Experimental validation of coal gasification with neutron imaging

This material is based upon work supported by the Department of Energy Award Number FWP-FEAB325.

James E. Parks II, Charles E.A. Finney,
Costas Tsouris
Oak Ridge National Laboratory

DOE-NETL'S 2021 INTEGRATED PROJECT REVIEW MEETING:
GASIFICATION SYSTEMS
May 4, 2021

Acknowledgements

DOE/NETL

David Lyons
Diane Madden
Lynn Brickett
Jonathan Leske
James Bennett
Bill Rogers
Mehrdad Shahnam

ORNL

Luke Daemen (SNS)
Yuxuan Zhang (HFIR)
Erik Stringfellow (HFIR)
Scott Palko (NTRC)
Jonathan Willocks (NTRC)
Madhavi Martin
Yarom Polsky
Edgar Lara-Curzio
Xin Sun
Hassina Bilheux (SNS/HFIR)

NIST

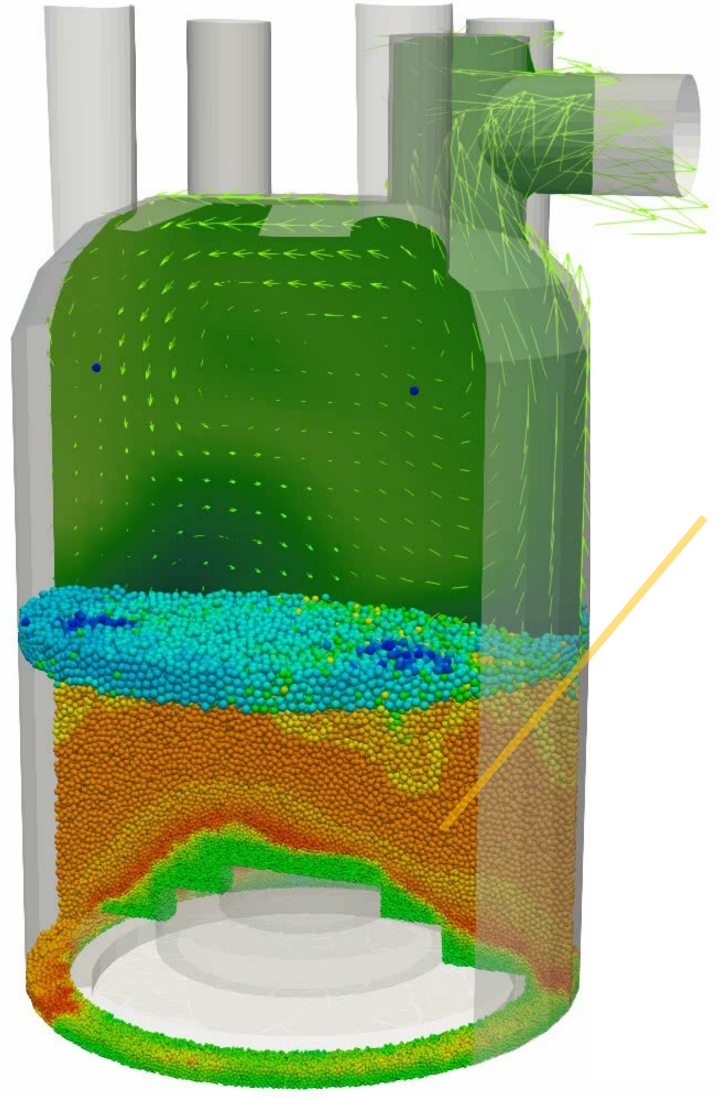
Jacob LaManna
Eli Baltic

Coal samples

Joe Sheets (3J Enterprises, Newburg WV) – Sample A (anthracite)
Jim Mullins, **Shelby Howard** (Covol Fuels No. 3, Beverly KY) – Sample B (Blue Gem bituminous)
Cosmin Dumitrescu (West Virginia University, Morgantown WV) – Sample C (Pittsburgh #8 bituminous)
Jeff Barron (WWC Engineering, Sheridan WY) – Sample D (sub-bituminous)
Mike Heger (BNI Inc., Center ND) – Sample E (lignite)
Chilkoot Ward (Usibelli Coal Mine), **Brent Sheets** (University of Alaska, Fairbanks) – Sample U (Usibelli sub-bituminous)

Research sponsored by the U.S. Department of Energy Office of Fossil Energy
This material is based upon work supported by the Department of Energy Award Number FWP-FEAB325.

This project aims to obtain nonintrusive model validation data from inside operating gasifiers



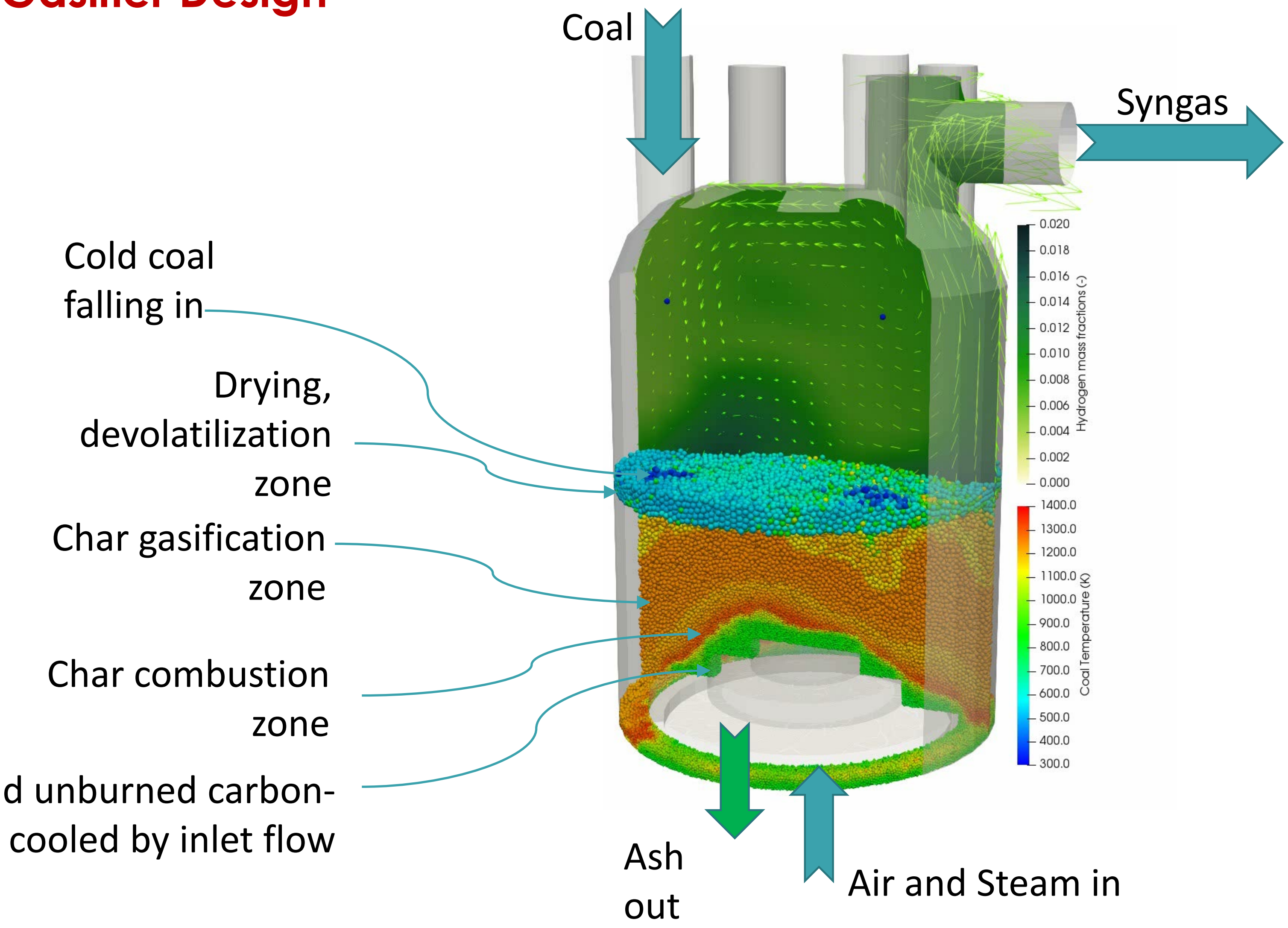
No known nonintrusive techniques to dynamically track coal gasification progression *in situ*

- Simulations are critical to designing next-generation advanced reactors
- Models such as MFiX rely on validation data for tuning and accuracy
- Measurement observations from inside operating gasifiers are difficult to obtain
- **Approach:** Use neutrons which interact strongly with H and weakly with metals, giving the ability to view coal pyrolysis and gasification *in situ*
- **Objective:** Obtain nonintrusive validation data from an operating gasifier, acquiring internal information and product-gas measurements to enable accurate simulations of coal gasification.

Graphics courtesy of W.A. Rogers (NETL)

An updraft, moving bed gasifier is our target design

See next presentation, "Advanced Gasifier Design" by Bill Rogers (NETL)



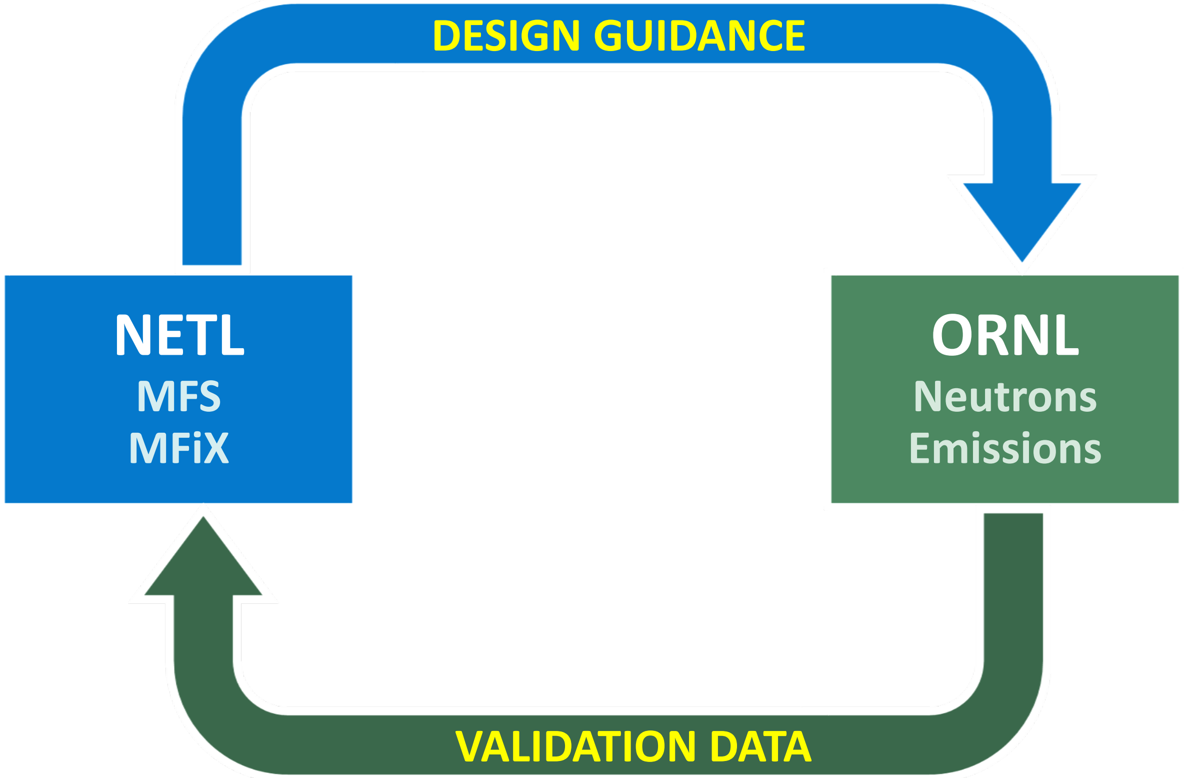
We aim to peer inside a similar reactor using neutrons to map the degree of gasification in space and time.

Graphics courtesy of W.A. Rogers (NETL)

ORNL research supports NETL in this project

NATIONAL ENERGY TECHNOLOGY LABORATORY

- Coal gasification expertise
- Multiphase flow experimental & computational expertise
- MFiX – Multiphase Flow with Interphase eXchange – CFD suite

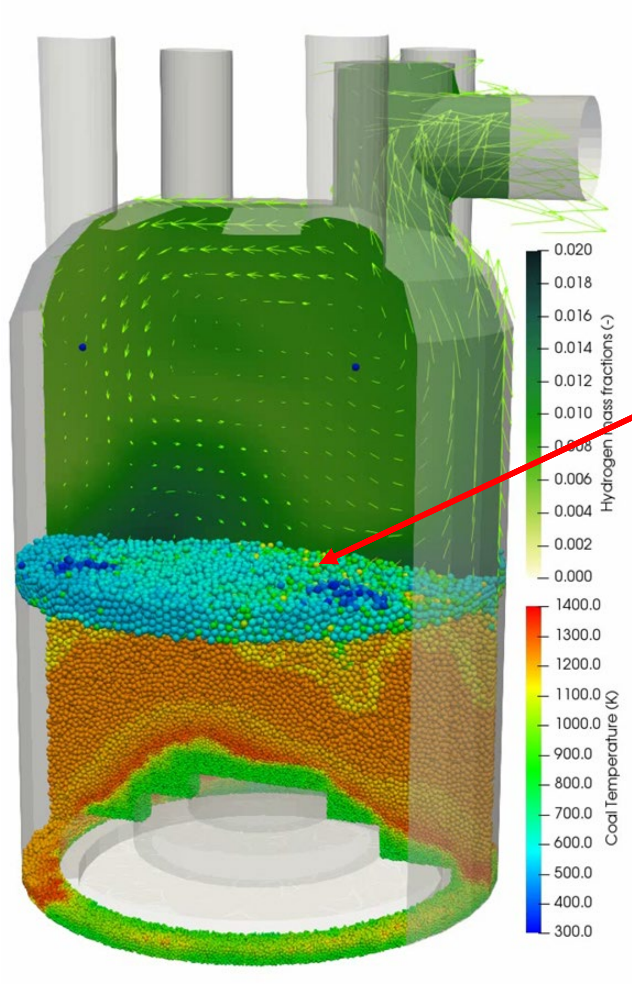


OAK RIDGE National Laboratory

- Neutron-scattering science facilities and expertise (High Flux Isotope Reactor, Spallation Neutron Source)
- Gaseous emissions facilities and expertise (National Transportation Research Center)

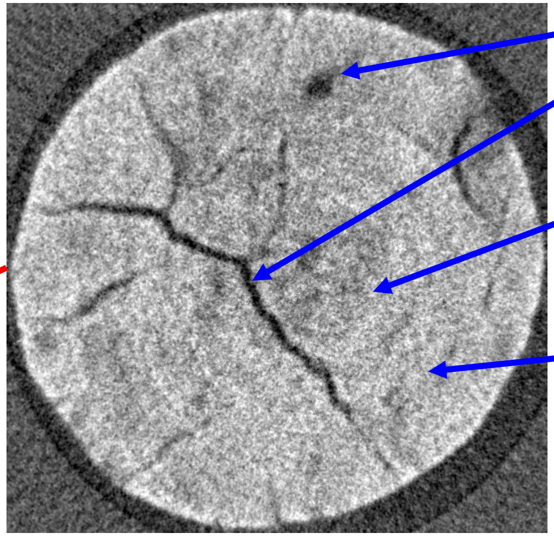
Science to Enable Accurate Reactor Modeling

via collaboration with NETL Team (Bill Rogers and Merhdad Shahnam)



Graphic courtesy of W.A. Rogers (NETL)

neutron tomograph (slice)

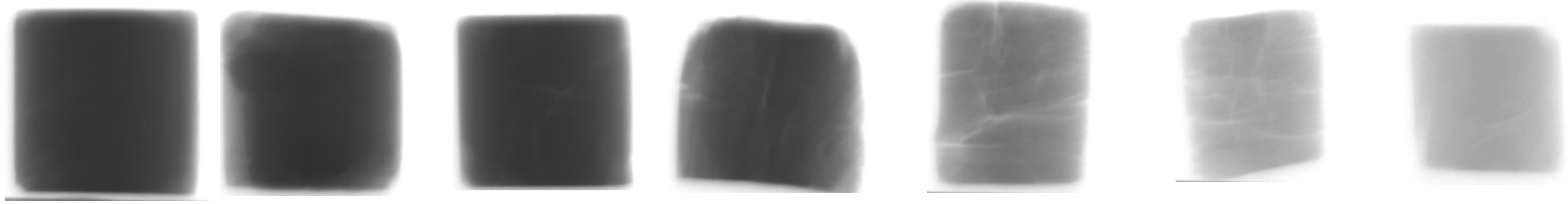


Macro pores and fissures affect mass and heat transfer in/out of particle

Microporosity/structure affect mass and heat transfer in/out of particle as well

Chemical composition affects gas product species and kinetic rates of reaction

Both physical and chemical properties of coal change as gasification occurs – the project uses advanced diagnostic tools to quantify changes

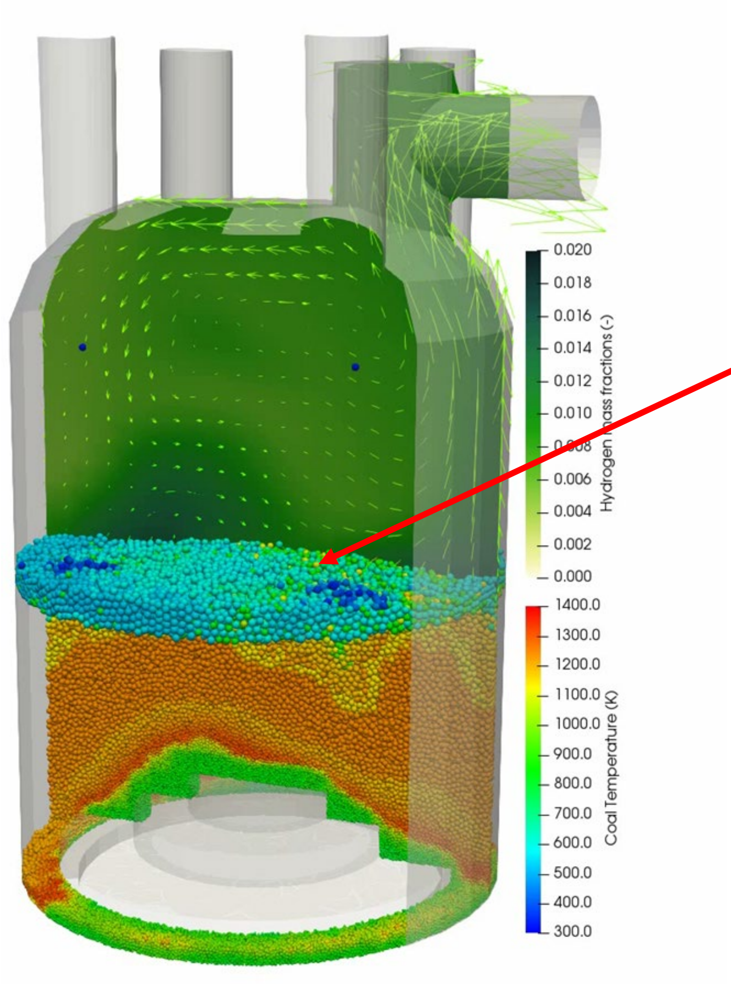


Raw **200 °C** **300 °C** **400 °C** **600 °C** **800 °C** **1000 °C**

Sub-bituminous Coal Shown. Relative image sizes approximate.

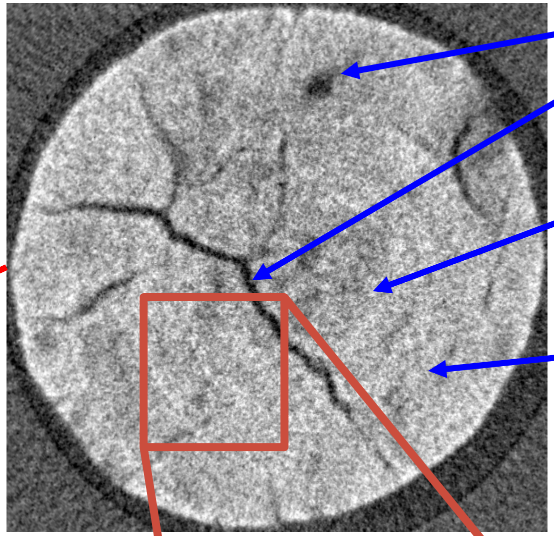
Approach has evolved to research microstructure characterization as well as dynamic gasification process

via collaboration with NETL Team (Bill Rogers and Merhdad Shahnam)



Graphic courtesy of W.A. Rogers (NETL)

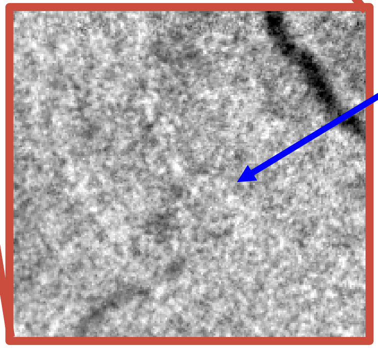
neutron tomograph (slice)



Macro pores and fissures affect mass and heat transfer in/out of particle

Microporosity/structure affect mass and heat transfer in/out of particle as well

Chemical composition affects gas product species and kinetic rates of reaction



(1) Dense regions of coal are difficult to characterize with conventional techniques (SEM, XCT)
(2) Dense regions limit diffusion and mass transfer of desorbed hydrocarbons
(3) Neutron scattering techniques employed for characterization

Summary of neutron experiments

Scheduled	Actual	Facility	Beamline	Samples	R&D Focus
February 2019	February 2019	NIST CNR	BT2 NIF	**Coal** (anthracite, bituminous(2), sub-bituminous, lignite), pre-pyrolyzed	**Coal species: neutron effects**
August 2019	August 2019	NIST CNR	BT2 NIF	Pyrolysis of **poplar** – 2 solid cylinders, 2 beds of solid rods, *in situ* & *operando*	**Pyrolysis (bio)** *in situ & operando*
December 2018	November 2019	ORNL HFIR	CG-1D	Pyrolysis of 2 beds of **lignite**, *in situ* & *operando*	**Pyrolysis (coal)** *in situ & operando*
July 2020	July 2020	ORNL SNS	VISION	Vibrational spectroscopy of **coal**, pre-pyrolyzed	**Chemical Composition**
May 2020	December 2020	NIST CNR	vSANS	**Coal**, pre-pyrolyzed – scoping study for neutron scattering	**Physical Structure (porosity, etc.)**
February 2021	TBD	NIST CNR	vSANS	**Coal**, pre-pyrolyzed – full experiment (scattering) pending scheduling	**Physical Structure (porosity, etc.)**
July 2020	TBD	NIST CNR	BT2 NIF	Pyrolysis/gasification of **coal** *in situ* & *operando*	**Gasification** *in situ & operando*
September 2020	Summer-fall 2021	ORNL HFIR	CG-1D	Pyrolysis/gasification of **coal** *in situ* & *operando*	**Gasification** *in situ & operando*

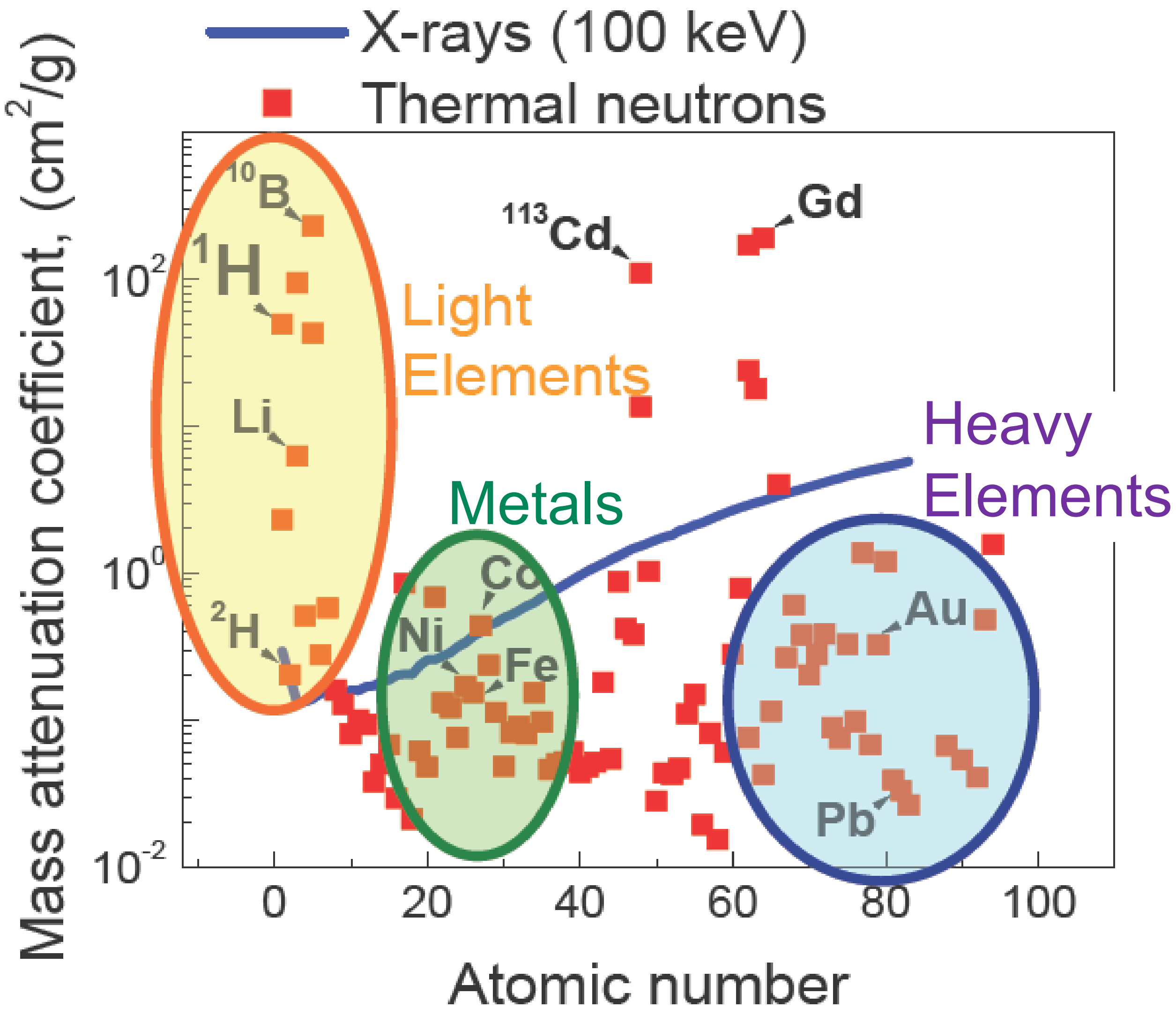
in situ & *operando* means that the pyrolysis and gasification is being imaged in the neutron beam in real time

OAK RIDGE National Laboratory | NATIONAL TRANSPORTATION RESEARCH CENTER

Neutron-Based Research

- Center for Neutron Research at the National Institute of Standards and Technology
- High Flux Isotope Reactor at Oak Ridge National Laboratory
- Spallation Neutron Source at Oak Ridge National Laboratory

Neutron-scattering measurements match our process well



Neutron interaction with light elements is why neutron imaging is a suitable diagnostic to view pyrolysis and gasification *in situ*. We have demonstrated utility and are refining technique.

Neutron attenuation for H >> attenuation for C

N. Kardjilov's presentation at IAN2006
http://neutrons.ornl.gov/workshops/ian2006/MO1/IAN2006oct_Kardjilov_02.pdf

Coal samples

Various samples of coal were acquired to determine suitability for neutron studies and for design of the experimental apparatus.

Sample	Rank	Source	Carbon [1] [wt %]	Moisture [2] [%]	Mass loss [3] [%]
A	Anthracite	Reading Coal Company (PA)	87–98	3	5
B	Bituminous	Blue Gem / Straight Creek (Pineville KY)	77–87	1	42
C	Bituminous	Pittsburgh #8	77–87	1	42
D	Sub-bituminous	Monarch PRB (Sheridan WY)	71–77	19	45
E	**Lignite**	Center Coal Mine (Center ND)	60–70	29	52
U	**Sub-bituminous**	Usibelli Coal Mine (Healy AK)	70 [4]	29 [4]	

[1] From USGS dry, mineral-content-free basis.
[2] Based on weights as-received and after desiccation.
[3] Based on weights after desiccation and pyrolysis in argon at 1000 °C.
[4] Usibelli Coal Mine.

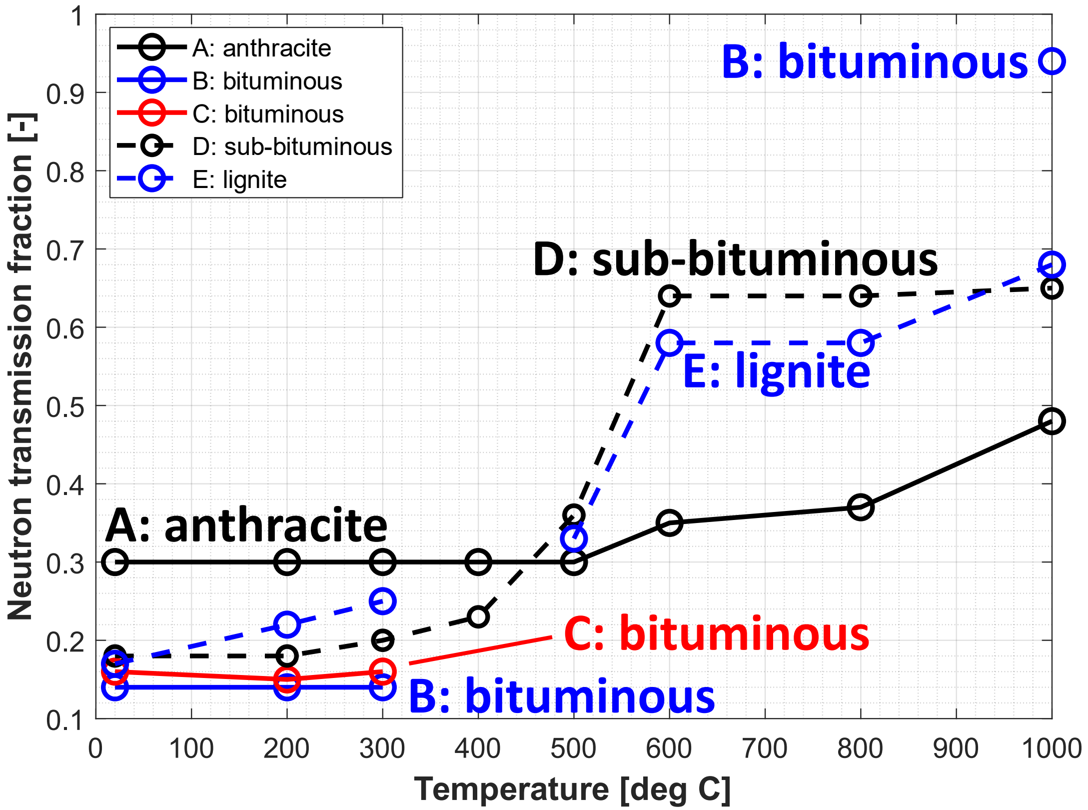
Current (Year 2) focus

Usibelli coal was obtained in April and added to ORNL studies.

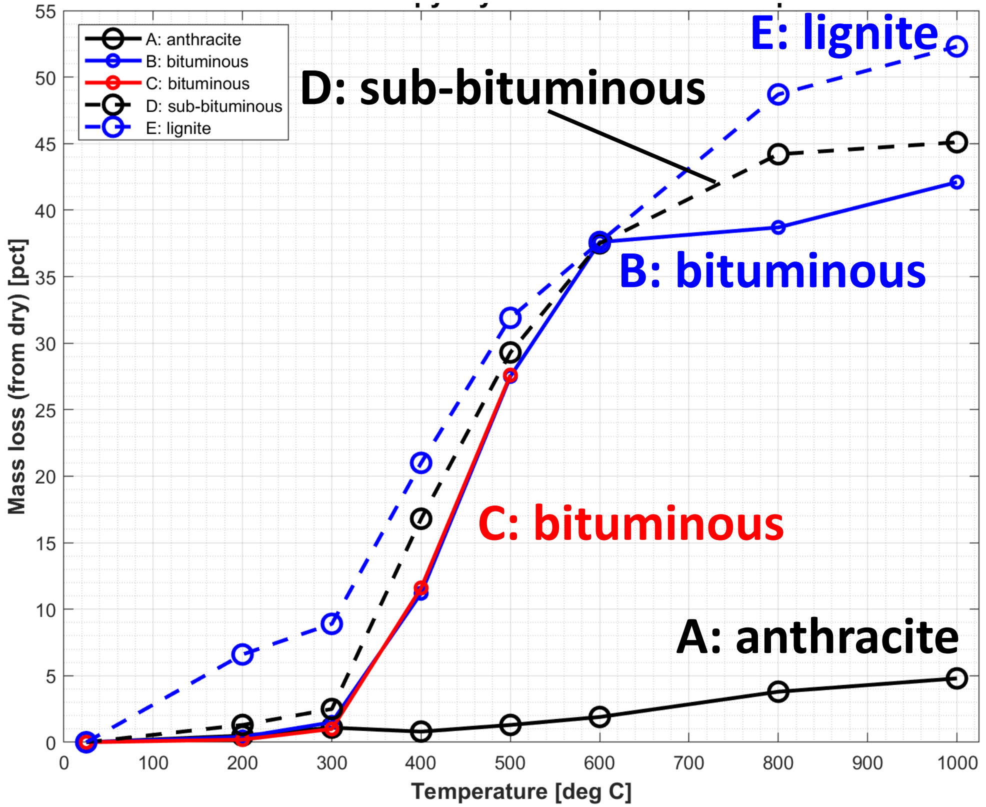
Mass loss correlates with neutron attenuation, which varies with degree of pyrolysis.

Neutron transmission increases with degree of pyrolysis

Neutron transmission / ~cm



Mass loss



Neutron interactions follow rough trends with mass loss, but there is a complex relation dependent on the pyrolysis chemistry.

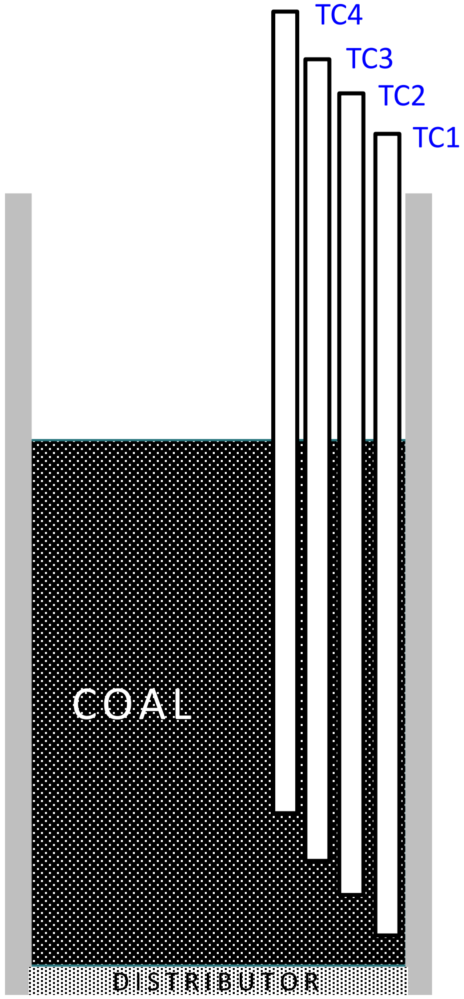
Analytical chemistry characterization enables correlation of chemistry and neutron attenuation data

These data provide guidance for gasifier design and experiments in the neutron beam.

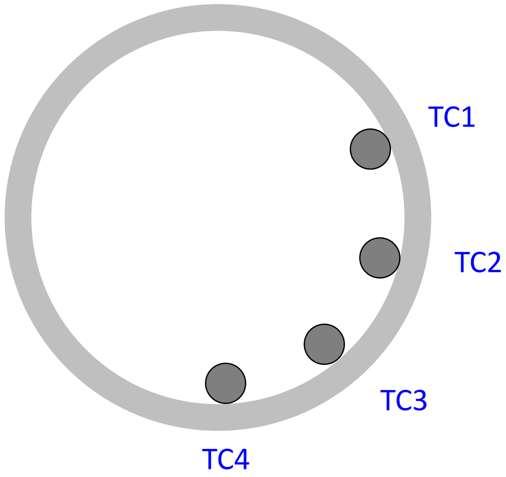
Pyrolysis (coal) in situ & operando

- High Flux Isotope Reactor at Oak Ridge National Laboratory (**HFIR**)
  - Imaging Beamline (CG-1D)

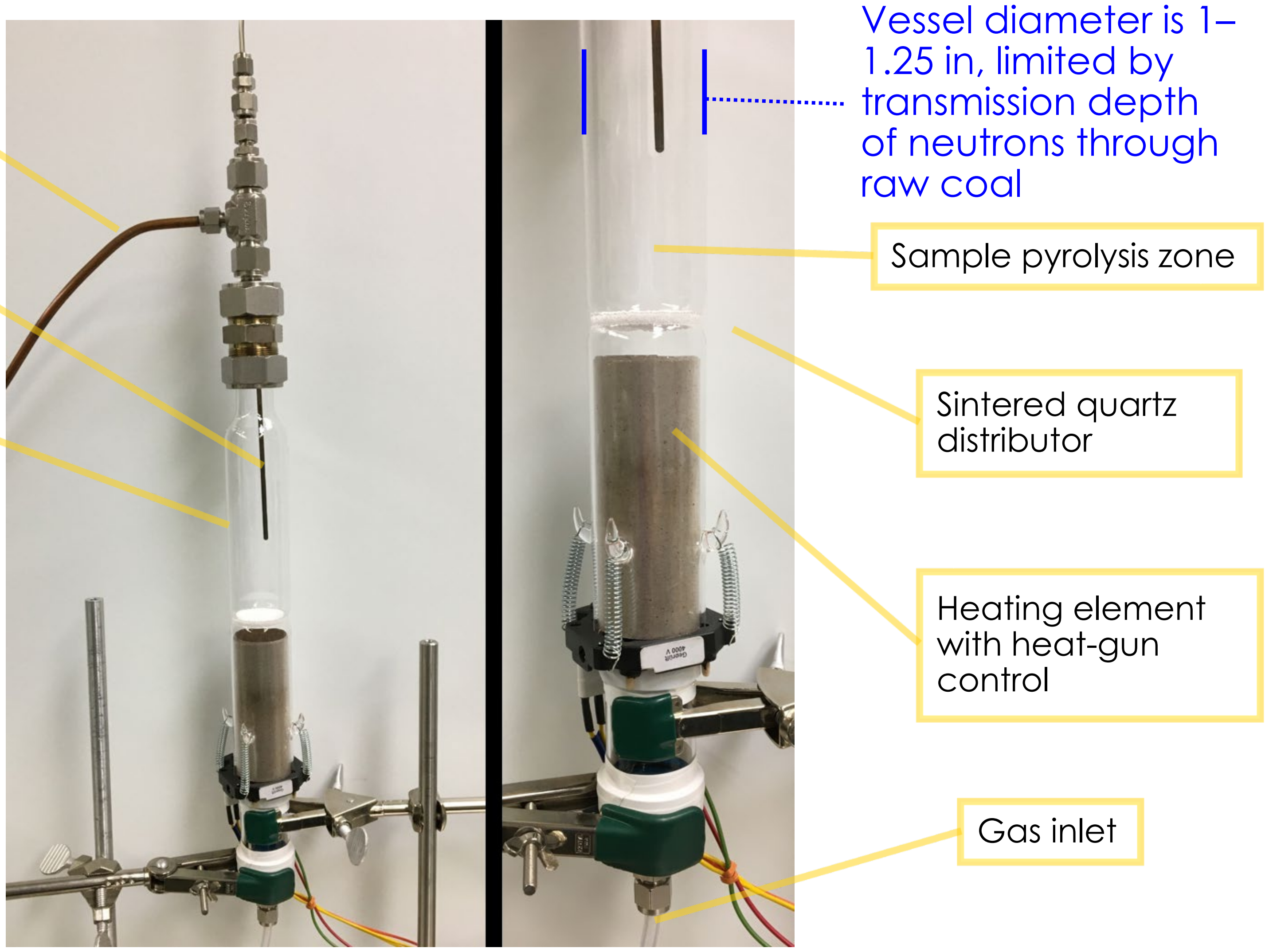
A portable pyrolyzer is used for both neutron & laboratory work



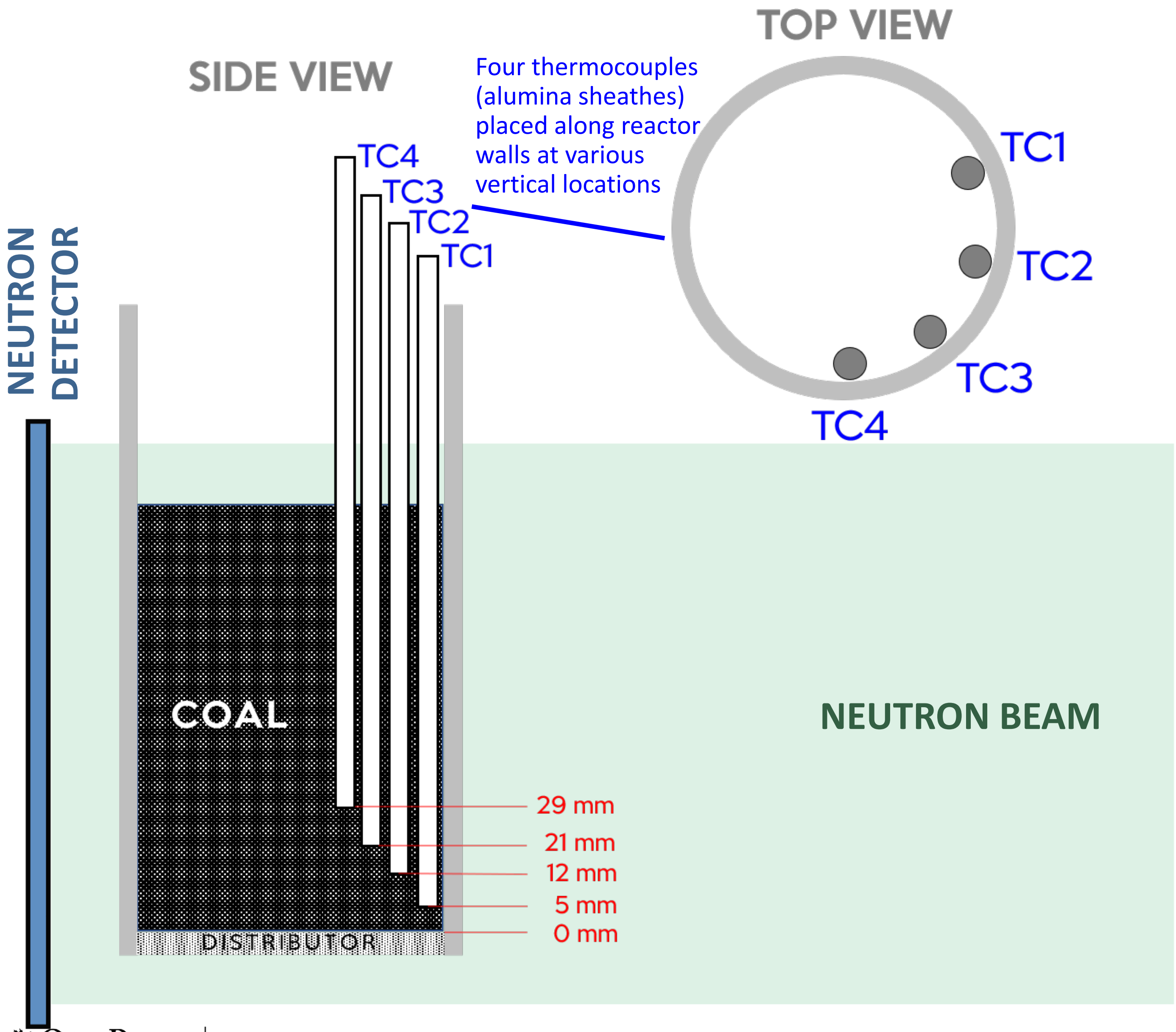
SIDE VIEW



TOP VIEW



HFIR – *in situ* real-time imaging of coal pyrolysis

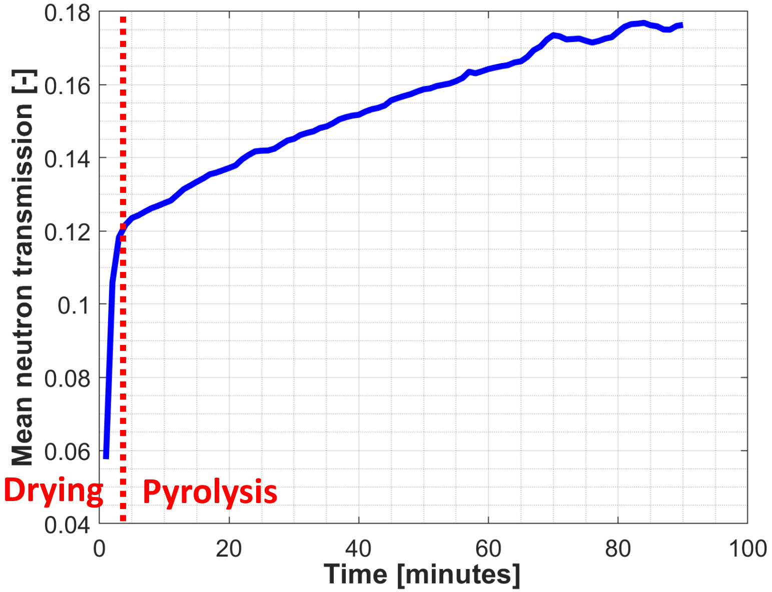


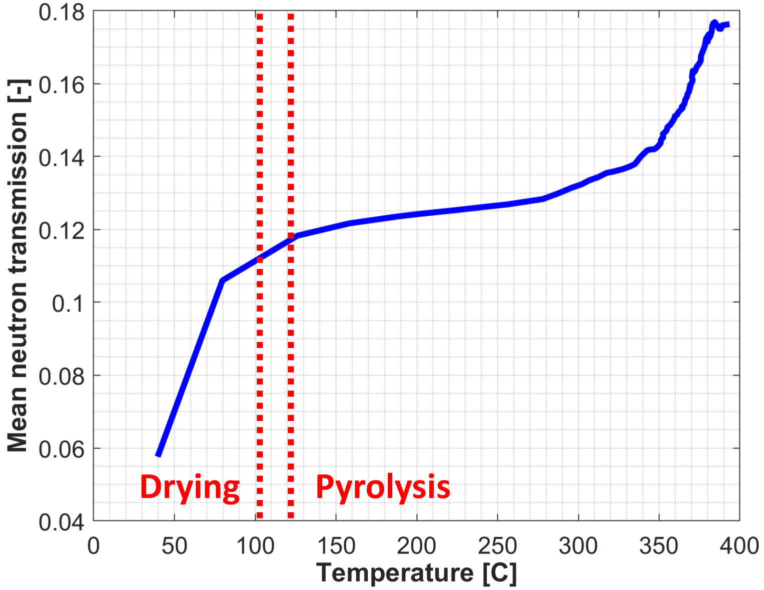
- Nonintrusive measurements for model validation
  - 2D map of gasification progress – transmitted neutrons projected onto detector screen
- Lignite
  - Sieved to 1000 – 2360 μm (8×18)
  - Low sphericity
- Type K exposed-junction thermocouples placed along reactor walls at various heights to estimate axial temperature profiles over time
- N_2 inert sweep gas
- Tube wrapped in Al foil for containment and to reduce radiative losses

HFIR – lignite bed – transmission radiographs

- Movie shows the neutrons transmitted through the coal bed over time, along with a 5-minute difference map
- Reaction rates, based on heat input, slowed down to see changes using 1-minute neutron exposures – can speed up as needed
- Takeaways:
  - Progressive pyrolysis is seen during the experiment – proof of principle
  - Bed settling will need to be accounted for or a continuous feed system implemented

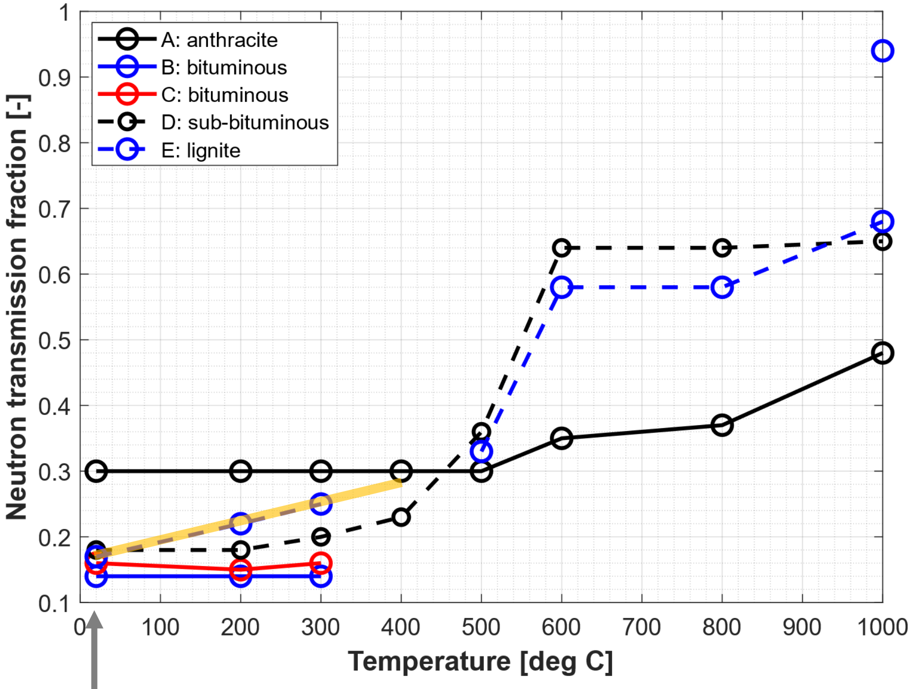
HFIR neutron transmission shows drying & pyrolysis stages





Compare

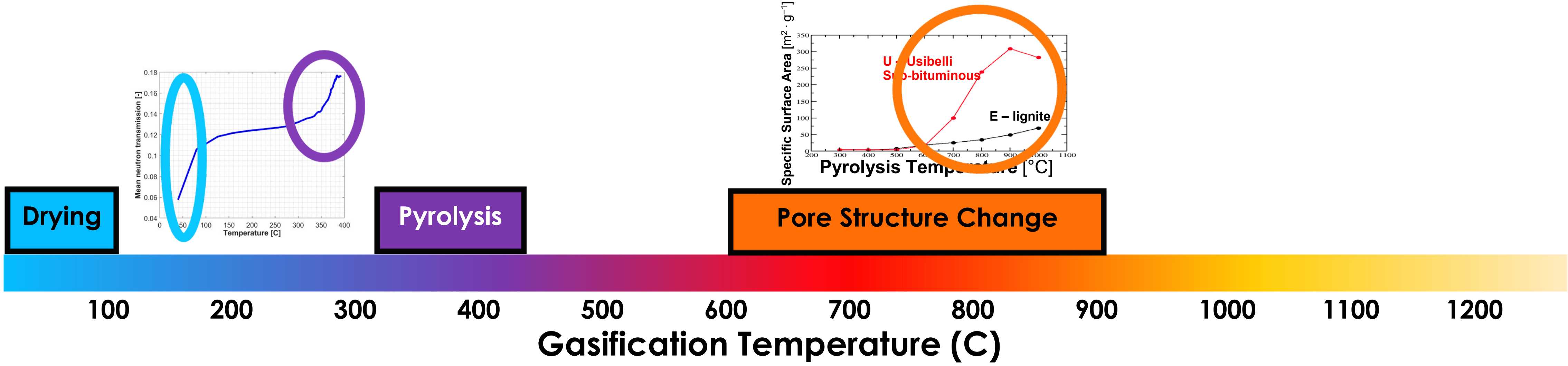
Compare with neutron transmission changes in 20–400 °C range



Note: room temperature data on this plot from post-dried samples

Path-length corrections in progress

Various phenomena occur over the vast temperatures experience during gasification with structural changes resulting



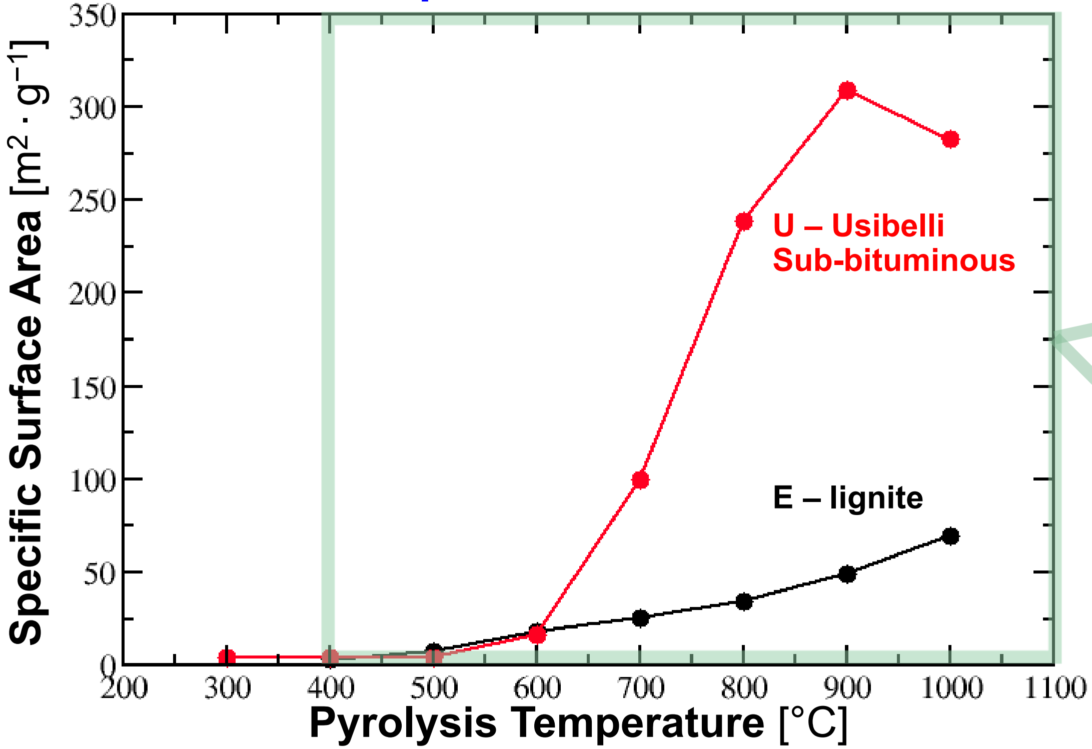
- Neutrons attenuation during the gasification process shows acceleration of H_2 loss during pyrolysis
- Subsequently, the continued gasification of the coal particle results in structural changes that accelerate the mass transfer and gasification process
  - Recent studies have focused on techniques to characterize the structural changes in the coal during gasification

Chemical Composition

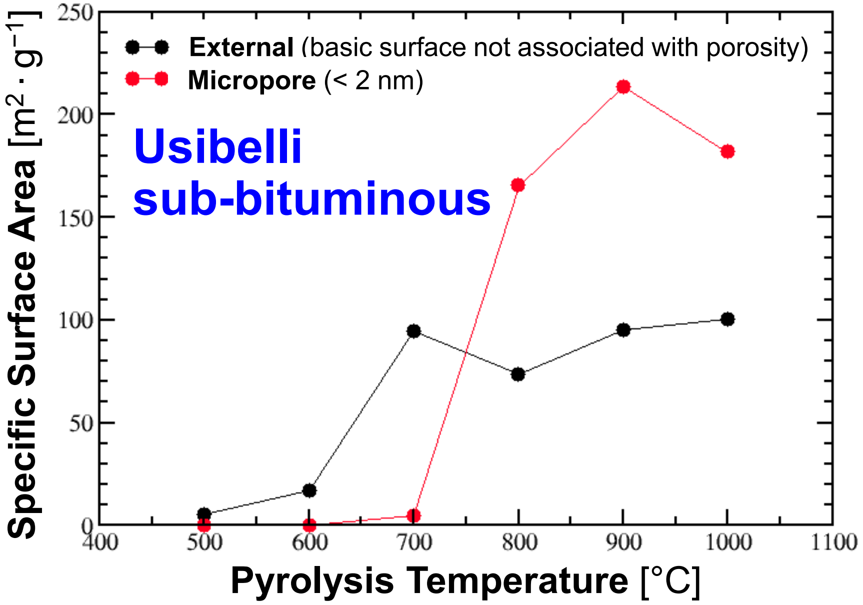
- Spallation Neutron Source at Oak Ridge National Laboratory (**SNS**)
  - **VISION** Beamline: Vibrational Spectroscopy

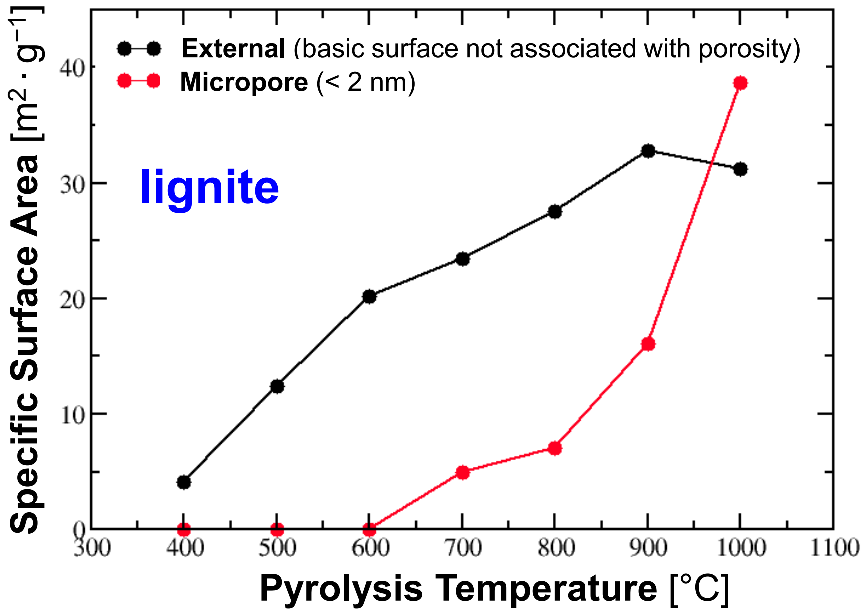
Coal porosity changes significantly with pyrolysis temperature

Total specific surface areas



Decomposed specific surface areas





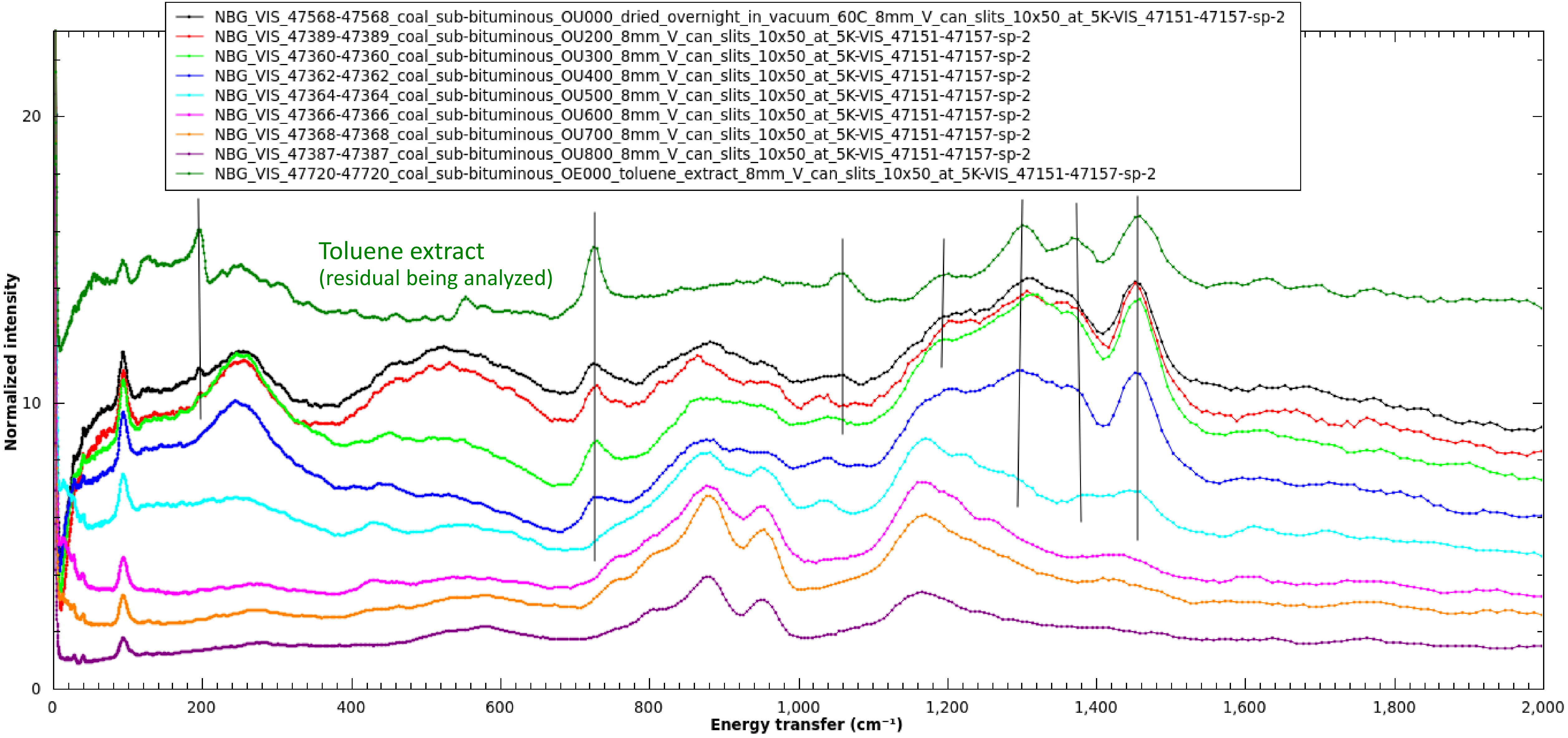
- **Off-line B.E.T. data shown**
- **Results for comparison to neutron-based experiments**
- **These results complementary to both VISION and vSANS neutron studies**

BET from Micromeritics Gemini VII
t-plot analysis based on Harkins-Jura equation
Pyrolysis: 20K/min; hold 20 min; open-loop cooling; Ar sweep

Neutron vibrational spectrographs of pyrolyzed Usibelli coal

IPTS-25475.1 (Finney&Tsouris) – July 2020 | ORNL/SNS/BL-16B (VISION) – L.L. Daemen

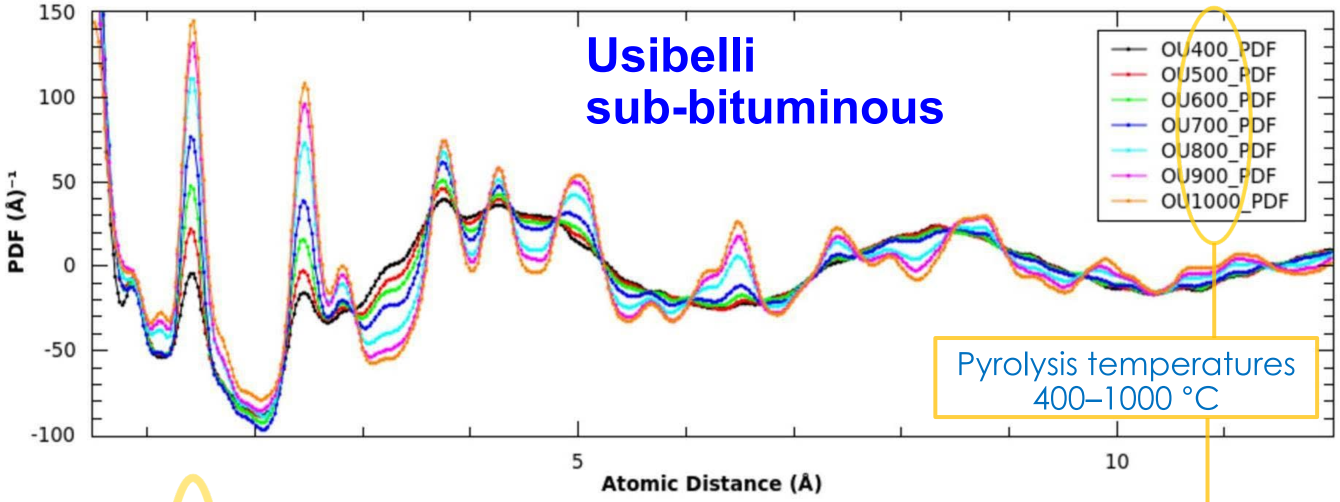
Pyrolysis: 20K/min; hold 20 min; open-loop cooling; Ar sweep



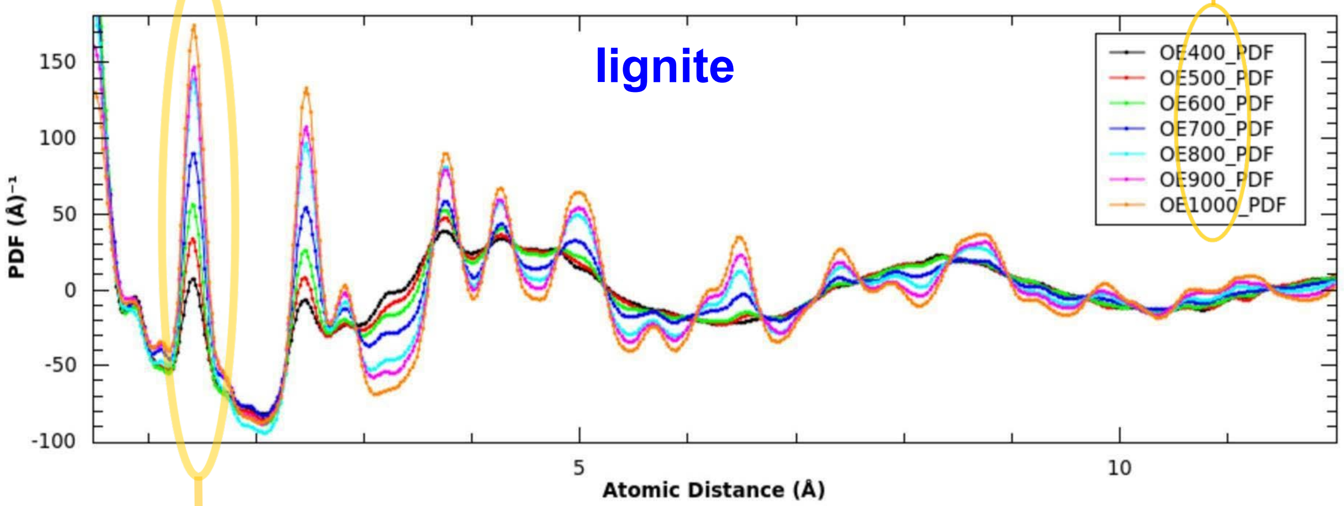
Pair distribution functions track structural evolution with pyrolysis

- Pair distribution functions (pdf) provide structural information in the absence of diffraction from periodic structures (e.g., with crystals)
  - Below 400 °C, background subtraction is difficult because of the incoherent scattering from hydrogen
  - Above 400 °C, concentration of hydrogen is sufficiently low that background can be subtracted reliably and the structure factor can be Fourier-transformed
- Data here from July 2020 SNS VISION experiments

This analysis is part of a comprehensive descriptive model of coal chemical–structural evolution under thermal degradation.



Pyrolysis temperatures 400–1000 °C



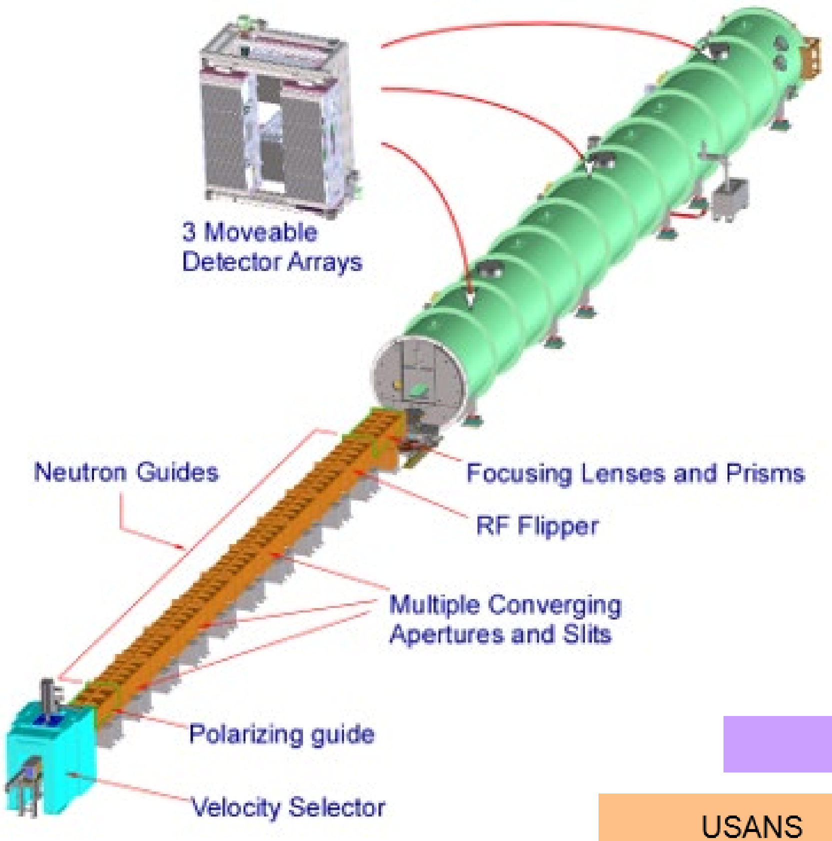
Peaks become more coherent with pyrolysis temperature, implying a more ordered structure in the coal (suggestive of increased porosity)

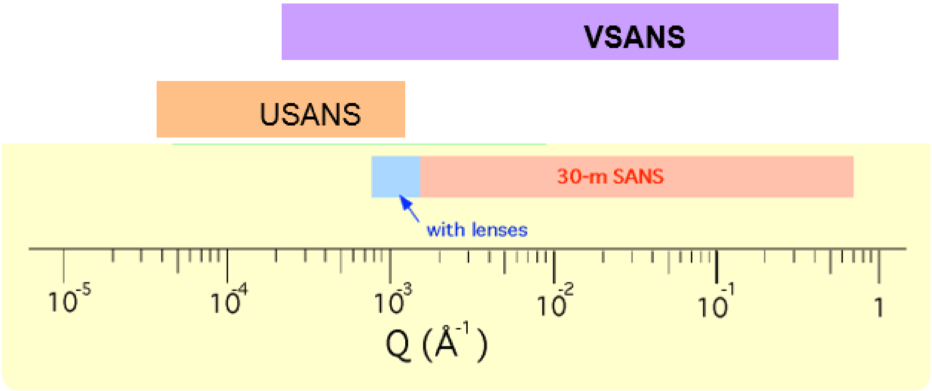
Physical Structure (porosity, etc.)

- Center for Neutron Research at the National Institute of Standards and Technology (**NCNR**)
  - **vSANS** Beamline: Very Small-Angle Neutron Scattering

vSANS: Very Small-Angle Neutron Scattering

- Small wavelength range of neutrons (0.4-0.6 nm) enables scattering from nano-scale pores/structures
- Non-crystalline structures extremely challenging to measure with conventional X-Ray Diffraction (XRD) techniques
- 1st experiments conducted on vSANS at NIST in December 2020





https://ncnr.nist.gov/equipment/msnew/ncnr/vsans.html

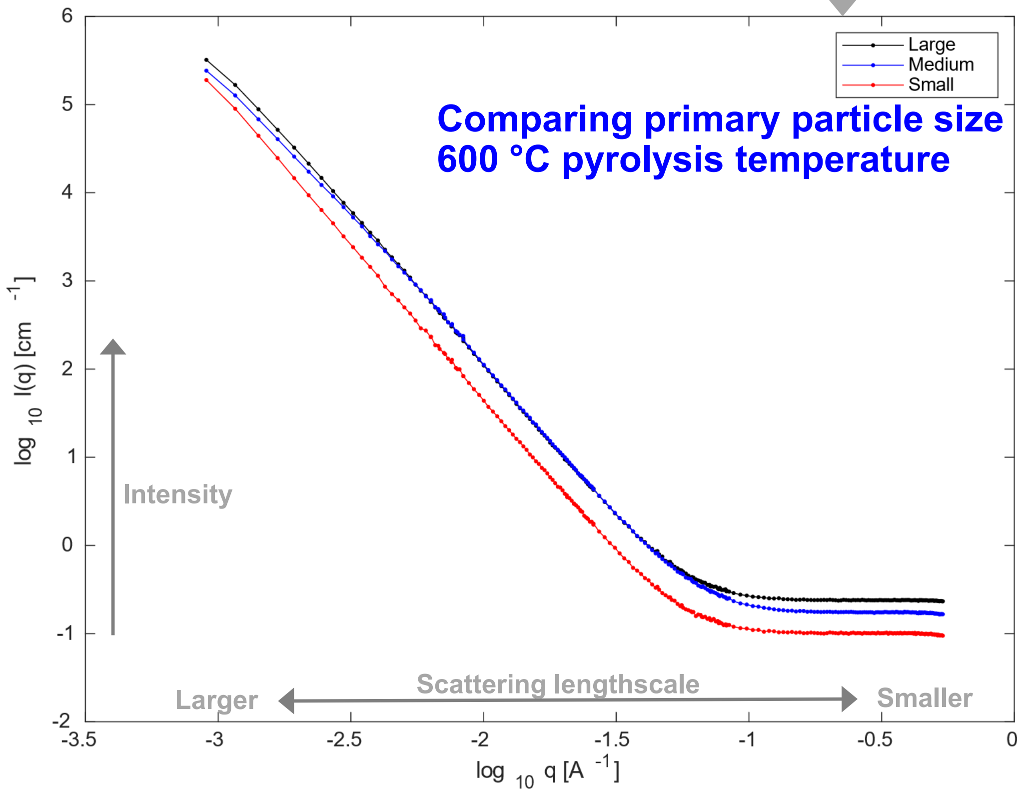
vSANS scoping experiments encourage full study

December experiment

- Scoping experiment to guide full study
- Limited range of samples (4 temperatures, 3 loosely sieved particle sizes, lignite)
- Instrument scientist could not control sample mass in beam

Full experiment (spring 2021)

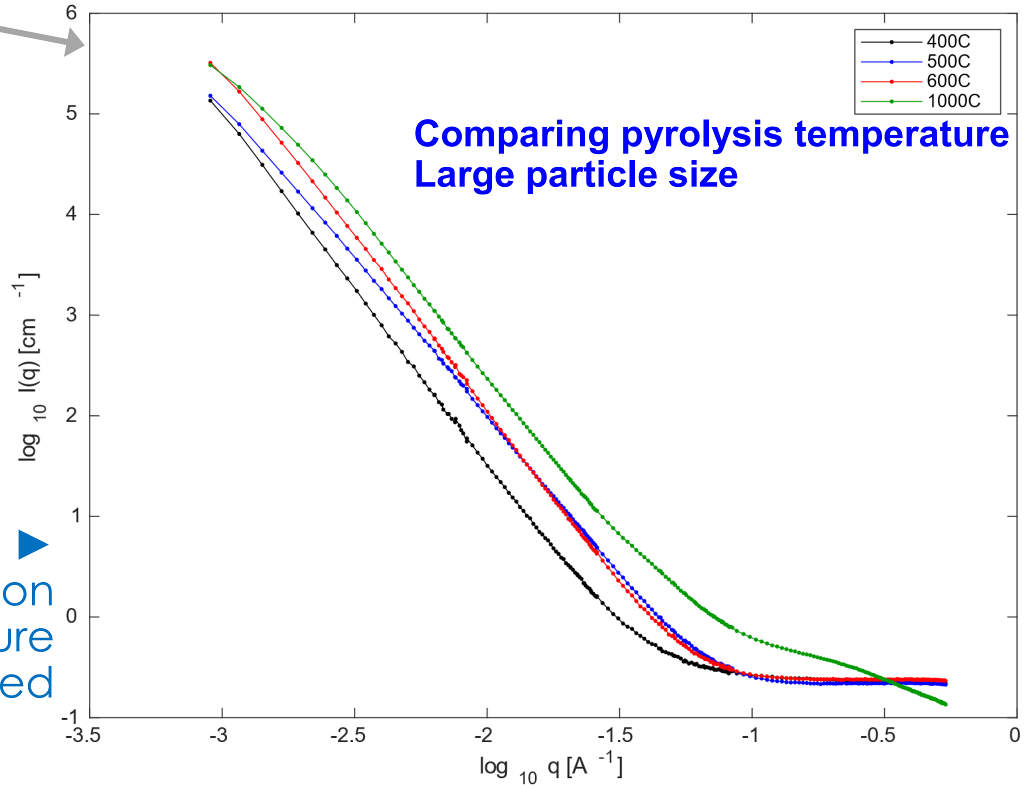
- Carefully prepared samples in sealed sample holders
- Known masses in beam, to normalize spectra
- Focus on full temperature range (400–1000 °C) and two coals (Usibelli and lignite)



Differences based on particle size are subtle

lignite

Differences based on pyrolysis temperature are more pronounced



Summary: Coal Gasification Characterization with Multiple Neutron Techniques

Dynamic *in situ* Gasification

- Dynamic *in situ* pyrolysis studies with coal capture complexity of process as a function of physical
- **Next step:** dynamic *in situ* gasification studies with coal
  - COVID has delayed neutron beamtime for this task
  - Preparations on going including high temperature safety review

Critical Data

Chemical Composition

- Neutron studies complete (VISION)
- Ongoing sample characterization (extracted hydrocarbons) for comparison
- Micro-pyrolyzer GC data represents good chemistry analysis for comparison

Supporting Data

Physical Structure

- Scoping neutron study complete (VSANS)
- Results promising, but additional study needed
- Relatively low resource intensity
- Conventional BET bench studies offer supplementary data for micro and macro pores (BET not capable of probing smaller pores that neutrons can characterize)
- 2nd campaign planned

Supporting Data

End Goal: Comprehensive fundamental science-based understanding of coal gasification