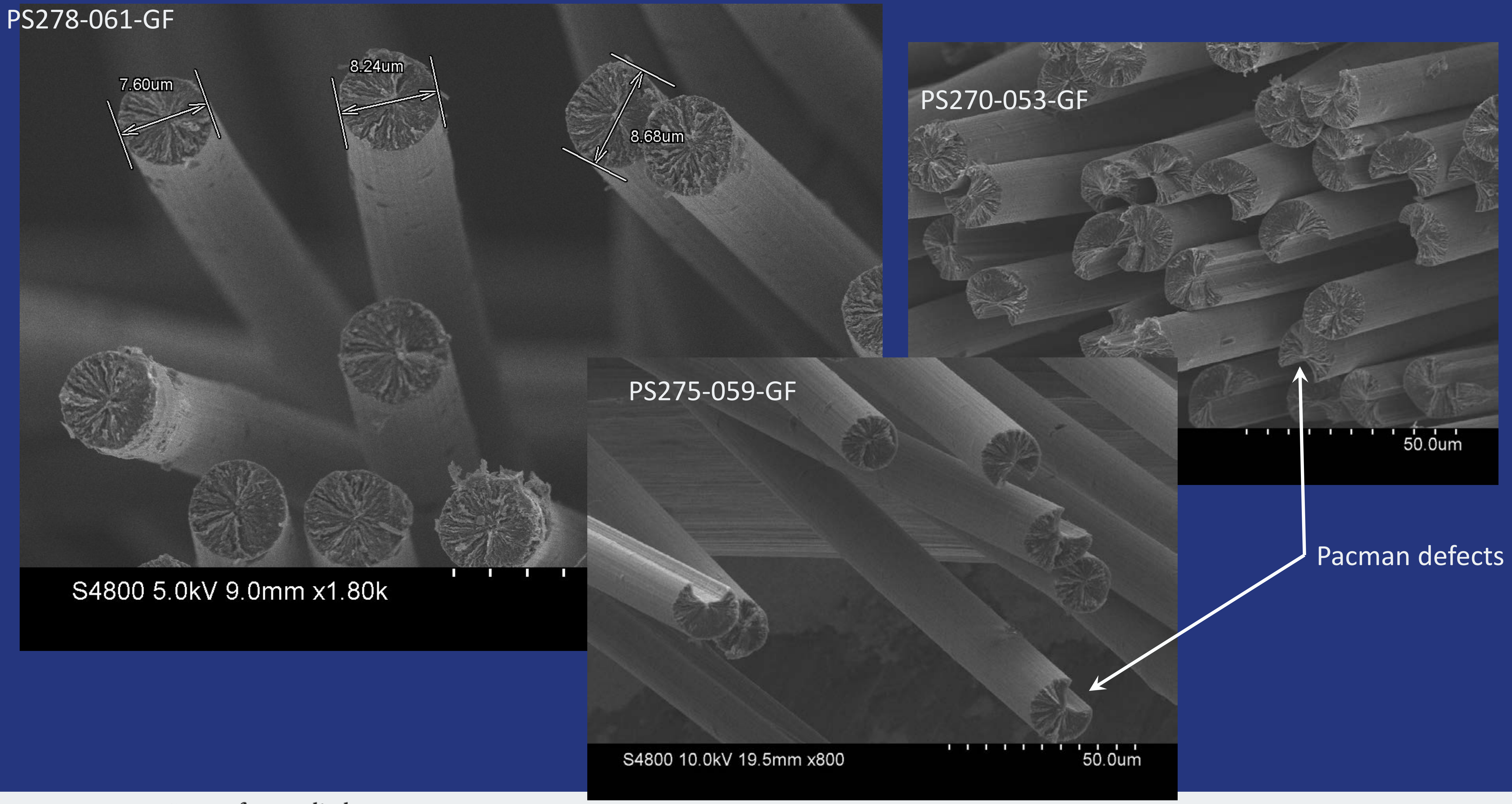
MS 3.2

Fiber	Mesophase	Break Load (gf)	Break Stress (MPa)	Modulus (GPa)	Break Strain (%)	Resilience (kPa)	N
PS309 Green	KCTP-076 Coal tar mesophase	0.40	16.8	5.39	0.34	28.5	22
PS309 Ox		0.77	26.9	5.25	0.54	72.7	24
						+2.5x	
PS307 Green	SP271 Baseline	0.65	22.3	4.65	0.50	55.8	23
PS307 Ox		1.91	66.6	7.10	1.52	506.8	18
						+9.1x	

Green Fiber is incredibly FRAGILE.
Oxidized fibers demonstrate an increased strain to failure and resilience, relative to green fiber.
Important for weaving.



Radial texture of graphitized fibers


PS278-061-GF
7.60um
8.24um
8.68um
S4800 5.0kV 9.0mm x1.80k
PS270-053-GF
50.0um
PS275-059-GF
S4800 10.0kV 19.5mm x800
50.0um
Pacman defects

Carbon Fiber Tensile properties

% Mesophase	Fiber	Diameter (um)	Stdev (um)	Stress At Break (MPa)	Stdev (MPa)	Modulus (GPa)	Stdev (GPa)	Strain at Break (%)	Stdev (%)	N	CY %
59.4	PS252a-052-GF671	17.70	0.75	1061	297	624	42	0.17	0.05	40	79
	PS252b-052-GF671	17.62	0.95	1022	379	592	67	0.17	0.06	40	79
77.5	PS253a-053-GF671	15.18	2.21	882	201	609	40	0.14	0.03	40	72
	PS253b-053-GF671	15.18	2.21	902	280	613	61	0.15	0.05	40	80
60.3	PS267a-059-GF678	10.93	0.72	1424	286	542	60	0.26	0.04	48	79
60.3	PS267b-059-GF678	12.90	1.03	1400	366	611	36	0.23	0.05	40	78
77.5	PS270-053-GF678	13.92	1.87	986	240	390*	97	0.26	0.06	40	78
60.3	PS273a-059-GF675	12.23	0.95	1234	328	755	58	0.16	0.04	42	73
60.3	PS275a-059-GF674	15.61	1.52	1145	215	464*	62	0.25	0.05	39	80
60.6	PS278-061-GF676	7.72	0.61	1607	215	448	29	0.36	0.05	40	72

*Pacman defects observed

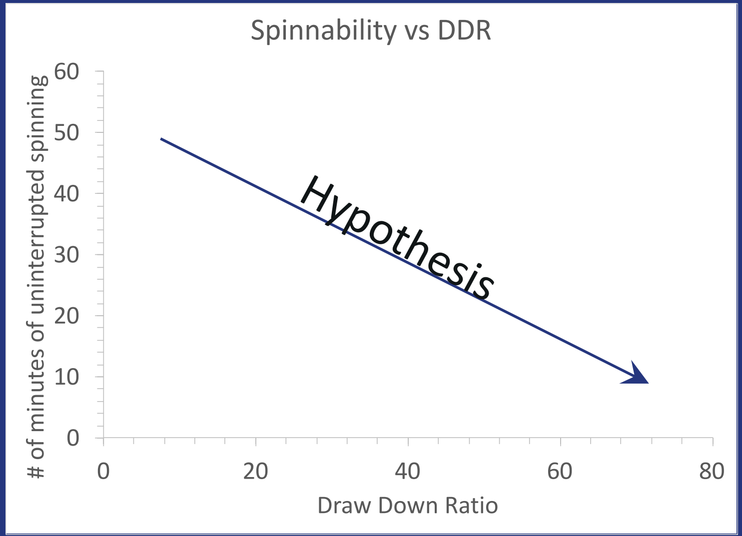
- Most had moduli ~ 600 GPa (87 MSI)
- Most ~ 80% CY
- Working to improve strength (strain to failure)

37% 'missing' area for PS270:
390 → 619 GPa

Review of Progress

- Coal tar derived mesophase production at 1s kg scale
  - Progress defining a ‘spinnable’ mesophase
- Multifilament melt spinning achieved
  - Rheological insight
- Faster oxidation achieved
- Single filament tensile properties measured
  - Moduli at approximately 600 GPa (87 MSI)
  - Strength still low at ~ 1 GPa (145 ksi)
    - strain to failure low at 0.15 – 0. 25%

Future



- Stable multifilament melt spinning
  - Challenges:
    - Spinnable mesophase supply
    - Start up
    - Stability
    - Spinneret cleaning
- Build spinnability charts
  - # of minutes of uninterrupted spinning vs. draw down ratio
- Investigate chemistry of spinnable and non-spinnable mesophase
  - Mw distribution (mass spectroscopy)
  - Aromaticity (H NMR)
  - QS fraction of mesophase
- Tasks 3.2 – 3.4 requiring continuous multifilament tow
  - MS 3.3 – Weaving oxidized fiber (Sept. 2022)

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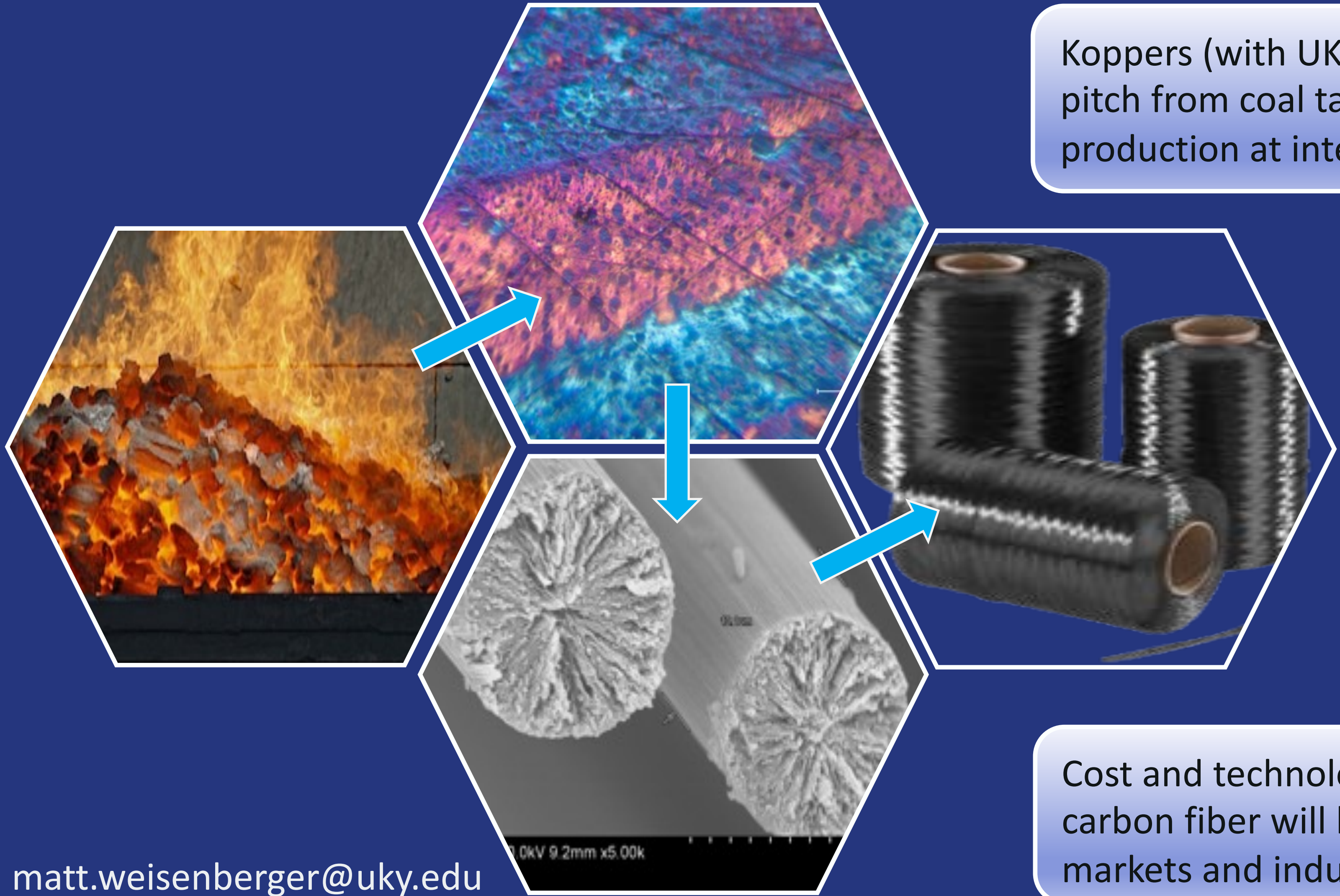

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