Sub-pilot Scale Production of Carbon Fiber from Coal

U.S. Department of Energy Award Number DE- FE0031880

June 1, 2020 – May 31, 2022

Department of Chemical Engineering

Scientific Computing and Imaging Institute

University of Utah

School of Energy Resources

University of Wyoming

Center for Environmental, Geotechnical and Applied Science

Center for Business and Economic Research

Marshall University

Project Objectives

- *Produce carbon fiber derived from coal tar pitch*
  - Will include coals from multiple coal-producing regions
  - Scale-up lab-scale R&D of coal-tar pitch production
- *Produce* high-value *Silicon Carbide (β-SiC) byproduct*
  - using carbon residue material (e.g., char) from carbon fiber production
- *Develop extensive 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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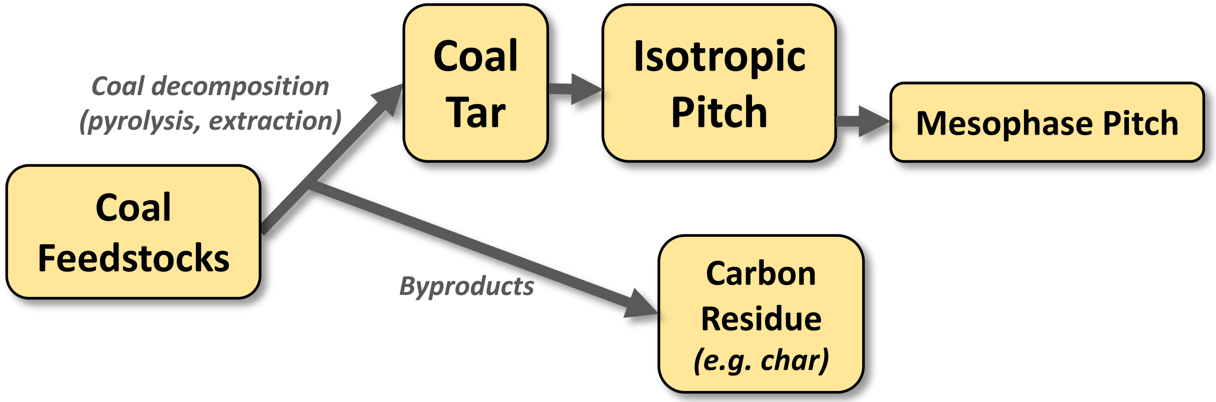

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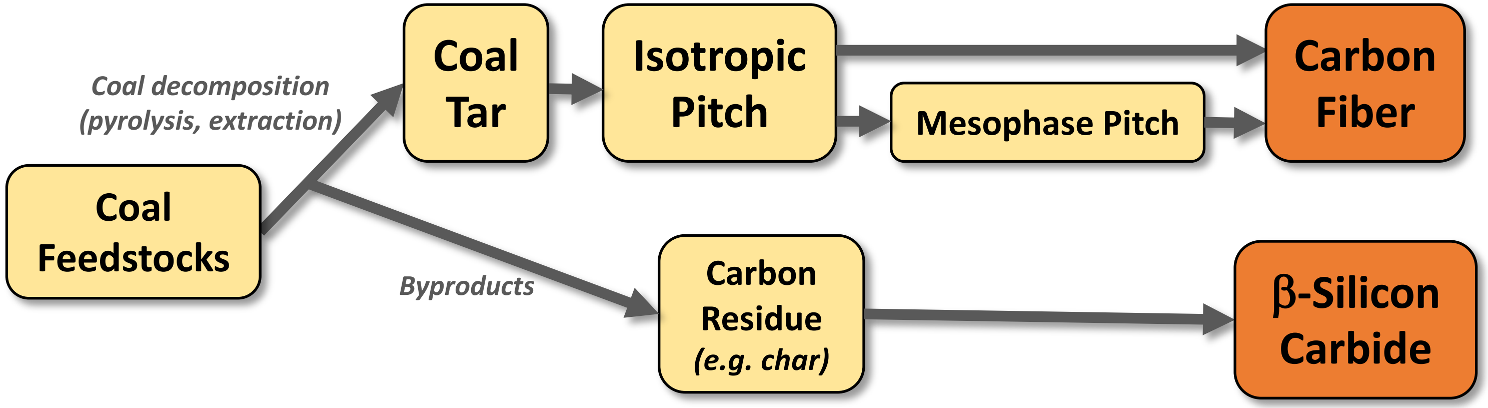

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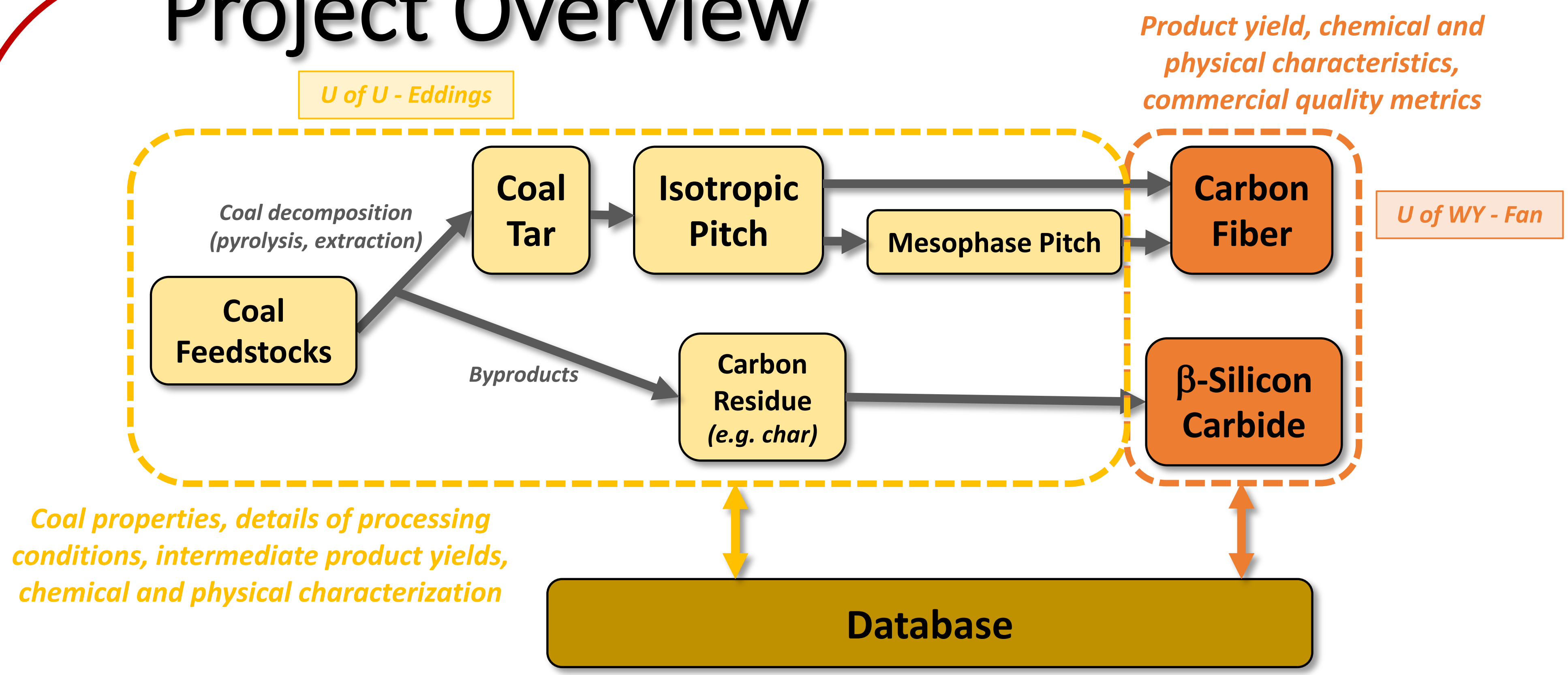

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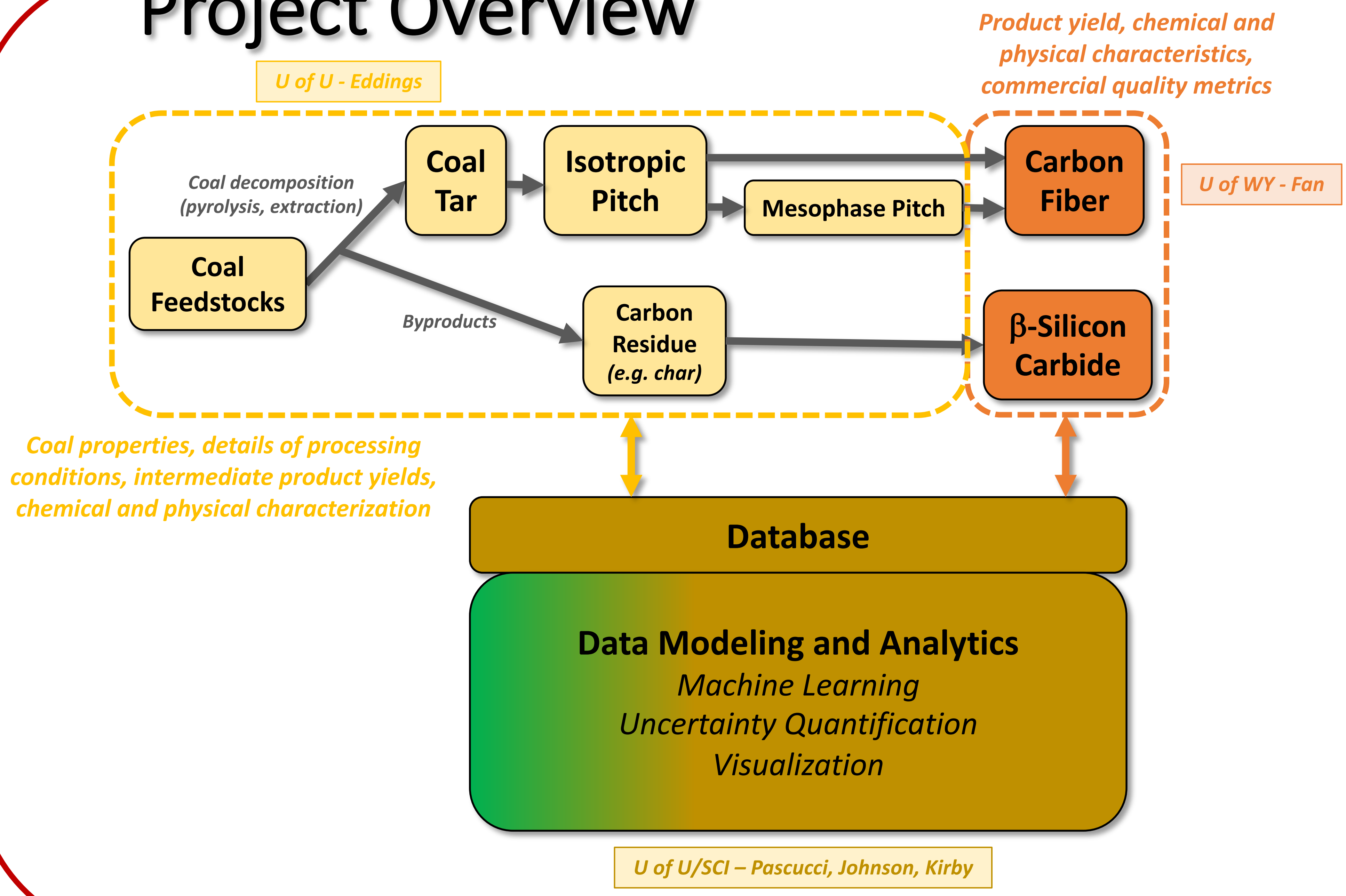

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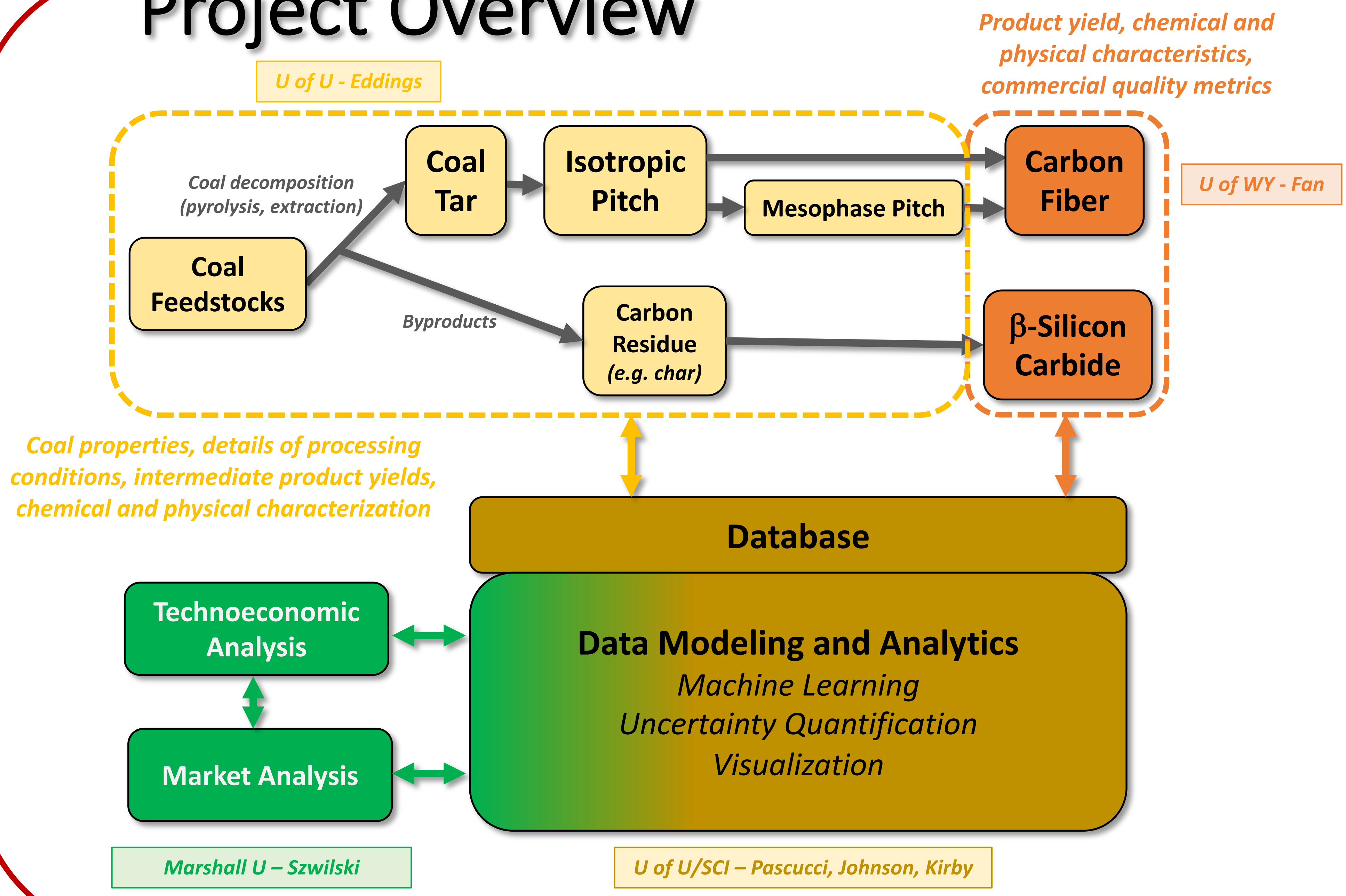

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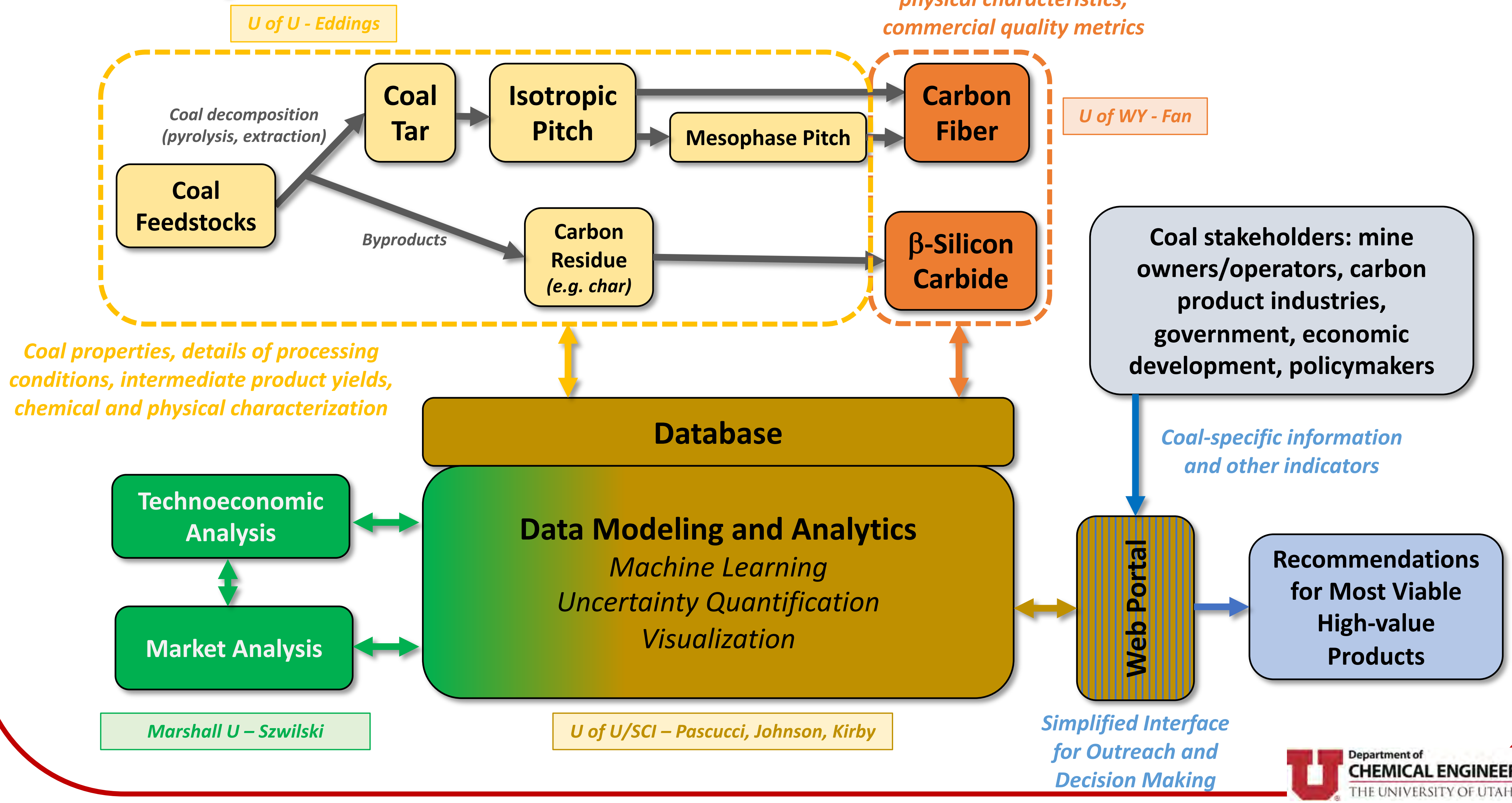

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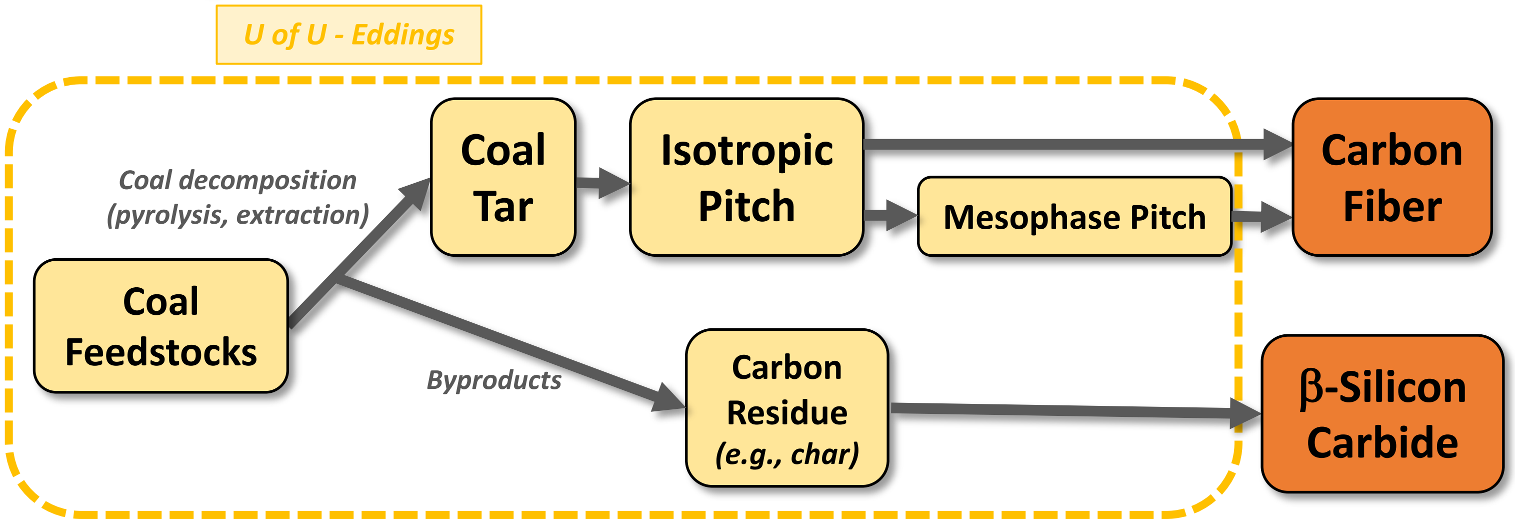

Three main focus areas:

I. Production of mesophase pitch via pyrolysis

II. Production of mesophase pitch via solvent extraction

III. Scale-up of bench-scale mesophase production

I. Production of Mesophase Pitch from Coal via Pyrolysis (Thermal Processing)

- Coal pyrolysis steps for tar production – two-stage process
  - Primary pyrolysis
  - Secondary pyrolysis (different conditions) for upgrading tar intermediates to produce higher-quality pitch product
    - Focus of current bench-scale optimization
  - Tar collection
- Tar characterization
  - FTIR, MALDI-MS, TGA, ^{1}H NMR
- Tar upgrading to produce pitch
- Pitch characterization
  - Microscopy, Optical Texture Index (OTI) determination
  - Softening point

Current Efforts

- Bench-scale pyrolysis work more mature
  - Was focus of previous grant
  - Optimizing conditions for scale-up
  - Matrix focused on exploring **secondary pyrolysis** conditions
    - Four different coals (UT, WY, IL, WV)
    - Conditions to yield highest-quality mesophase
    - Currently underway – matrix not complete
- Also developing Machine Learning models to link coal tar properties, analytical characterization, and associated operating conditions, to mesophase coal tar pitch (MCTP) quality
- Challenges:
  - Yield of heavy tar fractions is low -> yield of mesophase is low (order of a few percent)
    - Can be improved by upgrading other liquids/tars
    - Co-production of other products from the lighter liquids/tars also helps offset this

Experimental Matrix for Bench-scale Secondary Pyrolysis Studies

		Residence time (sec)			
Coal	**Temp (C)**	**0**	**1.5**	**3**	**6**
Sufco	600	X			
Sufco	600->800		X	X	X
Sufco	600->850		X	X	X
Sufco	600->900		X	X	X
PRB	600	X			
PRB	600->800		X	X	X
PRB	600->850		X	X	X
PRB	600->900		X	X	X
W Virg	600	X			
W Virg	600->800		X	X	X
W Virg	600->850		X	X	X
W Virg	600->900		X	X	X
Illinois	600	X			
Illinois	600->800		X	X	X
Illinois	600->850		X	X	X
Illinois	600->900		X	X	X

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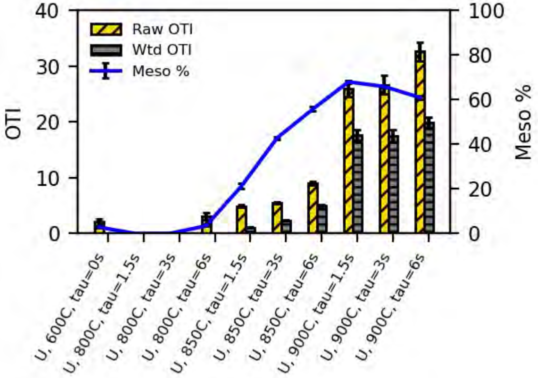
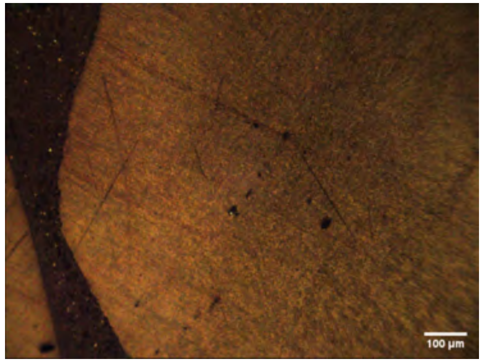
Utah Sufco MCTP





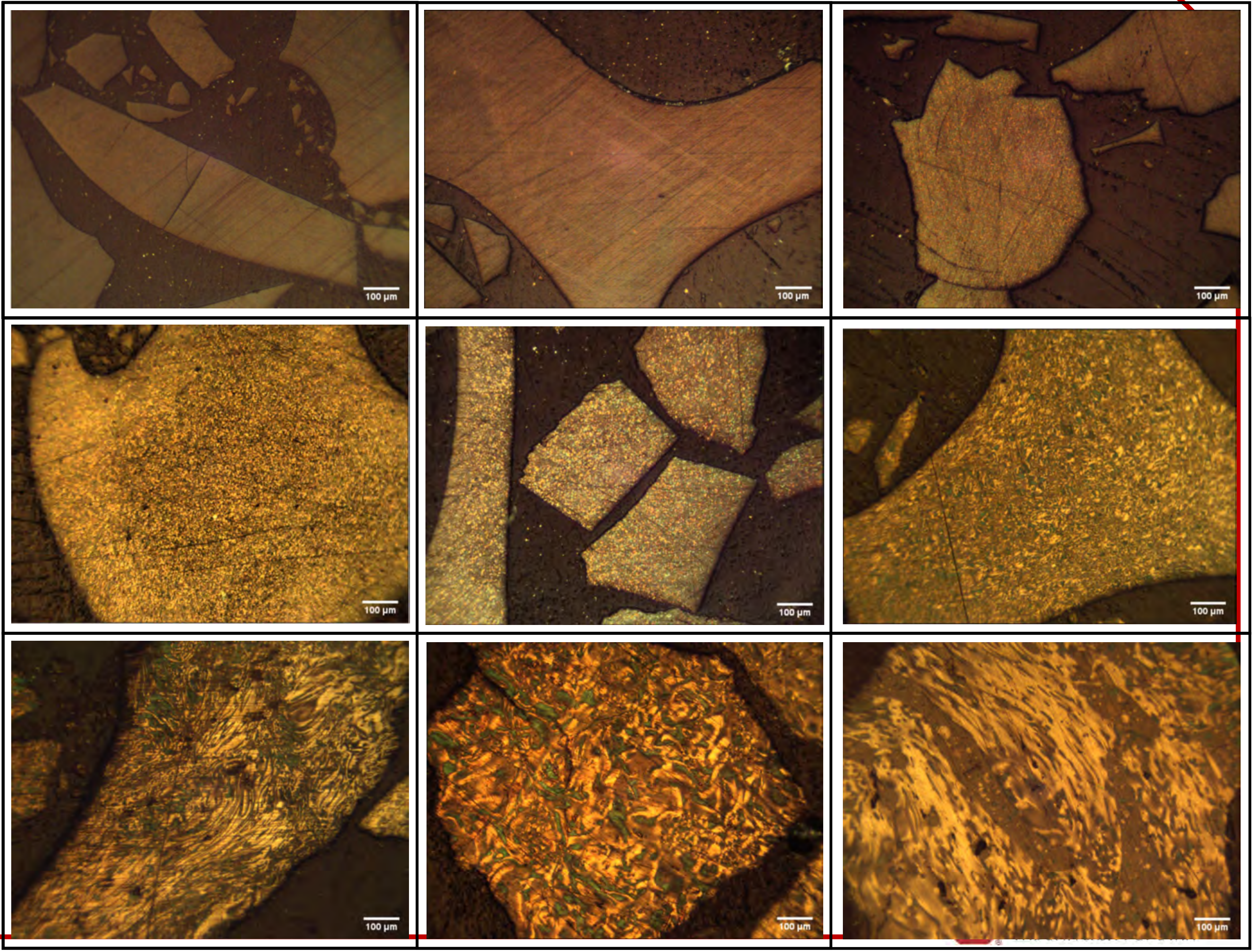
$T_1 = 600^oC$
$T_2 = 400^oC$
$\tau = 0$ sec

$\tau = 1.5$ sec | $\tau = 3$ sec | $\tau = 6$ sec

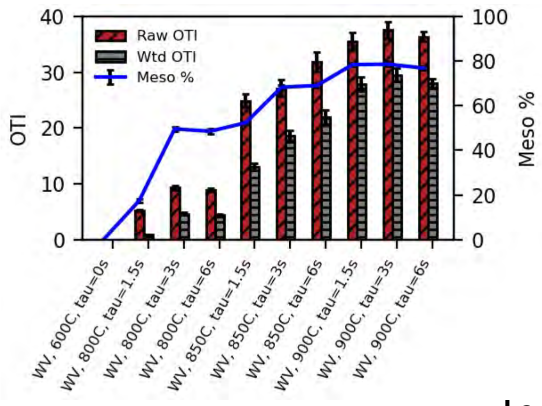
$T_2 = 800^oC$

$T_2 = 850^oC$

$T_2 = 900^oC$



West Virginia MCTP



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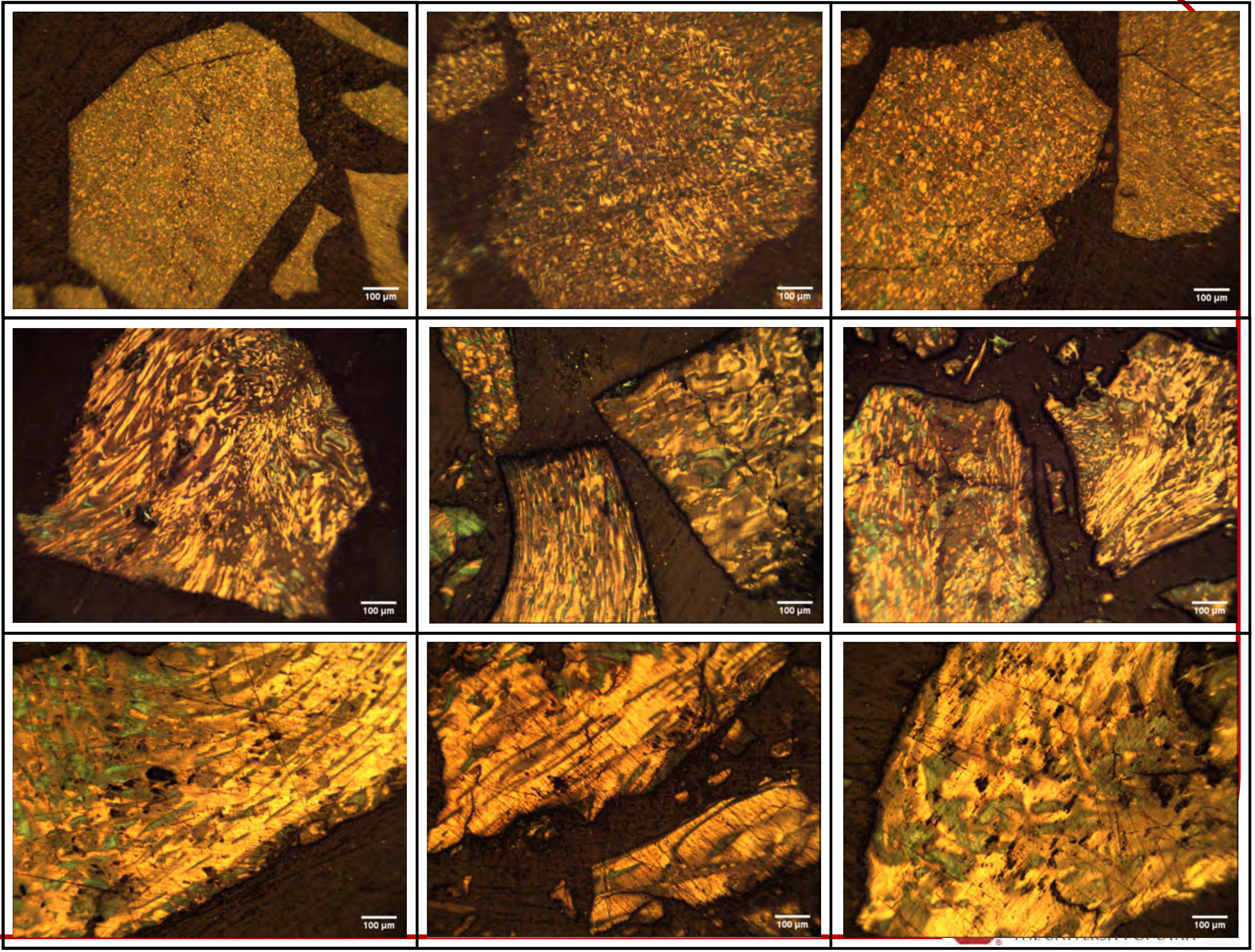
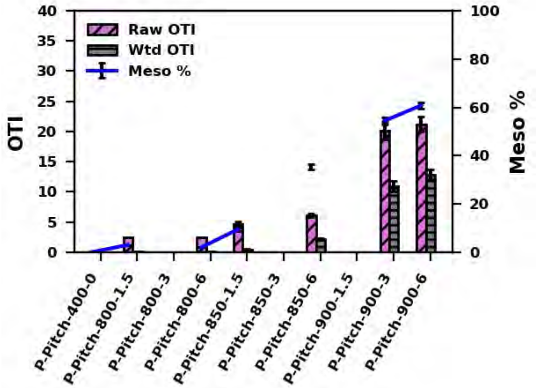


Wyoming PRB MCTP



$T_1 = 600^oC$
$T_2 = 400^oC$
τ = 0 sec

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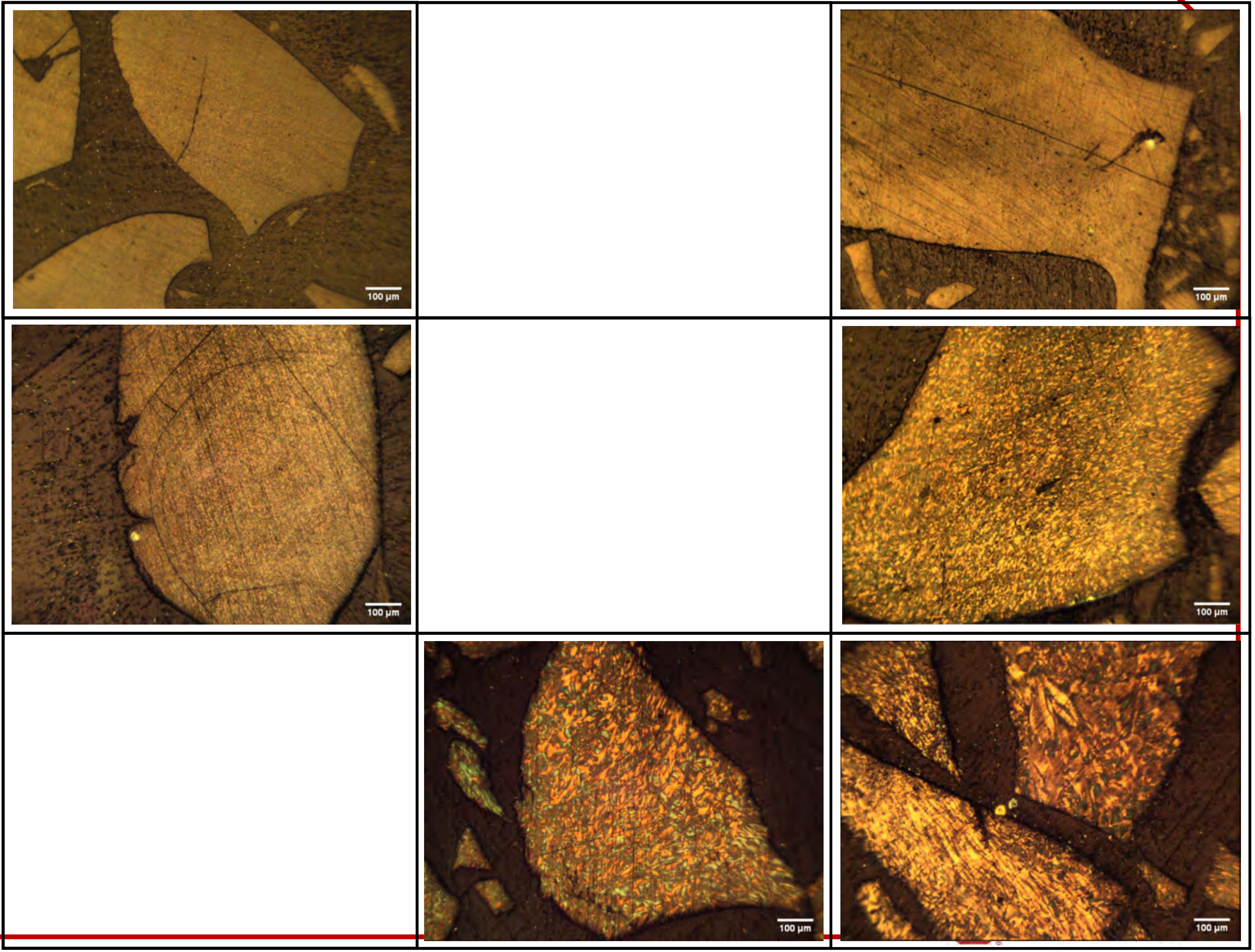
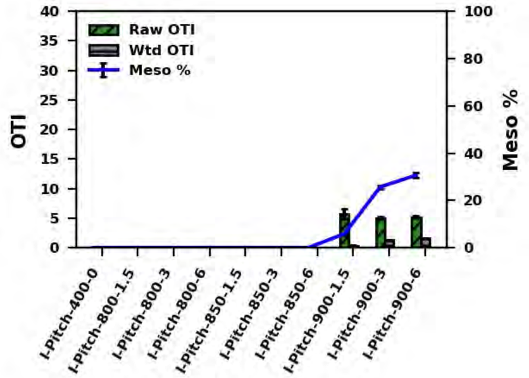
$T_2 = 900^oC$



Illinois #6 MCTP



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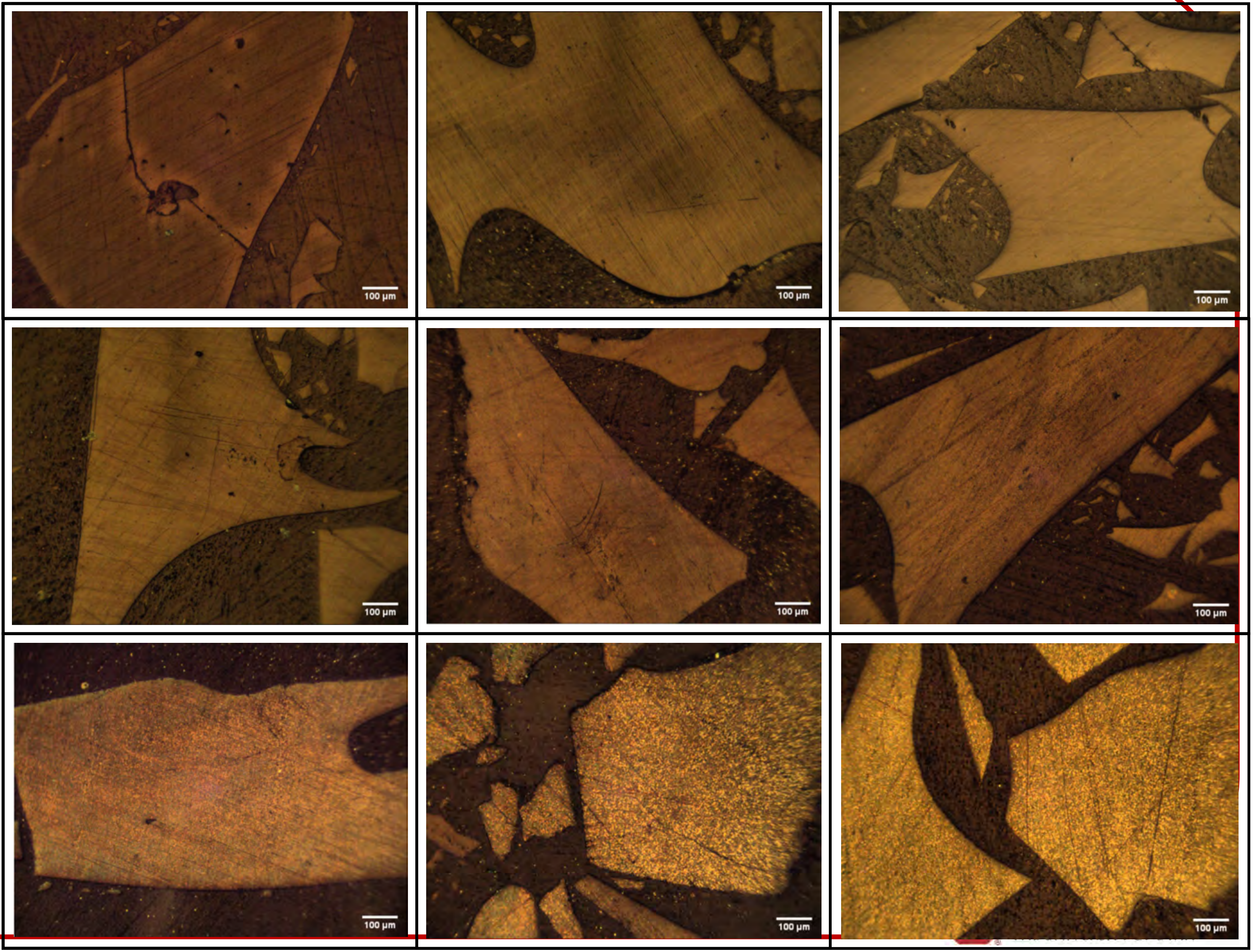

Challenges in Producing Mesophase Pitch from Low-rank Coal from Coal -> Coal Tar -> Pitch Pathway

Challenge	Approach
Low Coal to Tar Yield	• Increase coal to tar yield (other than gases or char)
Low Tar to Pitch Yield	• Provide a heavier coal tar (with more asphaltene and pre-asphaltene fractions)
Crosslinking Reactions	• In situ deoxygenation/hydrogenation of the tar (leads to less isotropic pitch)
Hydrogen Transferability of Tar	• Suppress over-coking/carbonization (semi-coke, less spinnability) • Provide enough flowability of tar @300-400 C for mesogen condensation (for larger mesophase domain size)

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II. Production of Mesophase via Solvent Extraction (Chemical Processing)

- Advantages
  - Provides for much greater yields of tars and important mesophase precursors
  - Utilizes in-situ hydrogenation
- Disadvantages
  - High-pressure operation
  - Uses hydrogen gas
  - Uses chemical solvents that need to be separated/recovered
- Our bench-scale work on solvent extraction is more recent, so more effort is required to identify optimized conditions for scale-up

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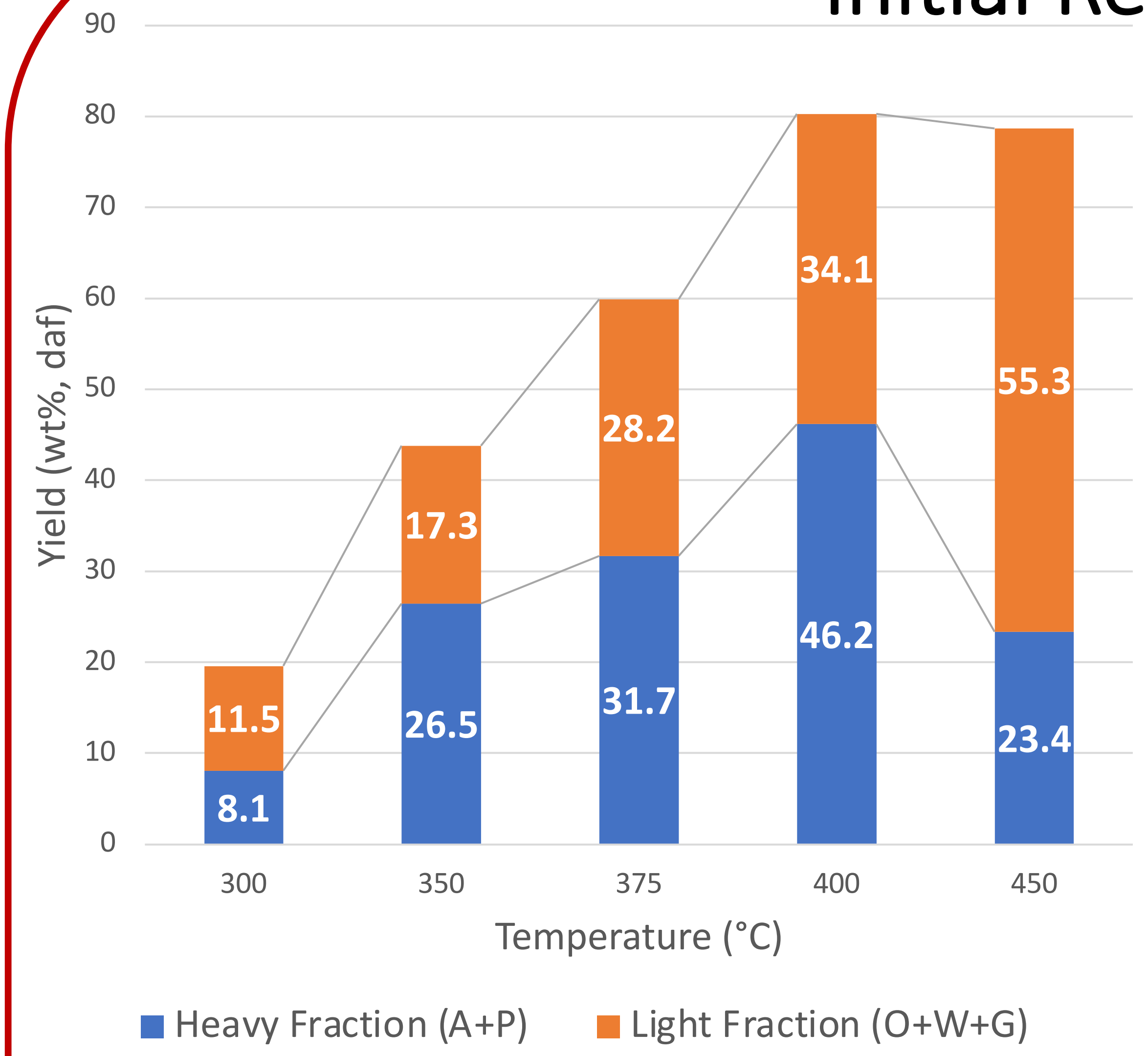
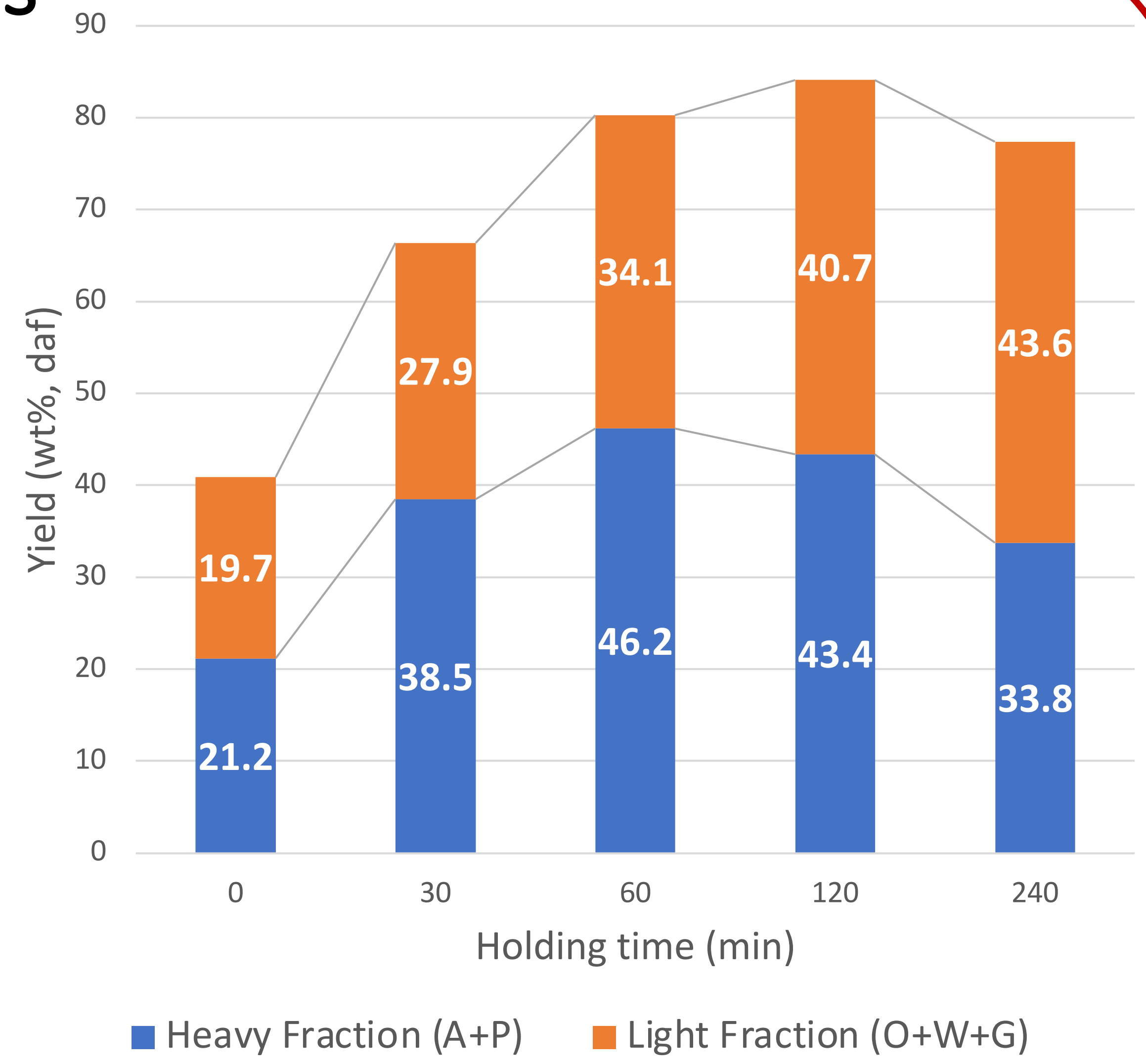
Initial Results

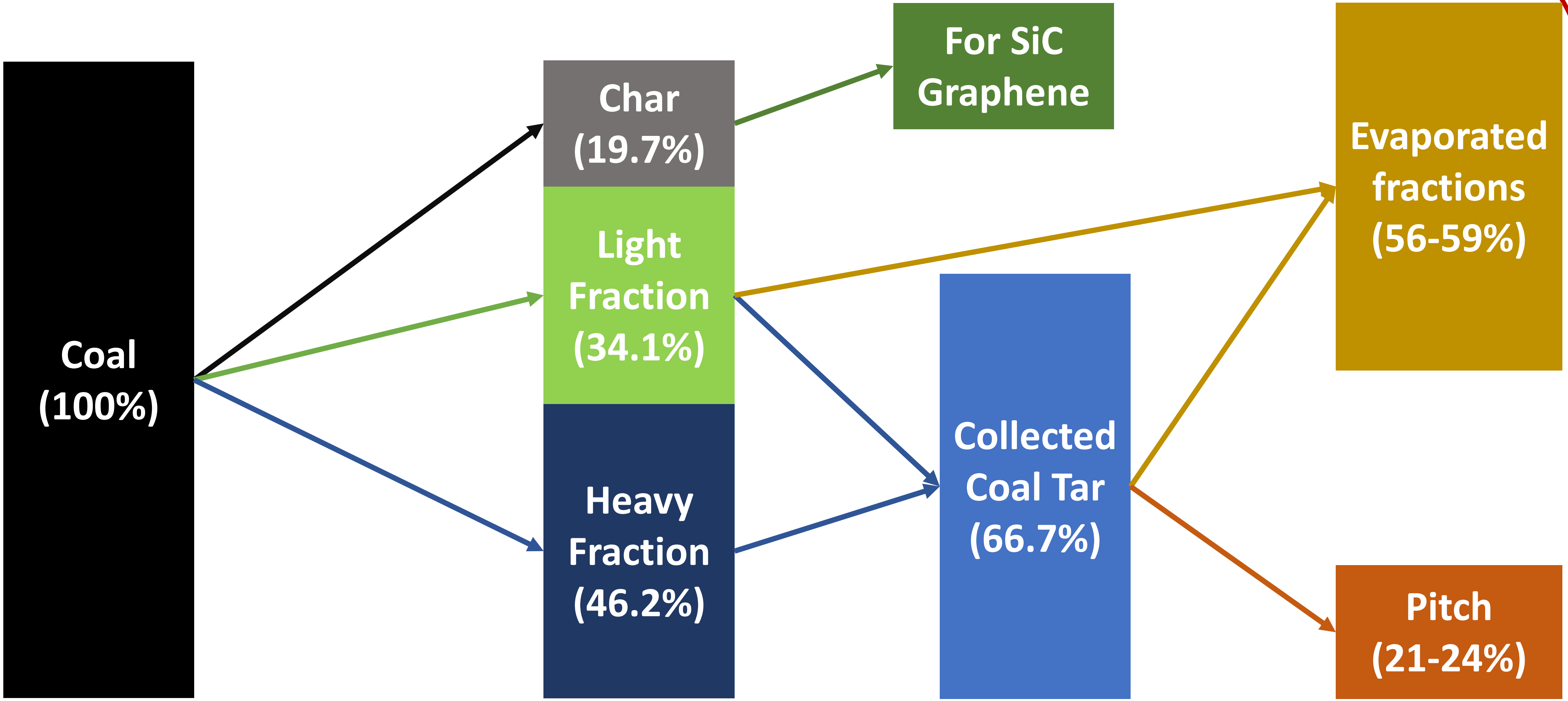


Effect of temperature on the conversion yield and product distribution of solvolysis extraction of Utah Sufco coal @ 60 min under 4 MPa of H_2



Effect of holding time on the conversion yield and product distribution of solvolysis extraction of Utah Sufco coal @ 400 °C and 4 MPa of H_2

Mass Flow from Utah Sufco Coal to Coal Tar Pitch Intermediates via Solvent Extraction



Note: Percentages based on the daf mass of coal and neglected the H_2 consumption less than 2% of coal

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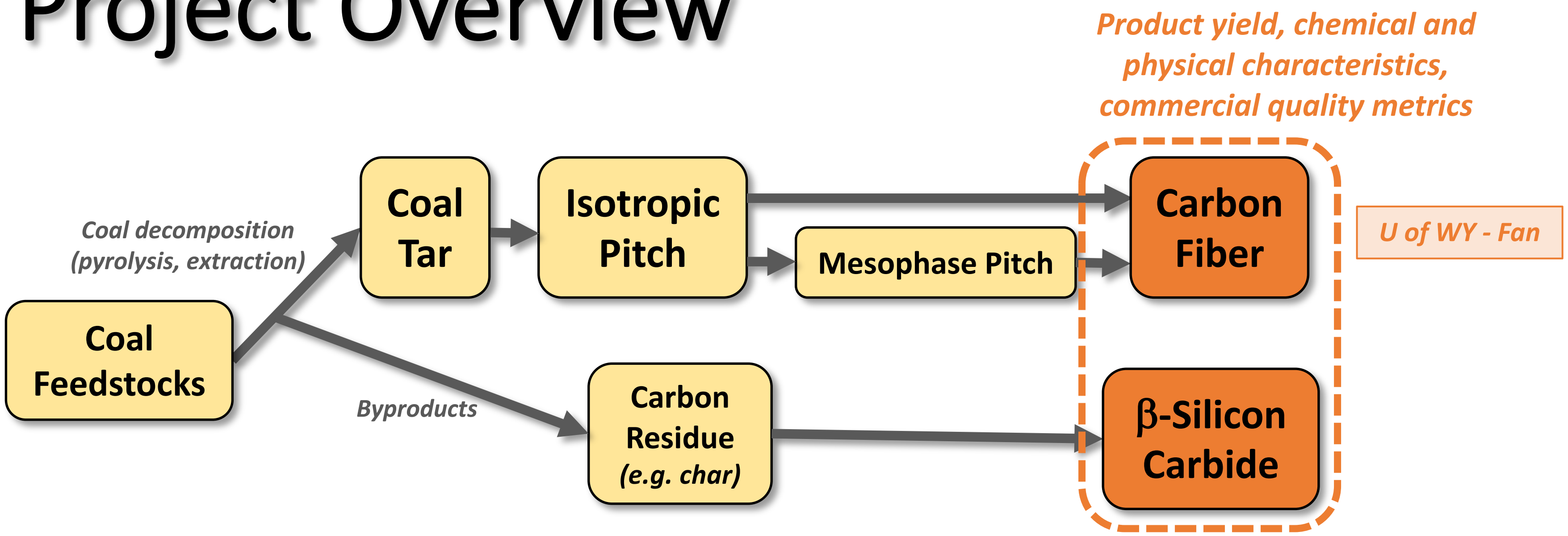

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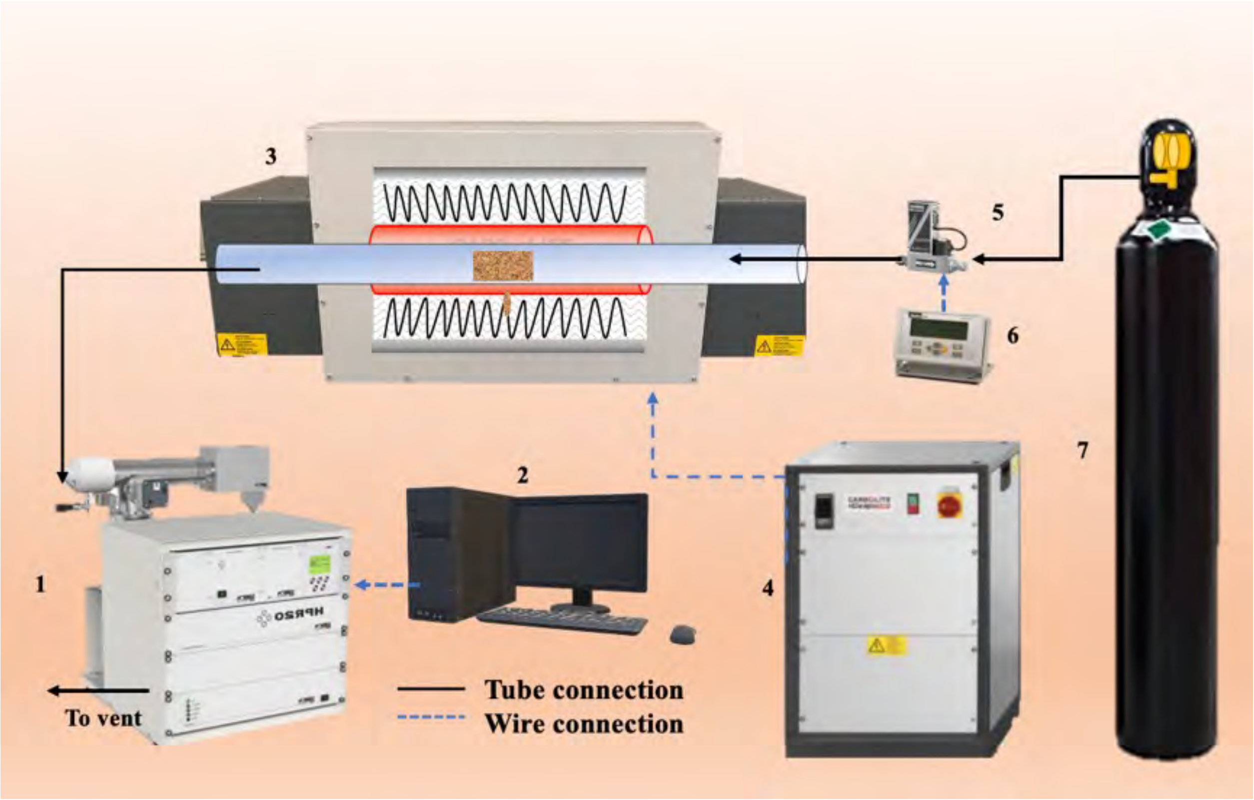
Subtask 2.4 – Production of silicon carbide byproduct from coal

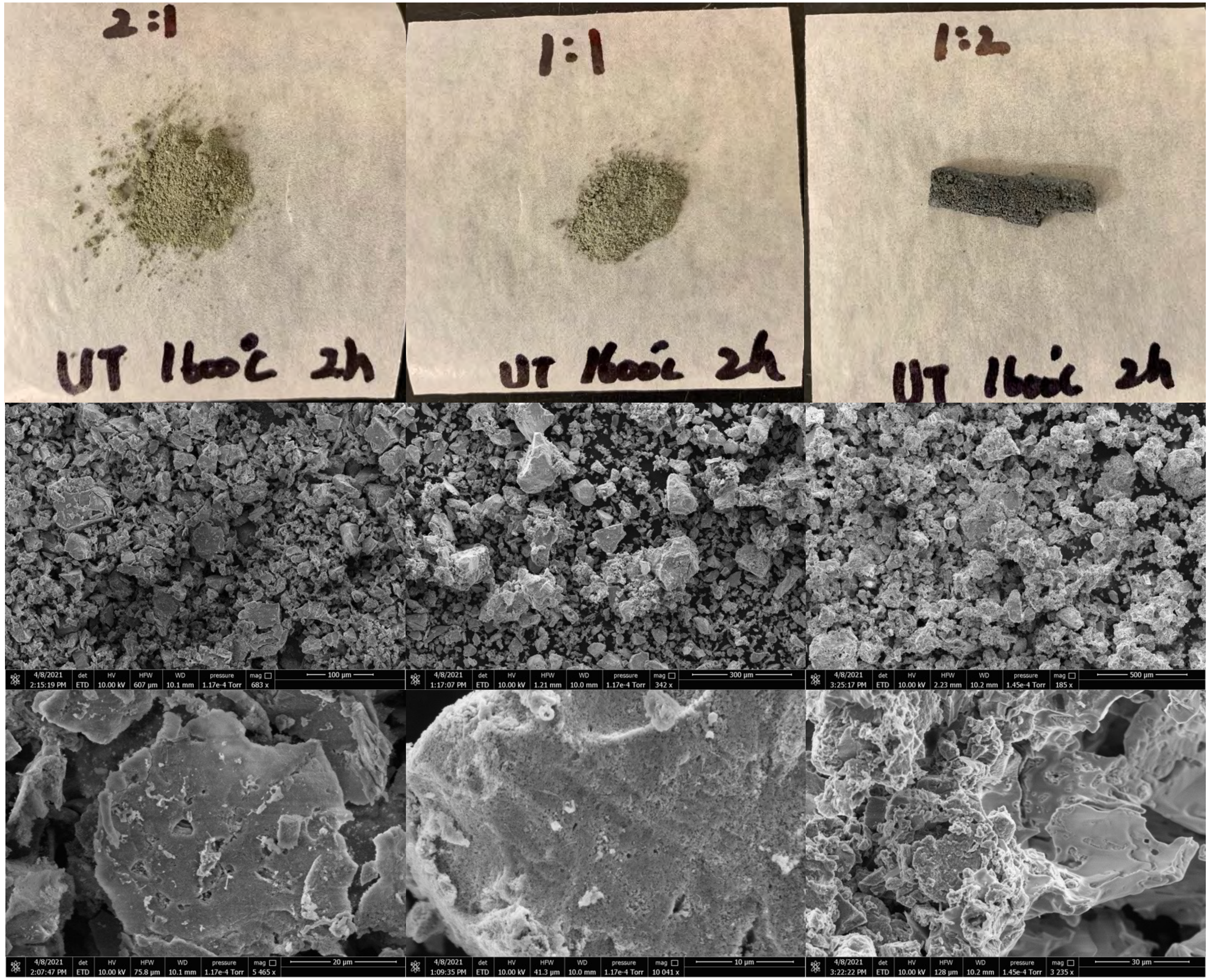
- The ***pretreated char*** and ***sandstone powder*** are combined and then carbonized in a **suitable temperature range** with **varying residence times** under **different atmospheres** to synthesize silicon carbide (SiC).



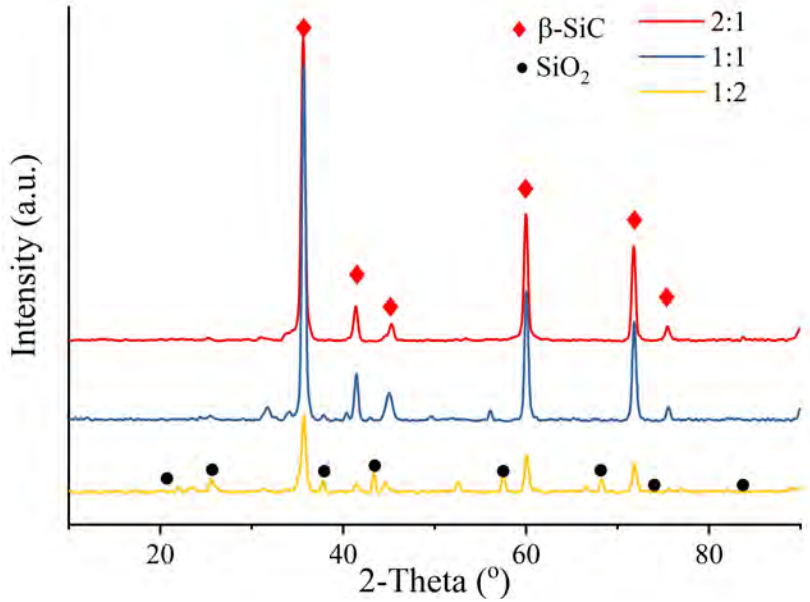
Schematic diagram of experimental set-up for synthesis of silicon carbide. [(1) mass spectrometer, (2) computer, (3) high-temperature horizontal tube furnace, (4) temperature controller, (5) mass flow controller (6) mass flow controller power supply/control module, (7) Argon cylinder]

1. Raw materials: coal chars from IL, UT, WV and WY coals, and sandstone powder.
2. Product: SiC (beta-SiC)
3. Reaction conditions:
   1) Ratio of coal char to sandstone (2:1, 1:1, 1:2)
   2) Temperature (from 1200 to 1600 ^{o}C)
   3) Holding time (0 to 4 hr)
4. Quantitative indicators: yield, purity
5. Major characterization: XRD, Raman, SEM, BET

Effect of ratio of UT coal chars and sand

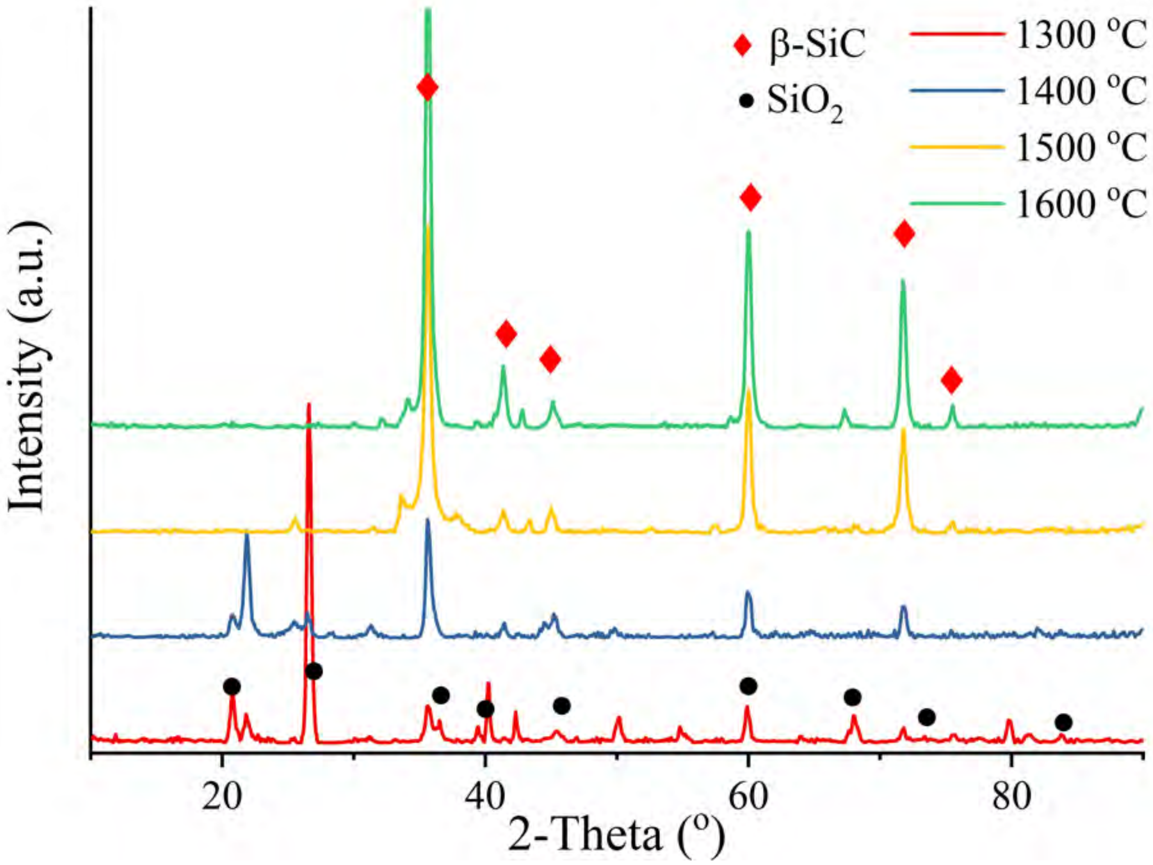


SEM images of product from UT coal chars and sandstone with different ratios

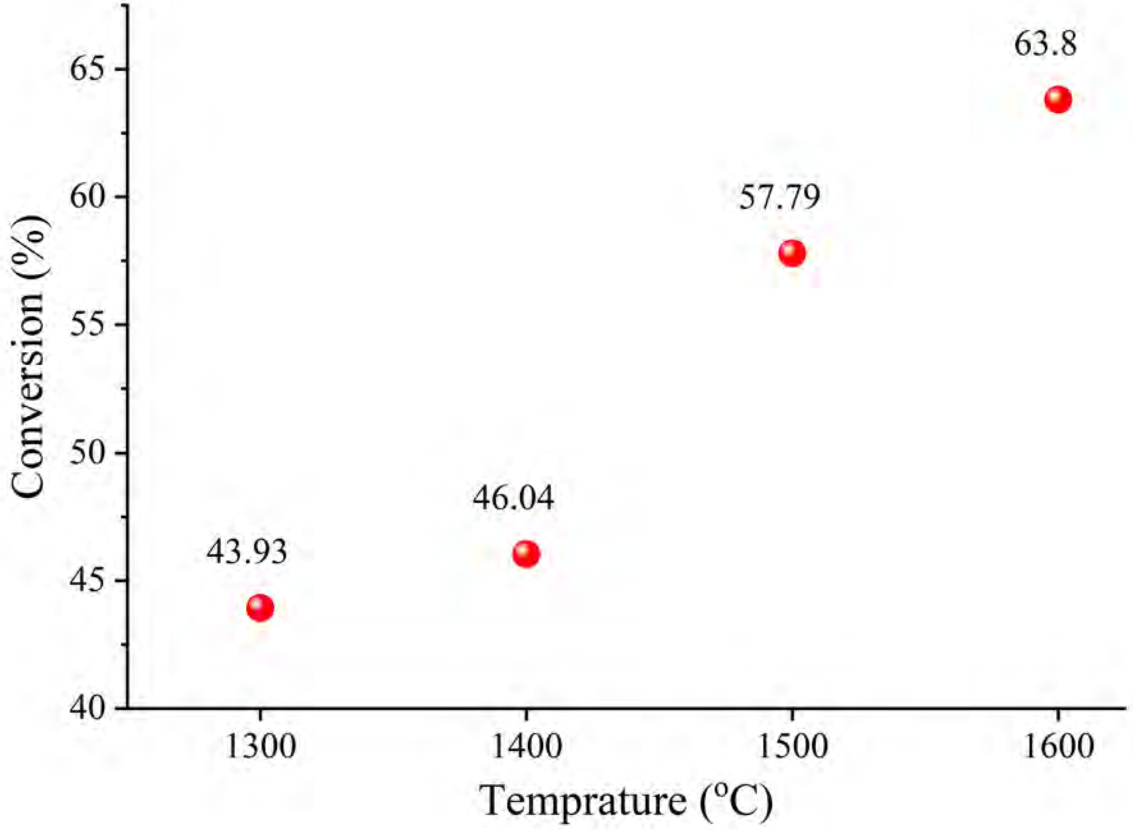


1. Reaction conditions: 1600 °C , 2hr, in Ar gas atmosphere
2. SiC product shows the green color that is characteristic of beta-SiC.
3. When the SiC ratio is 1:2, the product sticks together and forms a whole piece.
4. The SiC peak in 1:2 sample is very weak.
5. The ratio of 1:1 is a reasonable reaction ratio.
6. The yields of 2:1, 1:1 and 1:2 are 29.13%, 36.20% and 46.46%.

Effect of temperature on the SiC synthesis from UT coal char



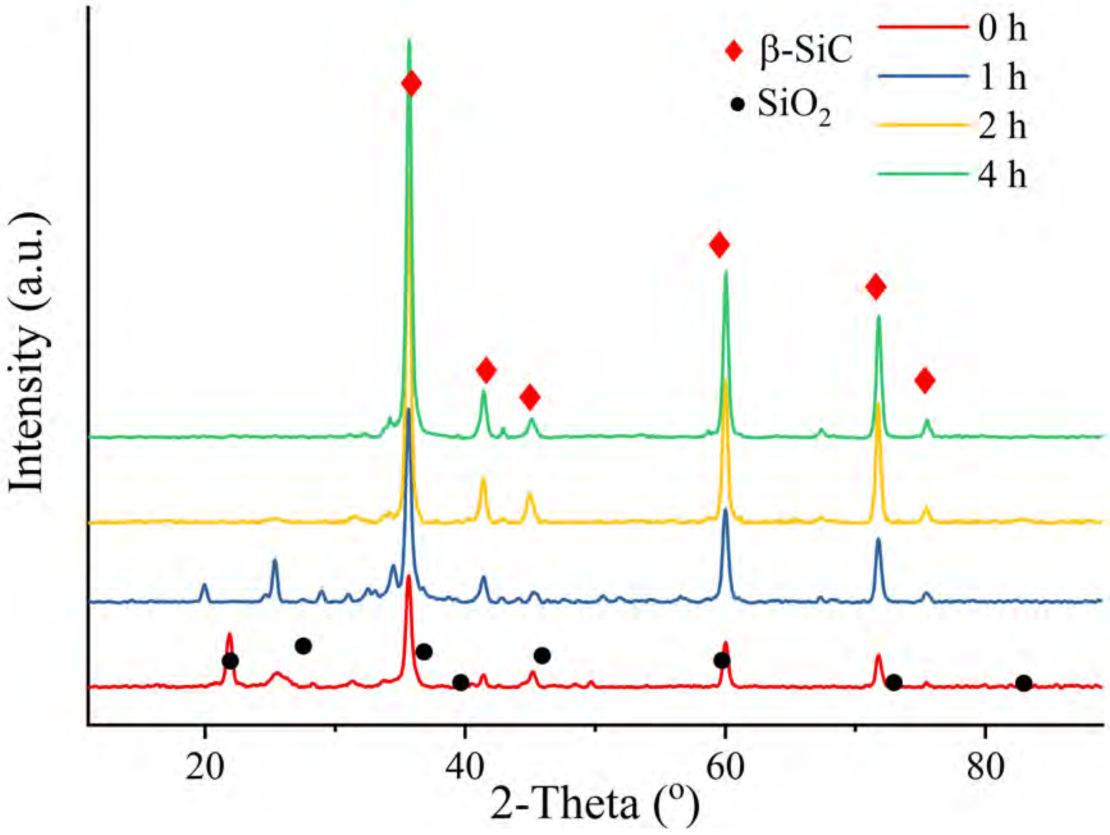
XRD patterns of the beta-SiC synthesis process from 1300 to 1600 °C for 2 hr.



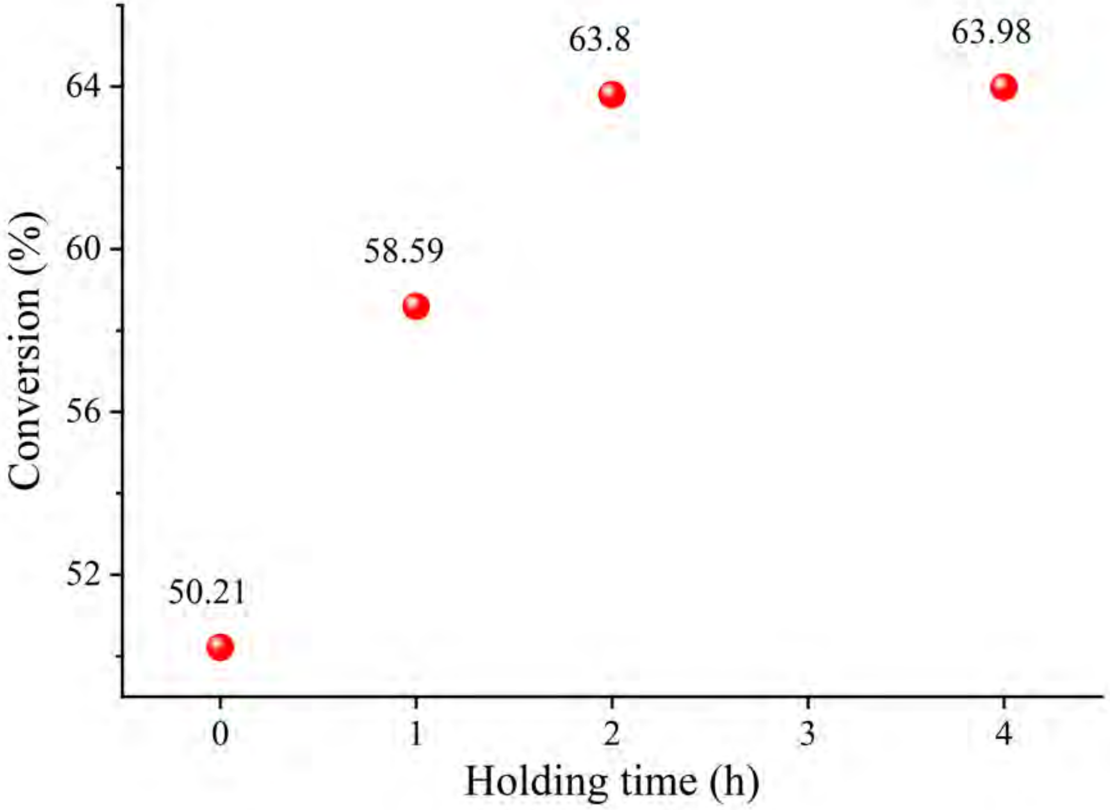
Conversion of coal tar and sandstone mixture during the beta-SiC synthesis process from 1300 to 1600 °C after 2 hrs of reactions

The reaction proceeds readily at 1600 °C to generate significant beta-SiC. The conversion of initial materials ranges from 43.9% at 1300 °C to 63.8% at 1600 °C.

Effect of holding time on the SiC synthesis at 1600 ºC using UT coal char



XRD patterns of the β-SiC synthesis at 1600 °C for 0-4 hr.



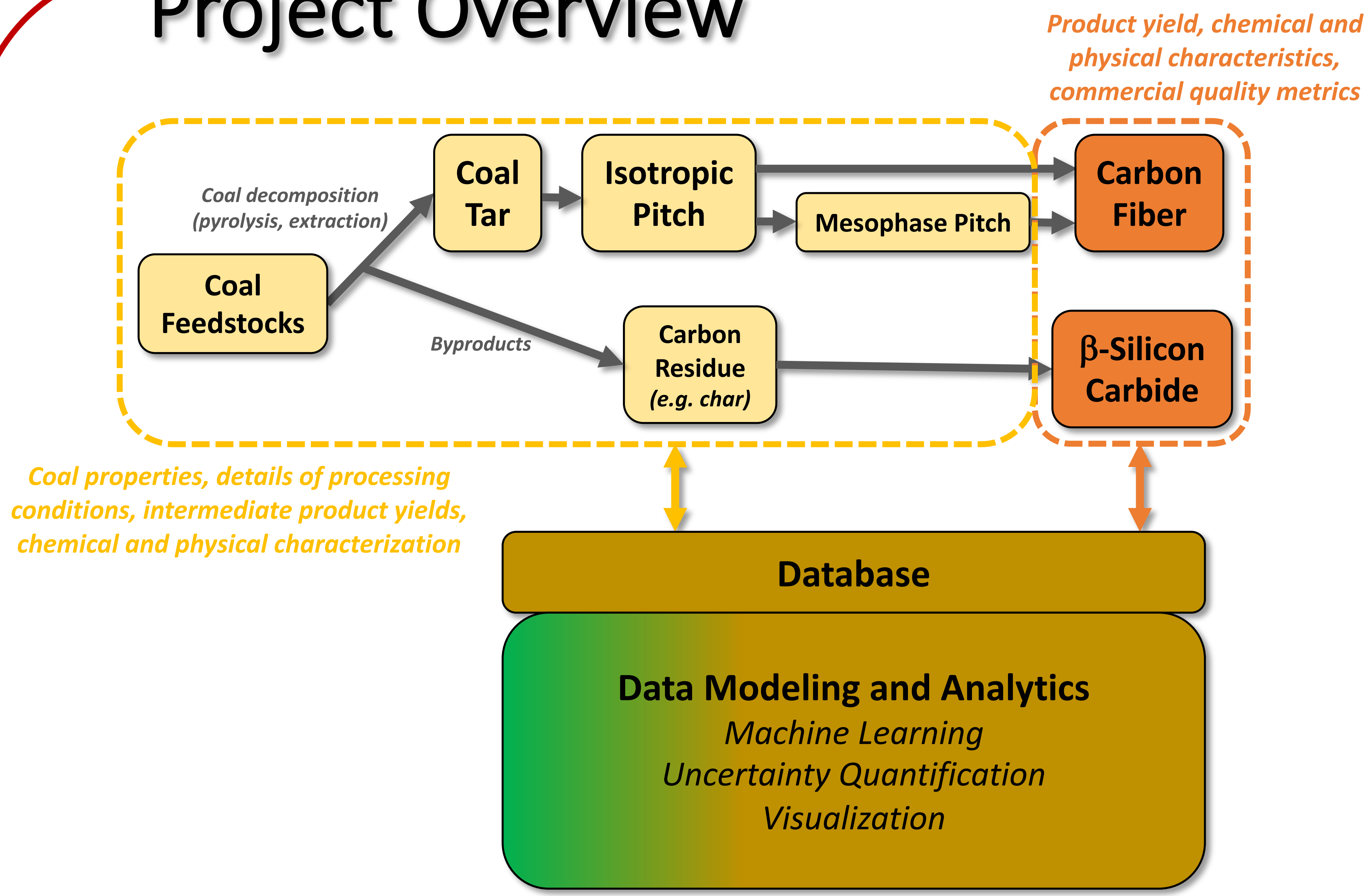
Conversion of the β-SiC synthesis at1600 °C for 0-4 hr.

The reaction proceeds readily at 1600 °C, and 2 hr is sufficient to generate significant beta-SiC.

Conclusions – SiC Production

1. Initial results show that the reaction proceeds readily at 1600 °C, and 2 hr is sufficient to generate a high yield of beta-SiC.
2. Suitable ratio for coal char and sandstone was found to be 1:1.
3. Preliminary results show that the beta-SiC produced exhibited a porous structure that may result from the the corrosive effect of SiO gas on the coal char.

Project Overview



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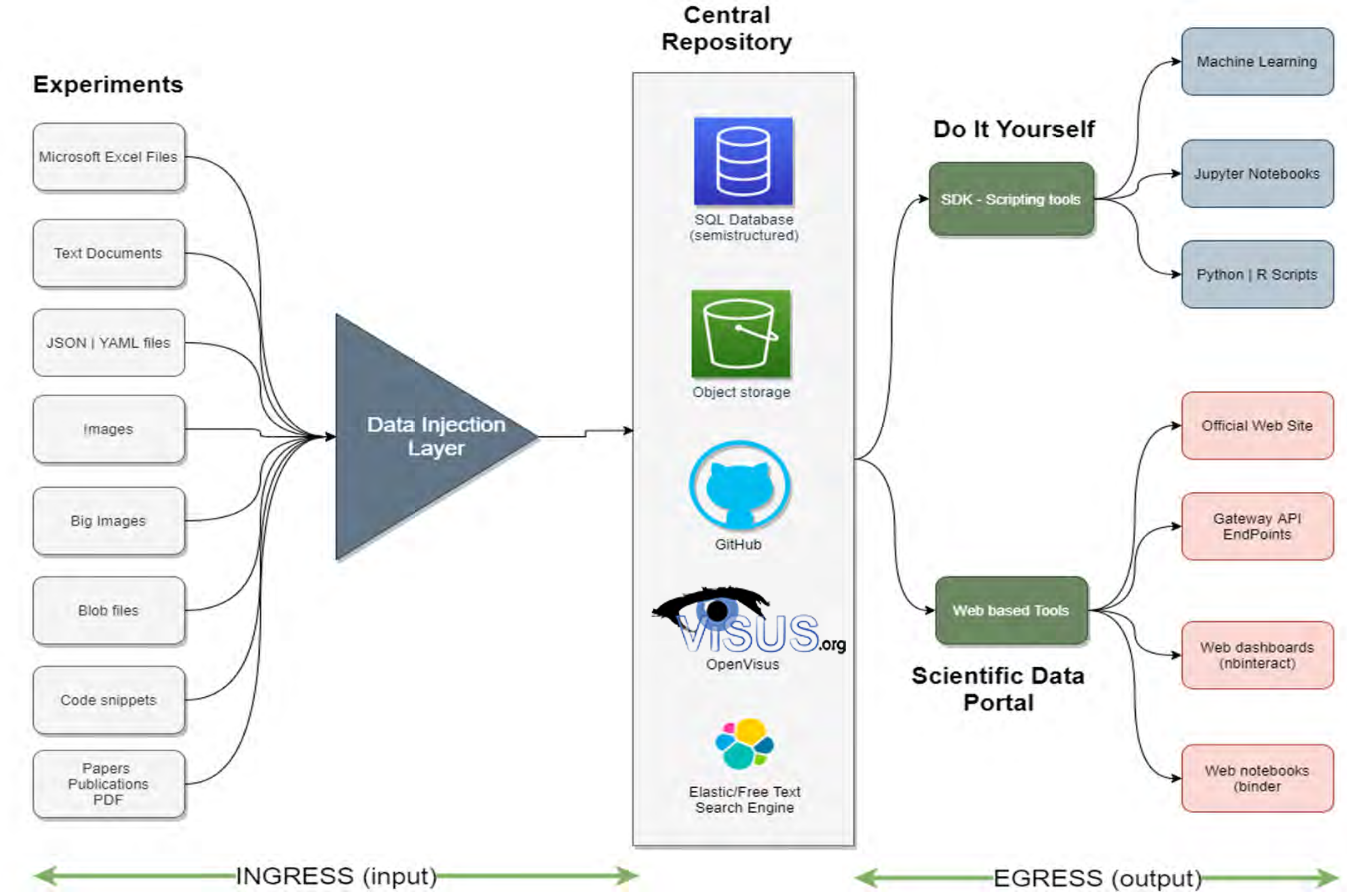
Data Pipeline



Data layer. INGRESS

Data templates and formats

- Staring with two **templates***:* Mesophase and Pyrolysis. More will be added as needed.
- **Python automation** to extract data directly from user files (Excel files, Google sheets)
- Fields are atomic-typed but nested structure are allowed for **unstructured data**: e.g., time sequences and object fields

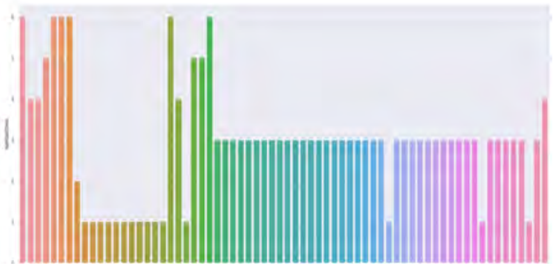
Central Repository

- **Database**. *Serverless DB* (small footprint, limited concurrency, portable data format, no user management SQLite); or *Production Ready DB* (open source, advanced security, speed and replication, website and web applications friendly MySQL); or *Big Data DB* (if data really grows BIG, advanced data integration Apache Spark)
- **Cloud object storage** stores object/images/blobs (Amazon S3, PyDrive, Google Python API)
- **GitHub**. Code repository for easy sharing and collaboration. DevOps.
- **Slack Channel**. Project oriented internal messaging.
- **OpenVisus**. Big image repository with web client. Possible to add annotations.
- **Elastic Search Engine**. Parse documents and store/search free text.

Data layer. EGRESS

Scripting Data Services

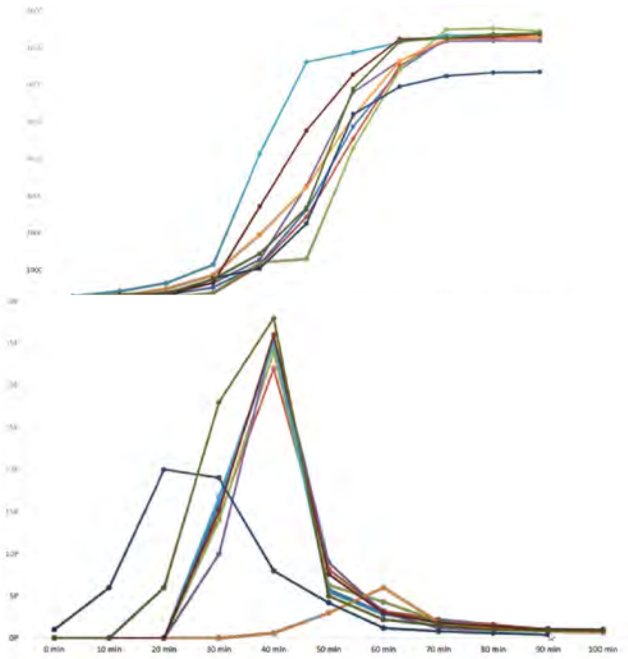
- Home made Python library for **Business Intelligence**
- Interactive **data extraction** and computing (Jupyter Notebooks)
- Machine Learning tools (scikit-learn, TensorFlow)



Python Pandas/Seaborn Bar Plot #batches/data

Data Portal and Web Based Services

- **Website** to browse/inspect data
  - Create a front end where the user can select the parameters
- **OpenVisus** server for big Images
- **RESTful API** to access data using HTTP web GET requests
  - Easy Integration with external sites and third part tools (Marshall University, ...)
- **Wide range of workflows,** configurable UI (JupyterLab)
- **Interactive web pages,** dashboards and notebooks built in support for interactive plotting; data driven Interactions; interactive data analysis
- **Custom Python layer.** We tried commercial tools but too convoluted (Azure Power BI, Microsoft Power Bi, Amazon Quick Sight, Amazon SPICE, Tableau).



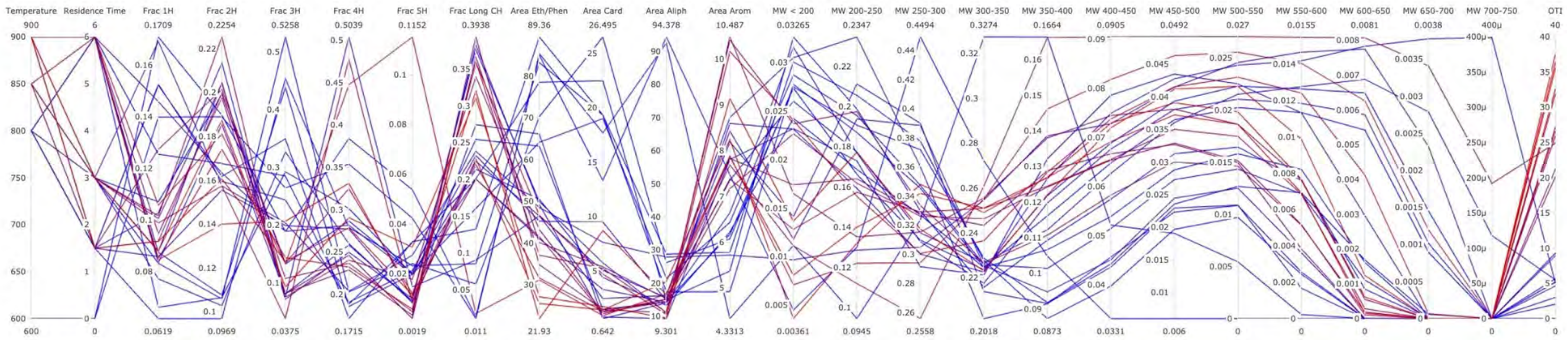
Char% vs temperature over time for some different coals. Bottom picture: char% vs Pressure (PSI) over time

Data Visualization

We have explored the use of **parallel coordinates plots** and a **scatter plot matrix** given their suitability to visualize high-dimensional data.

Interactive implementations:

- Python using Plotly library (simple, out-of-the-box charts)
- Javascript using D3 library (more complex, customizable)

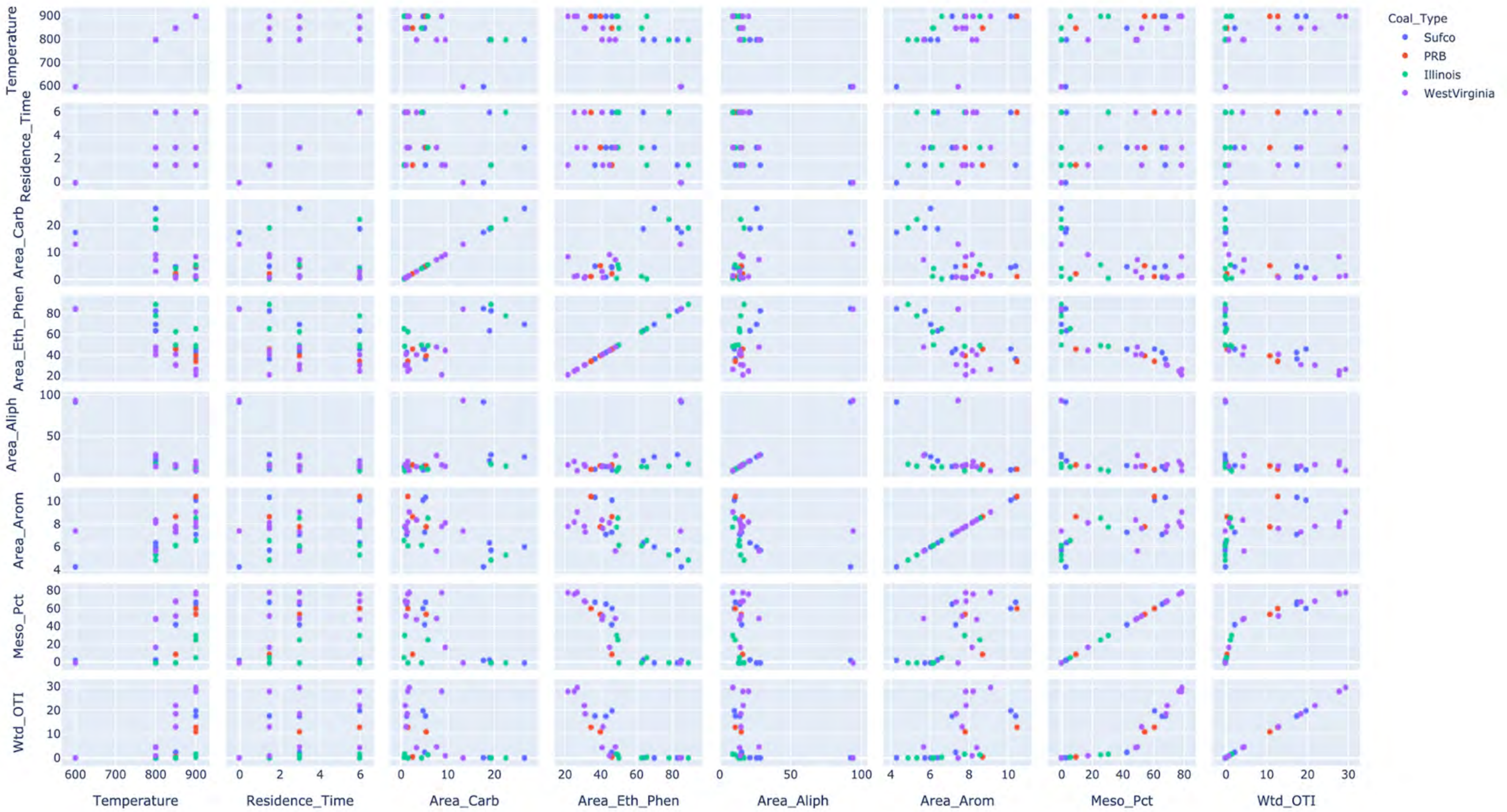


Example: Static Parallel Coordinates plot using Plotly

Scatterplot Matrix Example

- Allows interactive filtering of data points across the matrix.
- Relation between any two features is more easily observable.

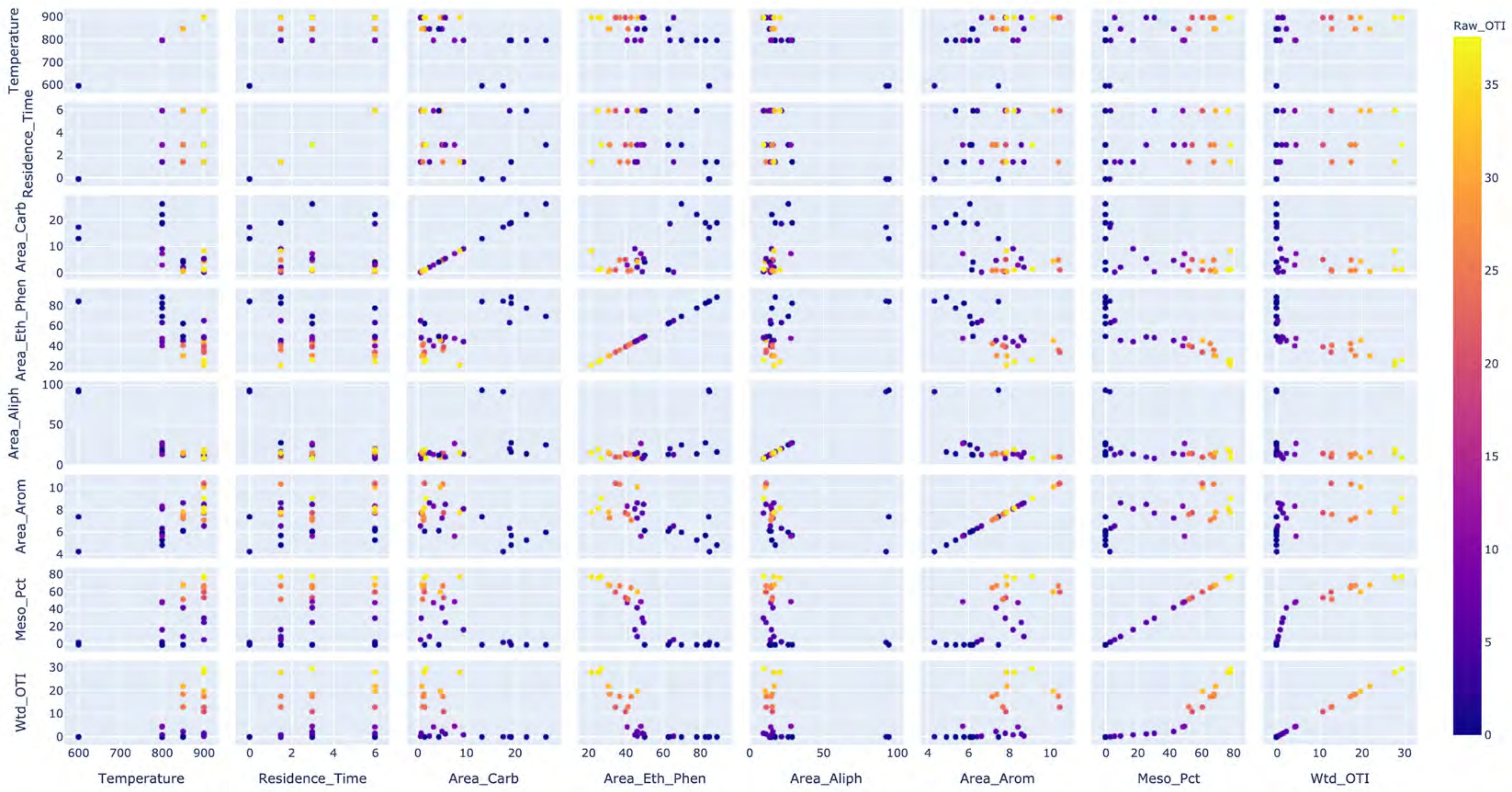
Data point color based on Coal Type



Scatterplot Matrix Example

- Allows interactive filtering of data points across the matrix.
- Relation between any two features is more easily observable.

Data point color based on Raw OTI



Machine learning methodology

- Target: **Robust prediction** of OTI, interpretability of **feature selection**

- Challenge: limited samples but much more features
  → easy trapped in **overfitting**
  → can't **over-complex** models(like deep learning)

- Toolbox: Ridge Regression, Lasso → **Elastic Net!**

$$\underbrace{\hat{\beta}}_{\text{Optimal model parameters}} \equiv \operatorname{argmin}\left(\underbrace{\|y - X\beta\|^2}_{\text{Linear Regression}} + \underbrace{\lambda_2\|\beta\|^2}_{\text{L2 norm: Robust regularization}} + \underbrace{\lambda_1\|\beta\|_1}_{\text{L1 norm: Sparse regularization(to select feature)}}\right)$$

Optimal model parameters

Linear Regression

L2 norm: Robust regularization

L1 norm: Sparse regularization(to select feature)

Machine learning

Next steps:

1. Explore more advanced machine learning tools, like **random forest**, **Gaussian Process** to boost the the prediction performance

1. Develop **smoothing** methods, like **ensemble learning**, increase the **robustness** of model

1. Further analysis with **domain knowledge**

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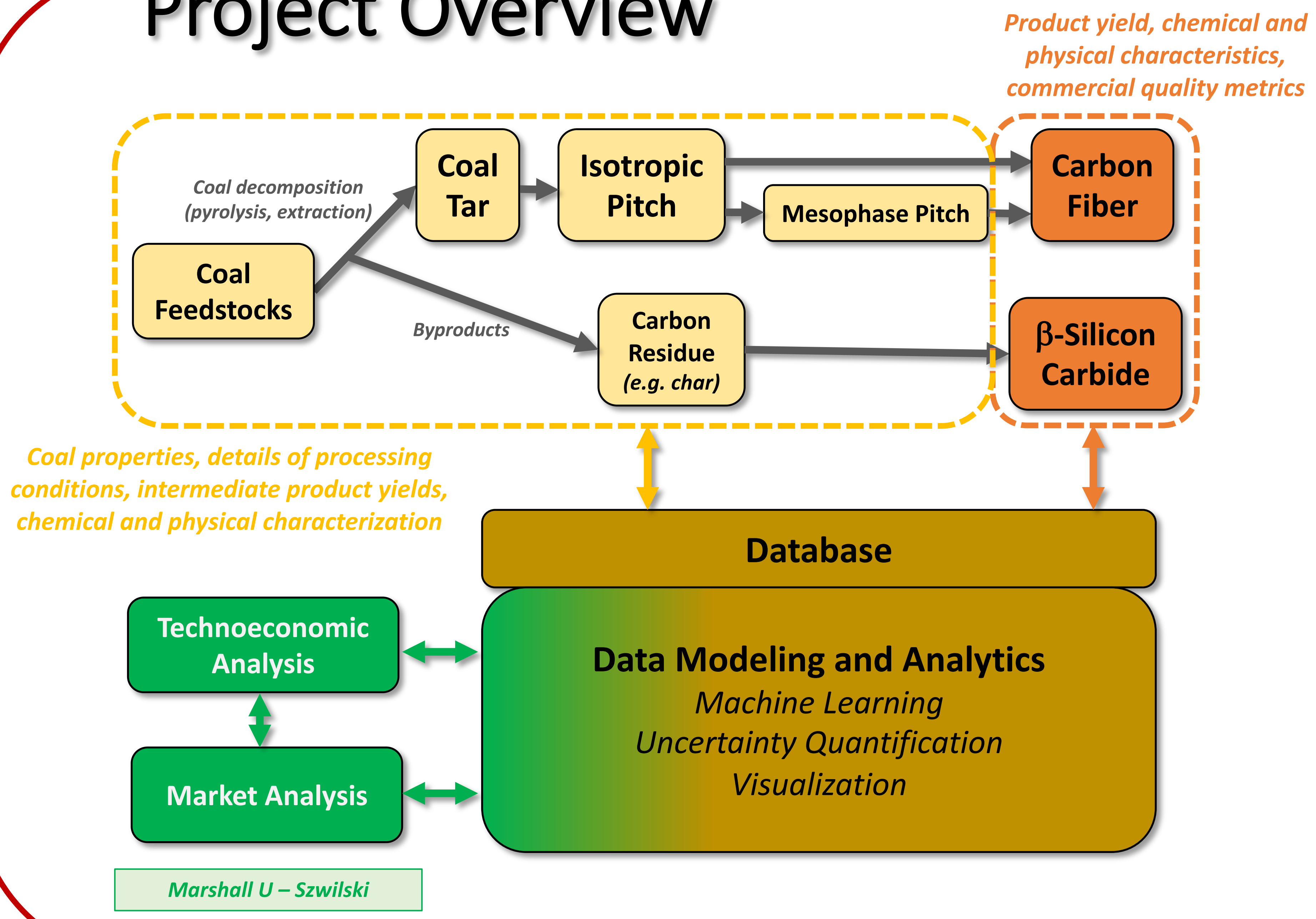

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Analysis of Pitch Production

- Possible production paths for coal-based pitch
  - Critical intermediate material input for high-modulus carbon fiber
  - Potential high-volume material input for automotive industry
  - Advantages of thermal vs. chemical conversion.
  - Lifecycle of coal-based pitch production, including co-products, by-products, and waste disposal requirements for the chosen conversion process.
- Lifecycle of petroleum-based pitch as a competing material

Market and Economic Analysis

- The best market opportunities for coal-based carbon fiber appear to be a function of the ability to replace aluminum or PAN-based carbon fiber in high-volume automotive parts production.
- Develop a cost framework for producing a competitive coal-based pitch, with stretch goals to be competitive with petroleum-based pitch and/or PAN.

Database Efforts

- A hierarchical **class-based schema** for characterizing heterogeneous **materials** with a variable ranges of compositions and properties like coal and most of the carbon-based intermediates leading to carbon products like carbon fiber
- A hierarchical class-based schema for characterizing **processes** and **process flows** involving heterogeneous materials like those above under a range of conditions, including costs and market factors, with a focus on the coal-to-carbon-product end-to-end flow, but including all by-product flows to allow for mass balance and total cost-value analysis
- An inventory of **material properties** and associated analytical methods for characterizing coal and many its derived carbon-based intermediates and products, with an emphasis on coal itself, carbon fiber precursors (tar, isotropic pitch, anisotropic/mesophase pitch, green fiber,..), and carbon fiber itself
- An inventory of regional "players" in coal-to-carbon-product research, development, advocacy, and related businesses
- Understanding coal-to-carbon-product chemistry and related processes

Concluding Comments – Overall Presentation

- Identifying optimal conditions for production of mesophase from four different coals via pyrolysis
  - Information will be used to determine operating conditions for sub-pilot-scale pyrolysis equipment
- Preliminary results with bench-scale solvent extraction are encouraging
  - Results for UT coal only, thus far
  - Pitch yields show 7-8X increase compared to pyrolysis
- Preliminary SiC product generated from coal char byproduct from pyrolysis process (above)
- Preliminary database structure in place utilizing detailed information on pyrolysis conditions, analytical results and product characterization
- Preliminary machine learning models to relate coal information, operating conditions, intermediate product composition to mesophase production
- Mapped out approach for techno-economic analysis

Acknowledgement

- This material is based upon work supported by the Department of Energy under Award Number(s) DE- FE0031880.
- Many faculty, graduate students, post-docs and research staff have contributed to this work, at the University of Utah, University of Wyoming and Marshall University.

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