Oak Ridge National Laboratory

C4WARD: Coal Conversion for Carbon Fibers and Composites: Project FEAA155

2021 Advanced Coal Processing Review Meeting

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ORNL is managed by UT-Battelle, LLC for the US Department of Energy

U.S. DEPARTMENT OF ENERGY

Project funded by DOE's Fossil Energy Program's Advanced Coal Processing Program

Outline

- Background
- Objectives
- Approach
- Results
- Summary and Future Work

Outline

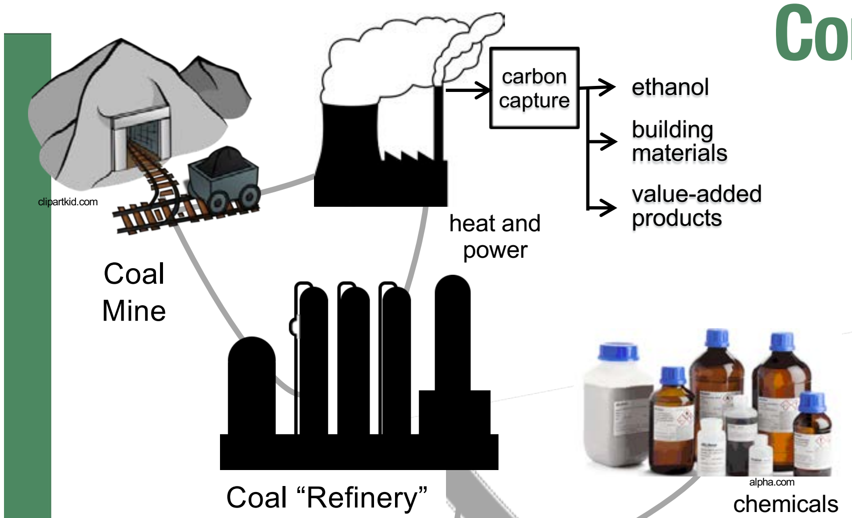
- Background

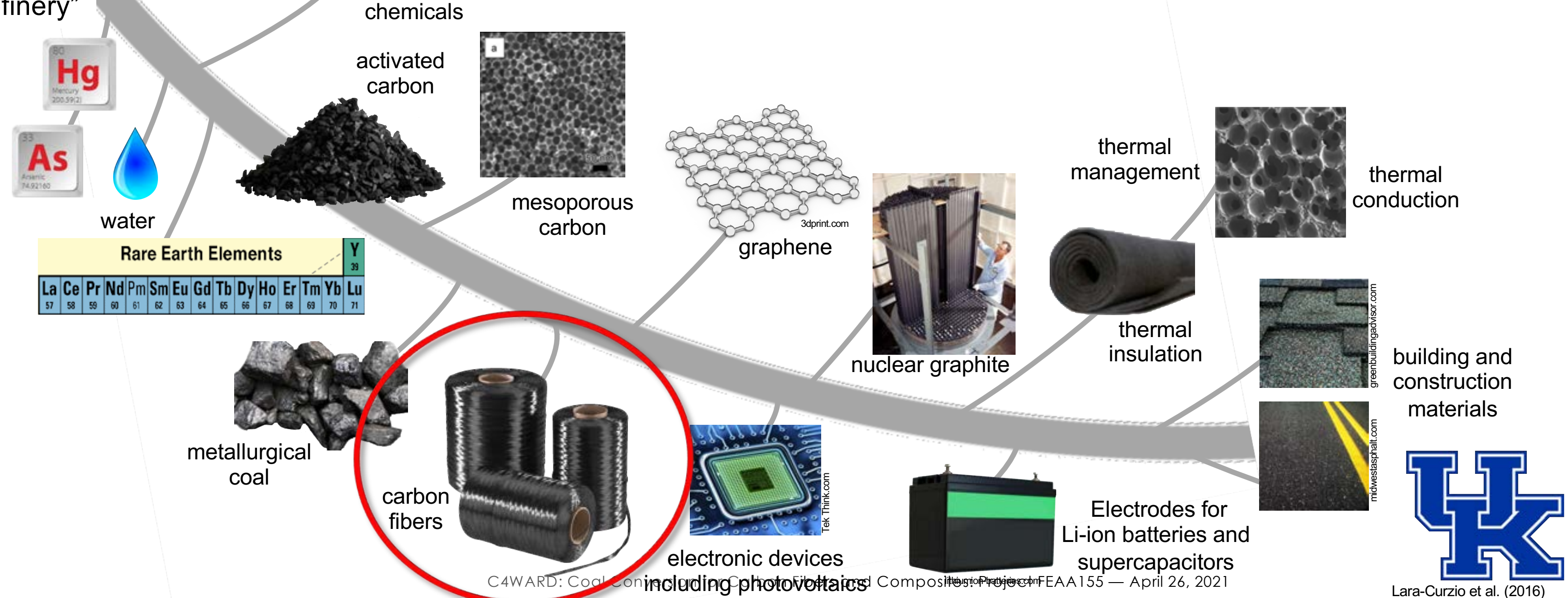
Converting Coal into Value-Added Products

Finding use for every molecule that is mined.

No molecule left behind!

Developing the underlying and translational science to enable the development and deployment of energy-efficient and cost-effective processes for: recovering rare-earth elements from coal and converting coal into high value-added products thus supporting the creation of new manufacturing industries and well-paying jobs in coal communities across the U.S.

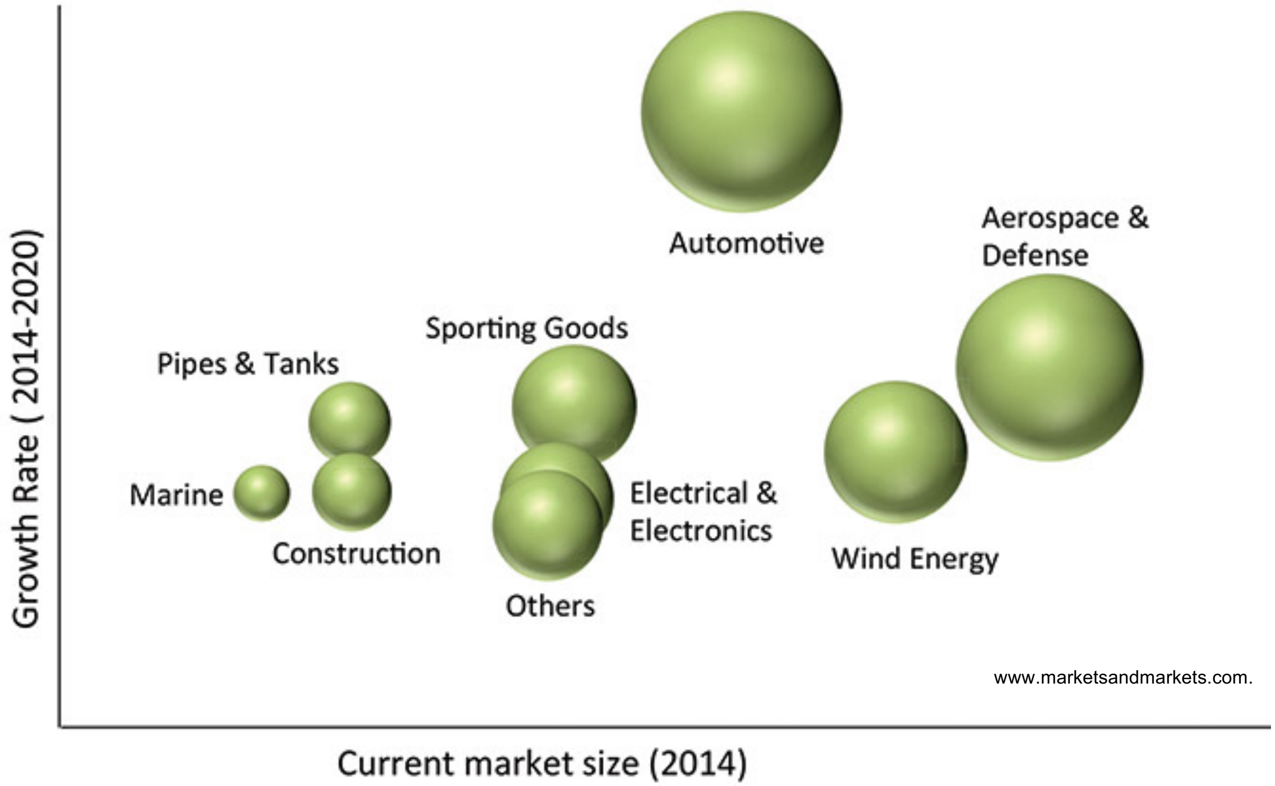




Carbon Fiber Composites are widely used in Aerospace Technologies…

and are expected to be widely used in highway transportation

Potential of Carbon Fiber Composites Market Growth



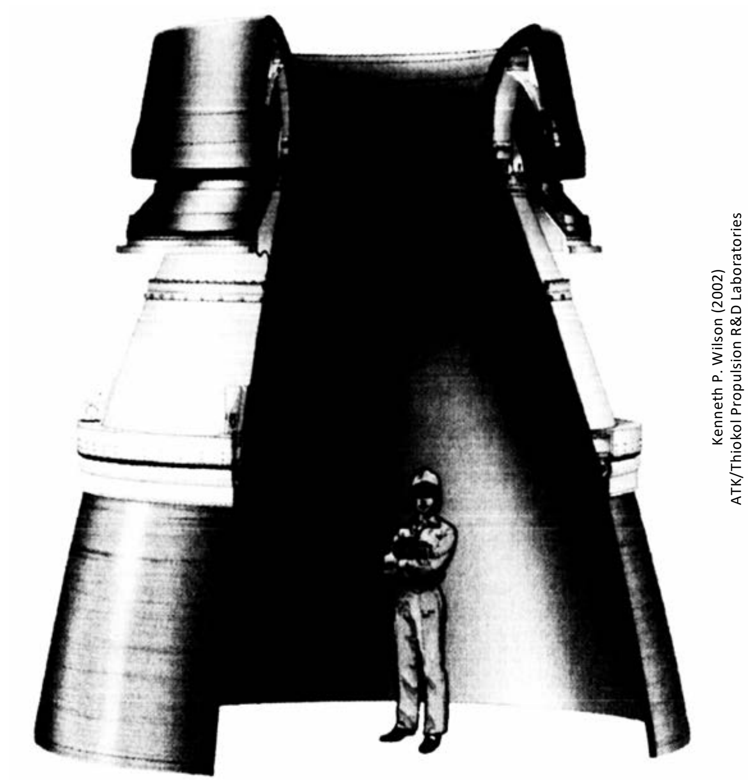
*** Size of the bubble describes market size in 2020**

Lara-Curzio et al. (2016)

But it is not only about stiffness and strength!

Low thermal conductivity carbon fibers could be used for building insulation

There is a need to replace rayon-derived carbon fibers for aerospace applications



Kenneth P. Wilson (2002)
ATK/Thiokol Propulsion R&D Laboratories

Outline

- Background
- Objectives:
  - To develop the underlaying and translational science to establish processing-structure-properties relationships for coal-derived carbon fibers that will enable energy-efficient, cost-effective and environmentally sustainable processes for manufacturing carbon fibers with tunable properties.
  - This project will address challenges associated with coal processing, variability in coal feedstocks, and with scaling up carbon fiber manufacturing from the laboratory bench to semi-production scale at ORNL's Carbon Fiber Technology Facility.

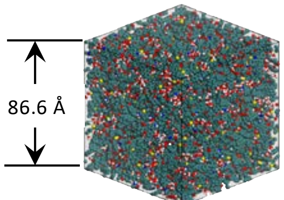
ORNL’s Carbon Fiber Technology Facility (CFTF)

Established in 2013, the CFTF is the Department of Energy’s only designated user facility for carbon fiber innovation.

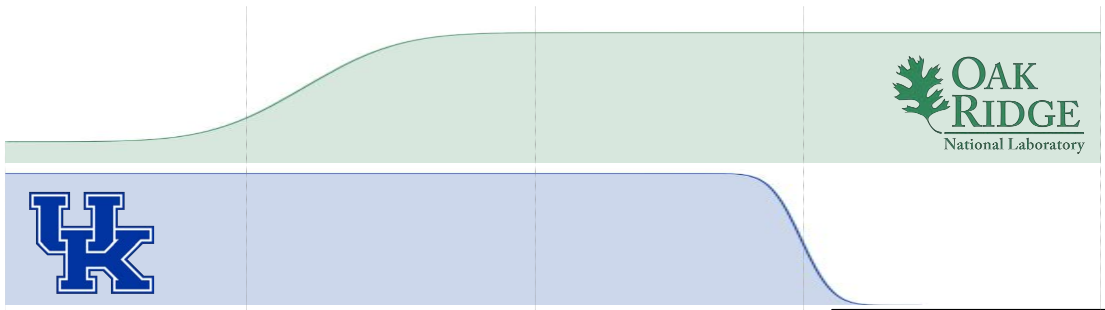
- 42,000 sq. ft. facility
- 390 ft. long processing line, capable of custom unit operation configuration
- Up to 25 tons per year

The ORNL-UK Partnership to Develop Coal-Derived Carbon Fibers

A Perfect Match



The molecular representation of coal will inform computational chemistry models to identify the most energy efficient and cost-effective pathways for processing coal into precursors best suited for manufacturing carbon fibers



Coal Processing → **Fiber Precursors** → **Fiber Production Laboratory Scale** → **Fiber Production semi-Production scale at ORNL's CFTF**

Continuous carbon fibers for structural applications

Short carbon fibers for structural applications

Short carbon fibers for thermal insulation

Composite Materials and Structures

Bringing new Industries to coal communities

Not all coals are the same

Together, ORNL and UK bring **complementary and unparalleled capabilities** in fundamental science and translational research and development expertise in:

- coal processing
- separation science and technology
- carbon science & technology
- computational chemistry and high-performance computing
- advanced characterization
- advanced manufacturing

to develop scalable, efficient, cost-effective, and environmentally sustainable processes for manufacturing coal-derived carbon fibers with tunable properties. A key element of this project is enabling scaling up fiber production from the laboratory benchtop level up to semi-production scale at ORNL's Carbon Fiber Technology Facility. This project will demonstrate a clear path for competitive industrialization of coal-derived carbon fibers and composites for a wide range of applications.

U.S. DEPARTMENT OF ENERGY | Office of Fossil Energy

Lara-Curzio et al. (April 2020)

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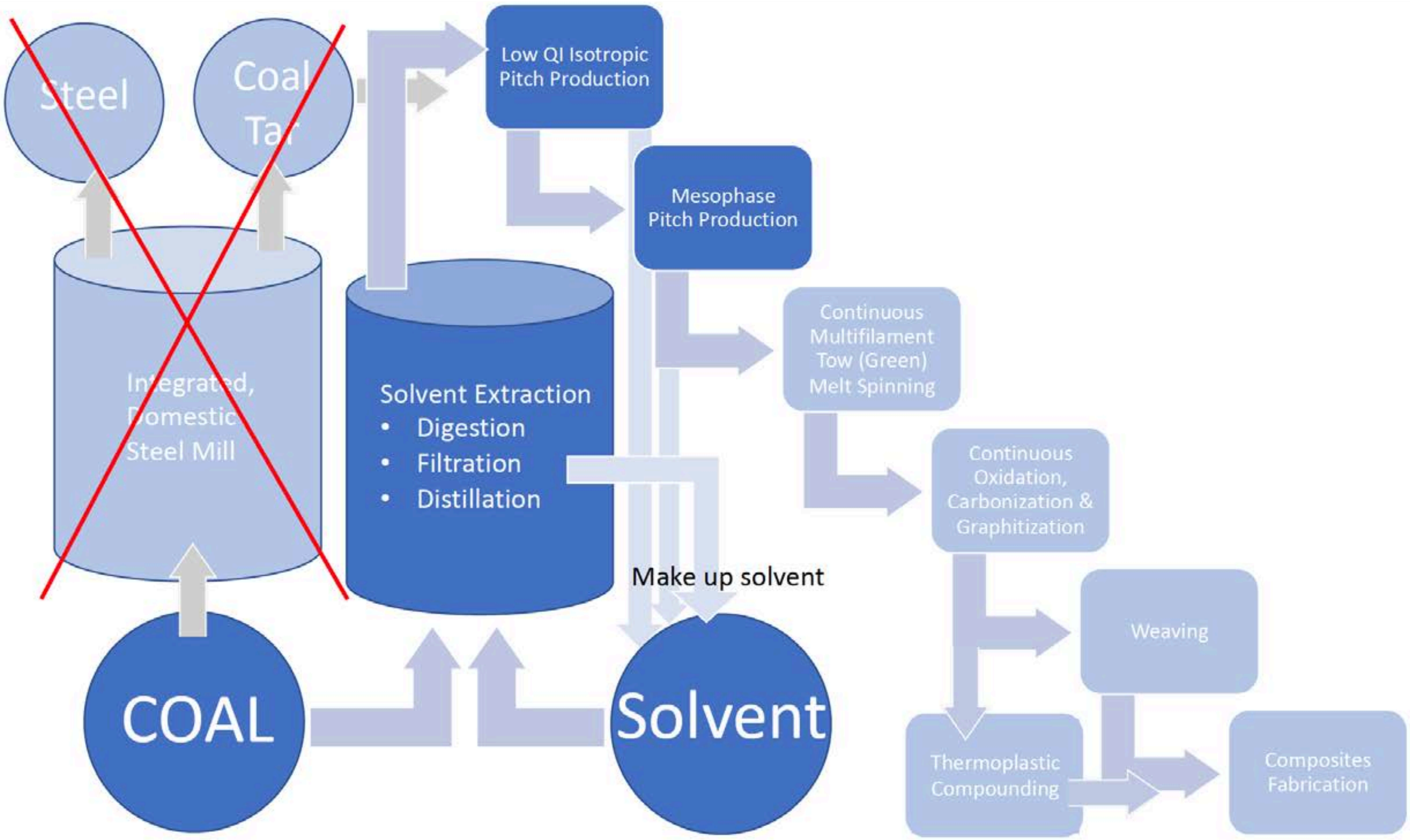
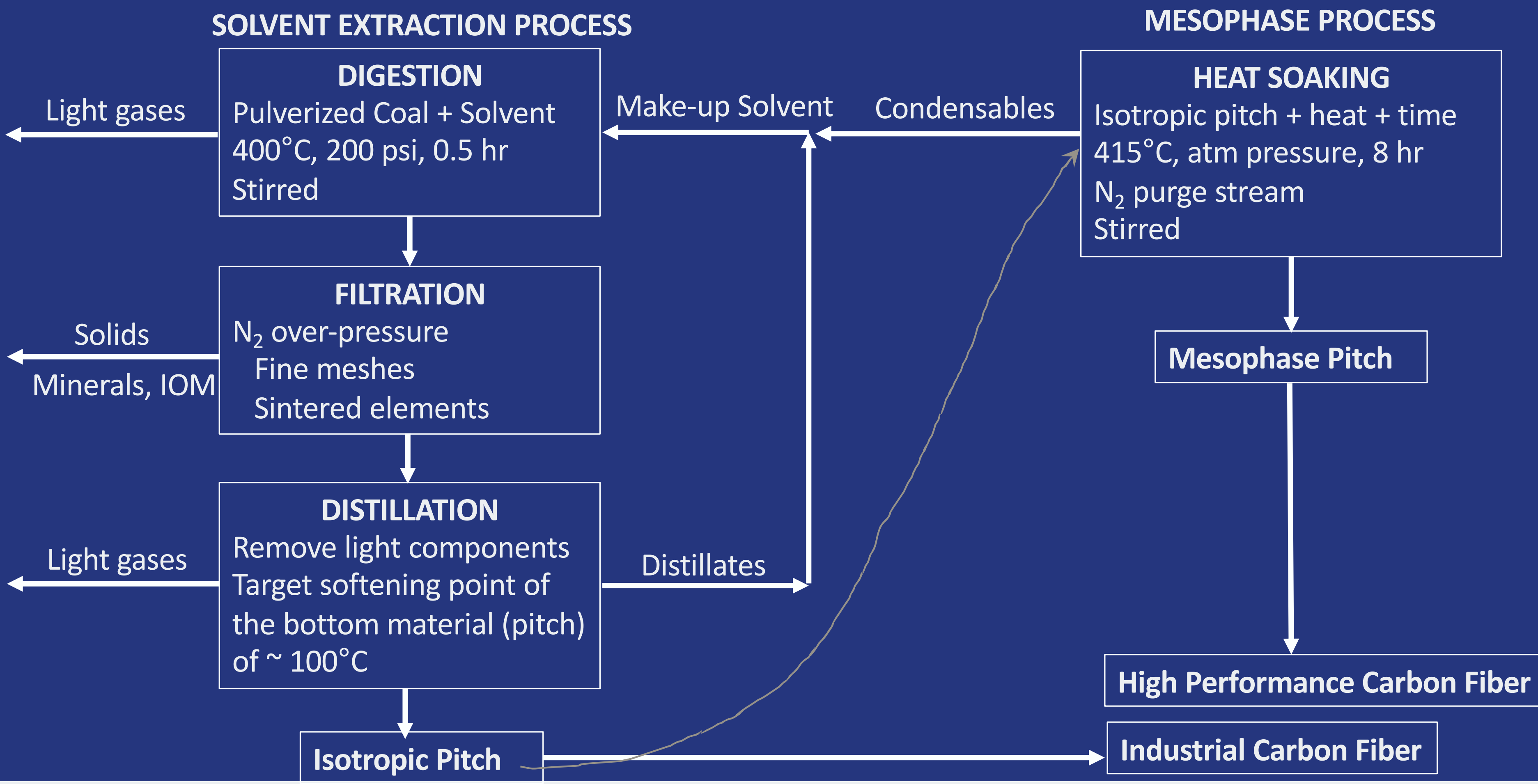
Advanced Coal Processing at UK-CAER



Overview – COAL & PITCH Processing



Coals and Solvents of Initial Interest

- **Bituminous**
  - Central Appalachian Basin
    - Blue Gem seam (low ash ~ 1 wt.%)
  - Illinois Basin
    - Springfield seam (Western Kentucky No. 9, Illinois 5, Indiana V)
    - Herrin seam (Western Kentucky No. 11, Illinois 6)
- **Sub-bituminous**
  - Powder River Basin – Wyoming and Montana
- **Solvents**: (heavy aromatics)
  - Anthracene Oil (from coal tar)
  - Creosote (from coal tar)
  - Decant Oil (from FCC of petroleum)
  - Make-up solvent ⟶ Condensates from our processing

Cost of solvents ~ $500 - $1000/tonne

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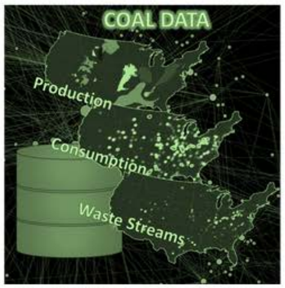
Data Management



ACD Coal Materials Resources
American Coal Database (ACD) is a database under dev at NETL to support coal...

♡ Favorite

EDX Workspaces

eXtremeMAT Consortium - IP Council
The objective of the eXtremeMAT consortium (XMAT) is to develop...

♡ Favorite

EDX Workspaces

NETL-ORNL Coal data share
Workspace to share coal data between NETL and ORNL

♡ Favorite

EDX will be the repository for all data generated in this project

Solvent Efficacy (microreactors)

Coals	Solvent	Solvent:Coal (g/g)	Temp. (°C)	Time (min.)	Coal Conversion (wt.% daf coal)
Blue Gem	FCC Slurry oil (decant oil)	2:1	400	30	42.7%
Blue Gem	Coal Tar Distillate (Koppers)	2:1	400	30	44.3%
Blue Gem	Creosote (Lone Star)	2:1	400	30	61.7%
Blue Gem	Coal Tar Distillate (Coopers Creek)	2:1	400	30	90.0%
Blue Gem	Anthracene Oil (Rain Carbon)	2:1	400	30	62.2%
Blue Gem	Petroflux (Rain Carbon)	2:1	400	30	83.3%
Blue Gem	New FCC Slurry Oil (decant oil)	2:1	400	30	
Springfield	FCC Slurry oil (decant oil)	2:1	400	30	60.0%
Springfield	Coal Tar Distillate (Koppers)	2:1	400	30	98.0%
Springfield	Creosote (Lone Star)	2:1	400	30	70.4%
Springfield	Coal Tar Distillate (Coopers Creek)	2:1	400	30	89.0%
Springfield	Anthracene Oil (Rain Carbon)	2:1	400	30	70.7%
Springfield	Petroflux (Rain Carbon)	2:1	400	30	86.4%
Springfield	New FCC Slurry Oil (decant oil)	2:1	400	30	
Herrin	FCC Slurry oil (decant oil)	2:1	400	30	94.1%
Herrin	Coal Tar Distillate (Koppers)	2:1	400	30	96.1%
Herrin	Creosote (Lone Star)	2:1	400	30	83.5%
Herrin	Coal Tar Distillate (Coopers Creek)	2:1	400	30	88.3%
Herrin	Anthracene Oil (Rain Carbon)	2:1	400	30	82.3%
Herrin	Petroflux (Rain Carbon)	2:1	400	30	72.4%
Herrin	New FCC Slurry Oil (decant oil)	2:1	400	30	
Monarch	FCC Slurry oil (decant oil)	2:1	400	30	
Monarch	Coal Tar Distillate (Koppers)	2:1	400	30	
Monarch	Creosote (Lone Star)	2:1	400	30	
Monarch	Coal Tar Distillate (Coopers Creek)	2:1	400	30	
Monarch	Anthracene Oil (Rain Carbon)	2:1	400	30	
Monarch	Petroflux (Rain Carbon)	2:1	400	30	
Monarch	New FCC Slurry Oil (decant oil)	2:1	400	30	

Coopers Creek coal tar distillate shows promising conversions with three coals

Herrin coal is the best performing in conversion to liquid – at this point–

- Work continues towards completion of study
- Replicates are planned to ensure reproducibility
- Based on results, solvent-coal combination will be down selected.

Distillation of Coal Liquids

- Currently running distillation of coal liquids on a 2L scale reactor
- Have successfully achieved softening points exceeding 100°C using decant oil

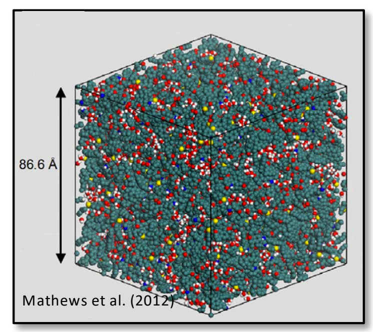
Summary of recent distillation runs

Run	Sample	Final Vapor T (°C)	DMA Softening Point (°C)	Mass Yield (%)
C4-dist-4	FCC decant oil	364	104	20
C4-dist-5	FCC decant oil	360	105	21
C4-dist-7	Blue Gem : FCC DO (1:3 ratio)	332	84	19

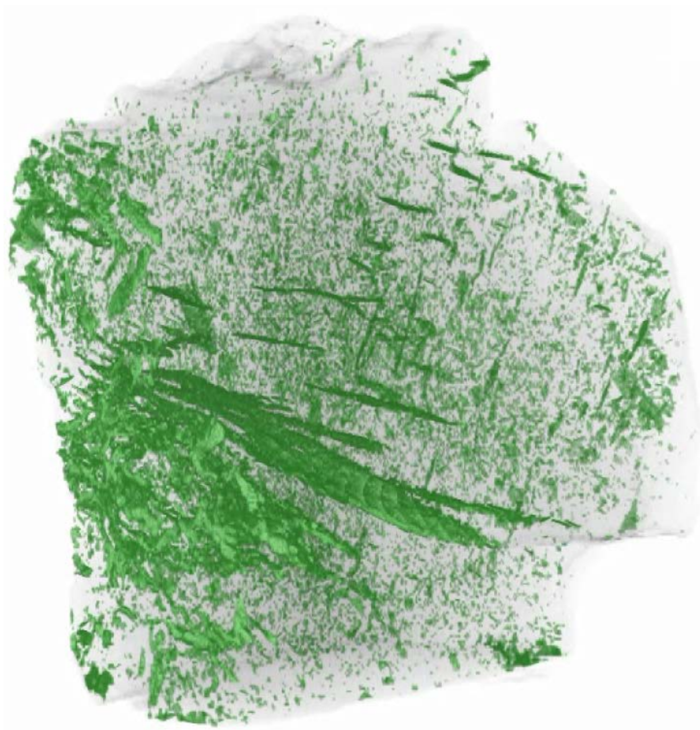
Advanced Characterization

The project is leveraging unique capabilities available at ORNL, UK, and DOE User Facilities to obtain descriptions of coals at different length scales from the mesoscale down to the molecular level.

- X-ray and neutron computed tomography
- Small-Angle Scattering (neutron and X-ray)
- X-ray Photoelectron, Raman, Infrared, Laser- Induced Breakdown Spectroscopy
- High-resolution Electron Microscopy
- Nuclear Magnetic Resonance
- Other

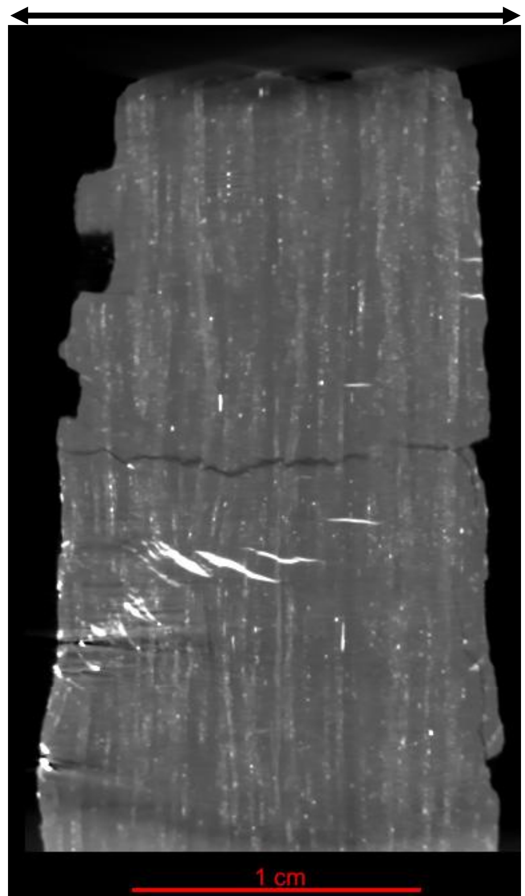


X-rays and neutrons are sensitive to different components in coal structure

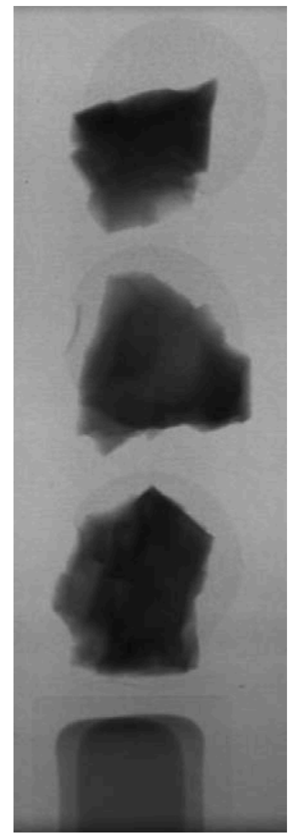


X-rays are more heavily absorbed by mineral matter in the coal structure (green in the 3D image).

A 2D slice image reveals the layered structure of Herrin coal



A neutron radiograph from a recent experiment at ORNL's HFUR



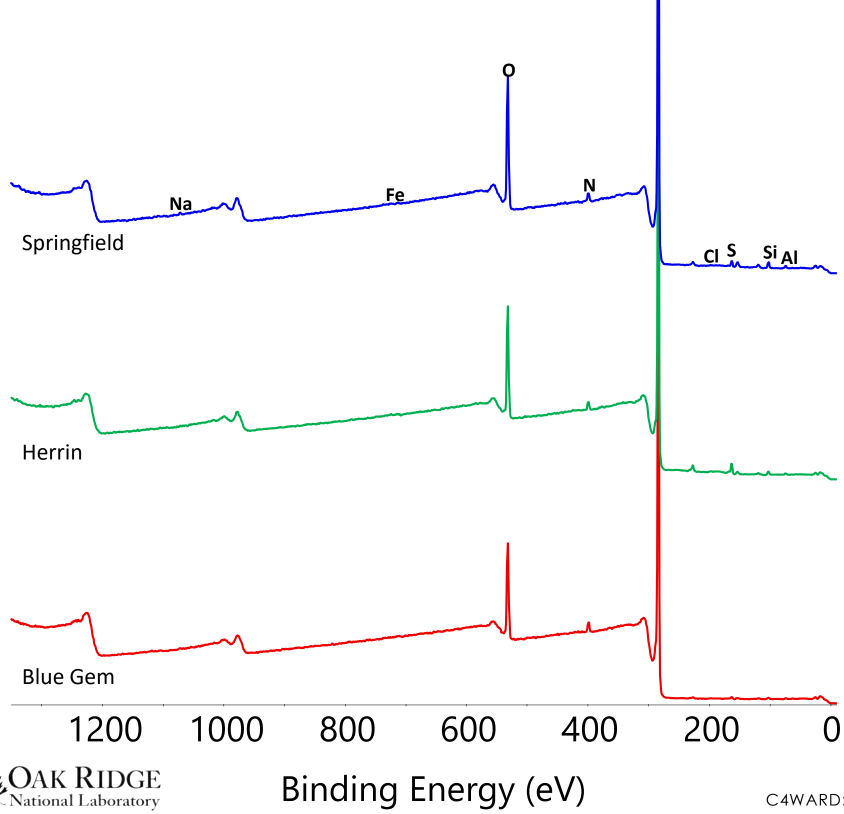
Neutrons are more sensitive to hydrogen.

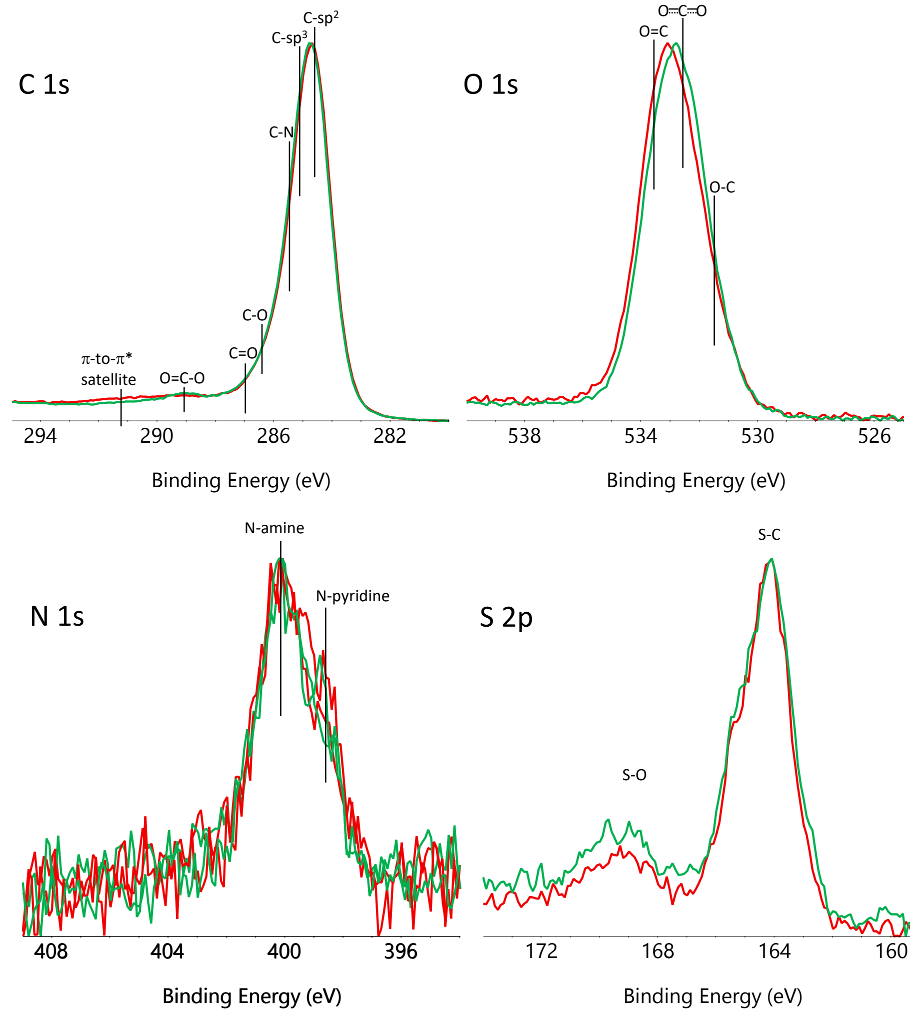
A comparison of XCT and NCT data of the same coals will help illustrate the distribution of the organic and inorganic compounds in the coals.

XPS data provides elemental quantification as well as quantification of organically bound O, N and S.

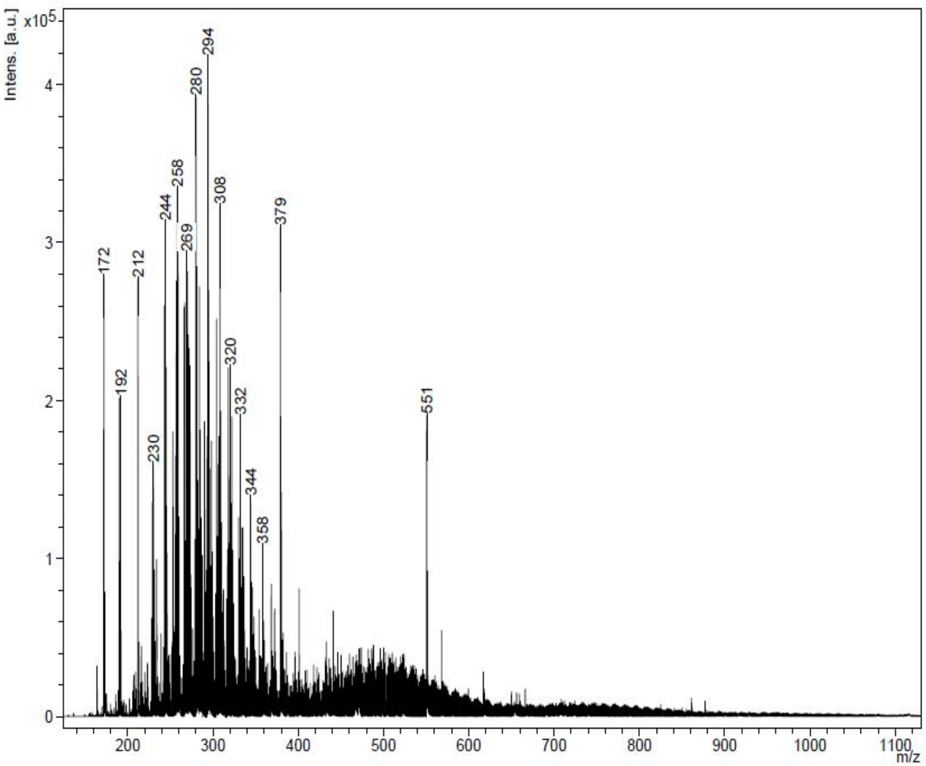
Surface Composition (at.%) – Analysis Area 1

	C	O	N	Si	S	Al	Cl	Fe	Na
Blue Gem	88.4	9.2	1.5	0.3	0.2	0.3	0.1	0.0	0.0
Herrin	85.5	10.4	1.1	0.9	1.3	0.7	0.1	0.1	0.0
Springfield	83.4	12.1	1.3	1.3	0.8	0.9	0.1	0.1	0.1

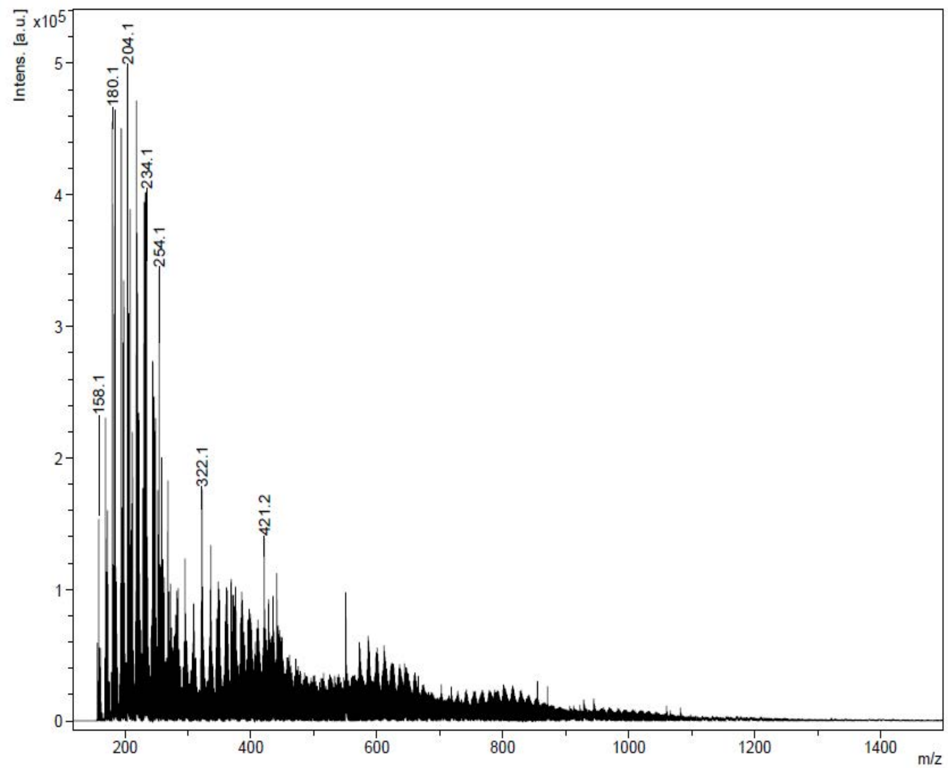




Chemical Characterization — Why do some solvents convert coal to liquids better than others?

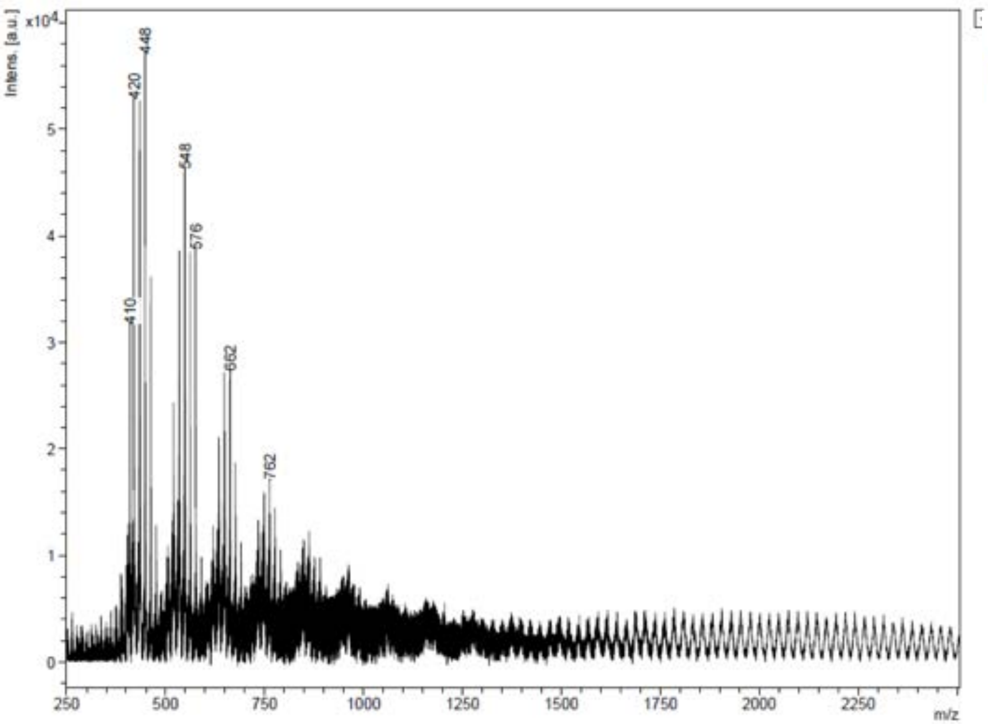


ACP Decant Oil

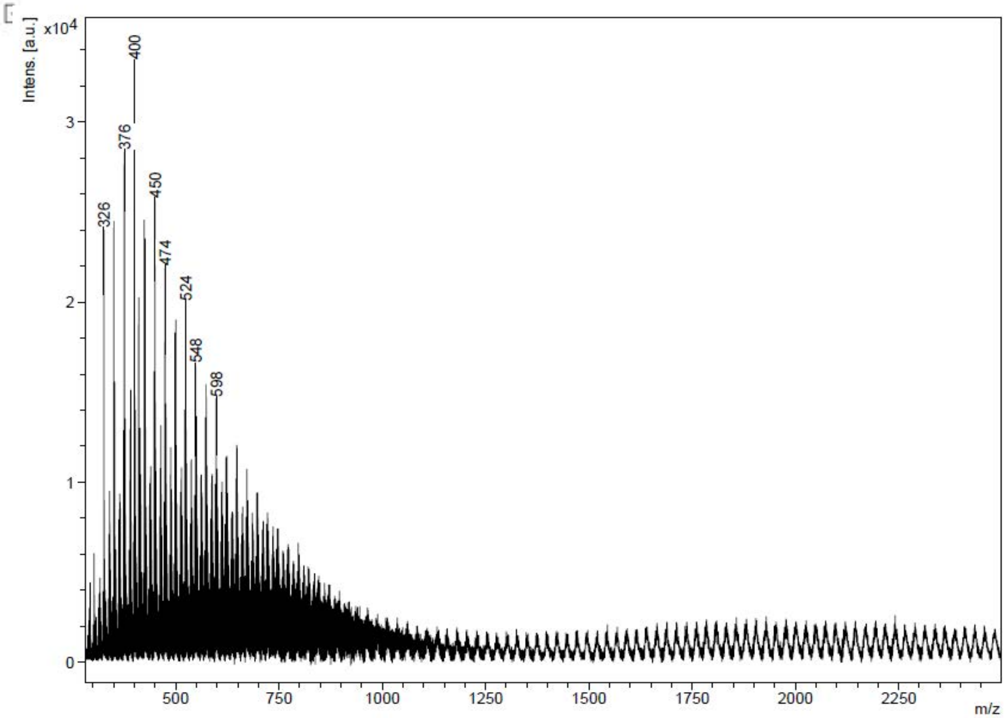


Coopers Creek Coal Tar Distillate

Chemical Characterization — Discrimination of pitch spinnability through Mass Spectroscopy

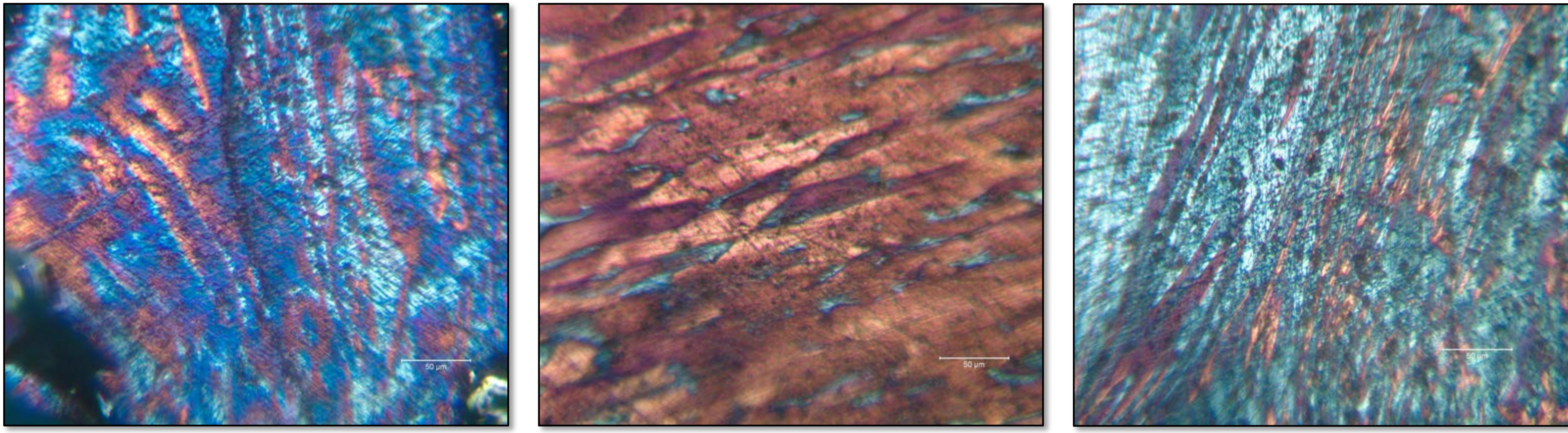


Mitsubishi Oil "SP 271" spinnable mesophase pitch



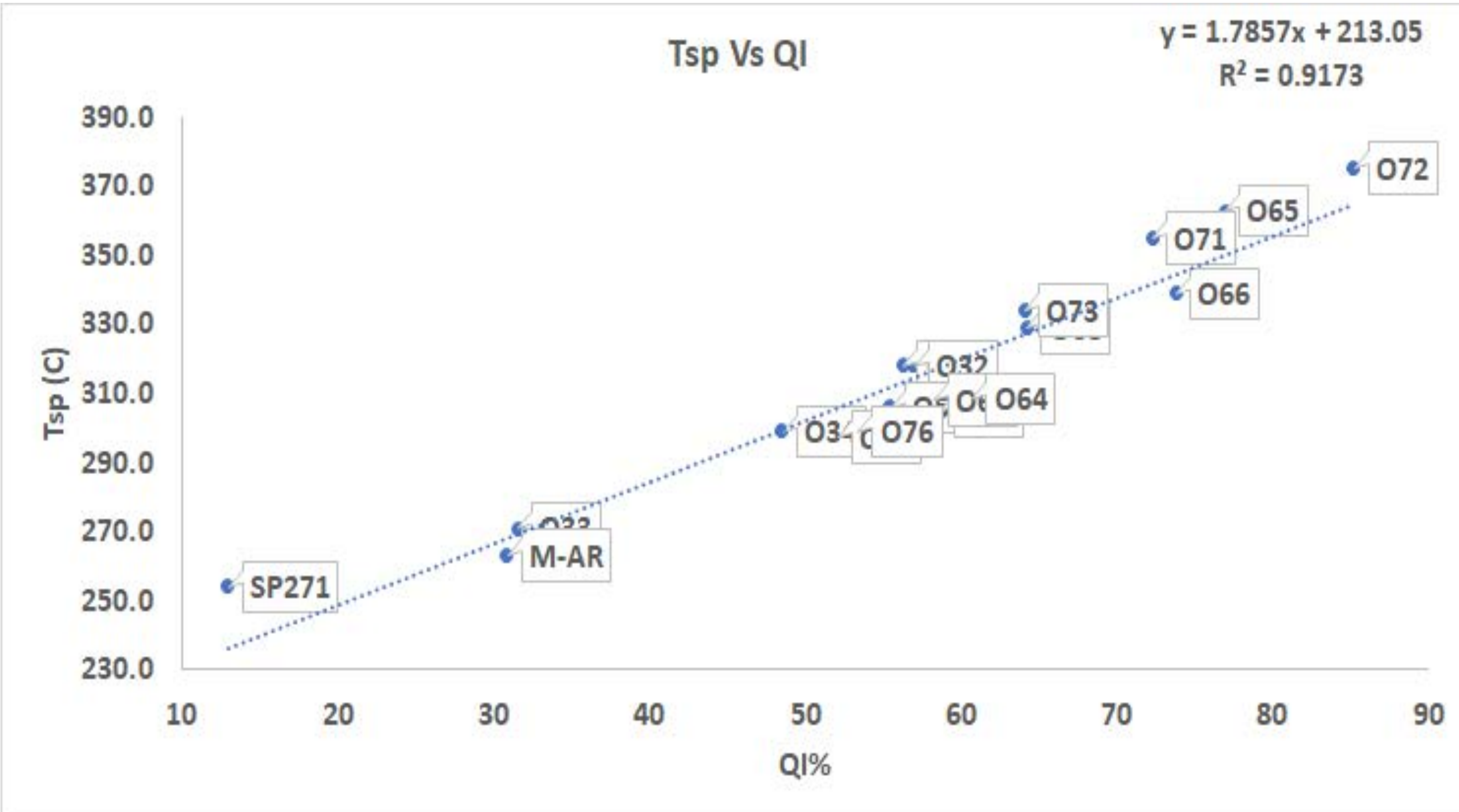
In-house coal tar-based non-spinnable mesophase pitch

Mesophase Formation

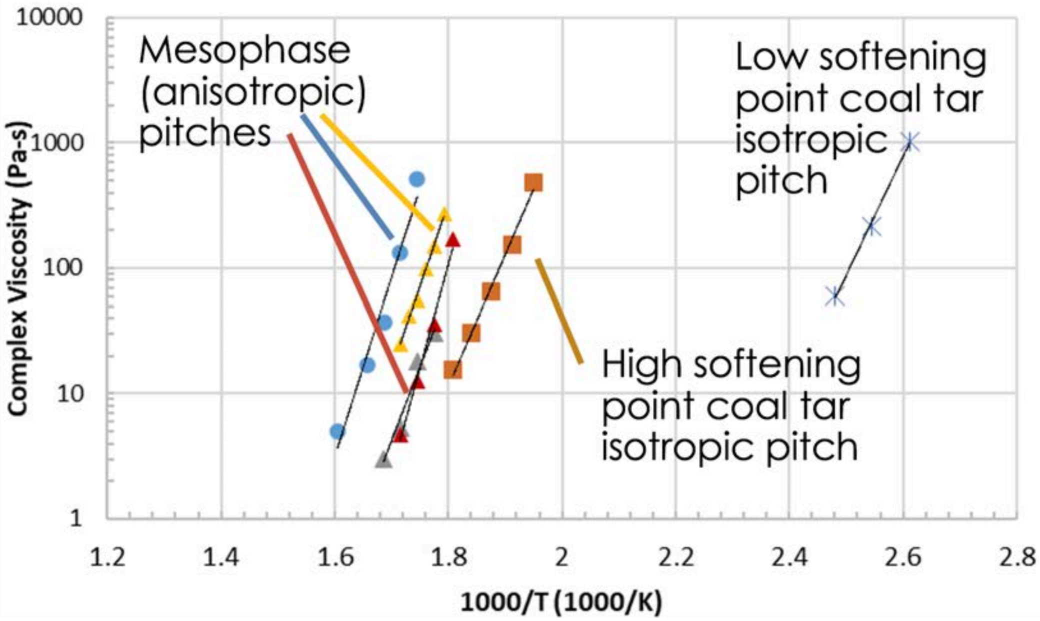


Reflected light, polarized optical micrographs of spinnable coal tar mesophase pitches. Recent pitches have achieved 100% mesophase at ~ 305°C softening point.

Correlation between Softening Point and QI for Mesophase Pitches



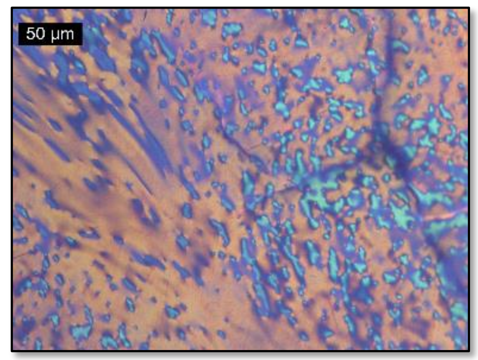
Pitch Rheology and Structure



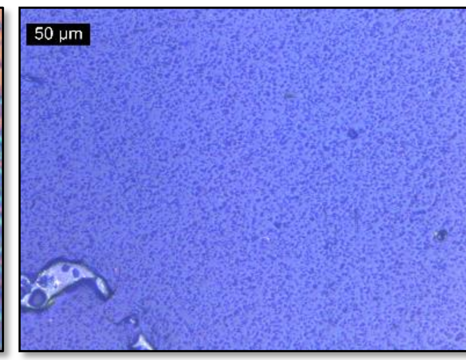
- Pitch viscosity is highly dependent on pitch composition and on temperature.
- Viscosity also depends on shear rate and may vary with time.

Source	Name	Type	Base	Comments
Mitsubishi	AR	Mesophase	Naphthalene	Reference.
Cytec	Mesophase	Mesophase	Petroleum	Reference.
Koppers	Mesophase	Mesophase	Coal tar	Reference.
Conoco	Mesophase	Mesophase	Petroleum	Reference.
Motorcarbon	Meso-C	Mesophase	Petroleum	Commercial product.
Lonestar	110 C SP	Isotropic	Coal tar	Commercial product.
Koppers	110 C SP	Isotropic	Coal tar	Commercial product.
Rain/Rutgers	Carbores	Isotropic	Coal tar	Commercial product.
Rain/Rutgers	250M	Isotropic	Petroleum	Commercial product.
Rain/Rutgers	270M	Isotropic	Petroleum	Commercial product.

Various commercial and reference samples have been screened. Focus on coal-based.



100% Mesophase (naphthalene pitch)



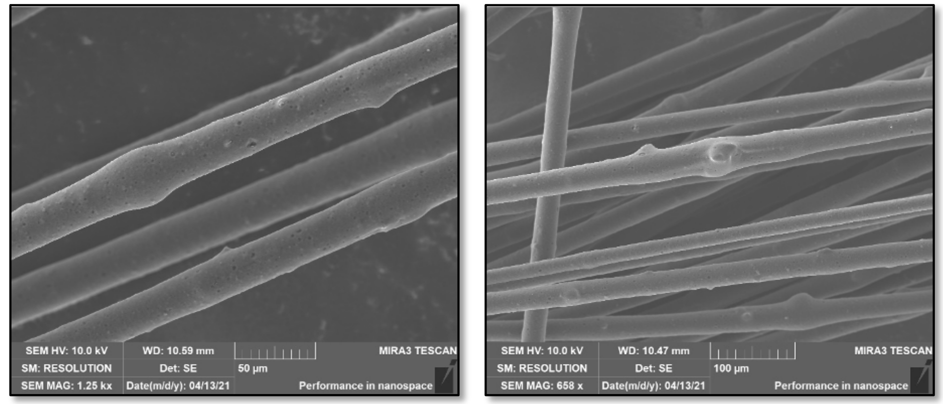
~0% Mesophase (coal tar pitch)

Mesophase (anisotropic) structures in pitch show optically active domains under cross-polarized light. Isotropic structures do not.

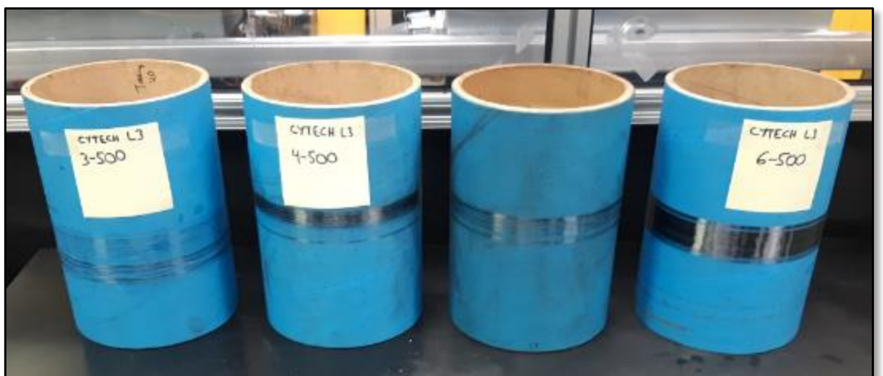
Bench Scale Melt Spinning of Fibers

ARA-24 mesophase pitch

Carbores isotropic coal tar pitch



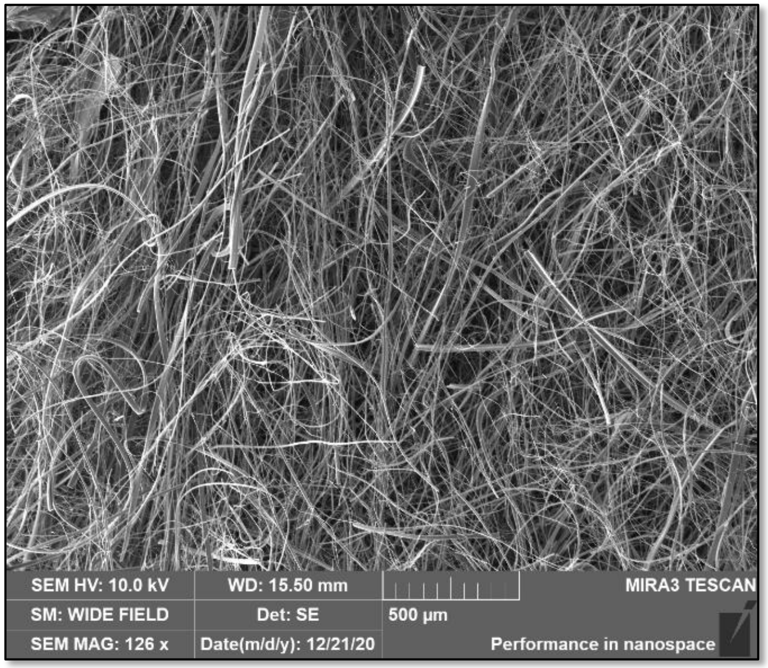
Carbores isotropic coal tar pitch

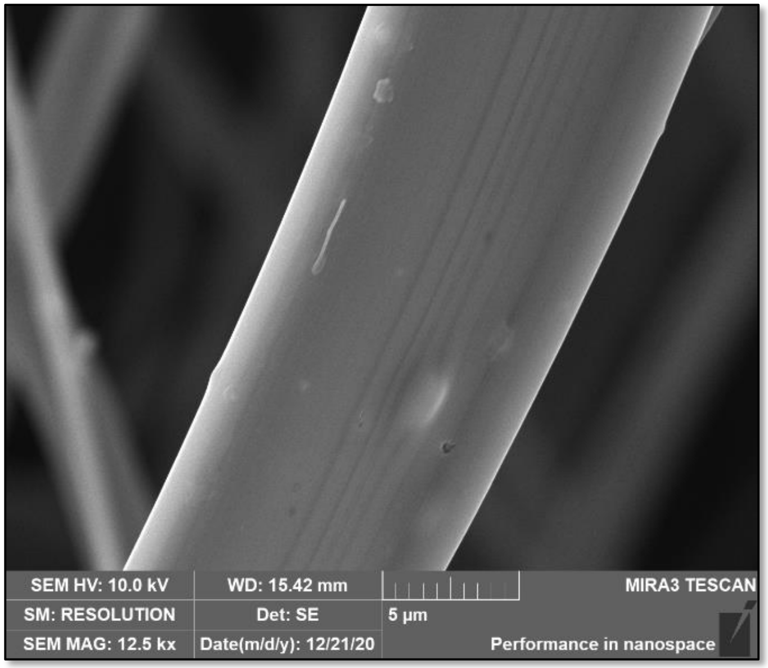


100% mesophase petroleum pitch

- Melt processing is not defined by one temperature or shear rate.
- Pitch materials are particularly challenging for melt spinning due to their heterogenous composition.
- rheology (temperature and shear rate dependence), thermal stability (volatilization)

Petroleum pitch fibers melt blown at CFTF scale

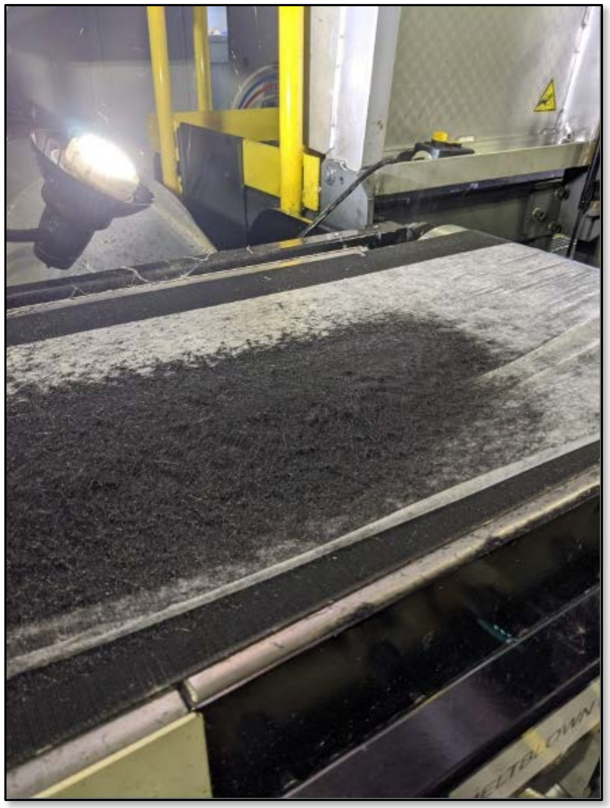




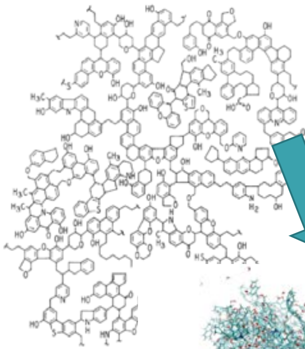
- Initial trial with high-softening point petroleum isotropic pitch fibers melt blown at CFTF.
- Average fiber diameter ~ 10 microns

Recent Results

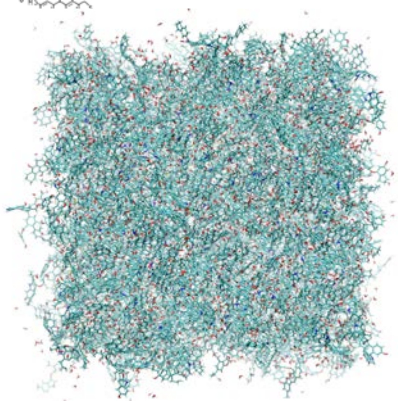
Melt-blown fibers from petroleum-derived isotropic pitch have been produced both at lab-bench scale and at the CFTF



Objective: Perform predictive simulations to efficiently break down different coals to pitches and then to fibers



Modeling: Analysis, structure generation, structure creation

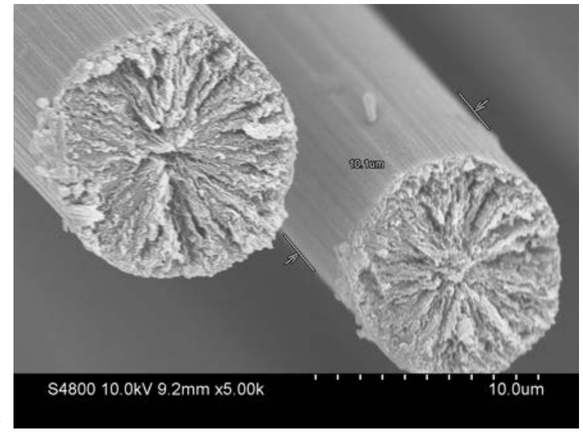


"Coal & Pitch Model DB"

DFTB LAMMPS

$$\hat{H}(\vec{R})|\Psi\rangle = E|\Psi\rangle$$

TORCHANI



Carbon Fibers (CFs)

Characterization: MS, optical, vibrational spectroscopy (Task 8)

Summit, 2018

Frontier, 2021

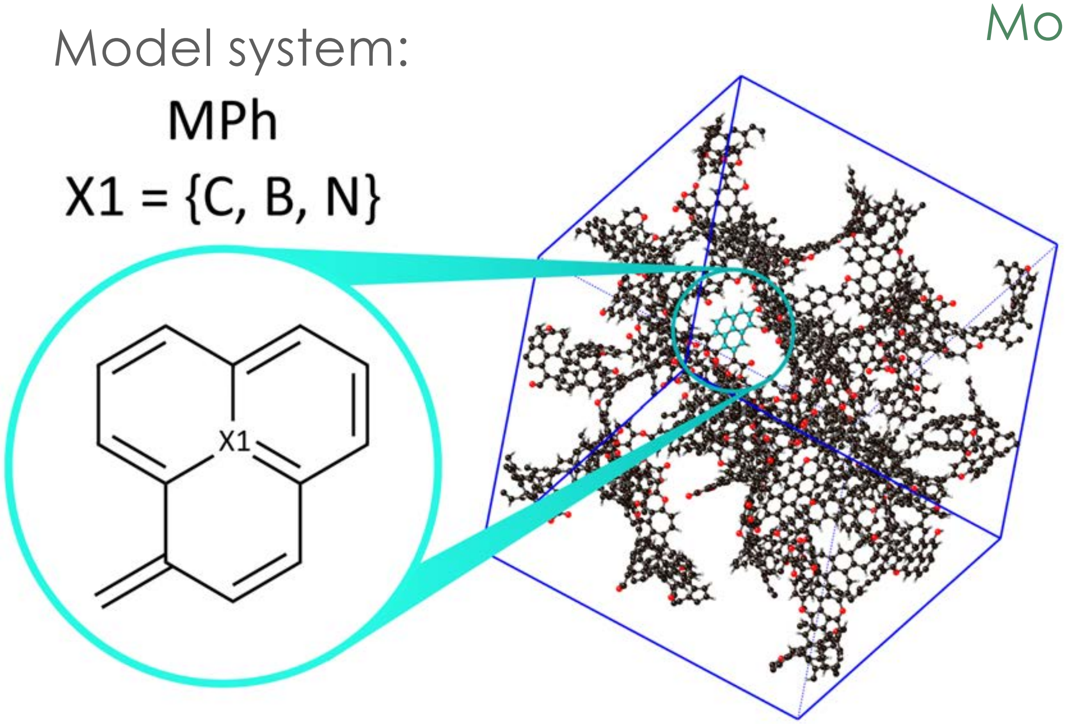
HPC: OLCF Oak Ridge Leadership Computing Facility

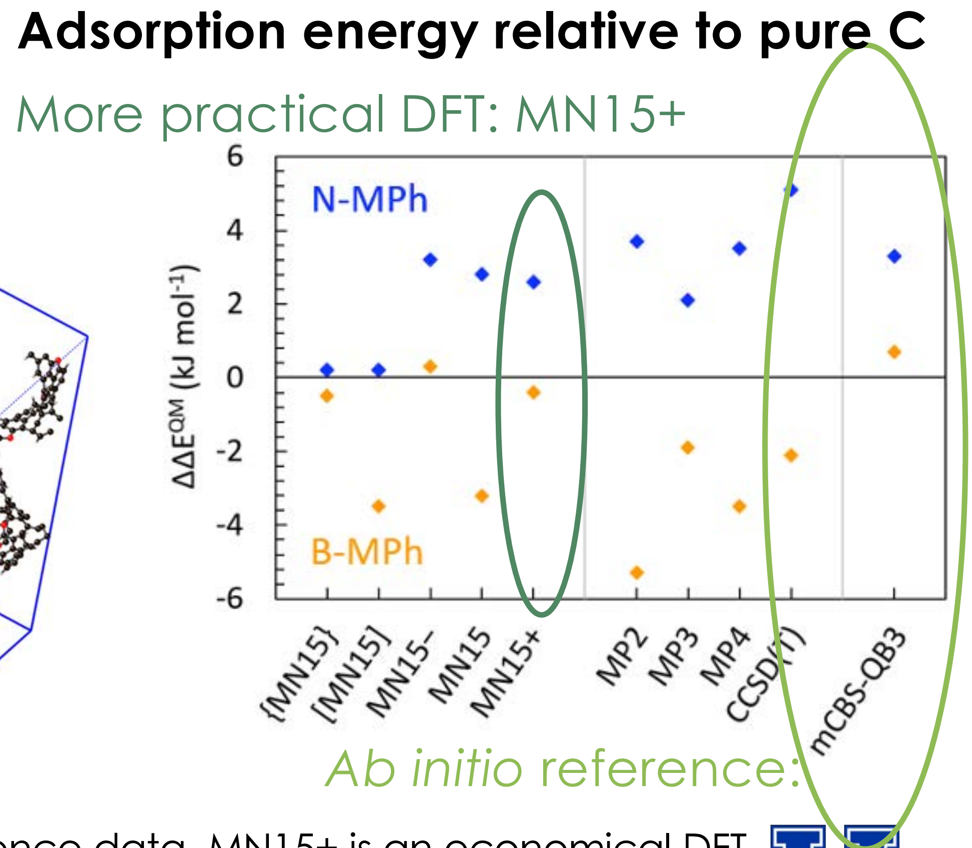
Efficient conversion by understanding structure/reactivity:

- Energy efficient
- Atom efficient
- Recover solvents

HPC Method Development

NN Training: Intermolecular interactions – Test case CH_4 adsorption in B and N doped porous nanocarbons



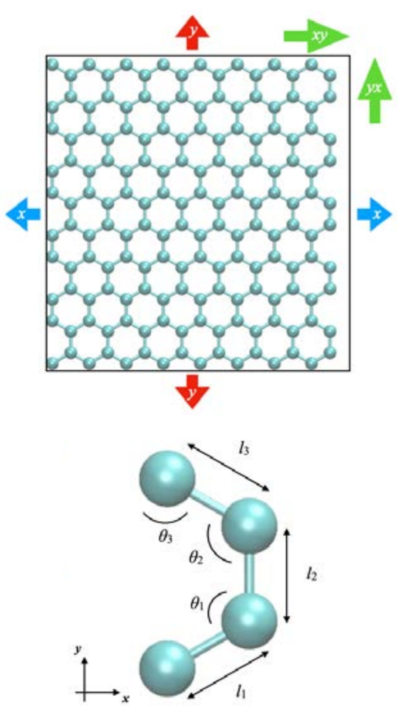


- Training NN potential requires high-level reference data, MN15+ is an economical DFT method for NN training!

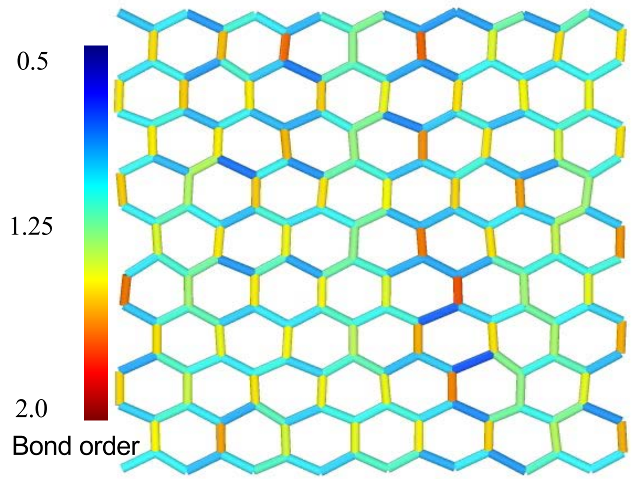
Irle et al, J. Phys. Chem. A, in revision

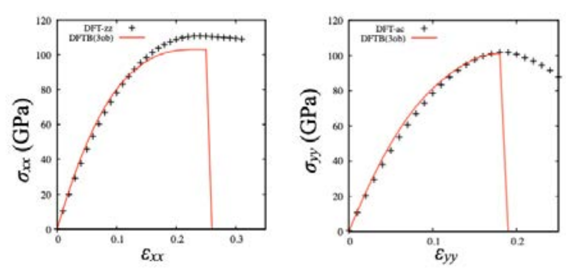
HPC Method Development

NN Training: Deformation & fracture of graphene with DFT and approximate DFT (density-functional tight-binding, DFTB)



Various Deformation & Failure





$\hat{H}(\vec{R})|\Psi\rangle = E|\Psi\rangle$

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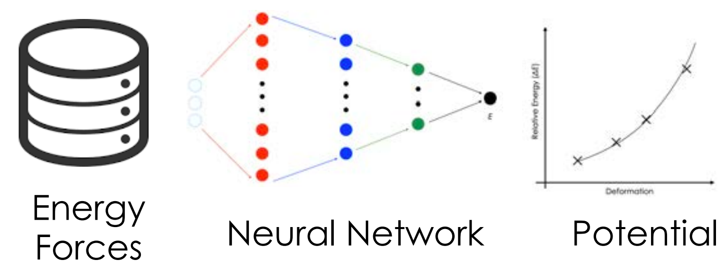
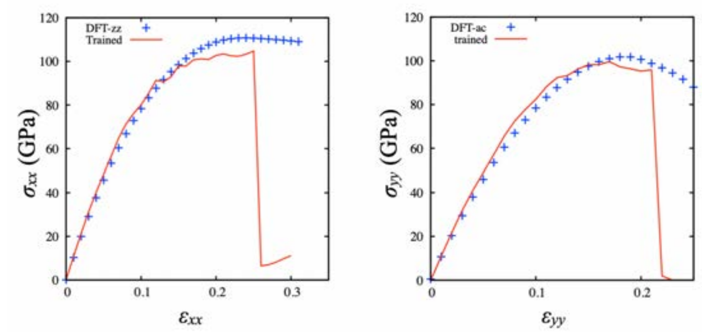
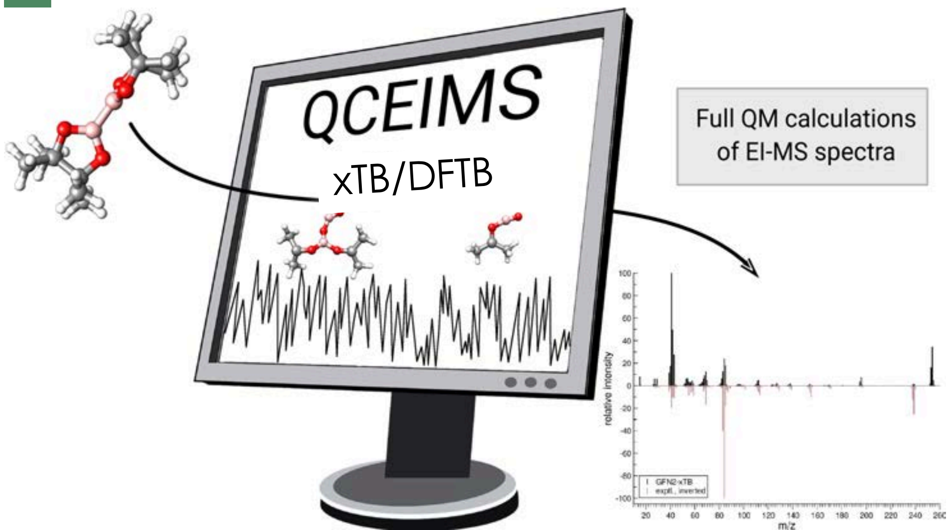
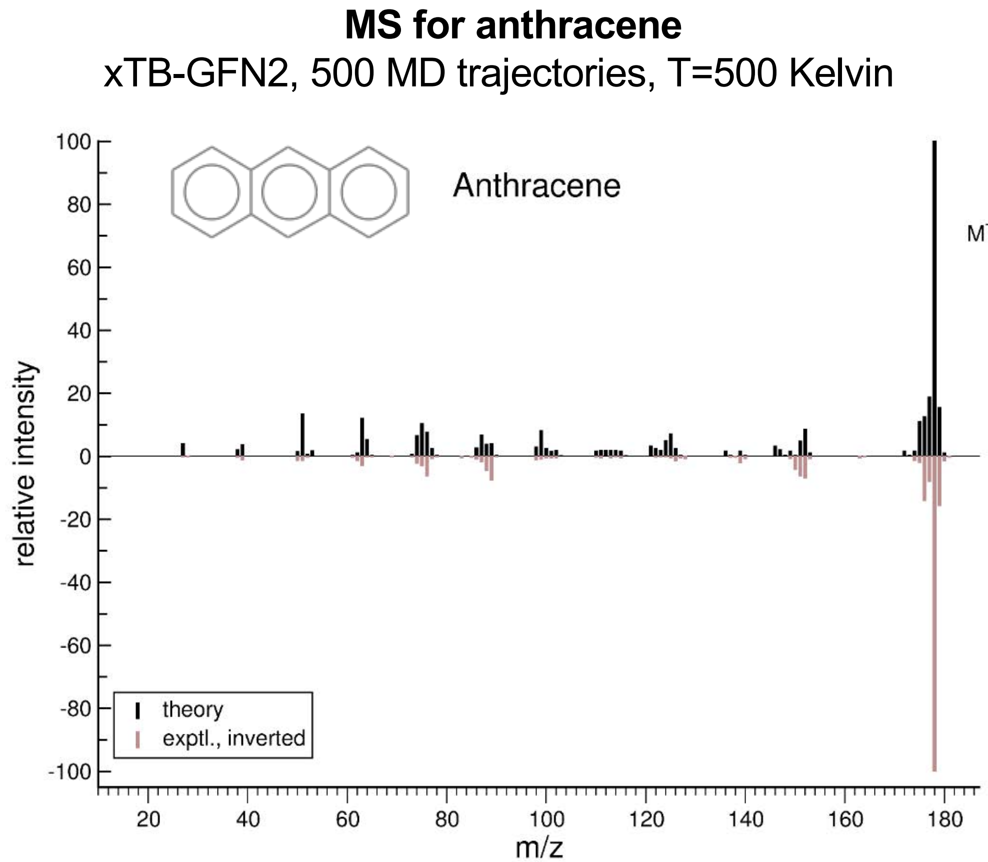




Fracture (Graphene) DFTB+/LAMMPS, *in preparation*

Database of Characteristic Spectra; Example: GC-MS





-. IR and Raman simulations
-. UV/Vis spectra simulations
-. NMR spectra simulations
-. GC-MS spectrum simulations

Life Cycle Technoeconomic Analysis of Coal-Derived Fiber Manufa

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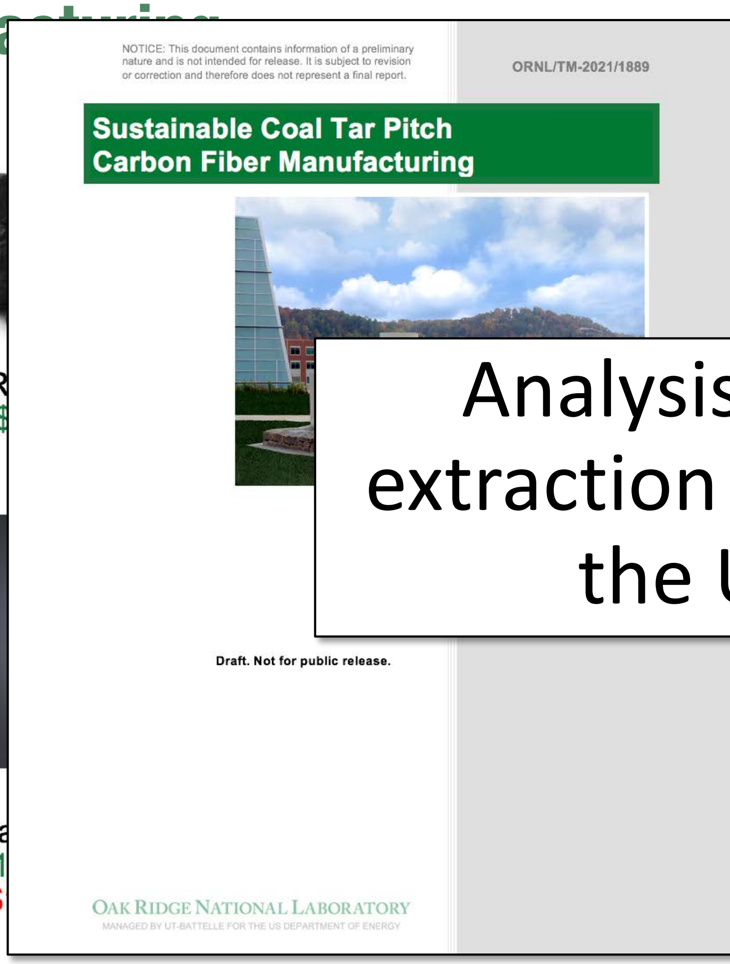
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ORNL/TM-2021/1889

Sustainable Coal Tar Pitch Carbon Fiber Manufacturing

Draft. Not for public release.

OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE US DEPARTMENT OF ENERGY

Analysis is in progress for solvent extraction process being developed by the University of Kentucky

itch Precursor

Coal Tar Pitch
$0.70/kg
$0.2B

OAK RIDGE National Laboratory

Outline

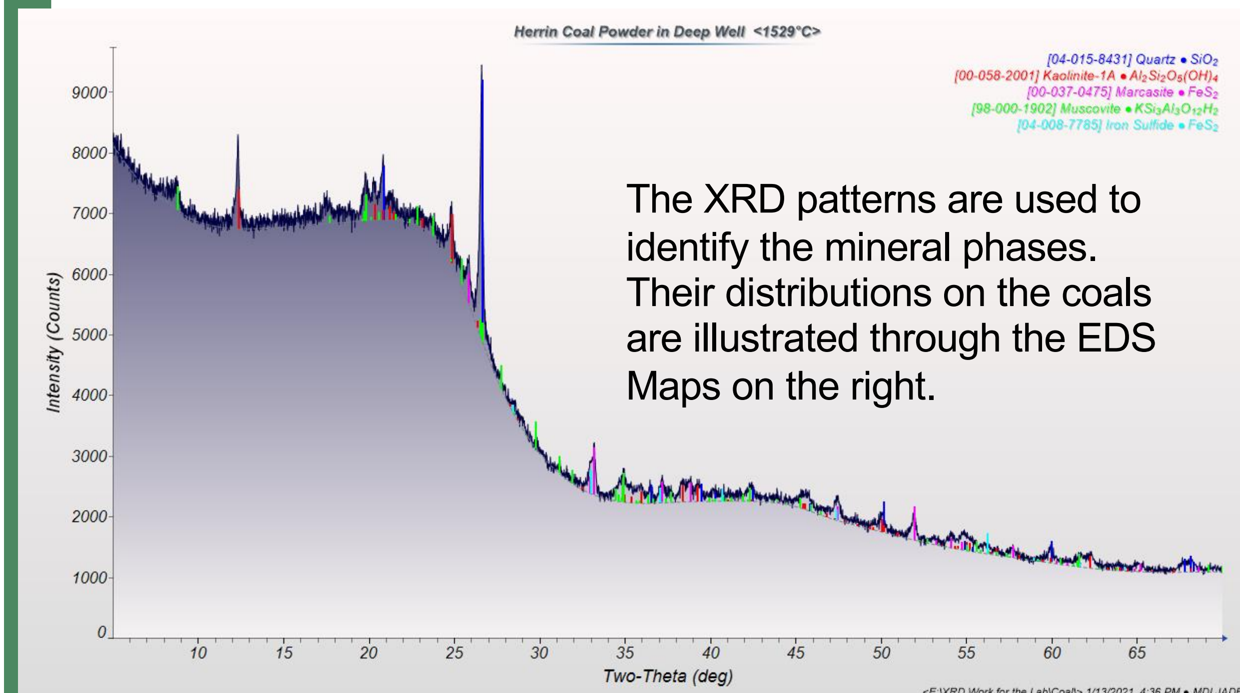
- Background
- Objectives
- Approach
- Results
- Summary

Summary

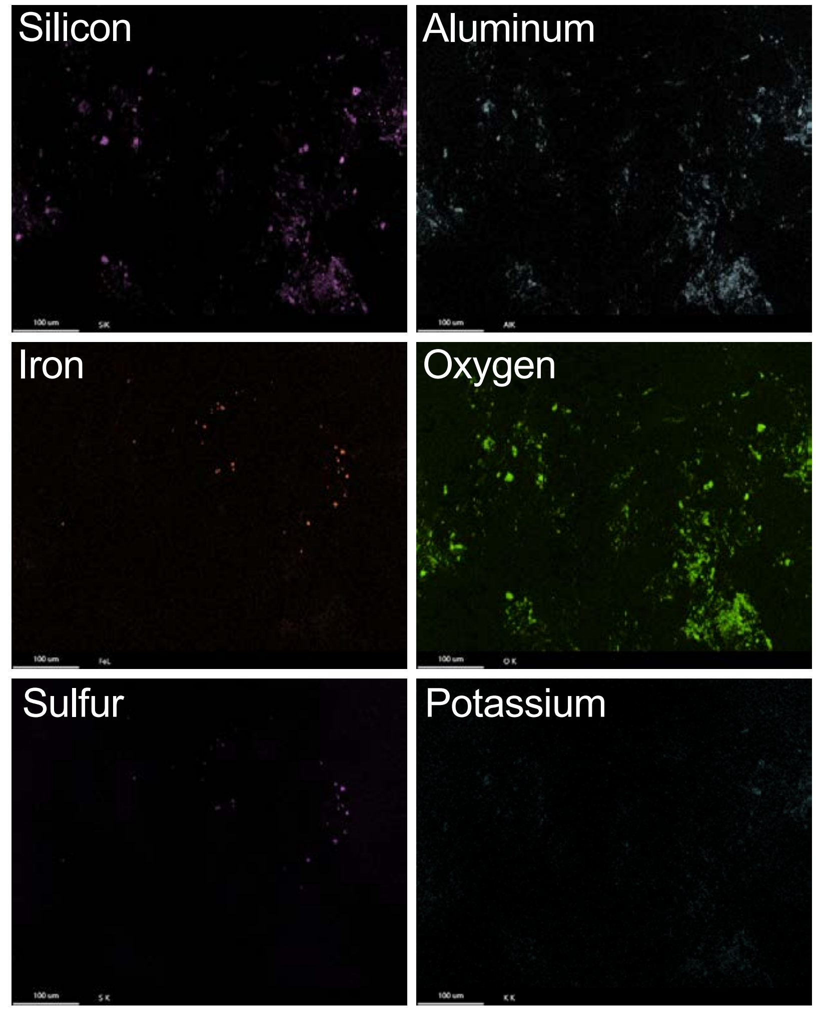
- Significant progress has been made to understand the effect of coal and solvent type on solvent extraction process to obtain spinnable pitches.
- Multi-scale chemical and structural characterization of coals and solvents continues using advanced characterization techniques.
- Scaling-up activities at the Carbon Fiber Technology Facility (melt-blowing) of petroleum-derived pitches are progressing with success.
- Interatomic potentials are being developed for molecular dynamics simulations towards the development of a virtual reactor. Preliminary results have successfully predicted mass spectra of relevant compounds.
- A technoeconomic analysis for coal tar pitch carbon fiber manufacturing has been completed.

Additional Slides

XRD data is supplemented by EDS in identifying the minerals present in the coals



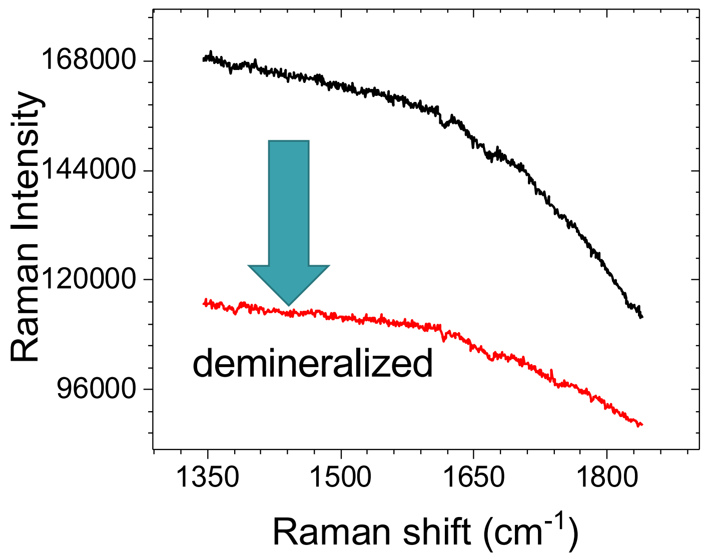
The XRD patterns are used to identify the mineral phases. Their distributions on the coals are illustrated through the EDS Maps on the right.

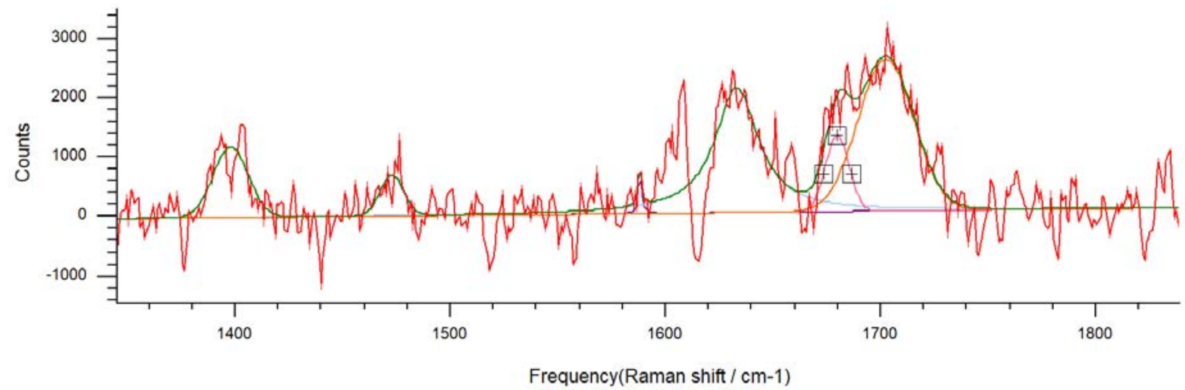


The coals are subjected to demineralization process to reduce/remove the minerals prior to FTIR and NMR measurements.

XRD will also be used to obtain structural parameters such as interlayer spacing, for each coal.

Preliminary Raman Spectroscopy results



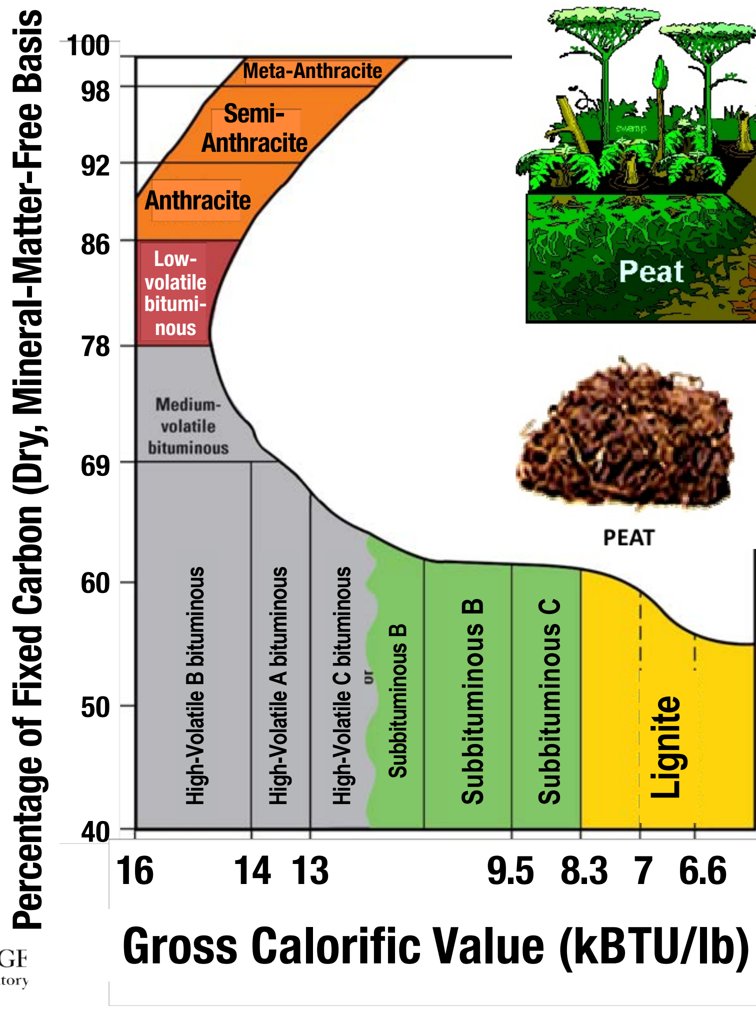


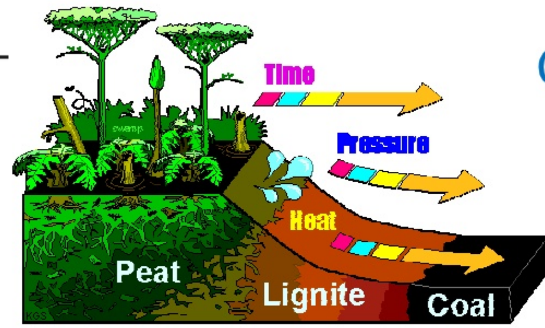
Curve Name	Centre	Width	Height	% Gaussian	Type	Area	ChiSq
Curve 2	1473.86	12.9721	695.671	100	Mixed	9606.1	5.69901
Curve 3	1398.78	19.2635	1211.08	100	Mixed	24833.6	
Curve 4	1589.37	2.10219	602.368	0	Mixed	1989.09	
Curve 5	1634.33	24.5391	2125.15	0	Mixed	81915.8	
Curve 6	1681.2	12.9322	1301.84	100	Mixed	17921	
Curve 7	1703.79	30.4591	2584.07	99.9111	Mixed	83818	

The Raman spectra are currently still being collected. The fits will be used to obtain structural parameters related to different coals.

2D Raman maps are also being collected on all the coals being investigated.

Not all coals are the same!

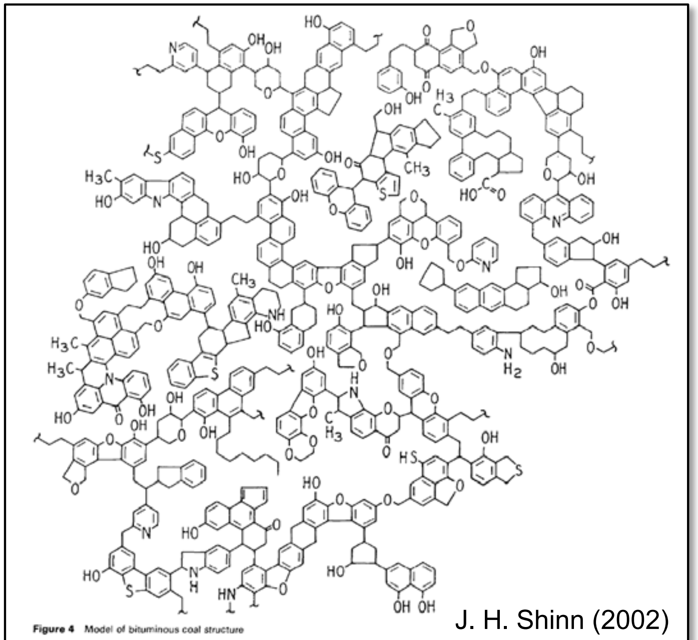




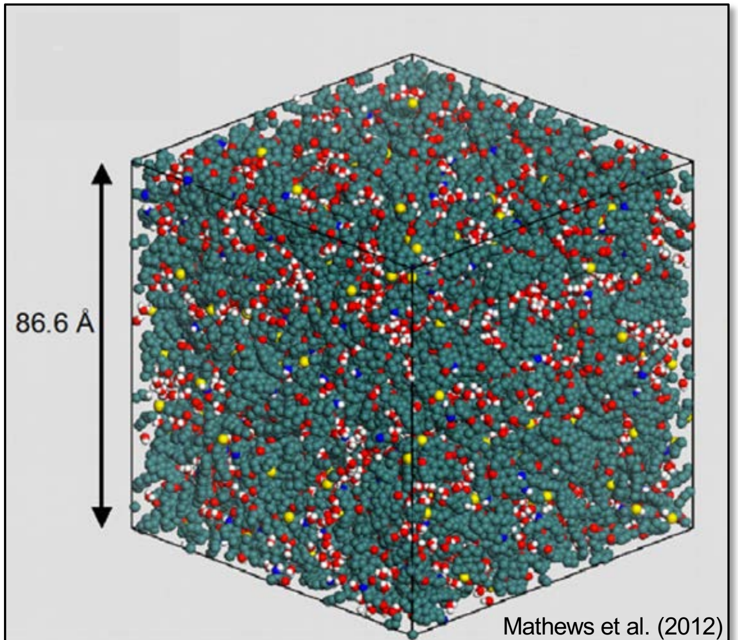
Coal – Stages of Formation

Fossil Fuels. Energy Information Association

The Molecular Structure of Coal



J. H. Shinn (2002)



Mathews et al. (2012)

This project will develop molecular models for several coals of interest

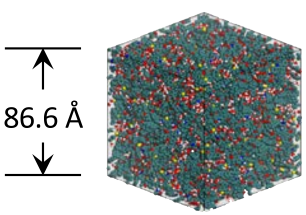
Coal-to-Fibers at ORNL's Carbon Fiber Technology Facility

By using **computational chemistry**, **machine learning** and **advanced characterization tools**, it will be possible to establish processing-structure-properties relationships for coal and coal-derived pitch at the molecular and mesoscale levels. This will accelerate the development of processes for fabricating coal-derived products with specific properties and performance (e.g., structural fibers or fibers for thermal management applications)

Not all coals are the same

Coal-Derived Pitch Processing

RAMACO CARBON



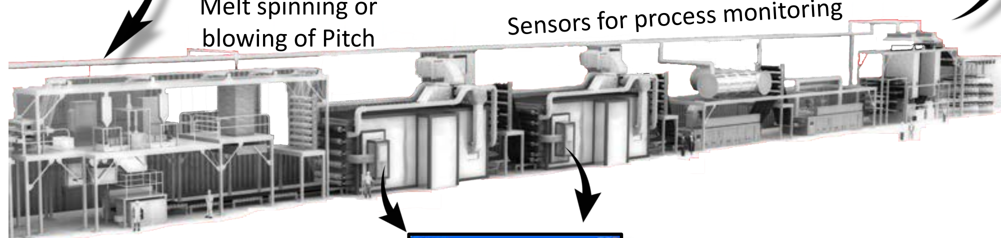
86.6 Å

Molecular Structure of Coal

High-throughput characterization tools will be used to determine the molecular structure of any type of coal.

Melt spinning or blowing of Pitch

Sensors for process monitoring

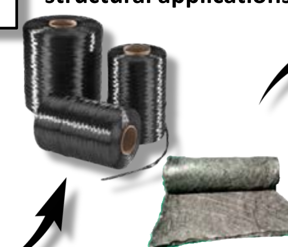


Process Control

Lara-Curzio (2019)

CFTF settings are selected based on the nature of the feedstock and desired final product

Continuous carbon fibers for structural applications



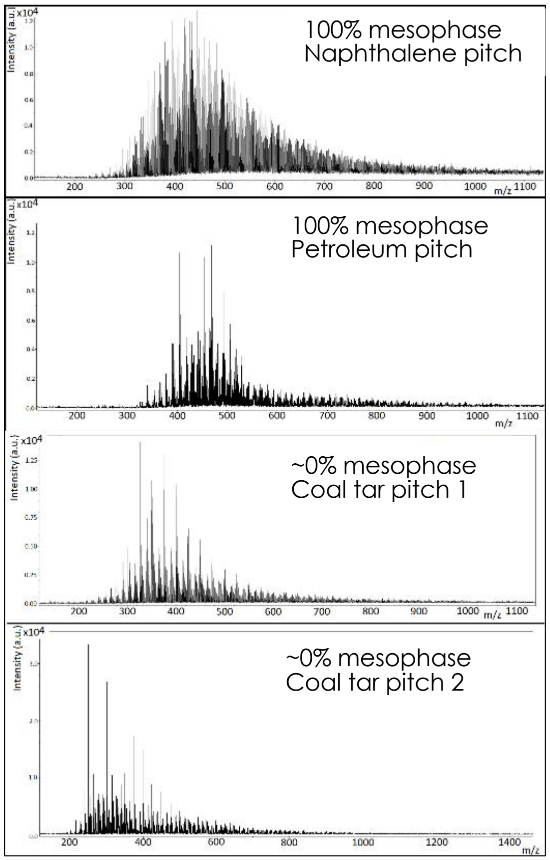
Composite Materials and Structures

Short carbon fibers for structural applications

Short carbon fibers for thermal insulation

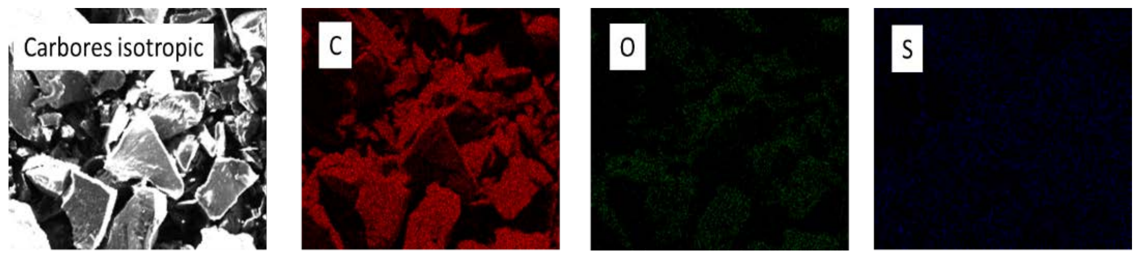
Molecular weight distribution and elemental composition

MALDI-TOF-MS



- Molecular weight distribution measurements (by MALDI-TOF-MS) shows the variety of pitch compositions
- SEM/EDS can be used to screen before applying more detailed tools

SEM/X-ray Energy Dispersive Spectroscopy



	C at.%	O at.%	S at.%
100% mesophase naphthalene pitch	98.15 ± 0.18	1.70 ± 0.18	0.15 ± 0.00
100% mesophase Petroleum pitch	96.31 ± 0.05	3.35 ± 0.12	0.34 ± 0.08
0% mesophase coal tar pitch 1	96.32 ± 0.55	3.40 ± 0.57	0.28 ± 0.02
0% mesophase coal tar pitch 2	96.93 ± 0.28	2.11 ± 0.23	0.96 ± 0.06