Sub-pilot Scale Production of High-Value Products from U.S. Coals

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Program Manager: Christian Robinson

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Project Overview

- Funding: $1,932,495 = Federal ($1,499,880) + Match ($432,615)
- Period of Performance: 06/01/2020 through 05/31/2023
- Project Participants:

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MARSHALL

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Project Objectives

- *Develop methodologies* *to produce* *coal tar pitch* *suitable for quality* *carbon fiber* *production*
  - Coals from multiple U.S. coal-producing regions
- *Develop method* for high-value *Silicon Carbide (β-SiC)* *production*
  - Use carbon residue byproduct material (e.g., char) from carbon fiber production
- *Develop database* and *tools for data analysis* and *economic modeling,* accessed by a web-based portal
  - Relate coal properties and process conditions to final quality of products
  - Assess the economic viability of coals from different regions for producing specific high-value products.

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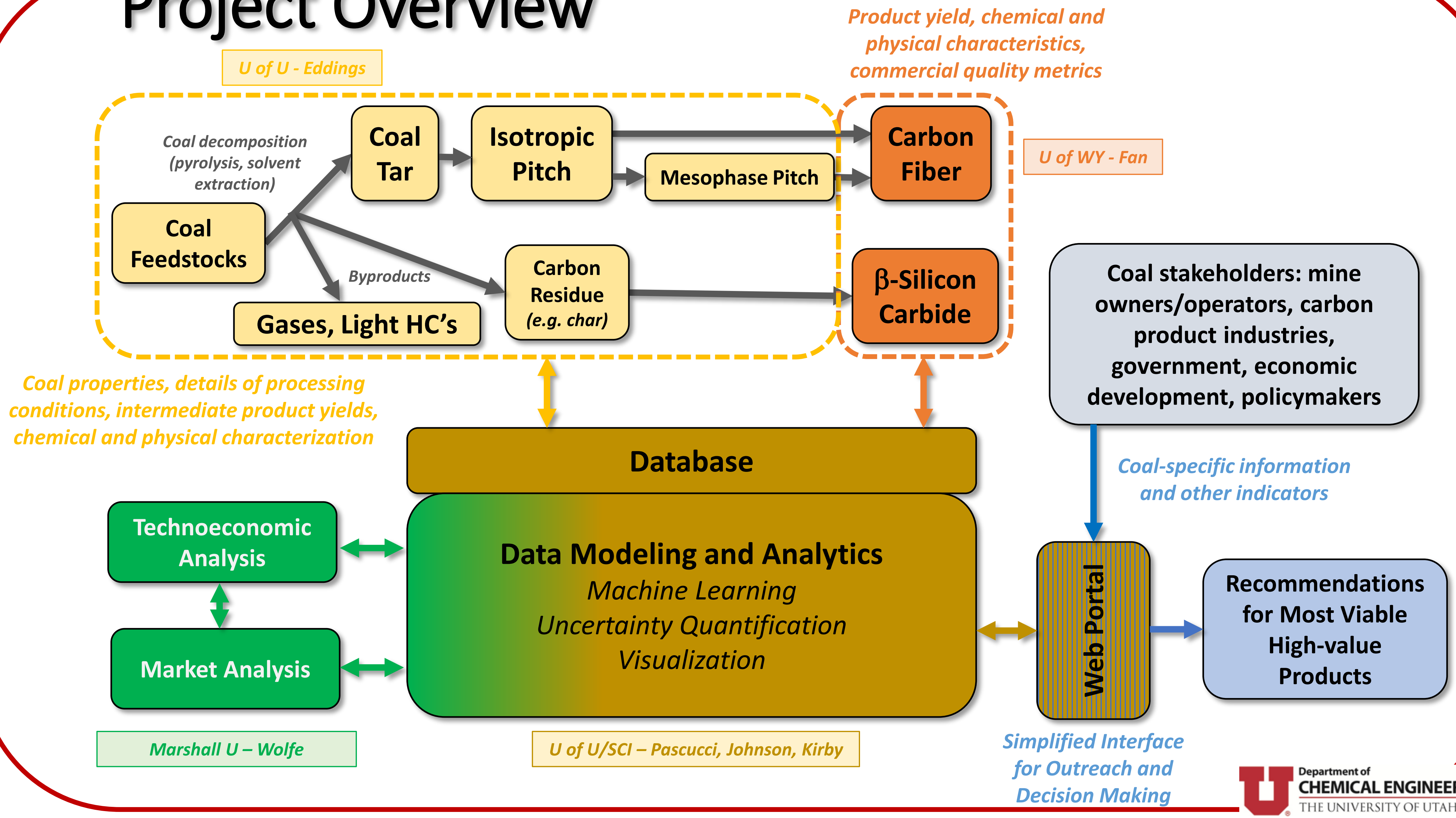
Project Overview



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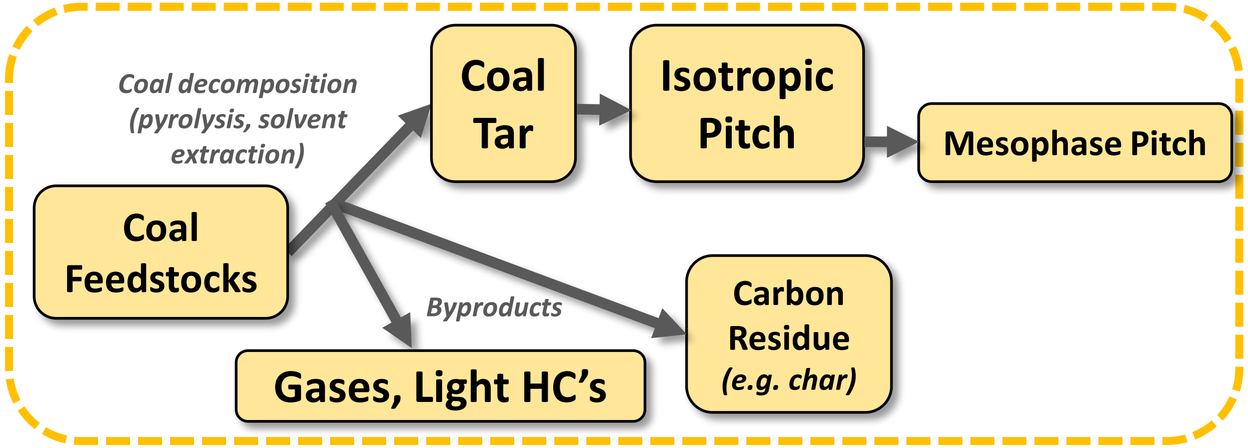
Project Overview

U of U - Eddings



Coal properties, details of processing conditions, intermediate product yields, chemical and physical characterization

Key question for many coal-producing regions:

How to produce high-quality mesophase pitch from a non-coking coal?

Investigating two different pathways for initial decomposition of the coal feedstocks:

- Thermal Decomposition (Pyrolysis)
- Chemical Decomposition (Solvolysis)

Thermal Decomposition Approach (Pyrolysis)

Current approach used in coke-making, and is primary commercial pathway for producing coal-derived pitch

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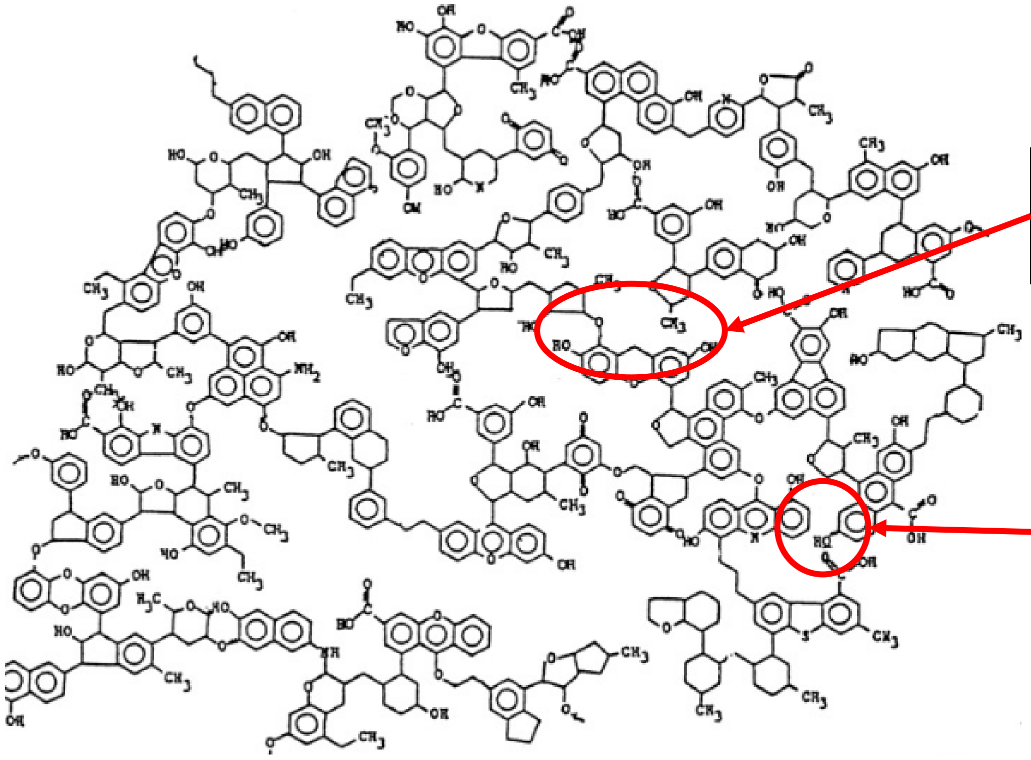
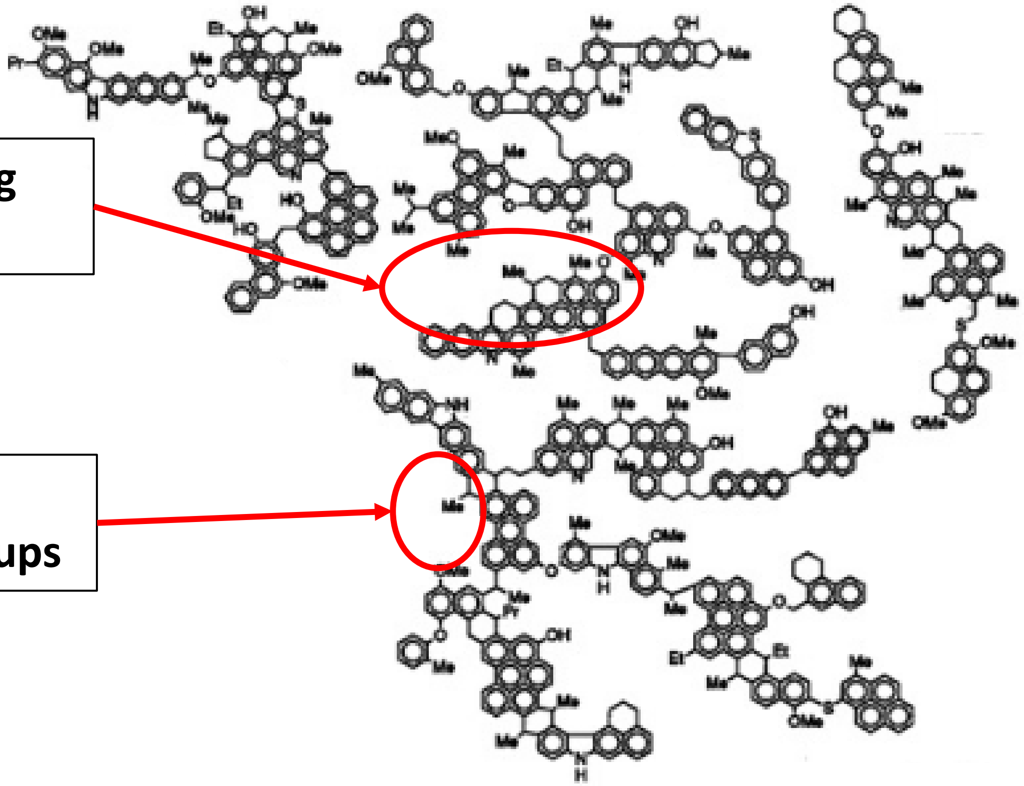
Problem: Non-coking coals have less-than-ideal properties for mesophase formation



Compare ring cluster sizes

Compare functional groups

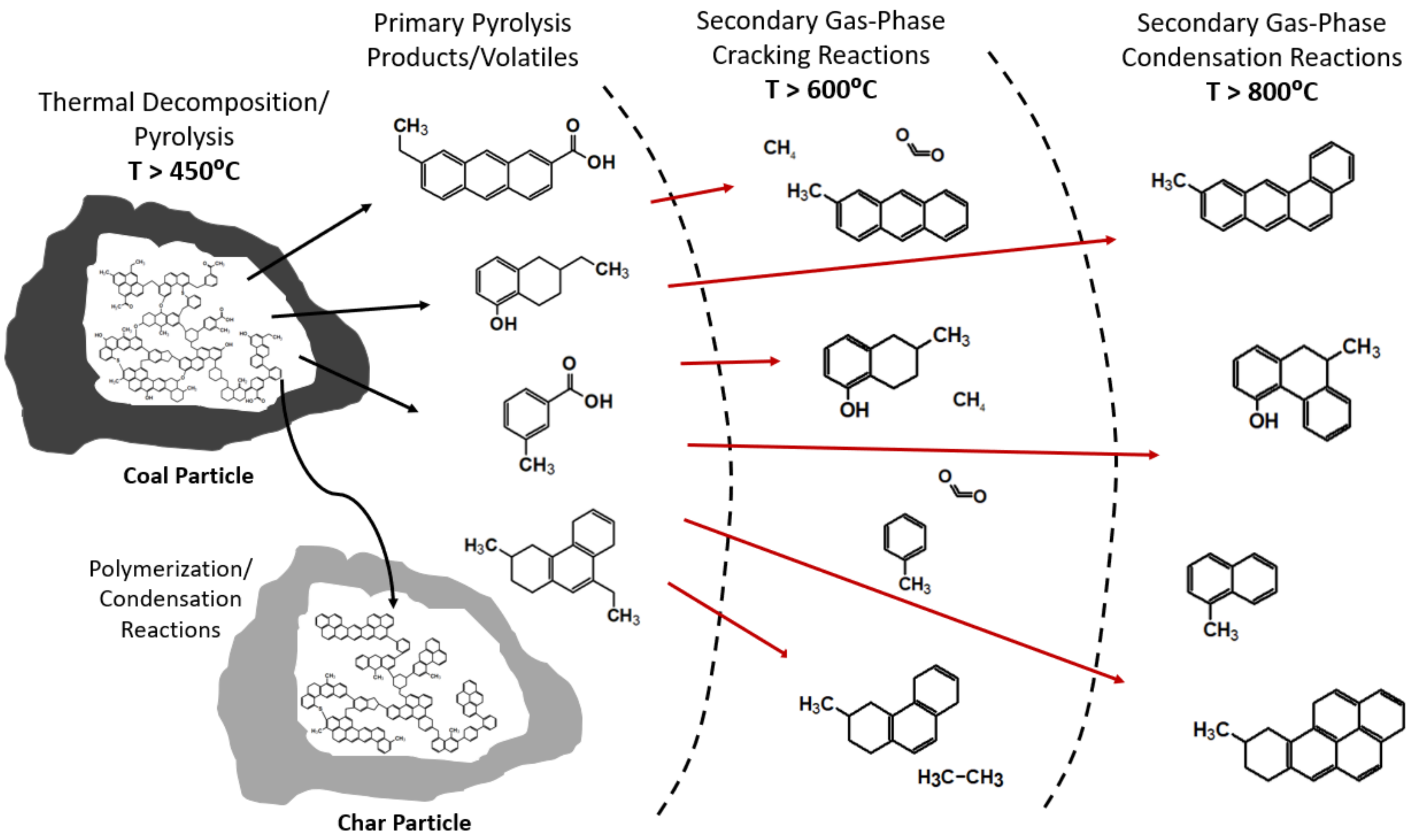


Depiction of sub-bituminous coal molecular structure (More like a <u>non-coking</u> coal)

Depiction of bituminous coal molecular structure (More like a <u>coking</u> coal)

Figures from J. Mathews and A. Chaffee, "The molecular representations of coal – a review", *Fuel*, 2012, 96, 1-14.

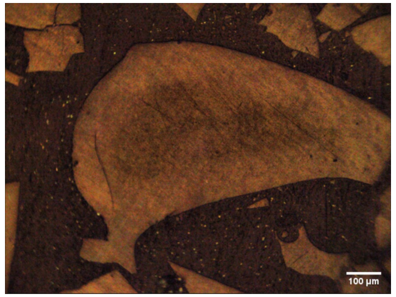
Solution: Utilize Secondary Gas-phase Reactions (SGR) in Pyrolysis to Modify Coal Tar Chemistry



This figure was adapted from K. Miura, "Mild conversion of coal for producing valuable chemicals", Fuel processing technology, 2000, 62, 119-135.

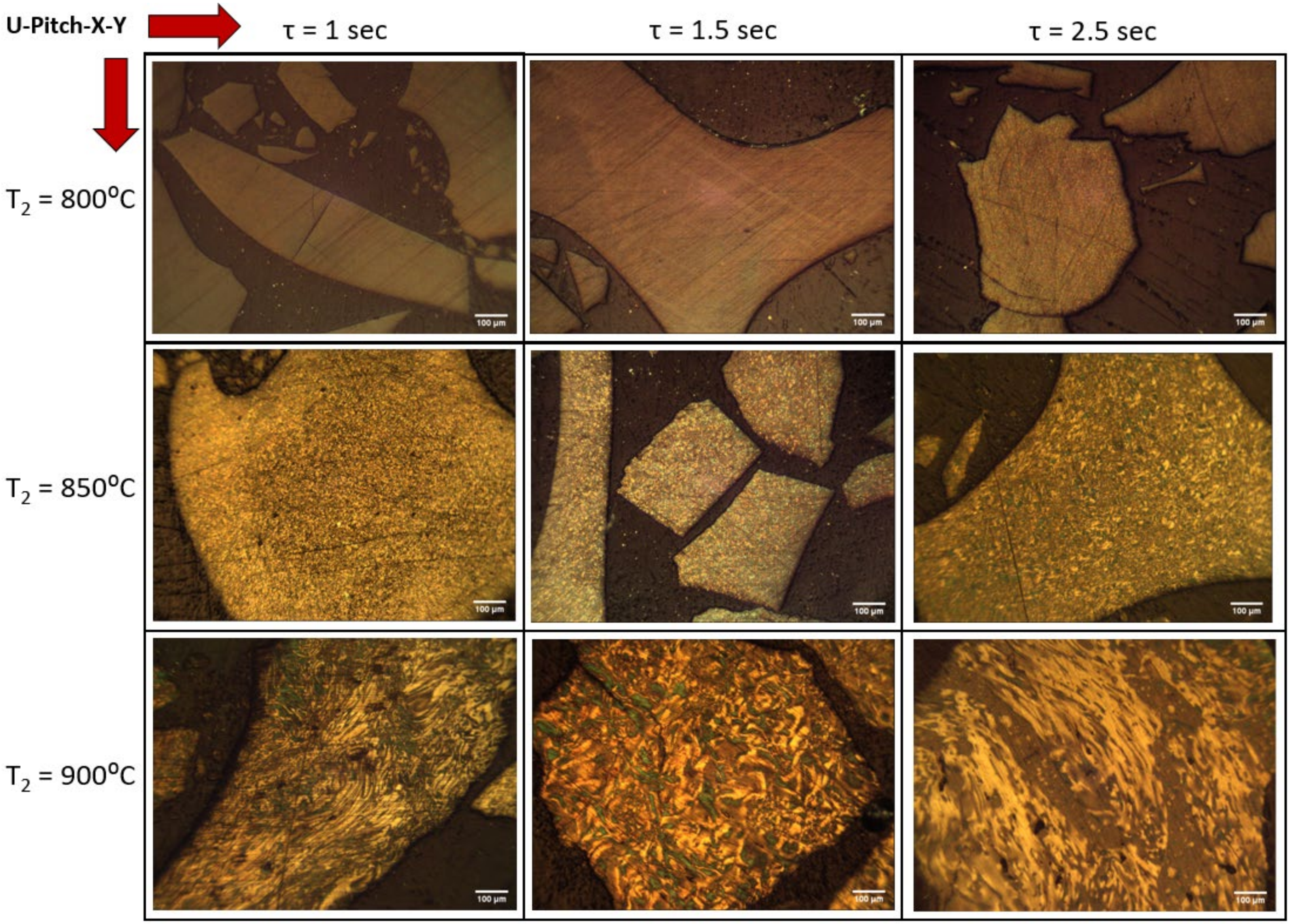
Pyrolysis: Conversion of Coal Tar to Anisotropic Pitch Material – Imaging Results*

Utah Sufco Pitch



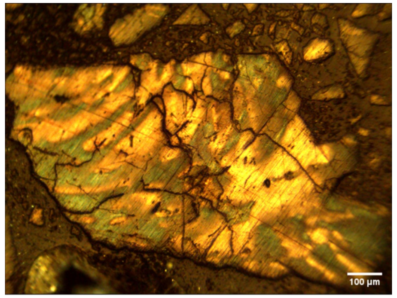
Primary Pyrolysis Only

Adding SGR



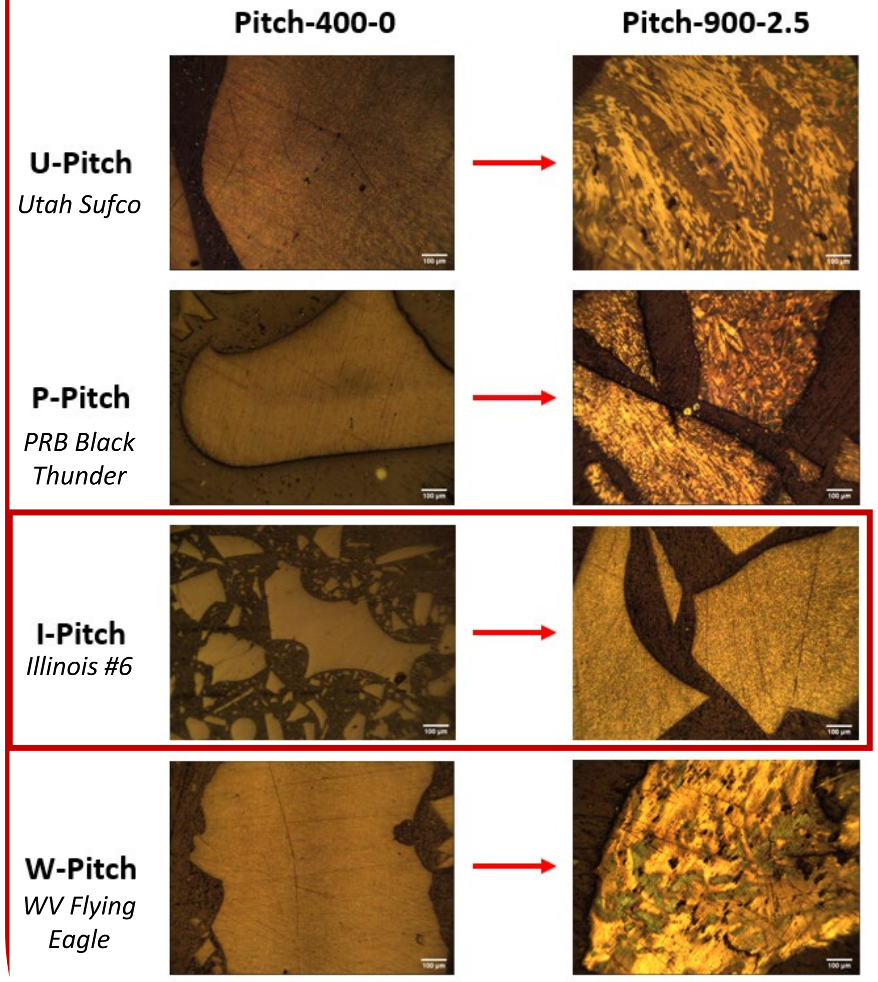
After Use of Secondary Pyrolysis Reactions for UT Coal

Commercial Coal Tar Pitch



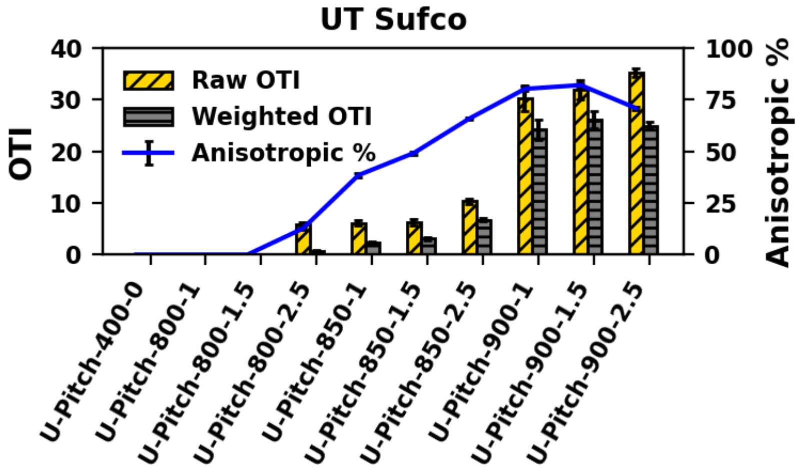
**as measured by Polarized Optical Microscopy*

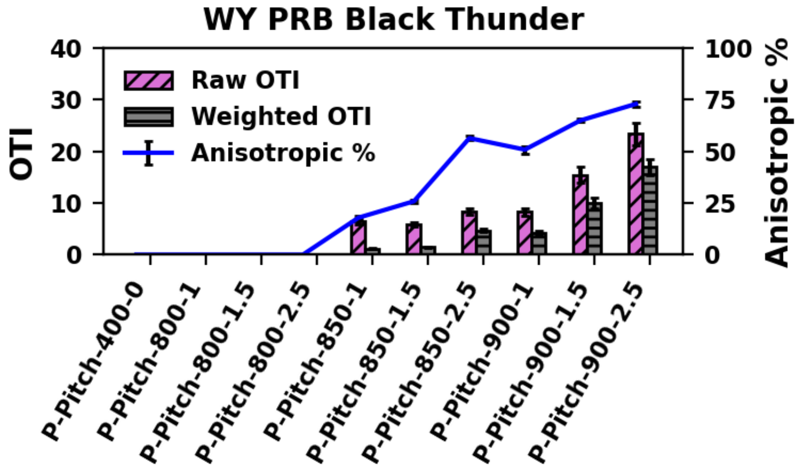
Pyrolysis: Mesophase (Anisotropy) Formation with Different Coals

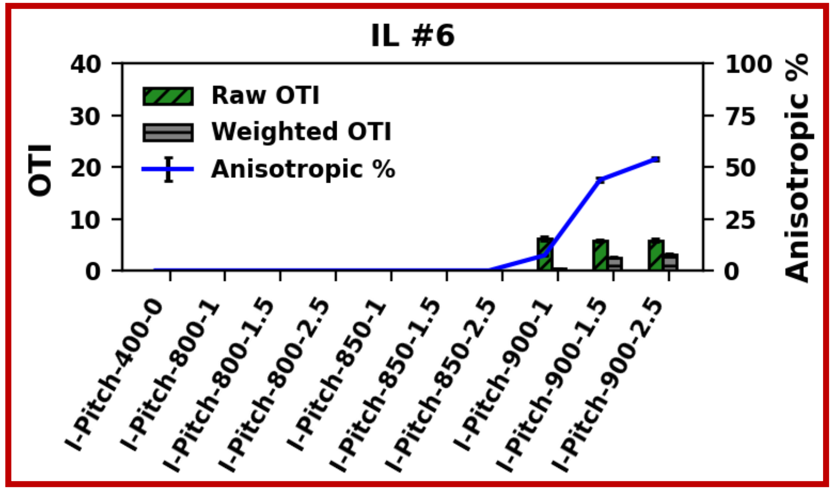


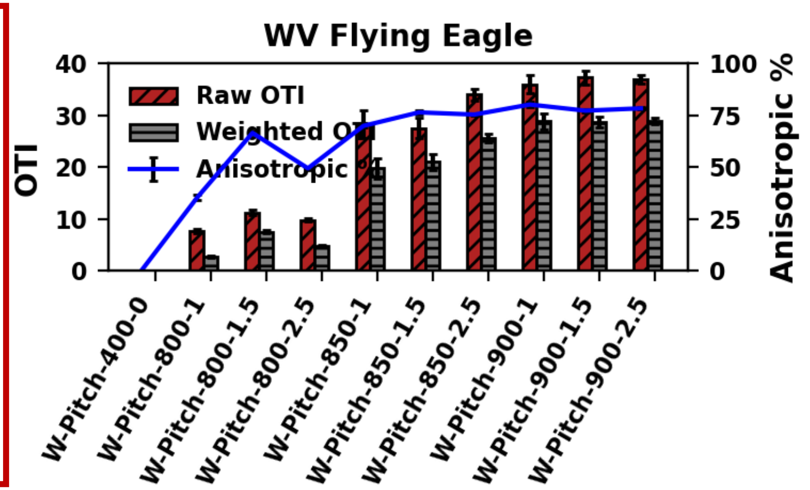
Primary Pyrolysis Only

After SGR



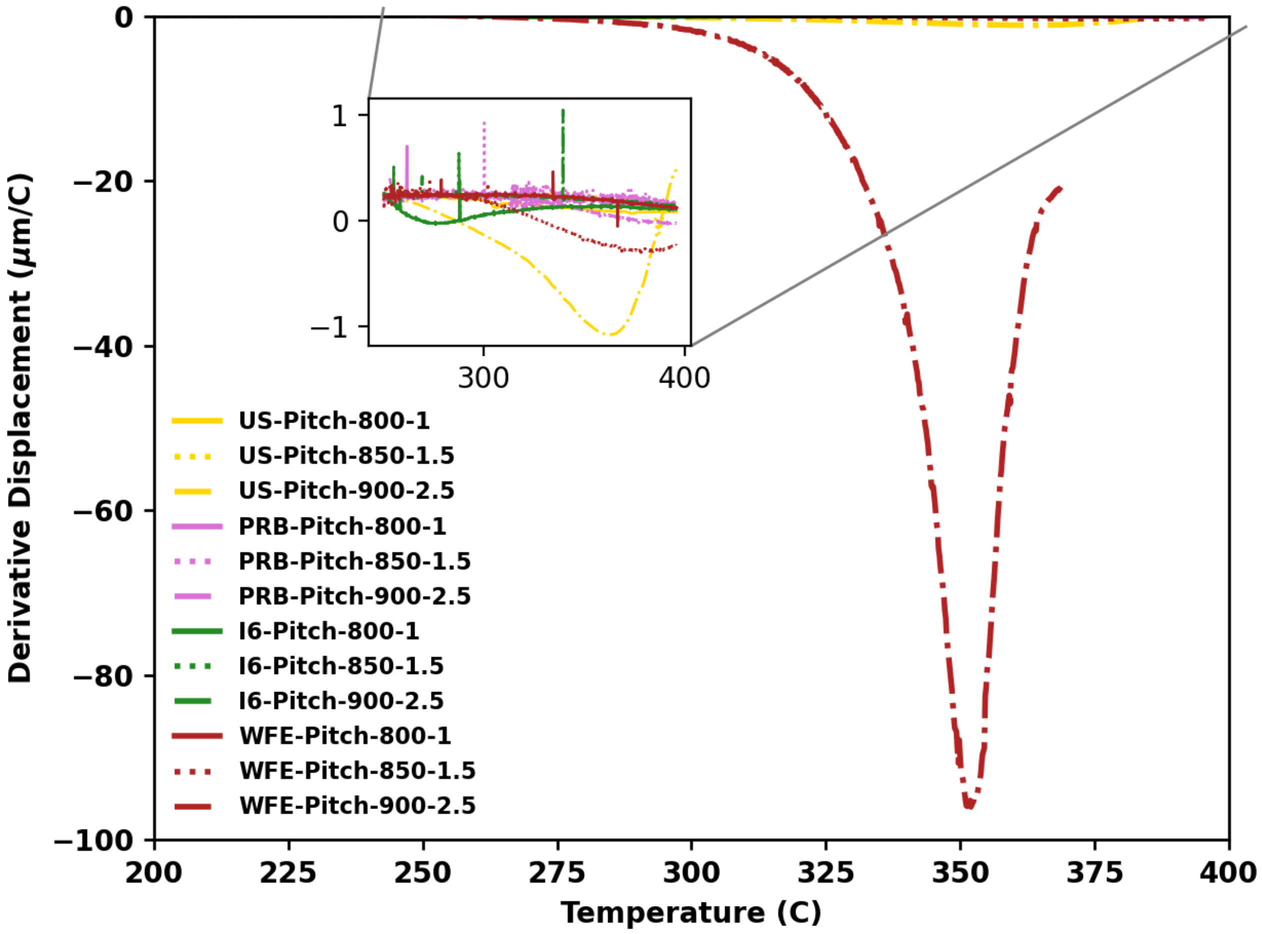






Pyrolysis: Pitch Sample Softening Points, T_{sp}*

- Softening point determined at max rate of change in sample displacement*
- None of the coal pitch samples (except WV) softened < 400 °C
  - *likely passed through mesophase formation to create semicoke*
- Desire T_{sp} < 350 °C for stable melt-spinning into carbon fiber



*as measured by Dynamic Mechanical Analysis (DMA)

Comments Regarding Pyrolysis Approach

- SGR in pyrolysis of UT Sufco coal led to substantially modified coal tar intermediates
  - Coal tar had lower oxygen and aliphatic contents, and higher overall MW with increased SGR conditions
  - SGR-modified coal tar intermediates led to improved pitch anisotropy
- SGR approach worked well for improving anisotropy for multiple coal types (UT, WY, IL-*worst performer*, WV)
- However, most pitch samples progressed beyond mesophase formation into anisotropic semicokes, not suitable for melt-spinning
  - Exception was WV coal, which is a coking coal
- Also, overall pitch yields were very low; e.g., ~1-2% of original coal mass (daf) for UT Sufco

Chemical Decomposition Approach (Solvolysis)

Used in direct coal liquefaction (DCL) traditionally for making liquid fuels

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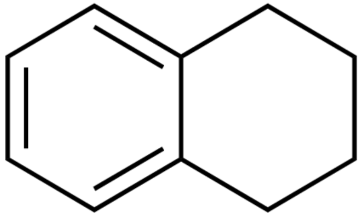
Mild Solvolysis Approach

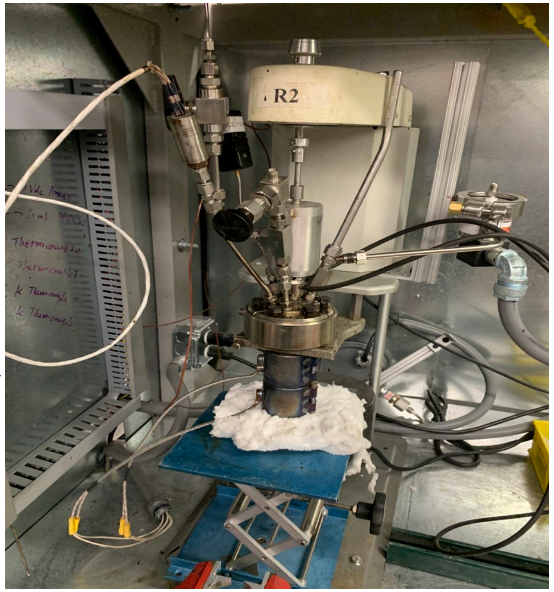
Coal

+



Tetralin (THN)

hydrogen donor solvent



Liquefaction System (100 mL)

Solid Residue

Light Fraction

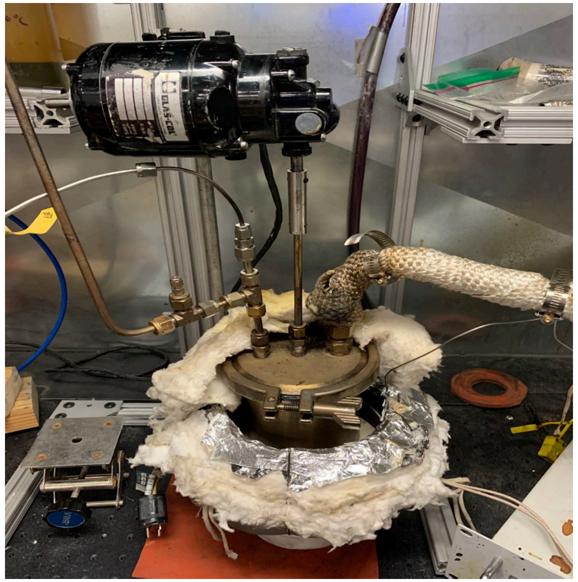
Heavy Fraction

Tetralin

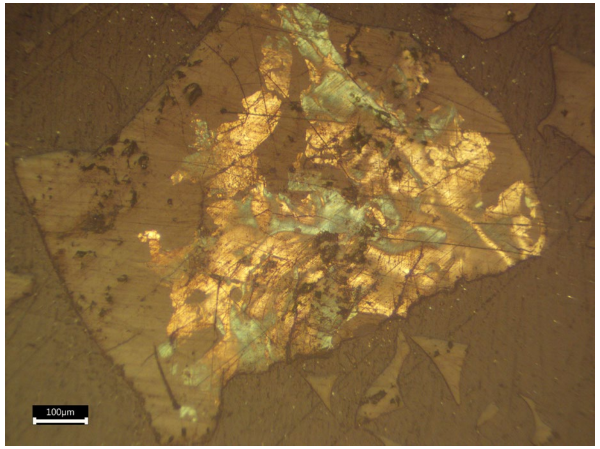
Extraction/ Separation

Some Light Fraction

Heavy Fraction (A+P)



Thermal Treatment System



Isotropic Pitch/Mesophase Pitch

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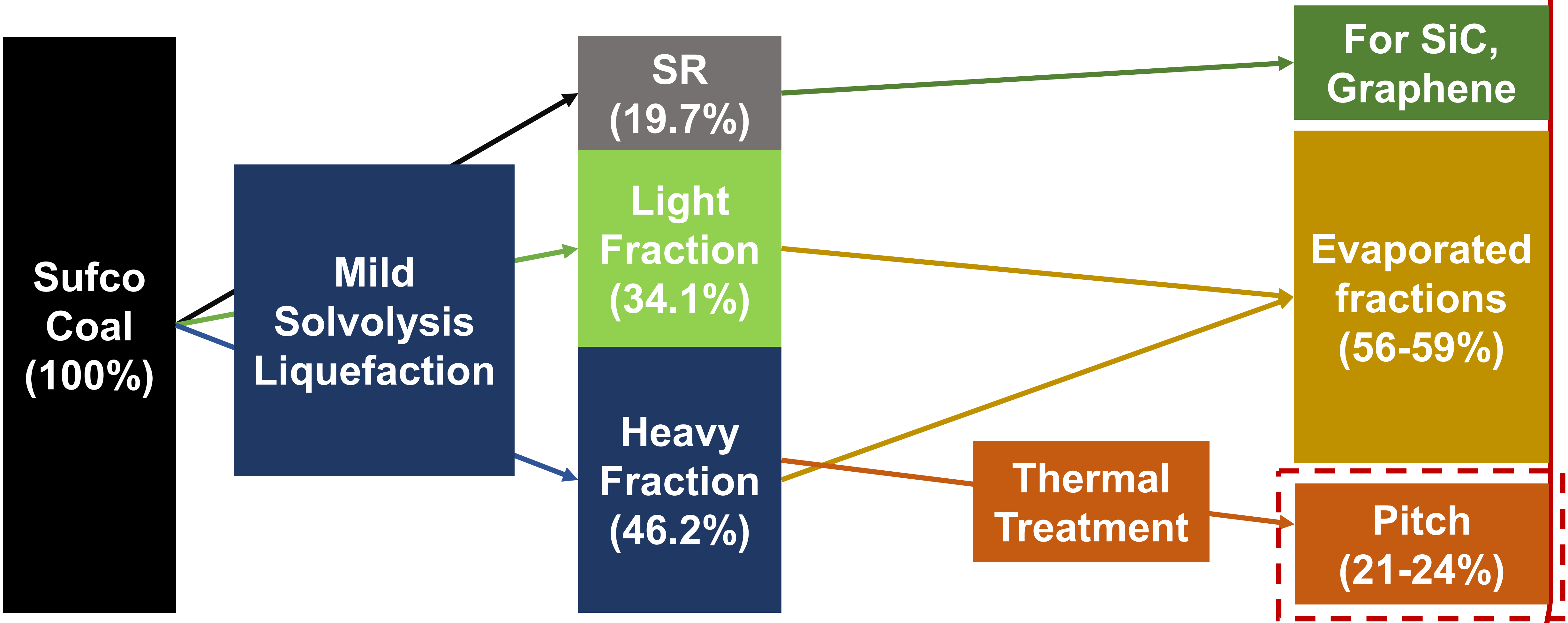
Mass Flow from UT Sufco Coal to Pitch Intermediate



Note: Percentages based on daf mass of coal and neglected H_2 consumption < 2% of coal

Solvolysis: Mesophase (Anisotropy) Formation Results in Pitch from Different Coals

Coal		Yield (wt%, daf)		Quinoline Insoluble Content (wt%)	Anisotropy (%)
State	Mine	Tar to Pitch	Coal to Pitch		
UT	*Sufco*	31.9	21.3	64.7	75.4
IL	*Illinois #6*	26.7	24.3	12.9	8.2
WY	*PRB Black Thunder*	22.8	26.6	43.5	32.7
WV	*Flying Eagle*	34.5	22.1	71.5	88.5

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Comments Regarding Solvolysis Approach

- Mild solvolysis liquefaction process effectively converted coals from different coal-producing regions into anisotropic material
  - UT Sufco coal and WV Flying Eagle coals showed good performance
  - WY PRB and IL #6 coals appear to face more difficulties, consistent with pyrolysis results.
- Softening points are still too high for melt-spinning to carbon fiber
  - Have similar problem of forming semi-coke during upgrading to form mesophase pitch
- The application of THN and other solvents can be costly and difficult to recycle. Need alternative hydrogen transfer/donating solvents
  - Consider use of materials such as waste plastic or renewable biomass

Addressing High Softening Points through Use of Additives

Co-processing with waste plastic material

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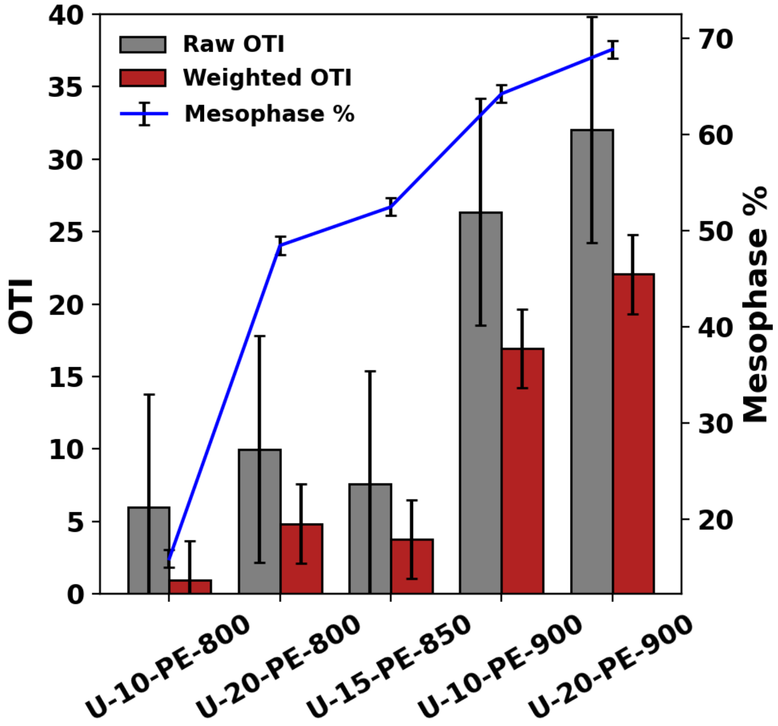
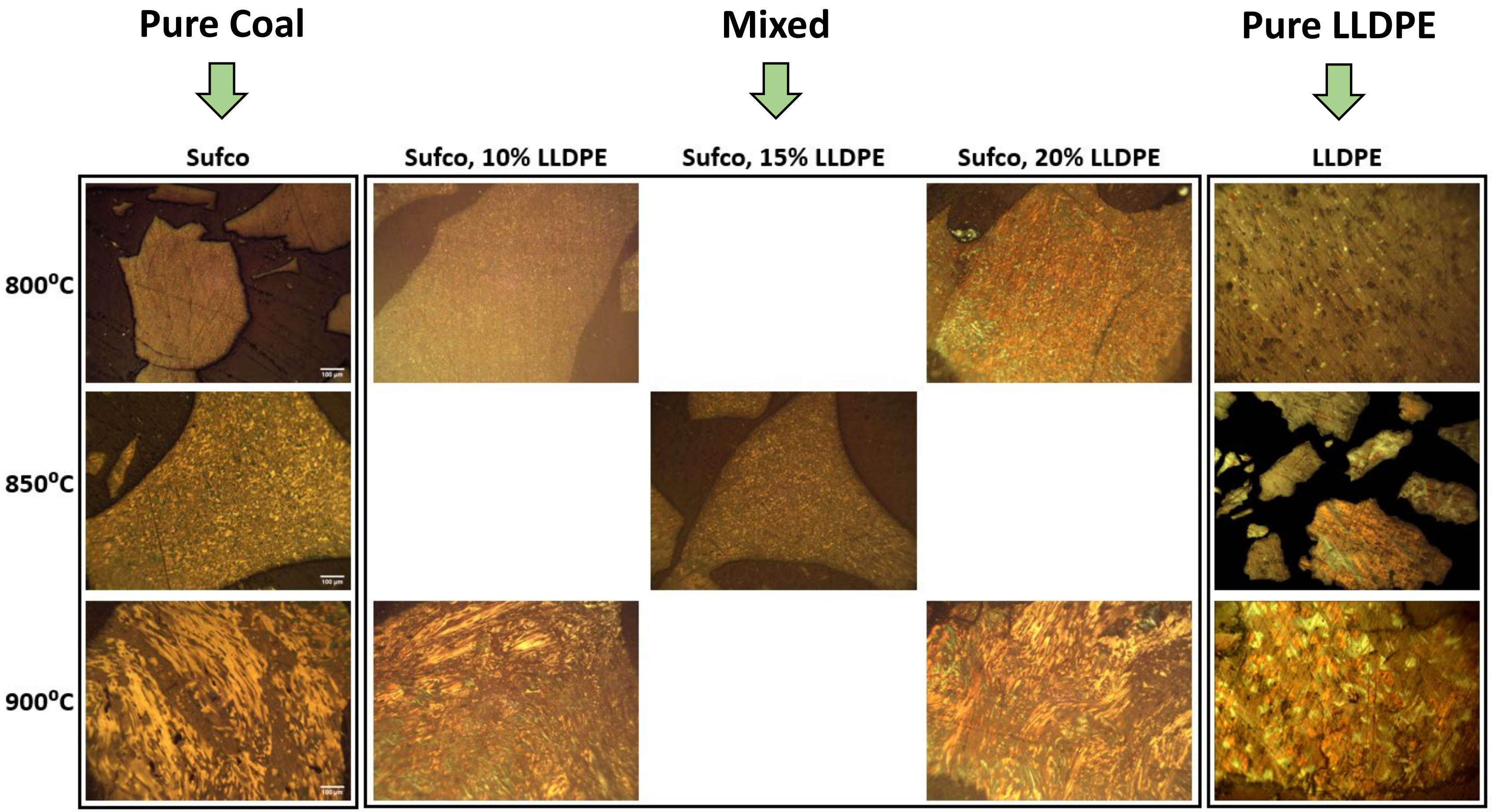
Pyrolysis: LLDPE Addition to Sufco Coal





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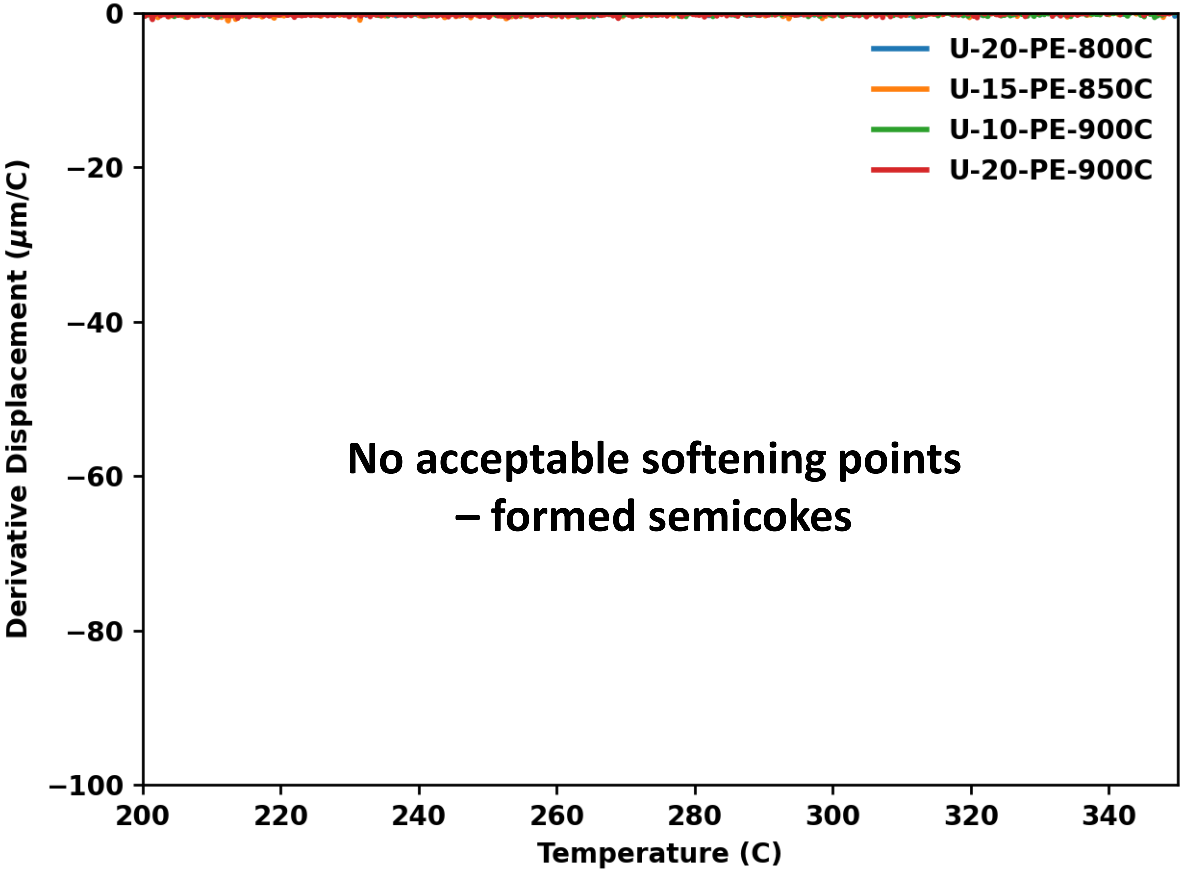
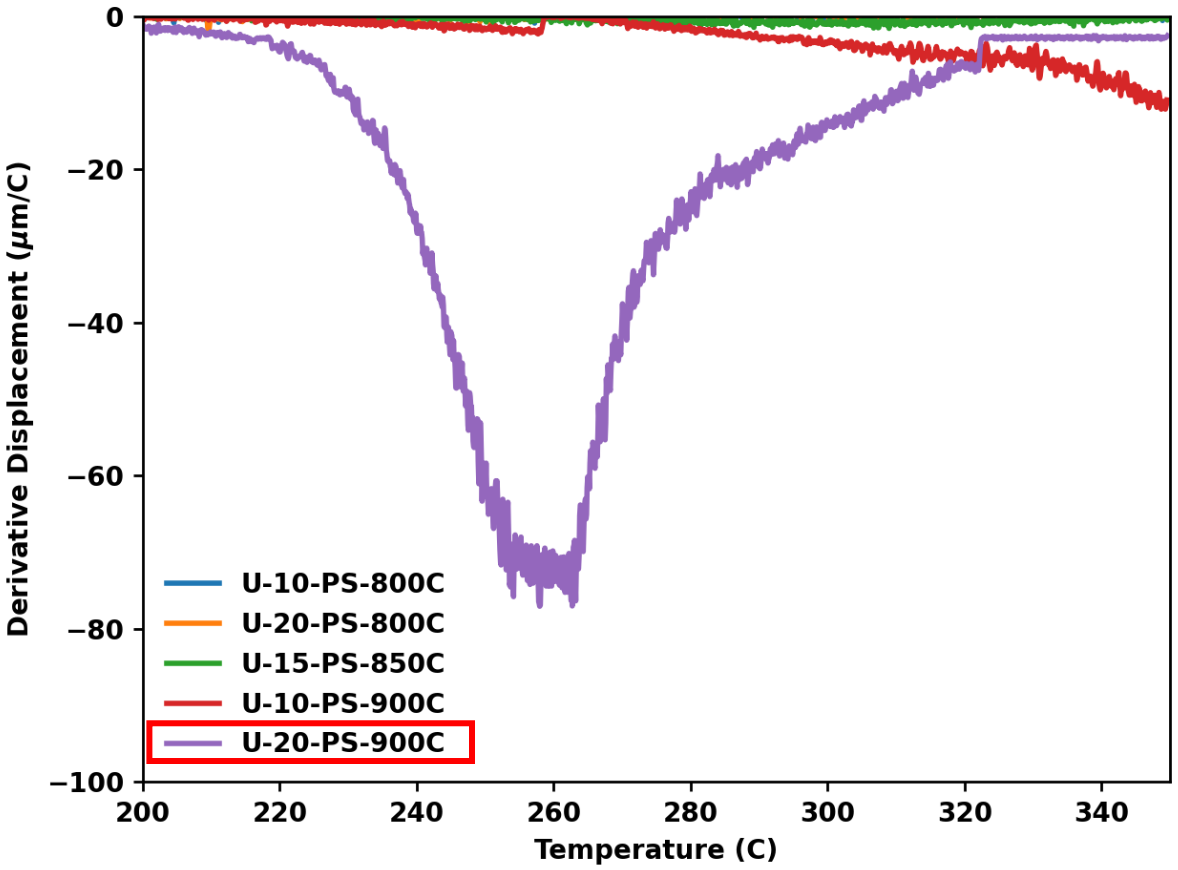
Pyrolysis: Pitch Softening Point T_{sp}*



Varying LLDPE Addition & SGR Reaction Temp



Varying Polystyrene (PS) Addition & SGR Reaction Temp

*as measured by Dynamic Mechanical Analysis (DMA)

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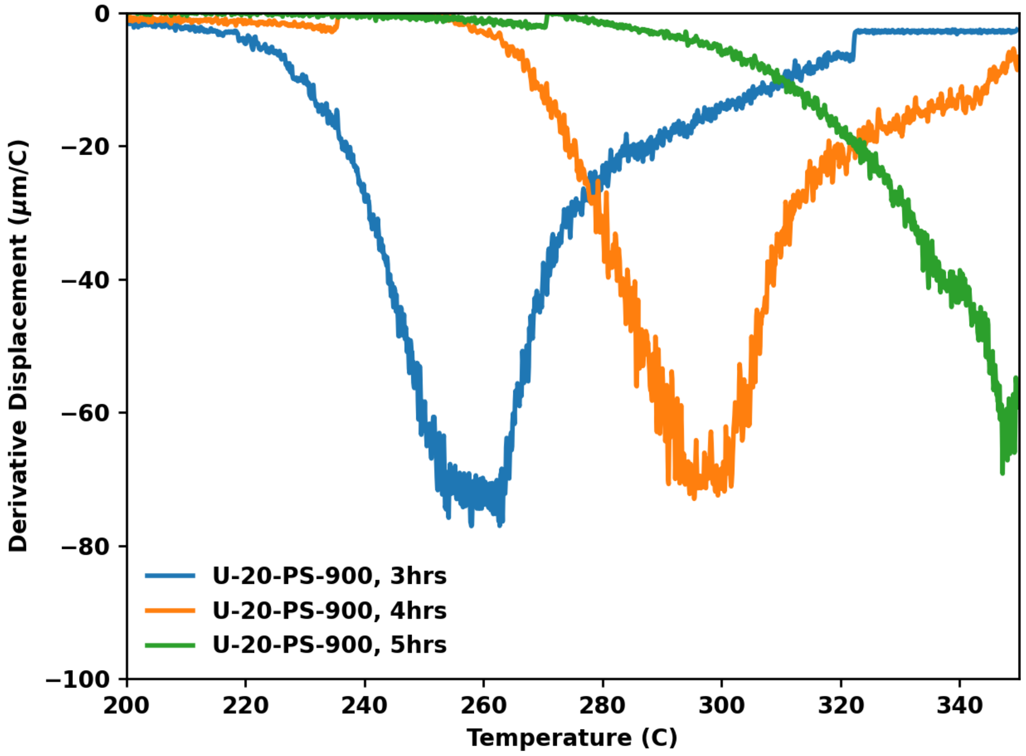
Pyrolysis: Effect of Increasing Thermal Treatment Time with 20% PS Addition



Sample	T_{SP} (^{0}C)	Mesophase %	Raw OTI	Weighted OTI
U-20-PS-900, 3 hour	257	37.2	28.8	10.71
U-20-PS-900, 4 hour	296	50.9	30.9	15.73
U-20-PS-900, 5 hour	347	71.9	35.3	25.38

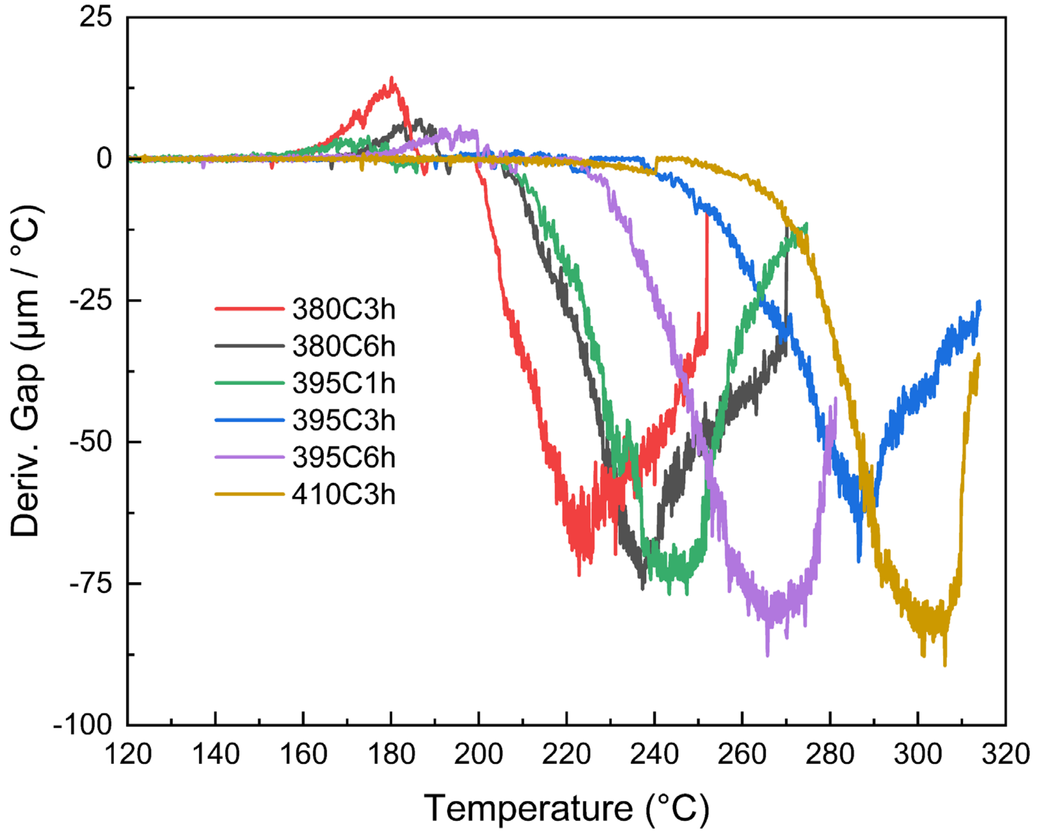
For melt-spinning mesophase pitch into carbon fiber, it is ideal to have softening point < 350^{o}C and mesophase content between 70-80%*.

*Y. Yao et al., "Tailoring structures and properties of mesophase pitch-based carbon fibers based on isotropic/mesophase incompatible blends", *Journal of Materials Science*, 2012, 47, 5509-16

Solvolysis: Results from Using Polyolefin Liquid to Replace Tetralin (THN) Solvent

Coal	Solvent	Anisotropy (%)
UT	THN	75.4
UT	HDPE	79.9
UT	LDPE	75.7
IL	THN	8.2
IL	HDPE	29.9
IL	LDPE	37.8

Production of anisotropic material (mesophase) with use of plastic-derived solvents vs tetralin



Softening Point results for Utah coal with HDPE at different pitch heat treatment temperatures and reaction times

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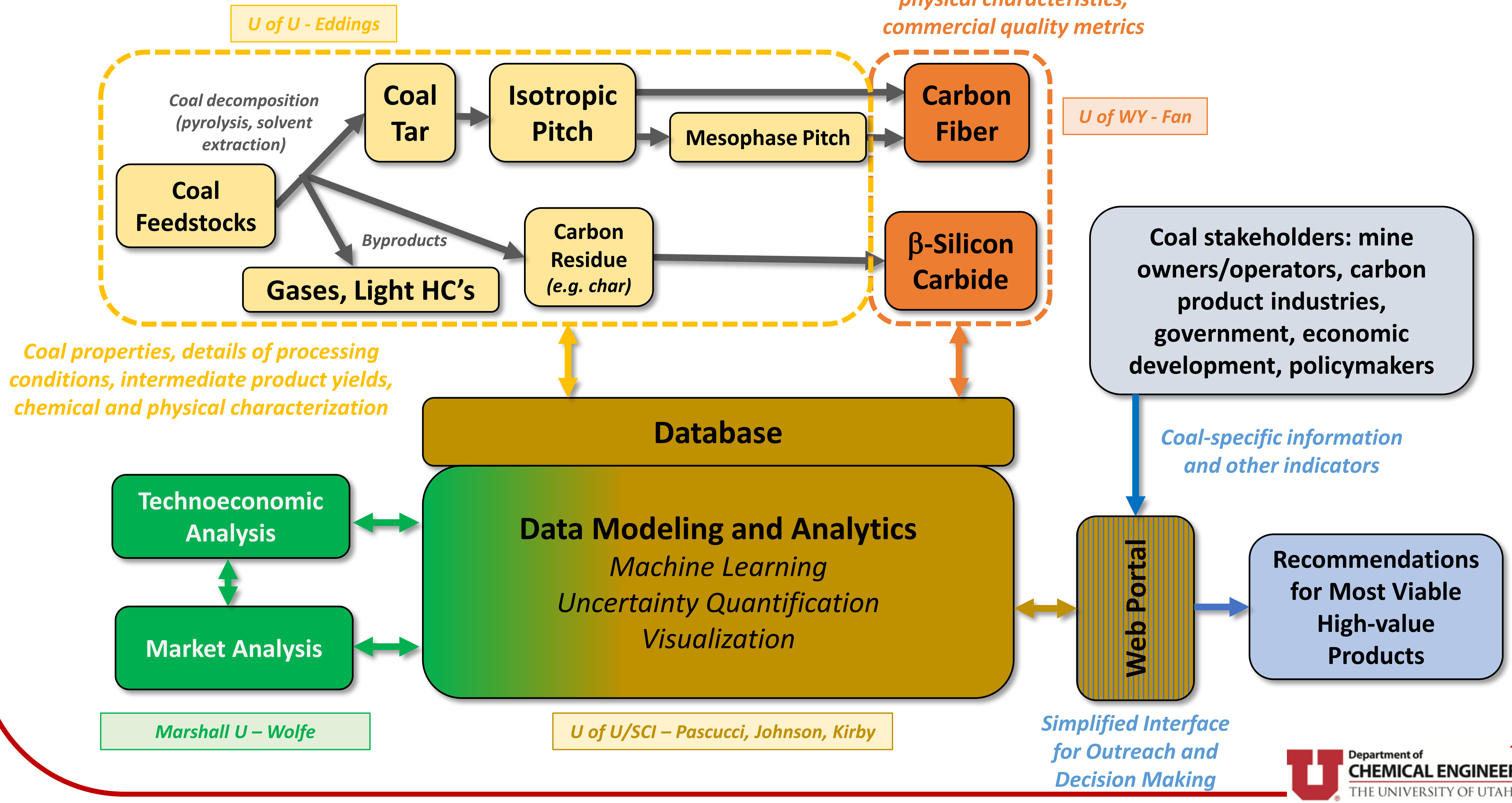
Comments on Co-processing Coal with Waste Plastics

- Pyrolysis: Co-processing with LLDPE and Polystyrene (PS)
  - Use of LLDPE was not effective in reducing pitch softening point to acceptable levels
  - Use of PS at the right conditions yielded acceptable softening points and mesophase levels for carbon fiber spinning
- Solvolysis: Co-processing with HDPE and LDPE
  - Generated good pitch intermediates with acceptable softening points
  - Softening point T and Mesophase % can be readily adjusted with thermal treatment conditions
  - Provided similar yields to use of tetralin solvent

Project Overview



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Project Overview

Product yield, chemical and physical characteristics, commercial quality metrics

Carbon Fiber

β-Silicon Carbide

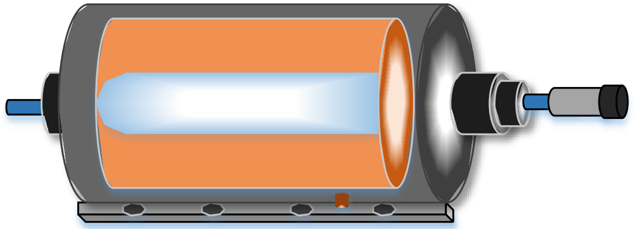
U of WY - Fan

High purity SiC from carbon fiber production residual and a sandstone

Treated residue powder

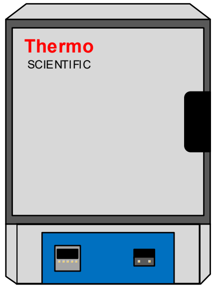
Treated sandstone powder

Mixture

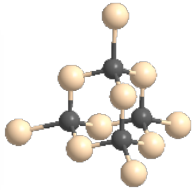


High temperature furnace

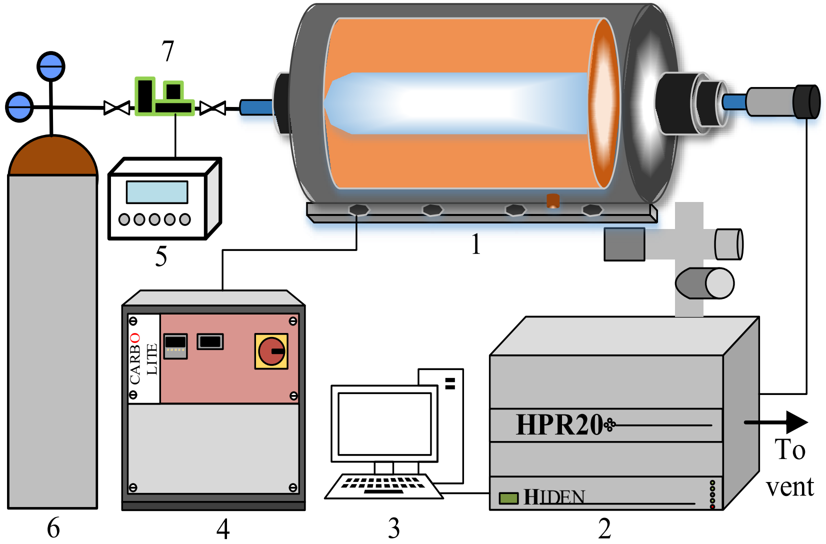
Solid product: remove excess carbon



Box furnace
850 °C, 6 h, Air

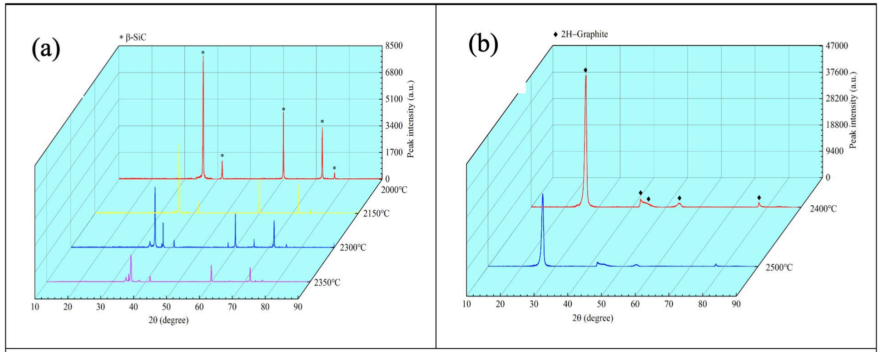


Beta-Silicon carbide (β-SiC)



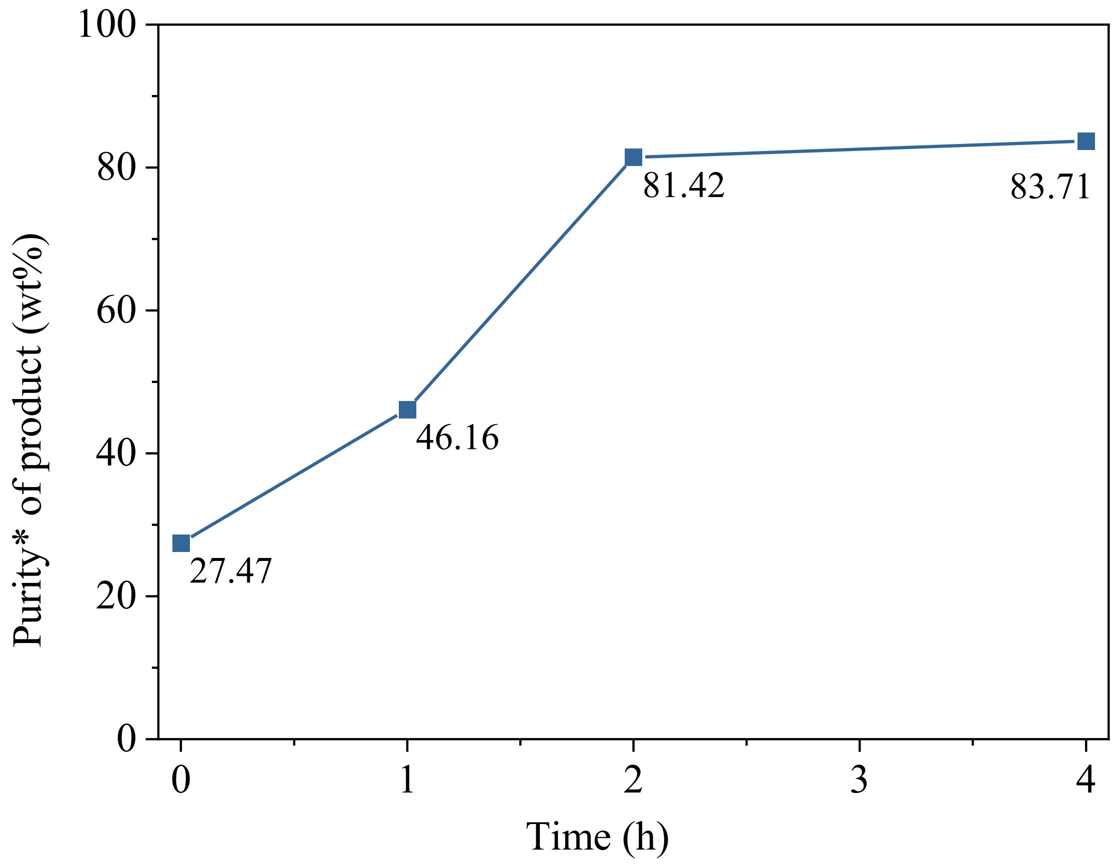
Reaction conditions
Reaction temperature: 1,300-1,600 °C
Holding time: 1-3 h
Atmosphere: Argon 50 ml/min
Pressure: Atmospheric pressure

Schematic diagram of experimental set-up for synthesis of β-SiC. [(1) high-temperature horizontal tube furnace, (2) mass spectrometer, (3) computer, (4) temperature controller, (5) Argon cylinder, (6) mass flow controller, (7) mass flow controller power supply/control module]

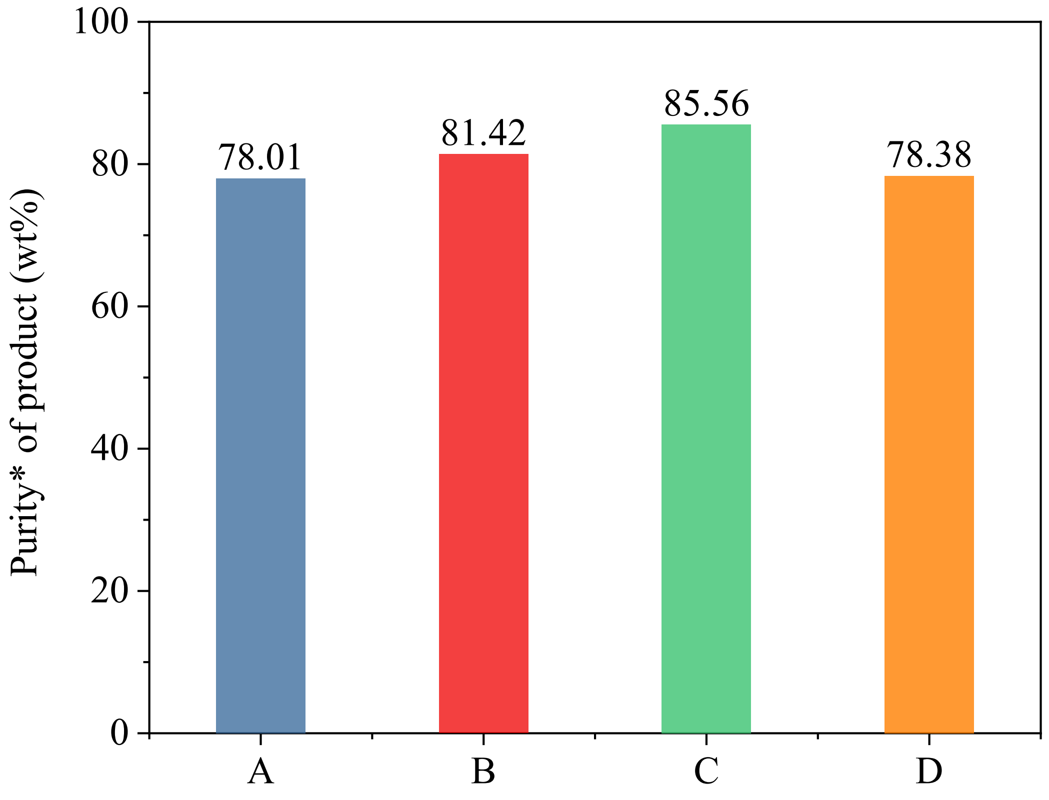


XRD pattern of products synthesized with PRB coal extraction residual and sandstone powder at different temperatures (α-SiC structure change with temperature).

SiC Production Results



SiC purity as a function of reaction time at 1600 °C

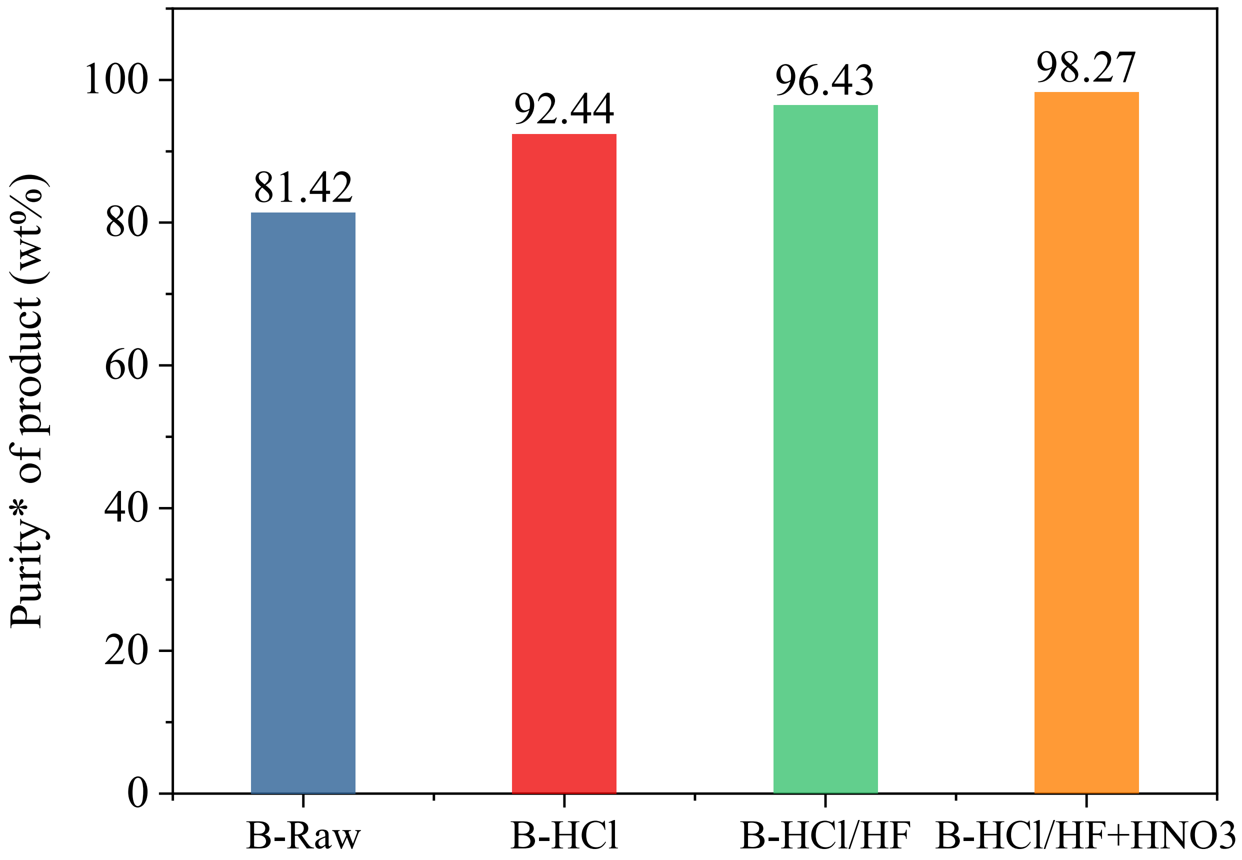


SiC purity as a function of coal type at 1600 °C and 2 hrs

A – Illinois char
B – Utah char
C – WV char
D – WY PRB char

For 50 wt% coal char mixed with sandstone

SiC Production Results



B-Raw: without acid-treatment
B-HCl: 10% HCl treated Utah coal char
B-HCl/HF: 10%HCl treated Utah coal char following 10%HF treatment
B-HCl/HF+HNO3: 10%HCl treated Utah coal char following 10% HF/4% HNO3 treatment

SiC purity as a function of acid treatment method of char for metallic element removal (e.g., Na, Ca, Fe, and Al)

For 50 wt% coal char mixed with sandstone

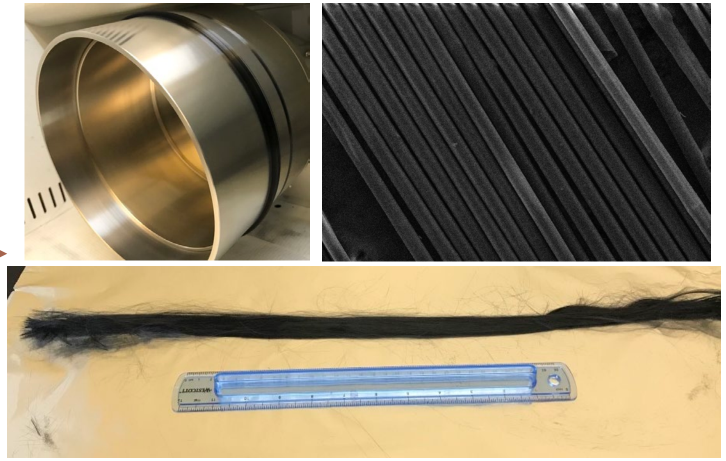
Carbon Fiber Production

From University of Utah

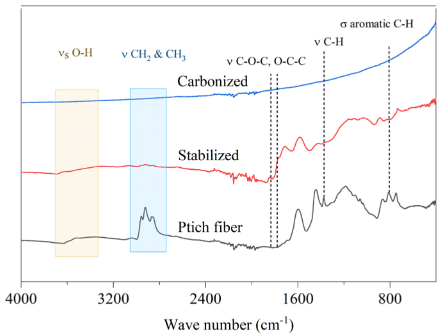
Isotropic & Mesophase Pitch

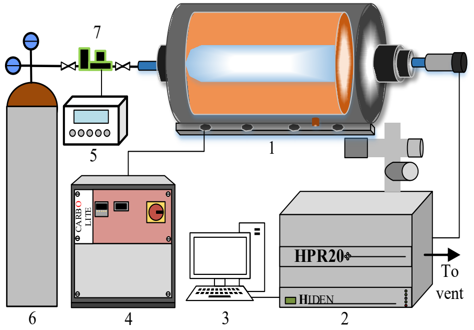
Melt-spinning Apparatus

The average diameter of fresh fiber is ~25.76 um.



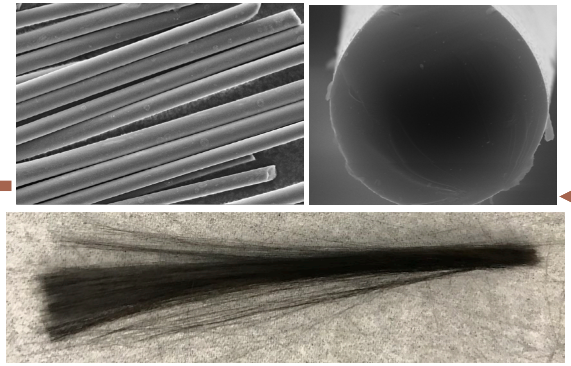
Fresh Fiber Filaments





Stabilization & Carbonization

The average diameter of carbon fiber is ~19.54 um.

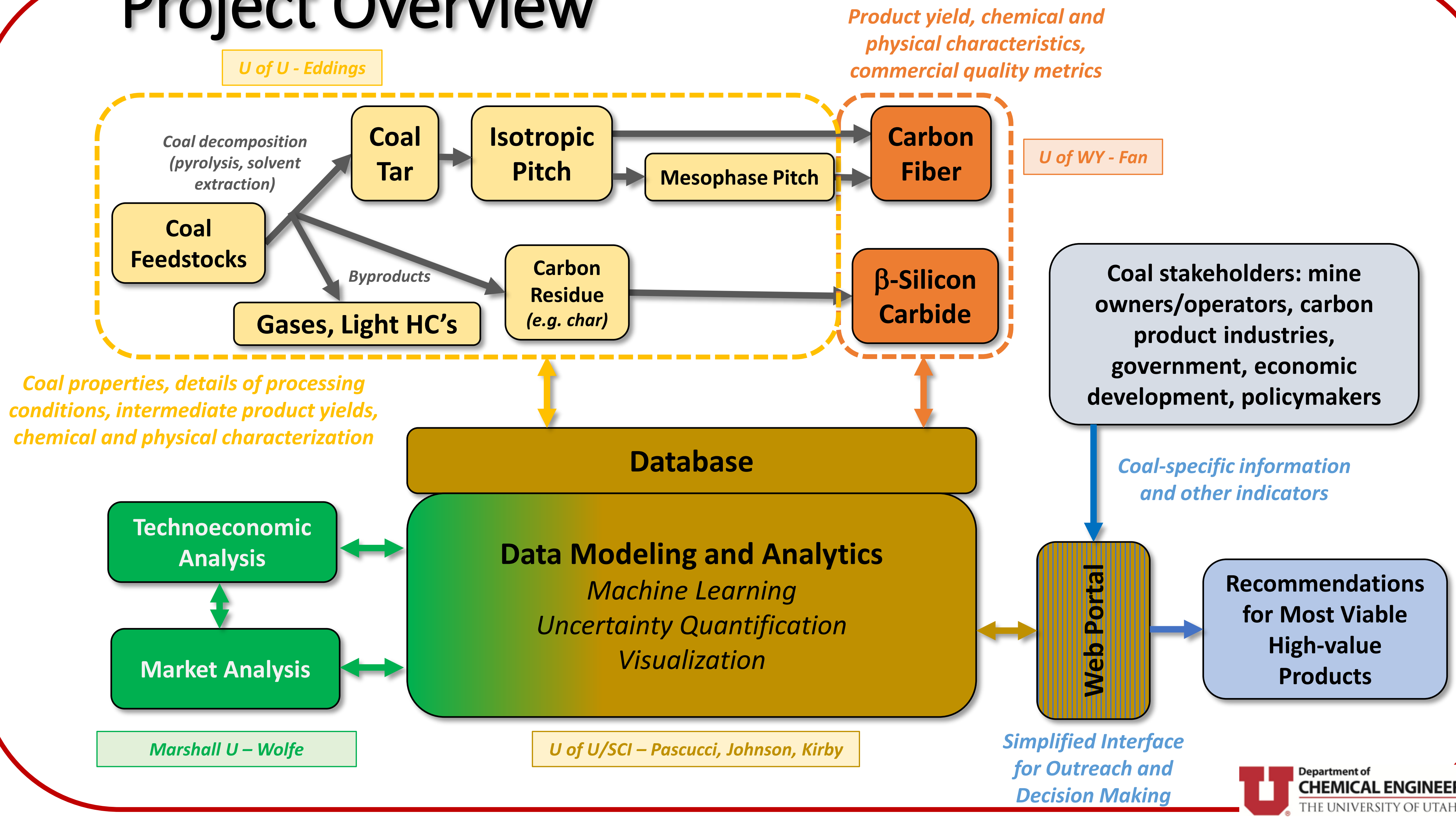


Carbon Fiber Product

Product Evaluation

Feedback on Processing

Project Overview



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Project Overview

Technoeconomic Analysis

Market Analysis

Marshall U – Wolfe

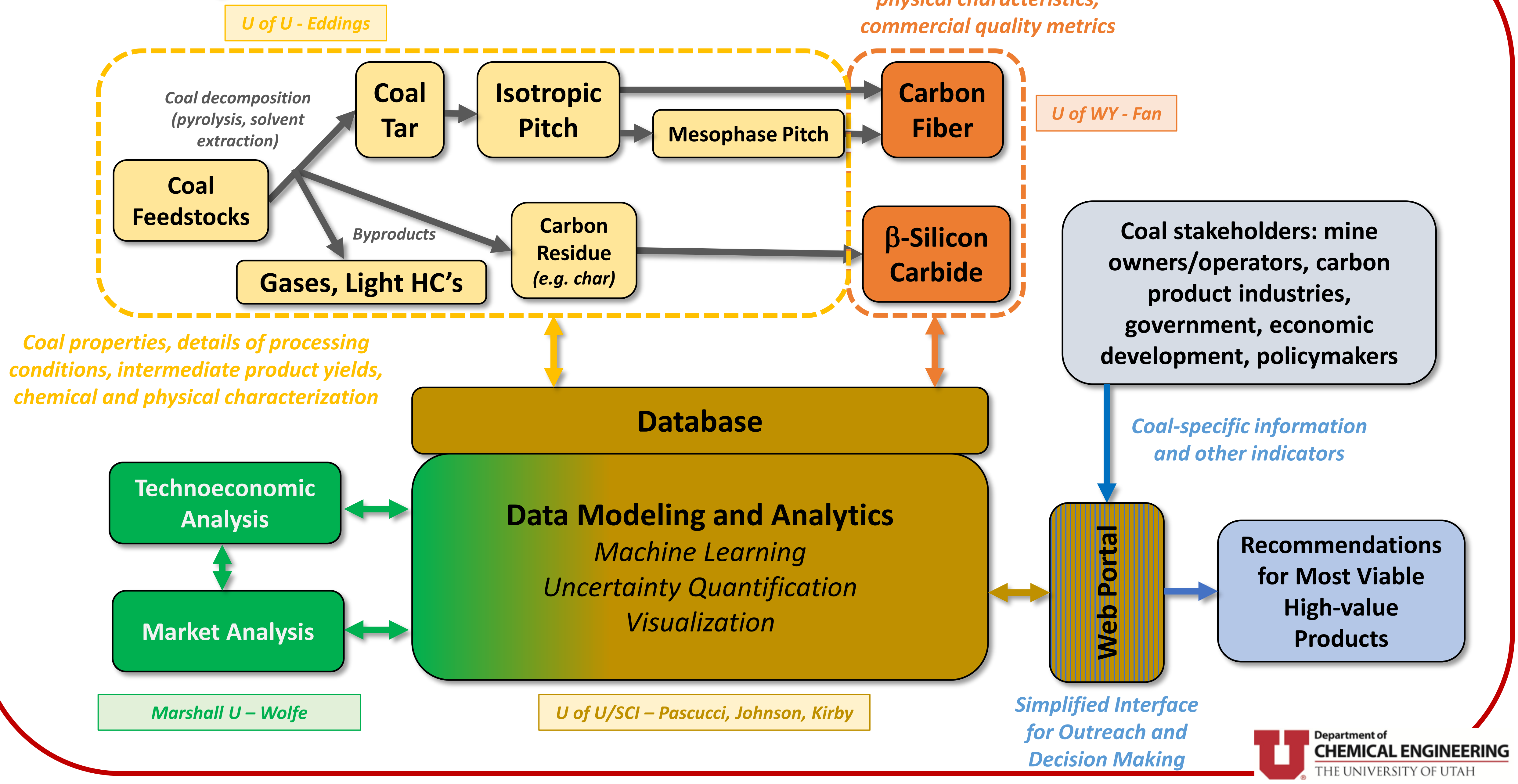
Technoeconomic Analysis

- Identify a suite of possible final and intermediate products suited to the coal conversion process, focusing on carbon fiber and precursor material (but not limited to those products)
- Identify metrics of the coal conversion process, by stages of production, that are indicators of commercial potential
- Connect key stages of production with cost targets that represent commercial viability
- Connect physical properties of regional coals to various products, based on prospects for material conversion

Market Analysis

- Track material sourcing developments in industries that can use coal-based carbon fiber products
- Provide product suitability information to coal operators and owners of coal reserves in various coal-producing regions
- Evaluate workforce needs for a future manufacturing industry based on these materials
- Identify potential production sites for manufacturing facilities

Project Overview



Project Overview

Database

Data Modeling and Analytics

Machine Learning

Uncertainty Quantification

Visualization

Web Portal

U of U/SCI – Pascucci, Johnson, Kirby

Simplified Interface for Outreach and Decision Making

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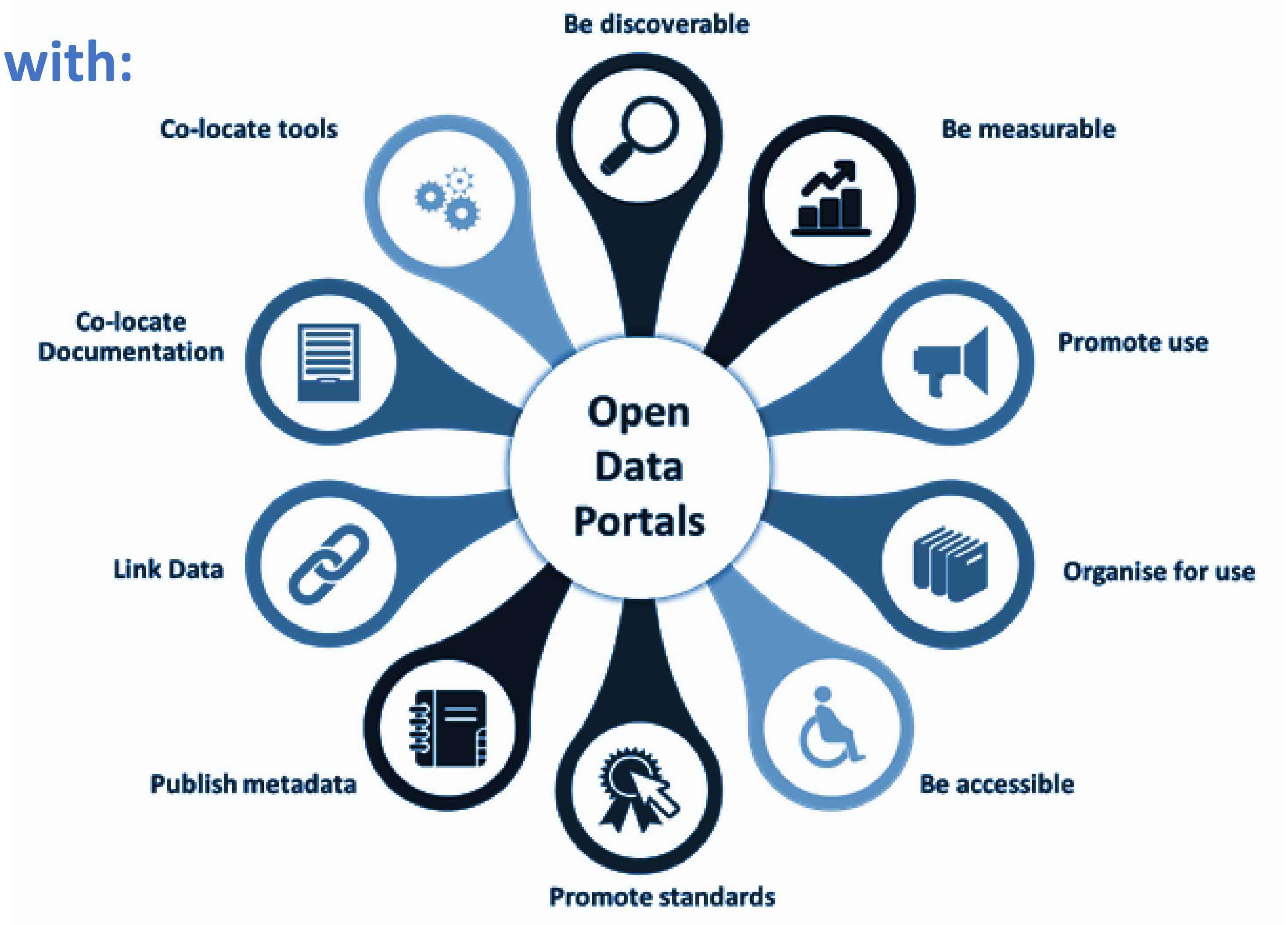
CoalToFiber Data Portal - Goals

- **Major goal**: **build a data portal with:**
  - Remote access
  - Distributed analysis
  - Interactive visualization and exploration
  - Web-based access
  - Shared data access
    - Utah users
    - other institutions
    - Guest/unregistered users
  - Advance query capabilities
  - Real time collaboration



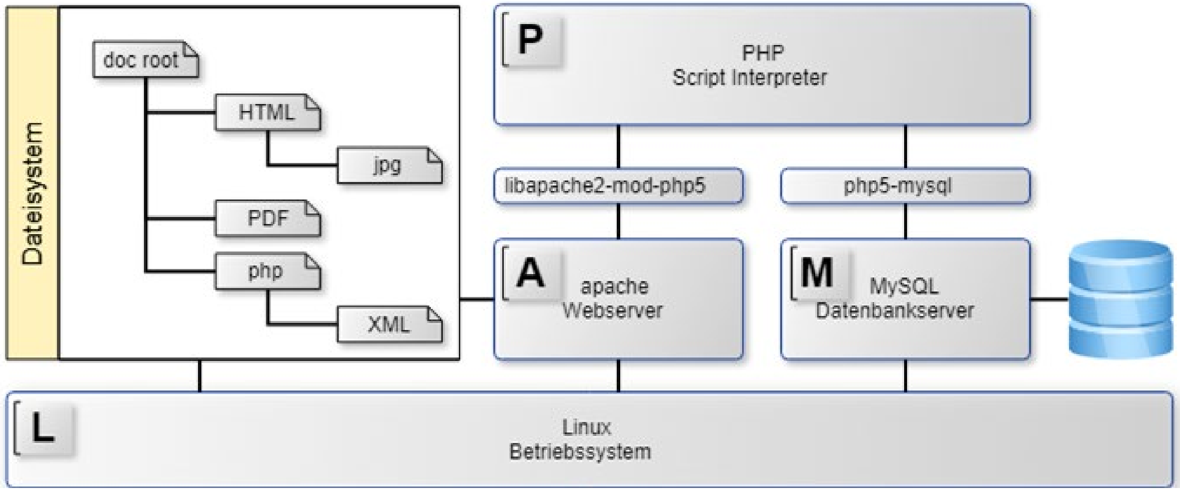
CoalToFiber - MCRDP

Deploy a *Modern Community Research Data Portal* (***MCRDP***) based on Material Commons (MC) 2.0 framework

- MIT - very liberal license
- Fantastic assistance from MC group
- We may need to customize it

Components (i.e. LAMP stack):

- **Front end** i.e., Laravel Apache Web Server PHP
- **Back end** i.e., MariaDB or MySQL SQL database
- RESTful **API** network services for programmability
- Command Line Interfaces (**CLI**) tools
- **Python** packages and Jupyter notebooks



LAMP software stack (Linux, Apache, MySQL, PHP)

Machine Learning Analysis

Overview

Coal → Tar → Pitch datasets

- Pyrolysis experiments
- Solvolysis experiments

Part 1. Output Optimization

- Given this material and these specific conditions, what is the highest mesophase content?
- Outputs of interest: mesophase content, pitch yield, softening point, QI

Part 2: Process Optimization

- Given this material, what process (temperature/reaction condition/reaction time/etc.) will produce the highest mesophase content?

Concluding Comments

- Have identified bench-scale conditions for producing highly anisotropic material from coking and non-coking U.S. coals
  - Evaluated both thermal (pyrolysis) and chemical (solvolysis) means for initial decomposition of coals
    - *Substantially higher pitch yields were obtained using solvolysis approach*
  - Identified methods and conditions for modifying pitch properties to avoid formation of semi-coke, by using waste plastic materials
  - Solvolysis system is being scaled-up 10x from 100 ml reactor to 1 liter to provide higher quantities of pitch for carbon fiber spinning
- Successfully produced β-SiC from chars derived from several U.S. coals
  - Identified optimal conditions to maximize yields and purity
- Establishing proof-of-concept database and analysis framework
  - Database is using Materials Commons platform
  - Includes machine learning models, uncertainty quantification and economic assessments
  - Can be expanded to include broader range of coal products and coals

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Questions?

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