OAK RIDGE National Laboratory

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

2020 Advanced Coal Processing Review Meeting

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UK-CAER—Rodney Andrews, Matt Weisenberger, John D. Craddock, David L. Eaton, and Ashley Morris

October 19, 2020

U.S. DEPARTMENT OF ENERGY

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

Outline

- Background
- Objectives
- Approach
- Results
- Summary

Outline

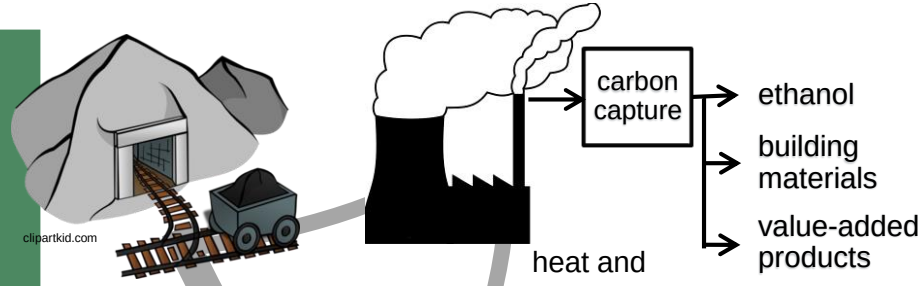
- Background

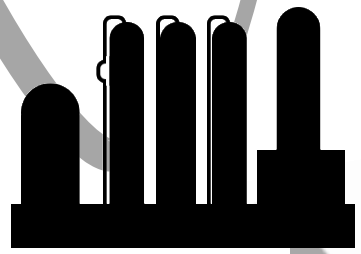
Converting Coal into Value-Added Pro

Finding use for every molecule that is mined.

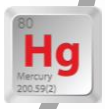
No molecule left behind!

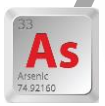
Developing the underlying and translational science to enable the development and deployment of energy-efficient and cost-effective processes for: recovering rare-earth elements from coal and converting coal into high value-added products thus enabling the creation of new manufacturing industries and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




Coal "Refinery"

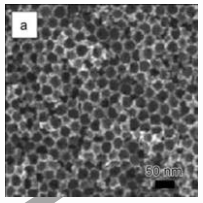
chemicals



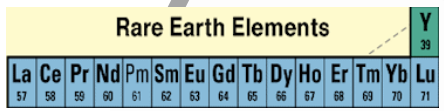


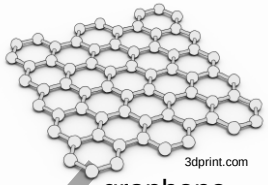

water

activated carbon

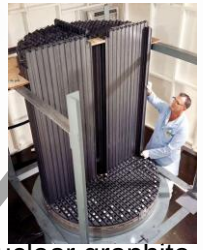


mesoporous carbon

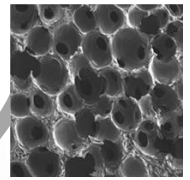




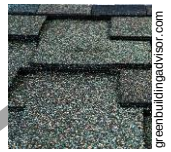
graphene


nuclear graphite

thermal management


thermal conduction

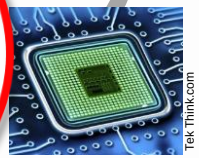

thermal insulation



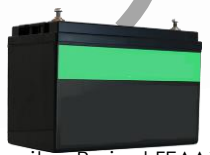
building and construction materials


metallurgical coal


carbon fibers



electronic devices including photovoltaics


Electrodes for Li-ion batteries and supercapacitors

Lara-Curzio et al. (2016)

Carbon Fiber Composites are widely used in Aerospace Technologies

Boeing.com

Boeing 787 fuselage

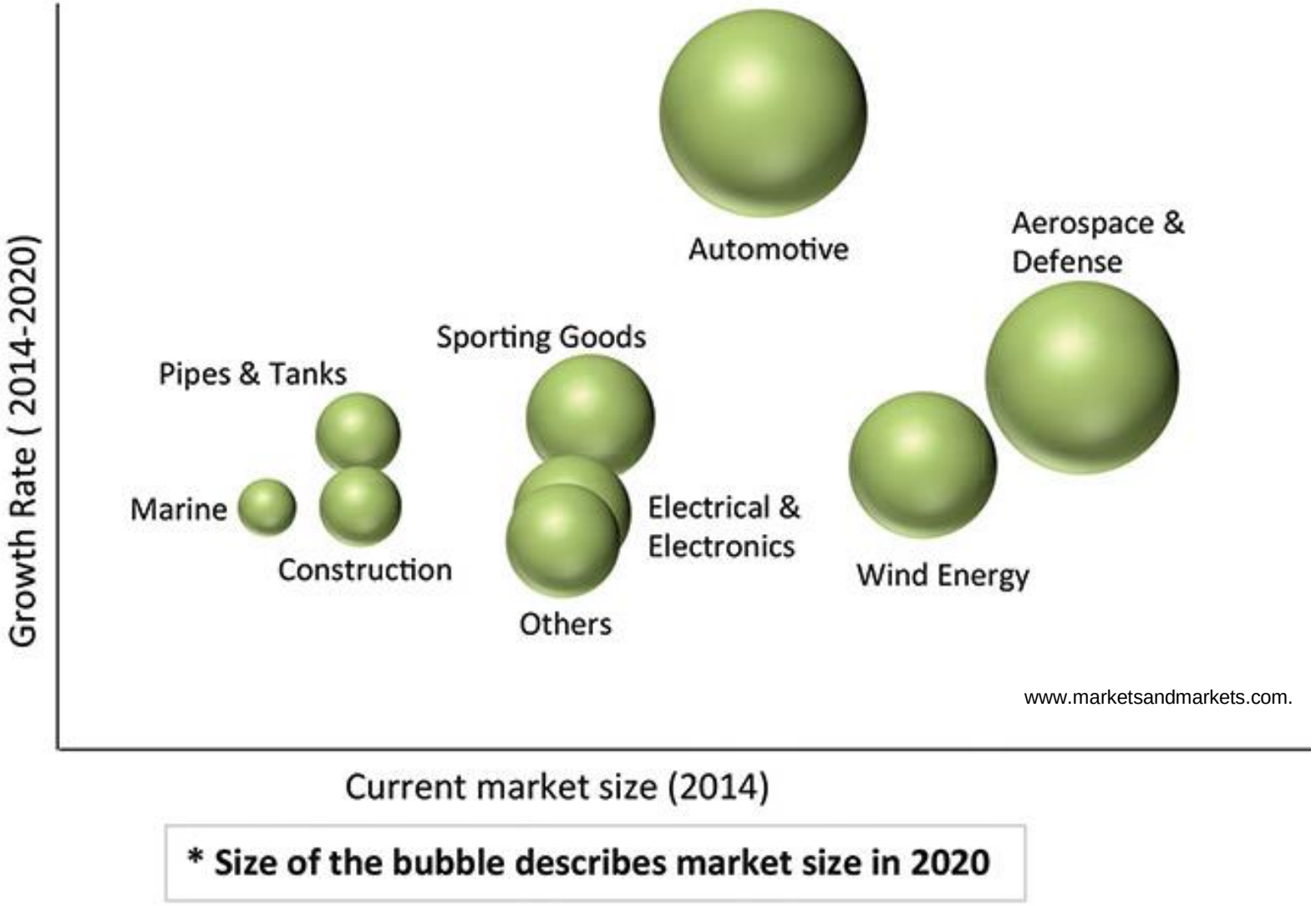
OAK RIDGE National Laboratory

Carbon fiber composites have started to be used in high volume in automobiles: BMW i3: mass-produced carbon fiber cars finally come of age

BMW.com

Lara-Curzio et al. (2016)

Potential of Carbon Fiber Composites Market Growth



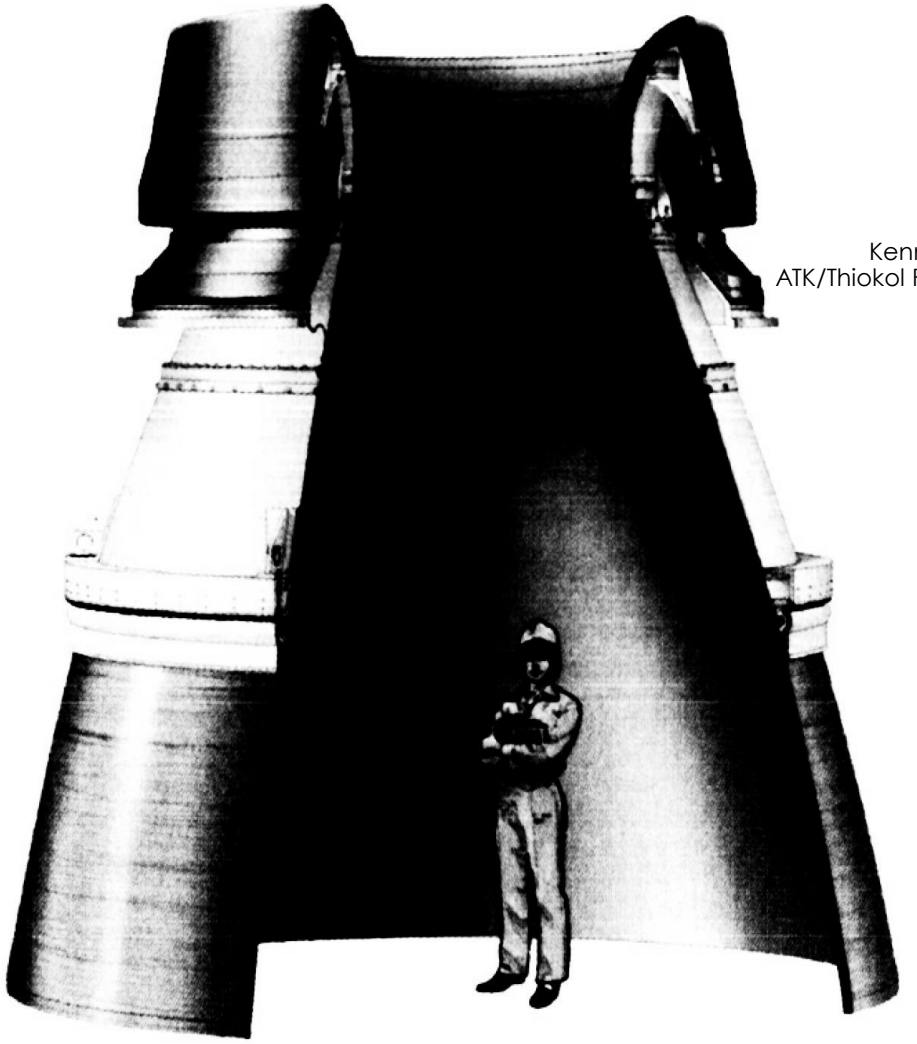
Lara-Curzio et al. (2016)

ut it is not only about stiffness and strengt

Low thermal conductivity carbon fibers could be widely used for building insulation

OAK RIDGE National Laboratory

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



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

Solid-rocket motor nozzle

Outline

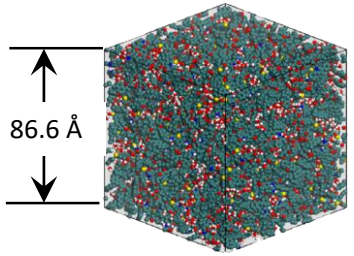
- Background
- Objectives:
  - To develop the underlaying and translational science to establish processing-structure-properties relationships for coal-derived carbon fibers, that will enable energy-efficient and cost-effective processes for manufacturing carbon fibers with tunable properties.
  - This 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 (

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



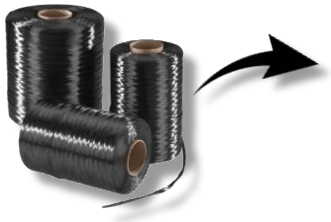
The molecular representation of coal will inform computational chemistry models to identify the most energy efficient and cost-effective pathways for processing coal into precursors best suited for manufacturing carbon fibers

Bringing new Industries to coal communities

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

Not all coals are the same

Continuous carbon fibers for structural applications



Composite Materials and Structures

Short carbon fibers for structural applications

Short carbon fibers for thermal insulation

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

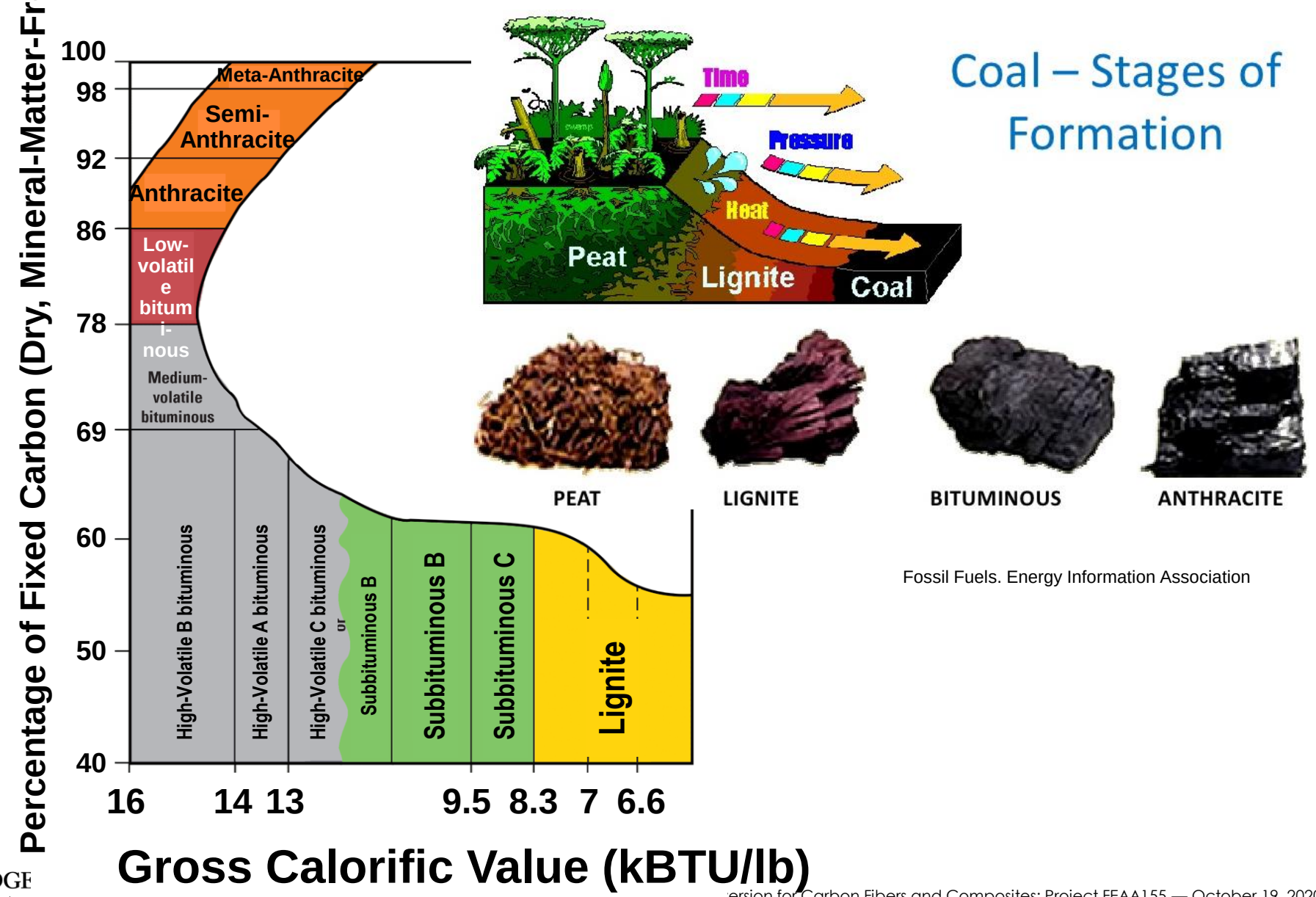
Lara-Curzio et al. (April 2020)

Outline

- Background.
- Objective
- Approach

Not all wines are the same!

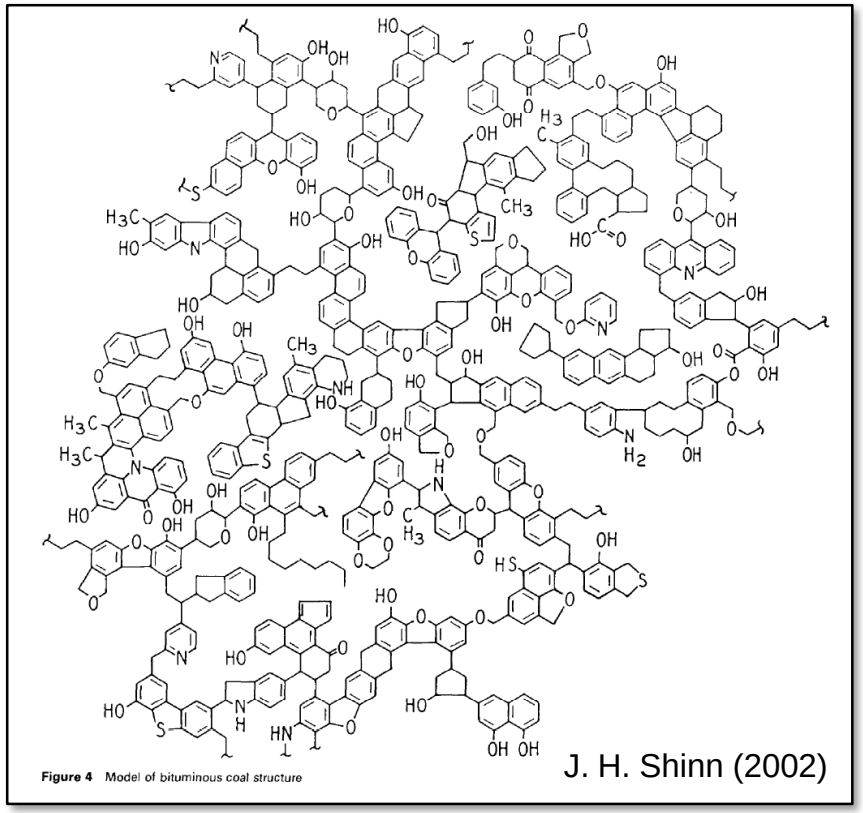
Not all coals are the same!



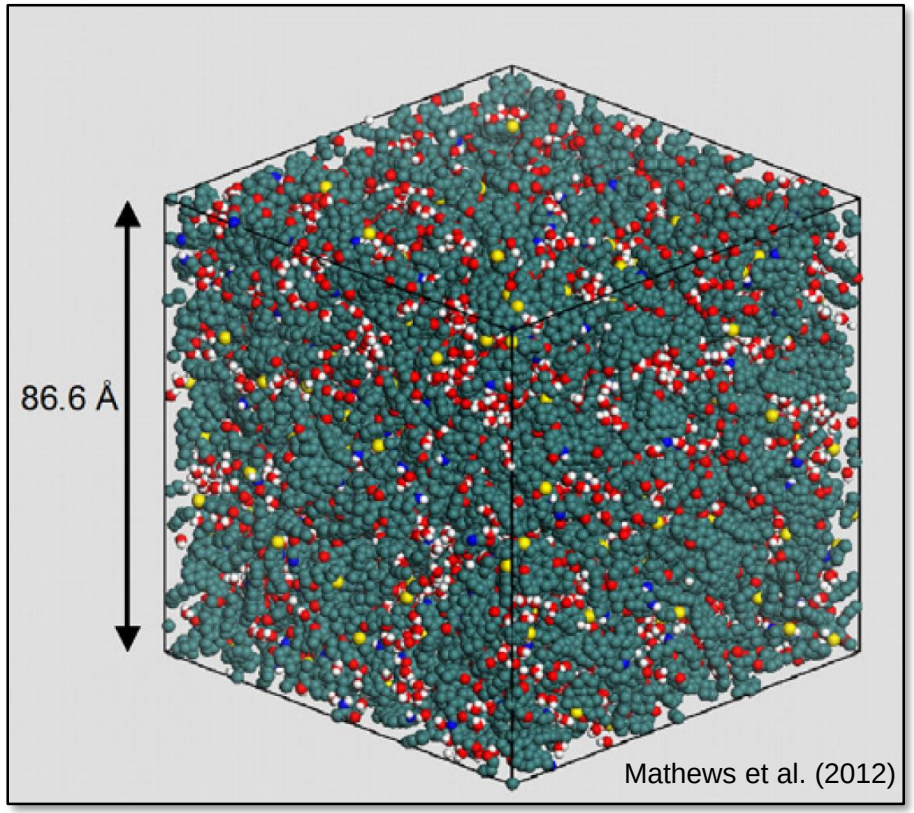
Coal – Stages of Formation

Fossil Fuels. Energy Information Association

The Molecular Structure of Coal



J. H. Shinn (2002)



Mathews et al. (2012)

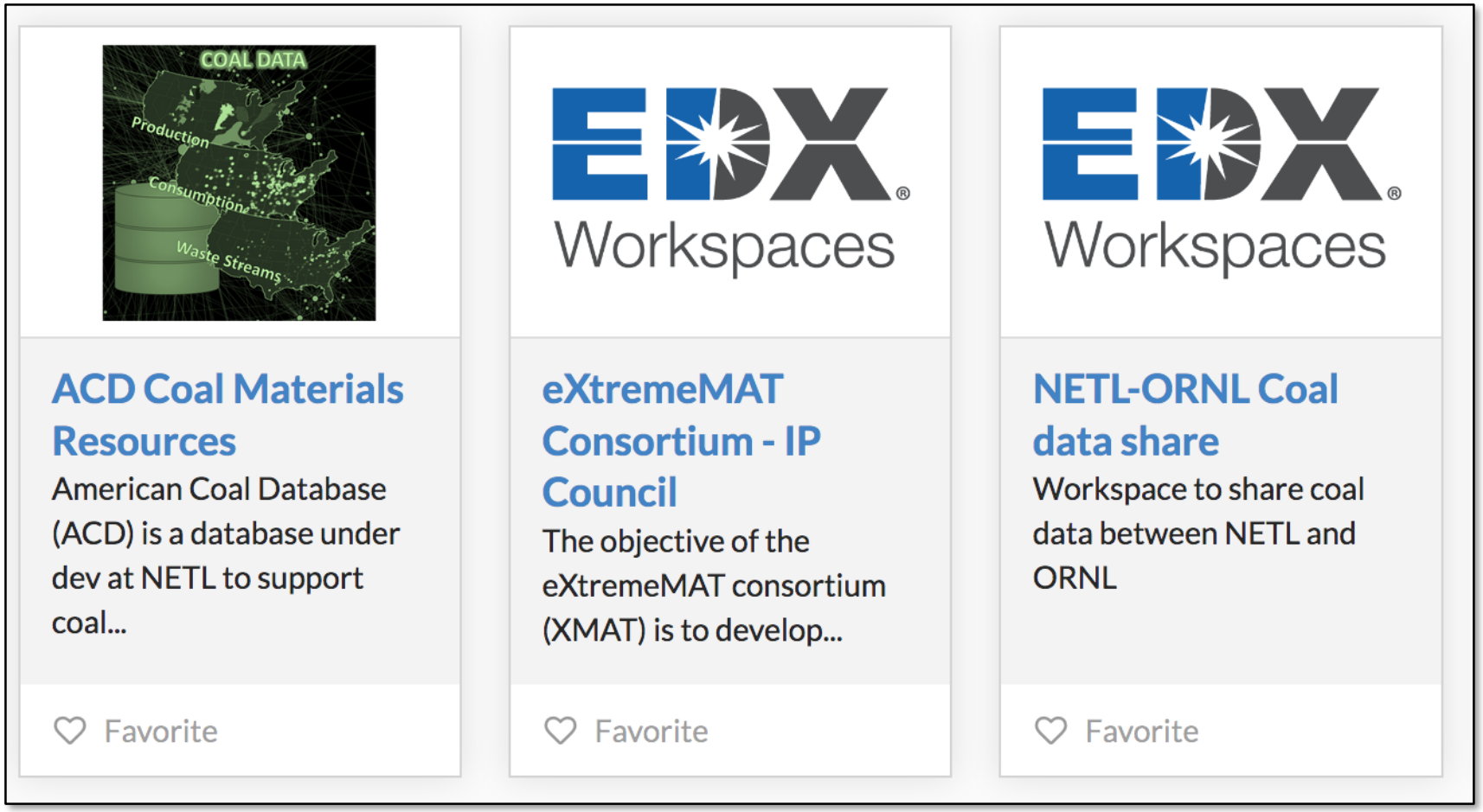
This project will develop molecular models for several coals of interest

Advanced Characterization

The project will leverage the unique capabilities available at ORNL, UK, and DOE User Facilities to obtain descriptions of coals at different length scales including at the molecular level.

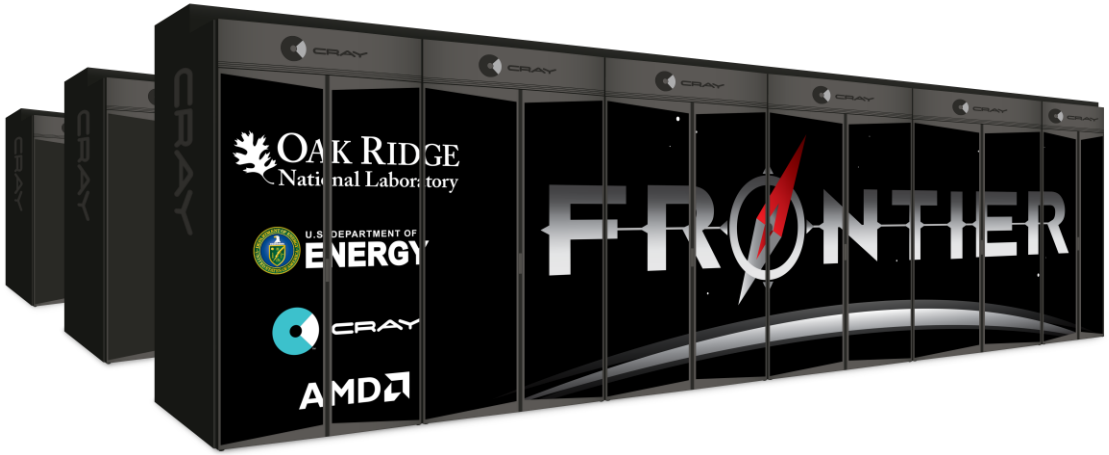
- Small-Angle Scattering (neutron and X-ray)
- X-ray Photoelectron, X-ray Adsorption Near-Edge Structure, Raman, Infrared, and Laser- Induced Breakdown Spectroscopy
- High-resolution Electron Microscopy
- Nuclear Magnetic Resonance
- Other

Data Management Plan



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

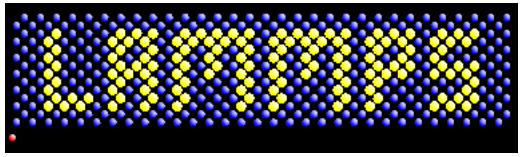
Computational Chemistry



ORNL will use the world's fastest high-performance computing systems to perform complex computational chemistry calculations. These systems provide unprecedented opportunities for the integration of artificial intelligence (AI) and scientific discovery.

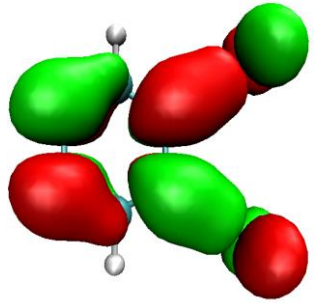
Density-Functional Tight-Binding (DFTB)

Hybrid between DFT and Tight Binding (TB)

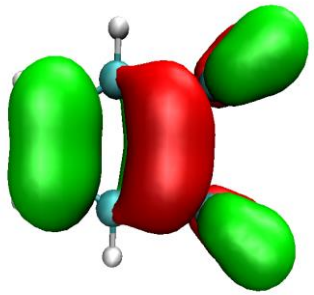


\+ GS Jung, ORNL

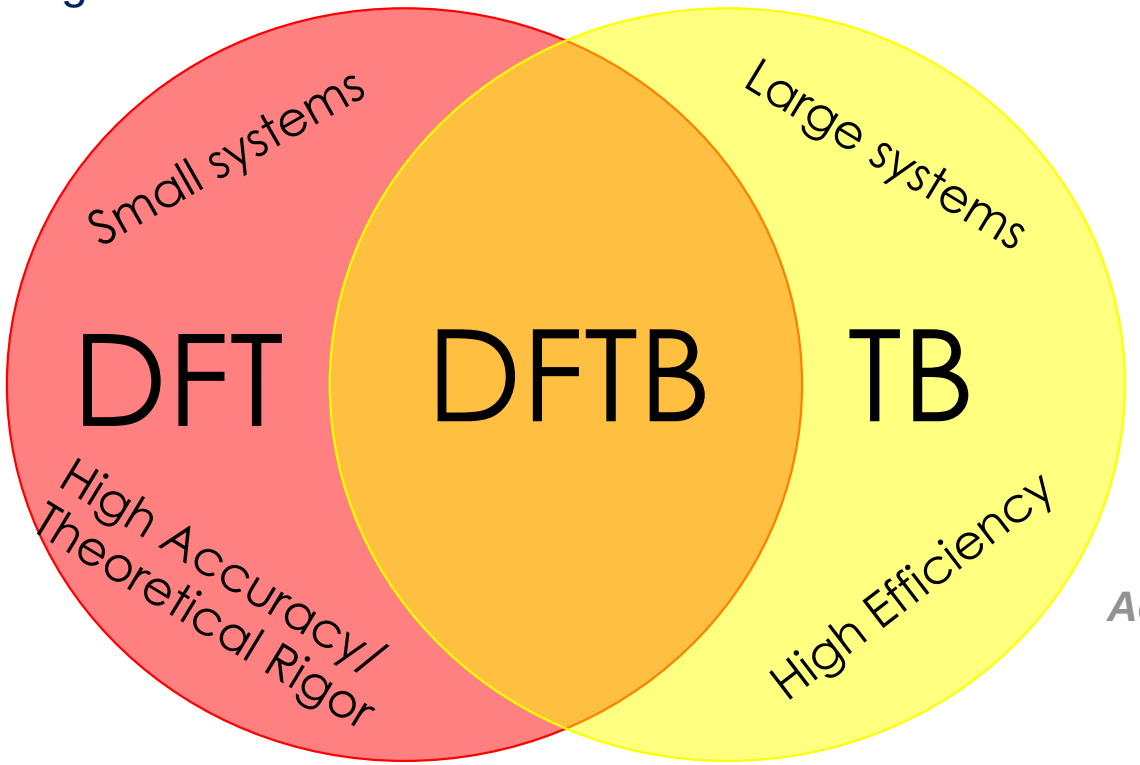
Self-Consistent Charge-DFTB/mio

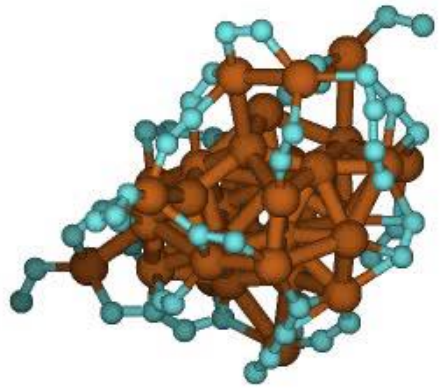


ε = -3.13 eV



ε = -7.39 eV





ACS Nano 2008, 2009; ***JACS*** 2011; ***Acc. Chem. Res.*** 2010; …; ***Carbon*** 2016

Eschrig, Seifert (1980's):

- 2-center approximation
- Nearest-neighbors only
- Minimum basis set
- Valence-electrons only

Main advantage: Pre-tabulated parameters!

Helmut Eschrig

Gotthard Seifert

Thomas Frauenheim

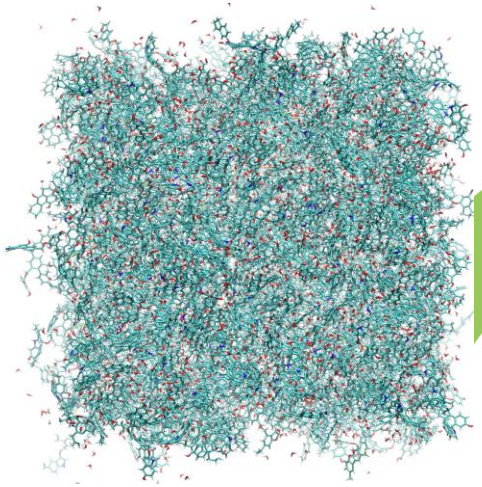
Classical reactive force field aware of π-electrons

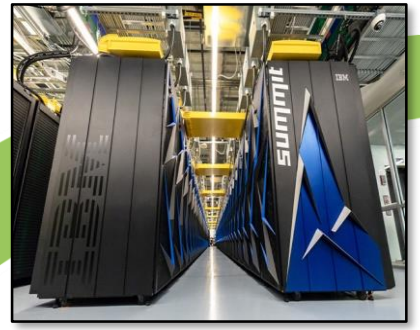
- DFTB training data
  - Energies, forces

Machine Learning (ML)

Reactive FF + ML

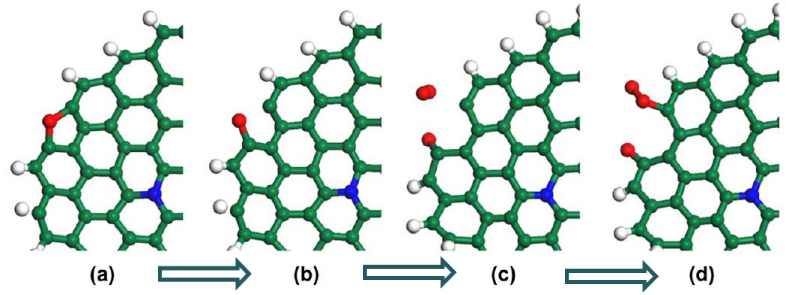
Based on charge-optimized many body (COMB) potentials, reactive bond order (REBO) force field, etc.





0.3 exaFLOPS, 2018

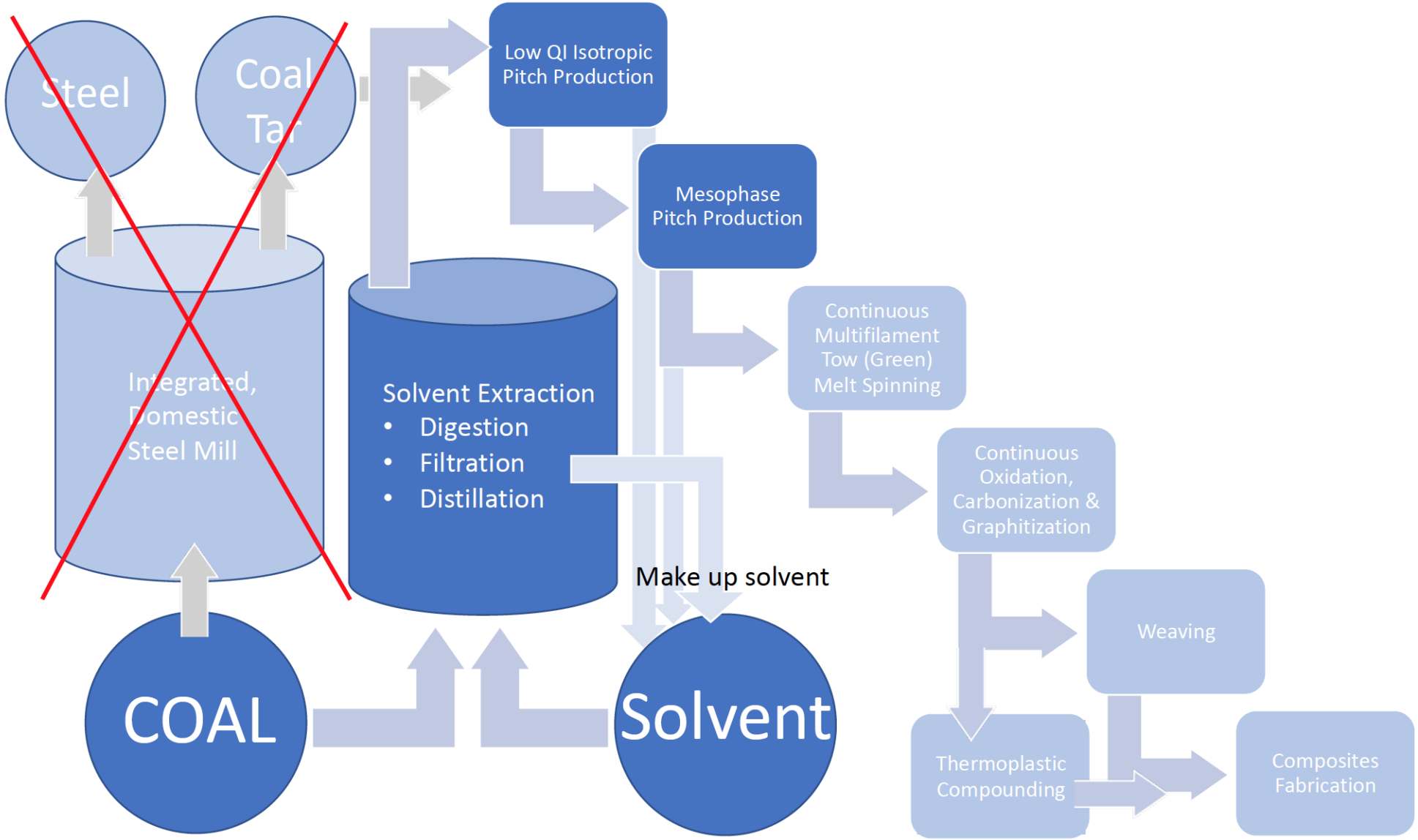
1.5 exaFLOPS, 2021



Δ , p

Reactive MD Simulations with high fidelity

Advanced Coal Processing at UK-CAER

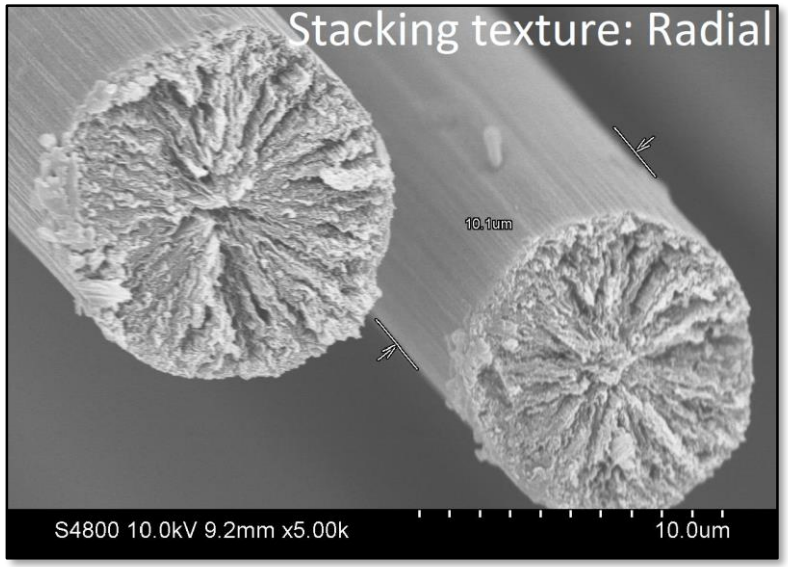


Coals and Solvents of Initial Interest

- **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

Lab-Scale Fiber Manufacturing

- Melt-Spinning
- Melt-Blowing



Challenges

- chemical heterogeneity
- Oxidation kinetics

Focus

- Close ORNL-UK collaboration
- Composition – rheology -spinnability relations
- Tailoring micro/nanostructure for optimization of mechanical and physical properties

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

Not all coals are the same

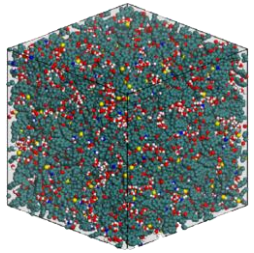
Coal-Derived Pitch Processing

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)

Continuous carbon fibers for structural applications

Composite Materials and Structures

86.6 Å

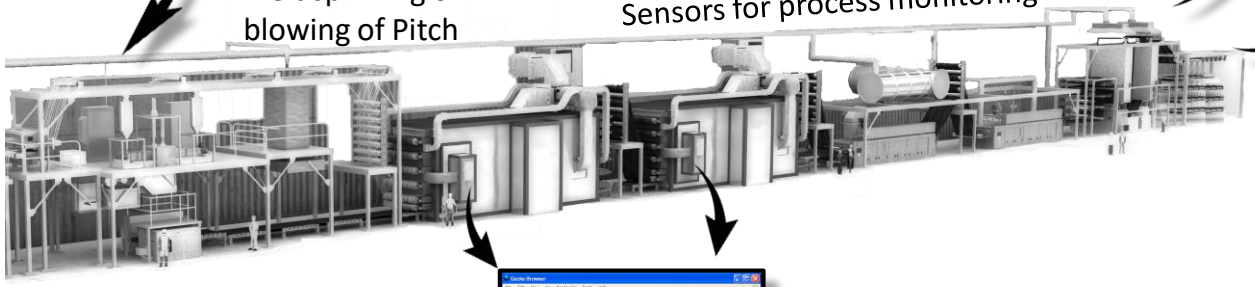


Molecular Structure of Coal

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

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

Short carbon fibers for structural applications

Short carbon fibers for thermal insulation

Lara-Curzio (2019)

OAK RIDGE National Laboratory

Life Cycle Technoeconomic Analysis of Coal-Derived Fiber Manufacturing

Re-analyzing old assumptions

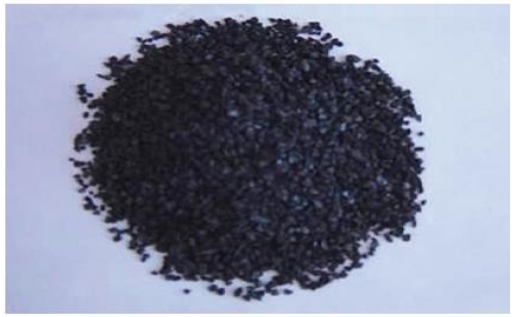
Raw Coal
$0.03/kg
$21B

Metallurgical Coal
$0.15/kg
$51B

Coke
$0.25/kg
$2.9B

Coal Tar
$0.40/kg
$0.24B

Coal Tar Pitch
$0.70/kg
$0.2B



Mesophase Coal Tar Pitch Precursor
$3.30/kg
$0.8B

Pitch Carbon Fiber
$11.00/kg
$1.9B

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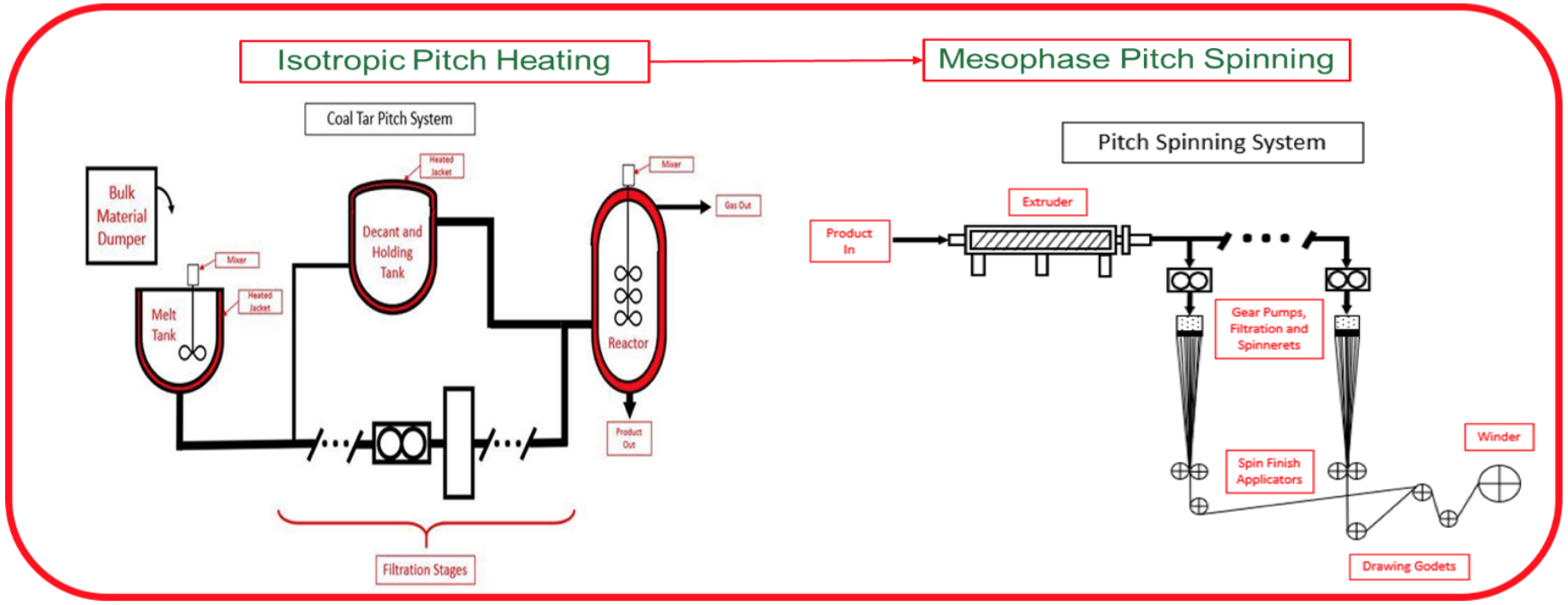
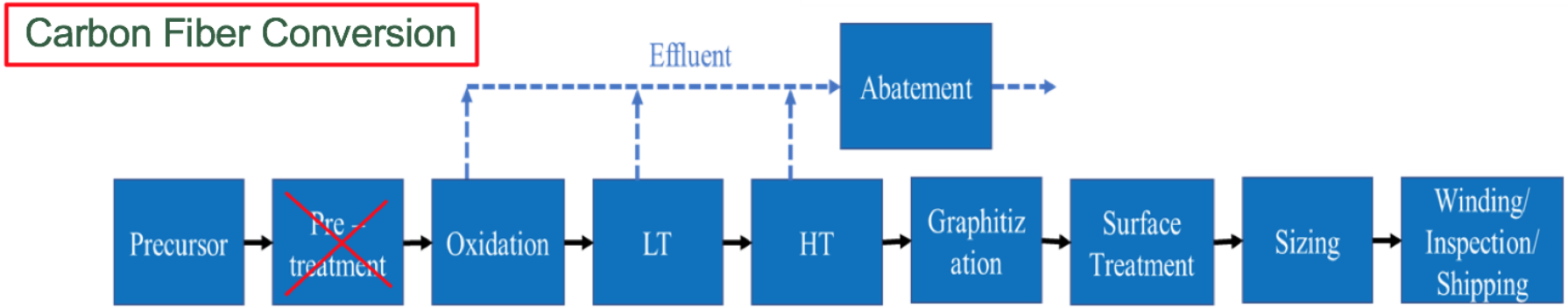
Life Cycle Technoeconomic Analysis of Coal-Derived Fiber Manufacturing

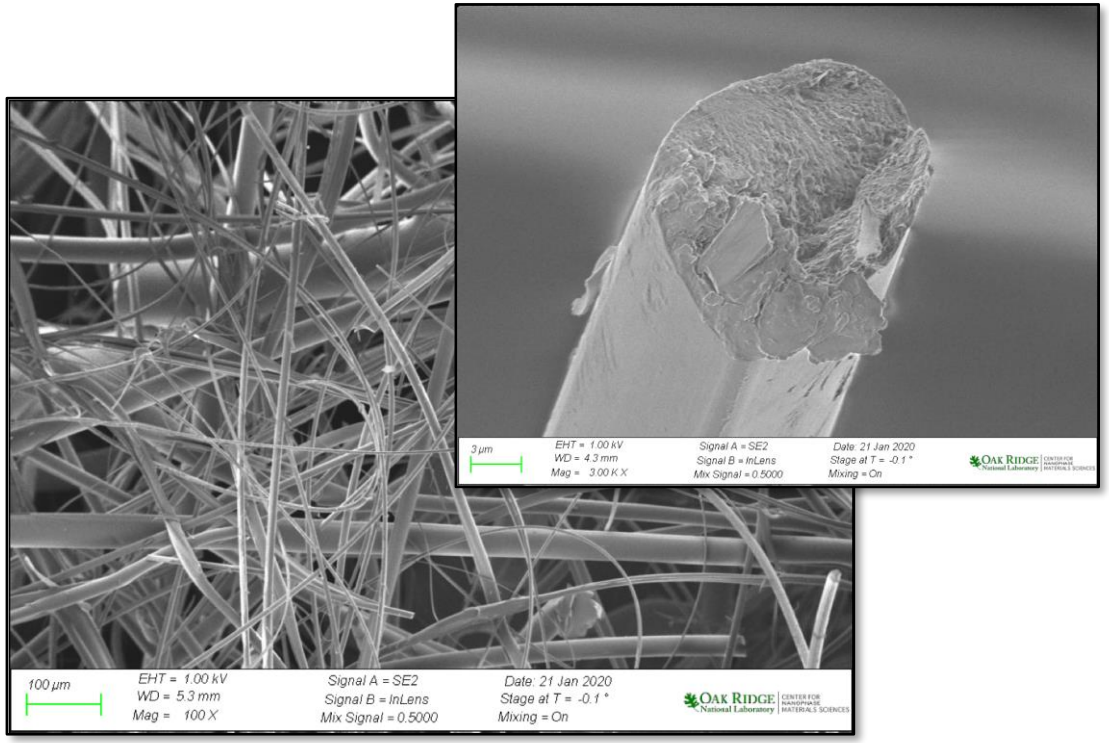
Direct
Coal Liquefaction
Isotropic Pitch





Recent Results

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



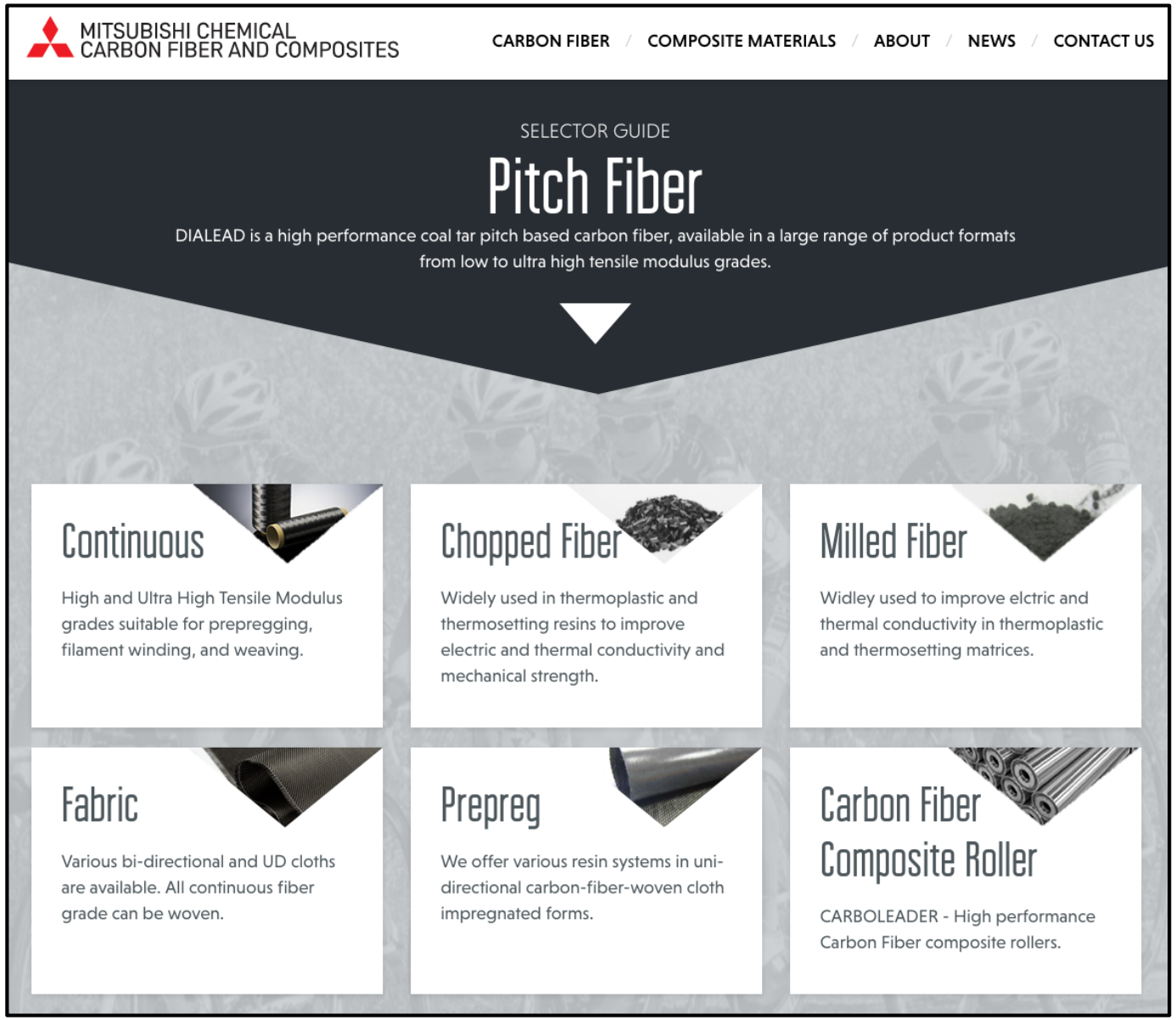
Thermal Conductivity ~ 0.04 W/m•K

Summary

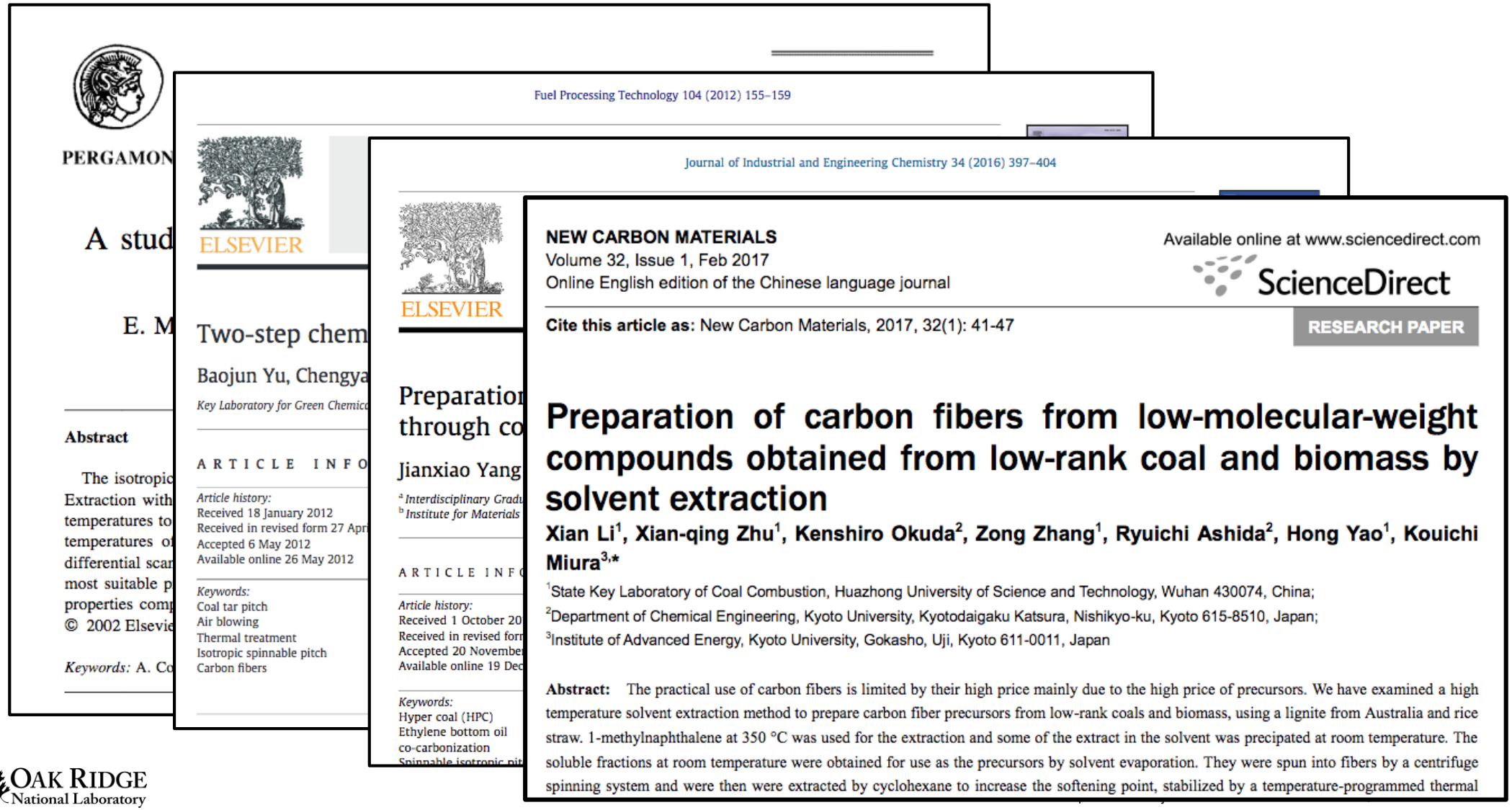
- A new project has been established to demonstrate the manufacture of coal-derived carbon fibers with tunable properties at semi-production scale at ORNL's Carbon Fiber Technology Facility.
- The project is built on deep and broad expertise at ORNL and UK-CAER in coal science and carbon fiber manufacturing, and it leverages extraordinary resources for advanced characterization and computational chemistry that did not exist 20 years ago, to accelerate the establishment of processing-structure properties relationships for coal-derived carbon fibers.
- Knowledge developed in this project will enable the processing of other coal-derived products.

So, what is new or different?

Coal Tar-derived Carbon Fibers have been commercialized



Background — Several groups are trying to develop Coal-Derived Carbon Fibers



PERGAMON

A stud

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Abstract

The isotropic
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© 2002 Elsevie

Keywords: A. Co

Fuel Processing Technology 104 (2012) 155–159

ELSEVIER

Two-step chem

Baojun Yu, Chengya

Key Laboratory for Green Chemica

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Coal tar pitch
Air blowing
Thermal treatment
Isotropic spinnable pitch
Carbon fibers

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Preparation
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Jianxiao Yang

[a] *Interdisciplinary Gradu*
[b] *Institute for Materials*

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RESEARCH PAPER

Preparation of carbon fibers from low-molecular-weight compounds obtained from low-rank coal and biomass by solvent extraction

Xian Li[1], Xian-qing Zhu[1], Kenshiro Okuda[2], Zong Zhang[1], Ryuichi Ashida[2], Hong Yao[1], Kouichi Miura[3,*]

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Abstract: The practical use of carbon fibers is limited by their high price mainly due to the high price of precursors. We have examined a high temperature solvent extraction method to prepare carbon fiber precursors from low-rank coals and biomass, using a lignite from Australia and rice straw. 1-methylnaphthalene at 350 °C was used for the extraction and some of the extract in the solvent was precipated at room temperature. The soluble fractions at room temperature were obtained for use as the precursors by solvent evaporation. They were spun into fibers by a centrifuge spinning system and were then were extracted by cyclohexane to increase the softening point, stabilized by a temperature-programmed thermal

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