Experimental validation of feedstock gasification with neutron imaging

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

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Oak Ridge National Laboratory

2022 FECM Spring R&D Project Review: Gasification Systems Program
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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)

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Experimental validation of feedstock gasification with neutron imaging

- **Project Objective:**
  Utilize unique DOE neutron user facilities to characterize physical and chemical conversion of ***feedstocks during gasification*** for cost-effective and efficient ***conversion to power and H_2*** for fuels and chemicals while ***managing carbon*** efficiently

- **Project Timeline:**

FY2019	Neutron imaging of conversion of biomass and various ranks of coal
FY2020	Continued focus on coal plus neutron scattering for characterization
FY2021	*In situ* studies of coal with neutron imaging
FY2022	Focus on conversion of municipal solid waste (MSW) and plastics

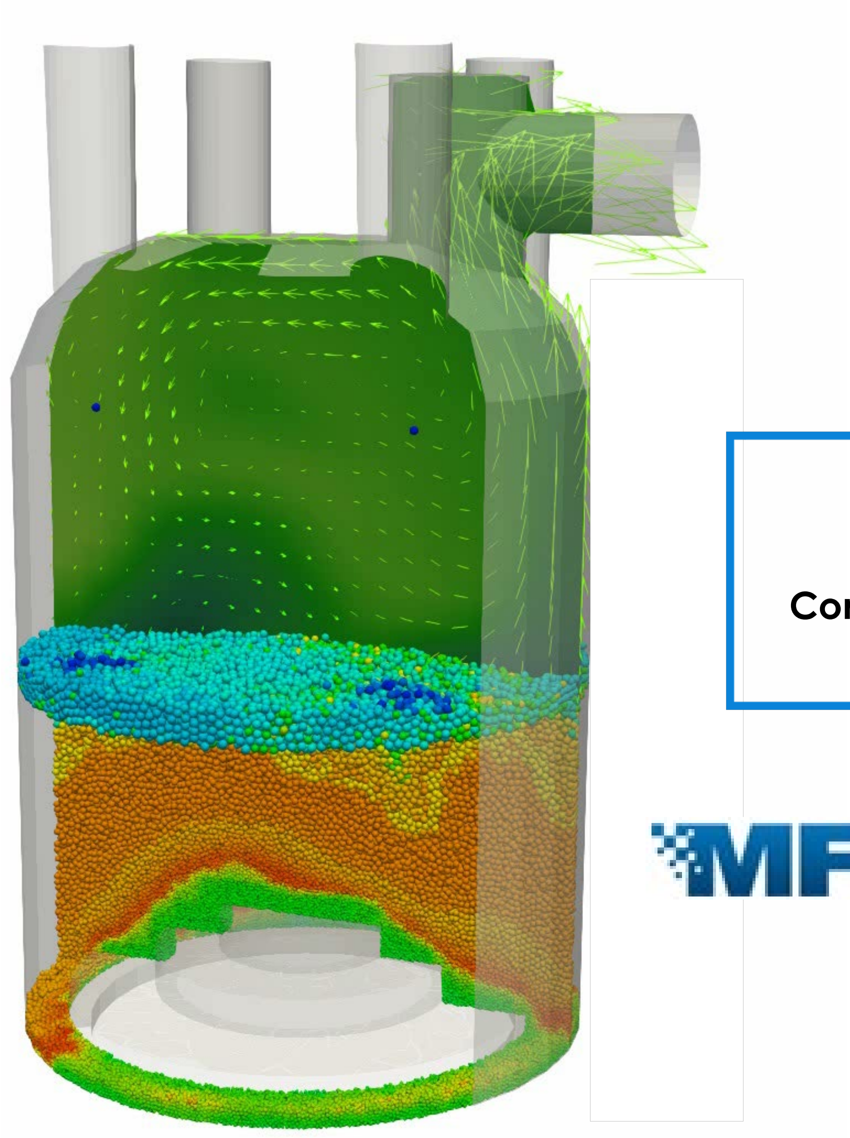
High Flux Isotope Reactor at Oak Ridge National Laboratory

HFIR

Spallation Neutron Source at Oak Ridge National Laboratory

SNS
SPALLATION NEUTRON SOURCE

Collaboration with NETL enables experimental-modeling coupling



MFiX

DESIGN GUIDANCE

NATIONAL ENERGY TECHNOLOGY LABORATORY

Reactor-scale modeling
Computational Fluid Dynamics
mfix.netl.doe.gov

OAK RIDGE National Laboratory

Particle-scale experiments
Neutron science
neutrons.ornl.gov

HFIR

SNS SPALLATION NEUTRON SOURCE

VALIDATION DATA

Graphics courtesy of collaborators Bill Rogers and Merhdad Shahnam (NETL)

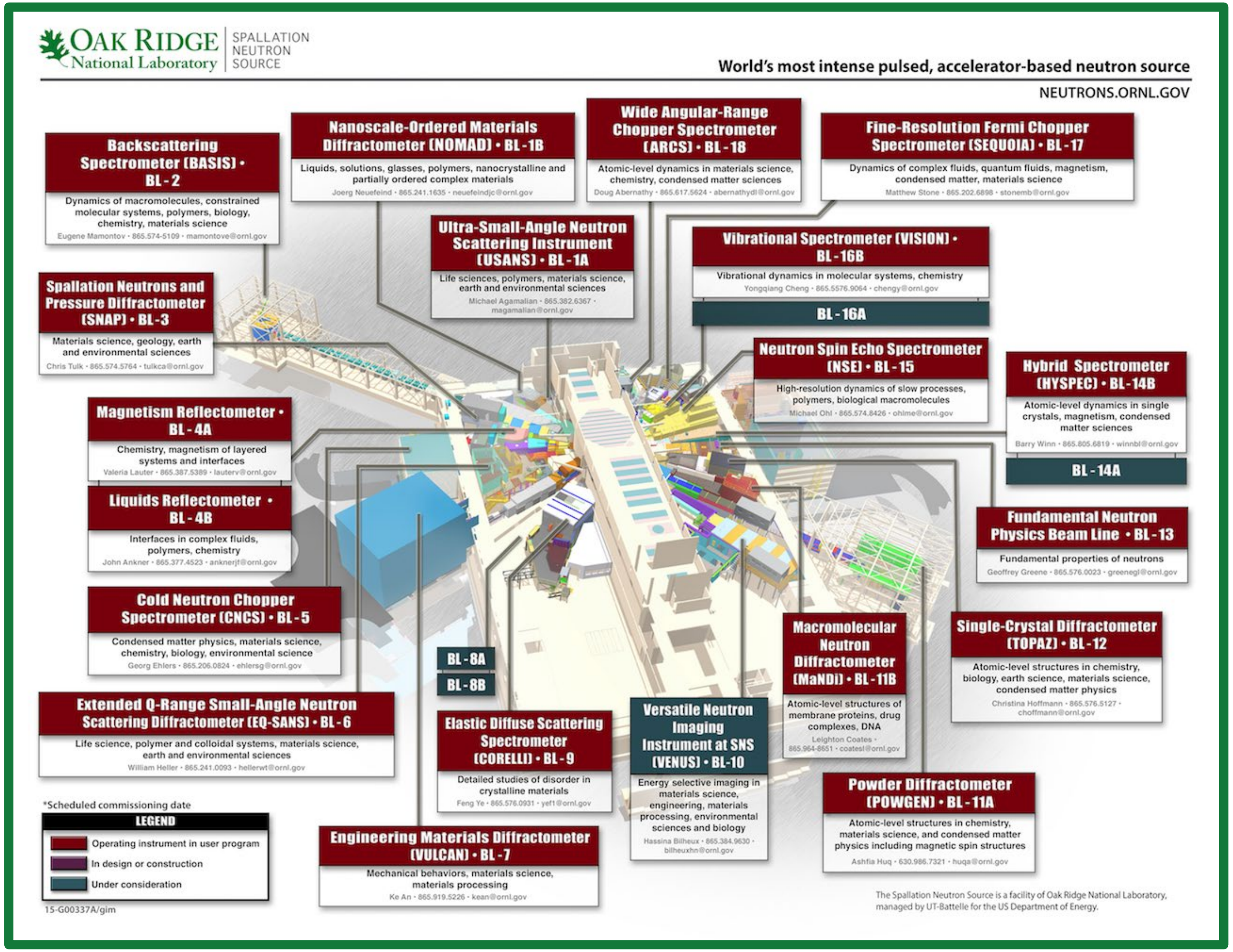
Neutron-Based Research

We have used the following facilities:

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

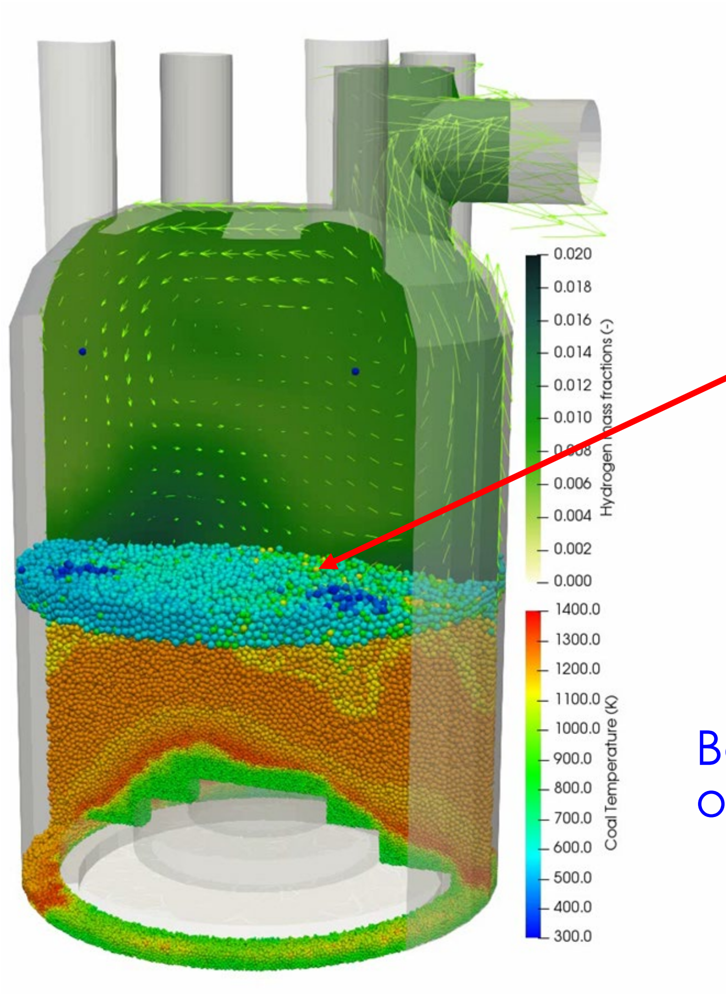
Multiple neutron techniques/beamlines utilized

- Neutron Imaging
  - ORNL HFIR CG-1D
  - NIST CNR BT2 NIF
- Small-Angle Neutron Scattering
  - ORNL HFIR GP-SANS
  - NIST CNR vSANS
- Inelastic Neutron Scattering (Vibrational Spectroscopy)
  - ORNL SNS VISION



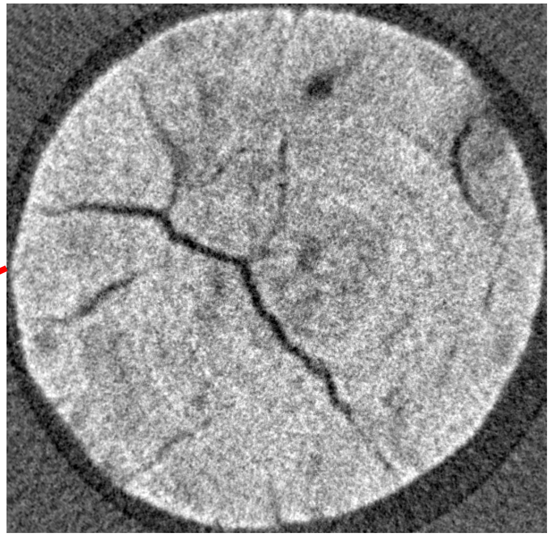
For more information on beamlines see: neutrons.ornl.gov and www.nist.gov/ncnr

Neutron imaging of feedstocks enabled by high attenuation coefficient for Hydrogen

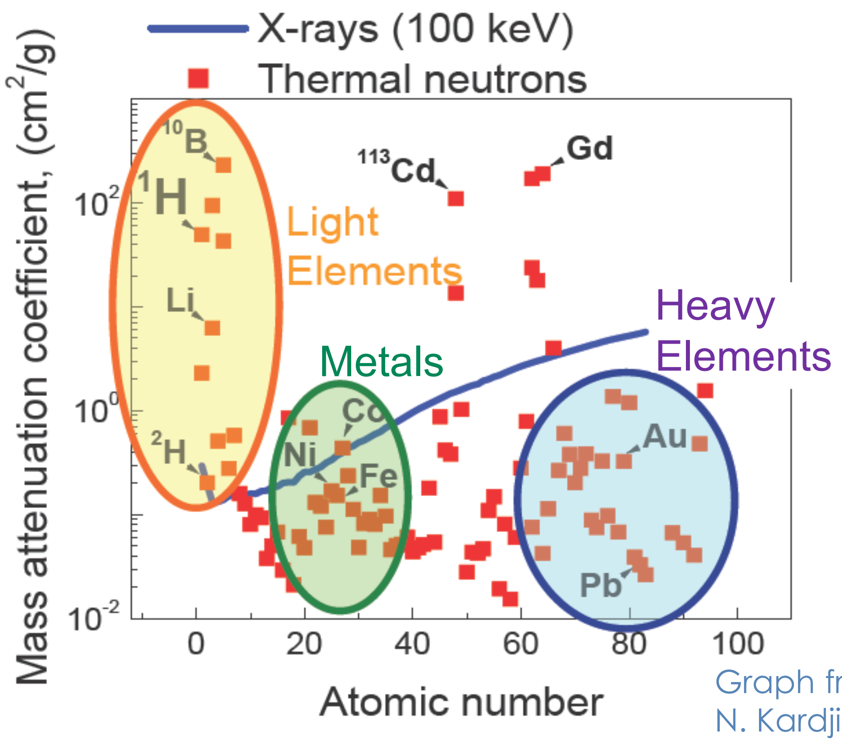


Graphic courtesy of Rogers & Shahnam (NETL)

Neutron tomograph (slice)

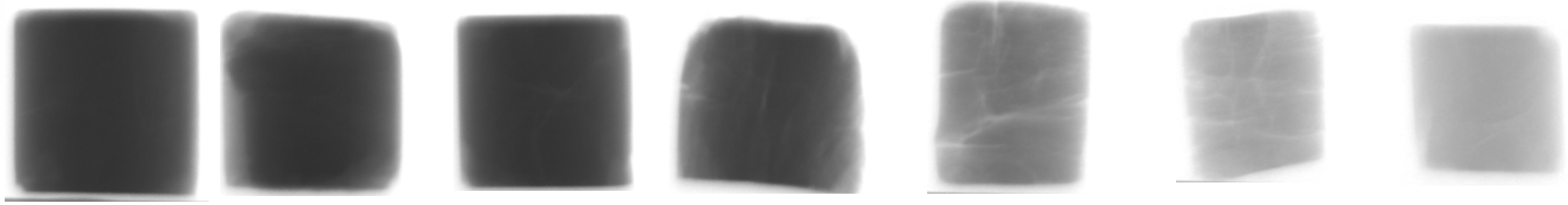


Neutron attenuation for H >> attenuation for C



Graph from N. Kardjilov

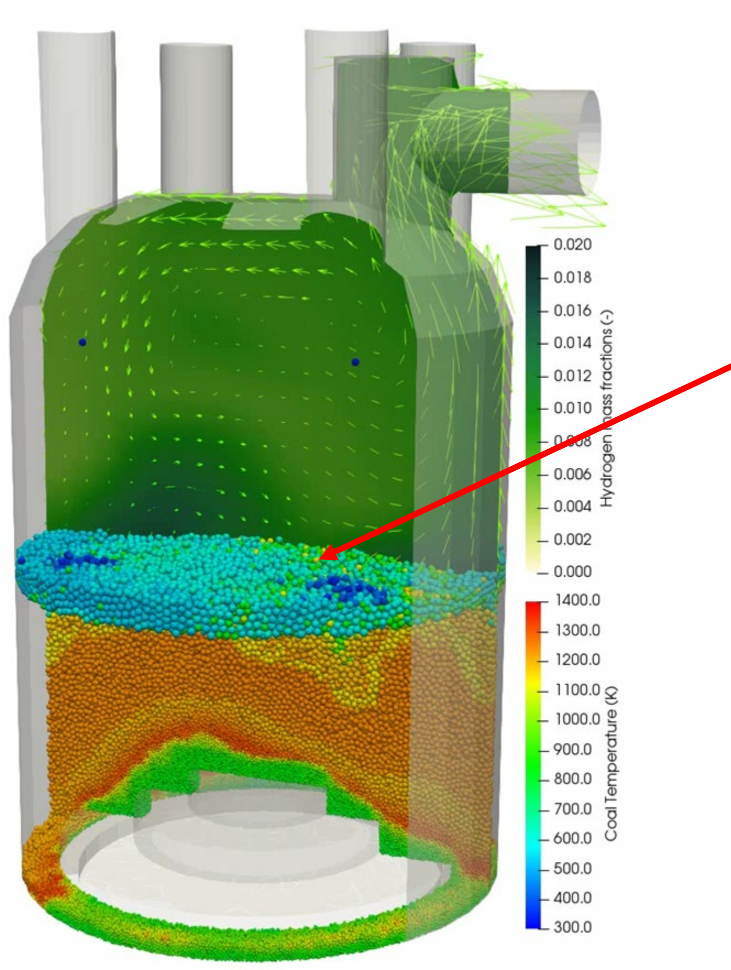
Both physical and chemical properties of coal change as gasification occurs – the project uses advanced diagnostic tools to quantify changes



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

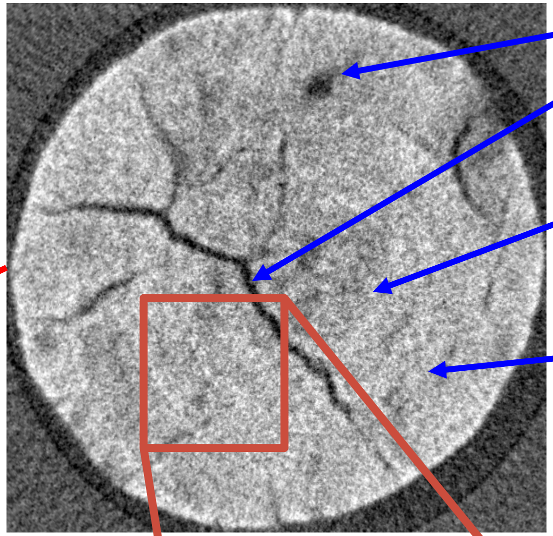
Sub-bituminous coal shown. Relative image sizes approximate.

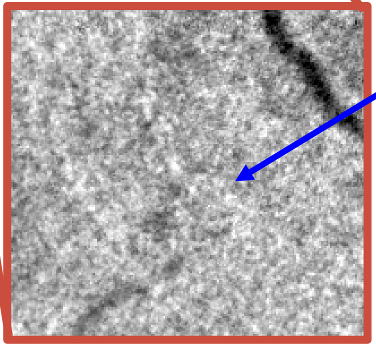
Neutron scattering enables characterization of microstructure and chemistry changes during dynamic gasification process



Graphic courtesy of Rogers & Shahnam (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

Multiple neutron instrument campaigns for measuring physical and chemical properties of feedstock conversion

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

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	Dynamic *in situ* pyrolysis of **poplar** – 2 solid cylinders, 2 beds of solid rods	**Dynamic *in situ* Pyrolysis (bio)**
December 2018	November 2019	ORNL HFIR	CG-1D	Dynamic *in situ* pyrolysis of 2 beds of **lignite**	**Dynamic *in situ* Pyrolysis (coal)**
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	*Pending NIST restart*	NIST CNR	vSANS	**Coal**, pre-pyrolyzed – full experiment (scattering) pending scheduling	**Physical Structure (porosity, etc.)**
Alternate	May 2021	ORNL HFIR	GP-SANS	**Coal**, pre-pyrolyzed	**Physical Structure (porosity, etc.)**
July 2020	*Pending NIST restart*	NIST CNR	BT2 NIF	Dynamic *in situ* pyrolysis/gasification of **coal**	**Dynamic *in situ* Py/Gasification**
September 2020	October 2021	ORNL HFIR	CG-1D	Dynamic *in situ* gasification of **coal**	**Dynamic *in situ* Gasification**
August 2020	August 2020	ORNL SNS	VISION	**Plastics**, pre-pyrolyzed	**Chemical Composition**

Proposed ▶

July–December 2022	ORNL HFIR	GP-SANS	**MSW** & **plastics**, pre-pyrolyzed	**Physical Structure (porosity, etc.)**
July–December 2022	ORNL HFIR	CG-1D	Dynamic *in situ* gasification of **MSW**	**Dynamic *in situ* Gasification**
July–December 2022	ORNL SNS	VISION	**MSW** & **plastics**, pre-pyrolyzed	**Chemical Composition**

Gasification of coal *in situ & operando*

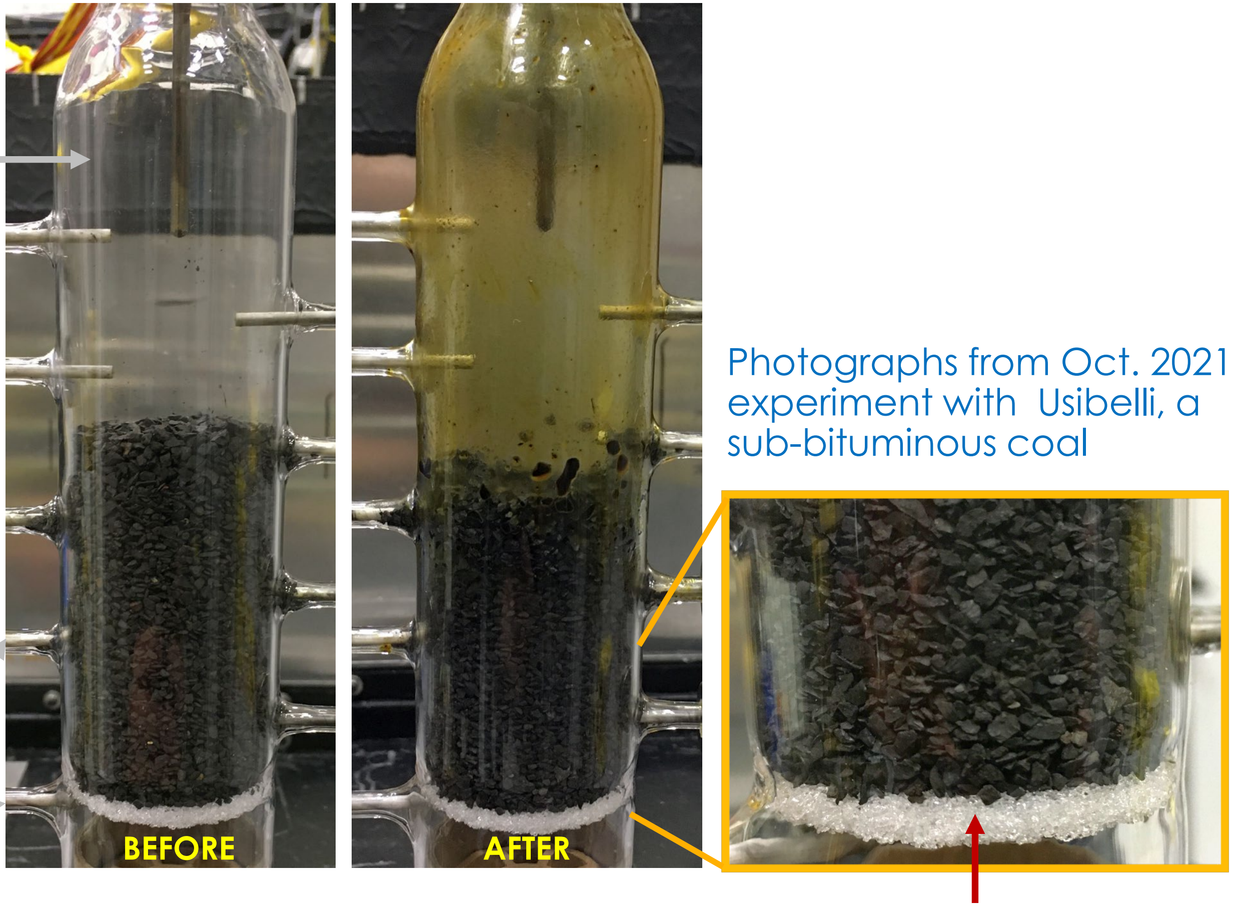
- High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory
  - Imaging Beamline (CG-1D)
  - GP-SANS Beamline: Small-Angle Neutron Scattering (SANS)
- Advanced Photon Source (APS) at Argonne National Laboratory
  - Small-Angle X-ray Scattering (SAXS)

Neutron imaging is used to map stages of progressive stages of gasification

- Objective: track gasification progress in coal bed with increased levels of oxidation
- Emphasis on early stages with pyrolysis then gasification
- Note: no steam in process gas
  - since neutrons adsorb H_2

Quartz reactor

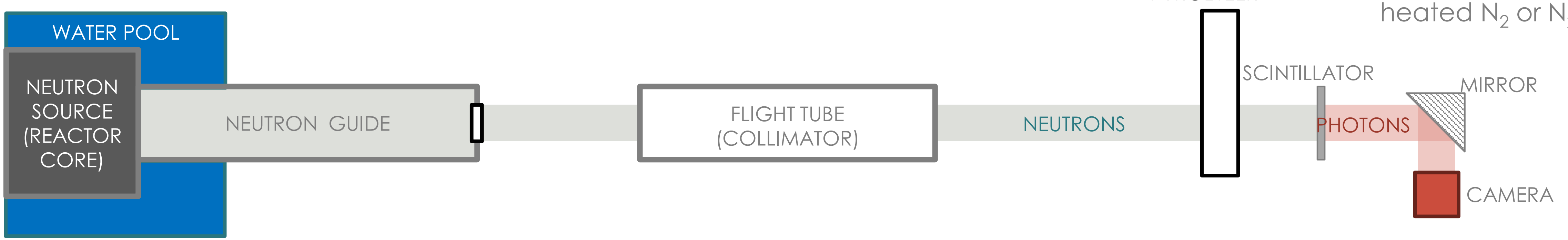
Thermocouples



Photographs from Oct. 2021 experiment with Usibelli, a sub-bituminous coal

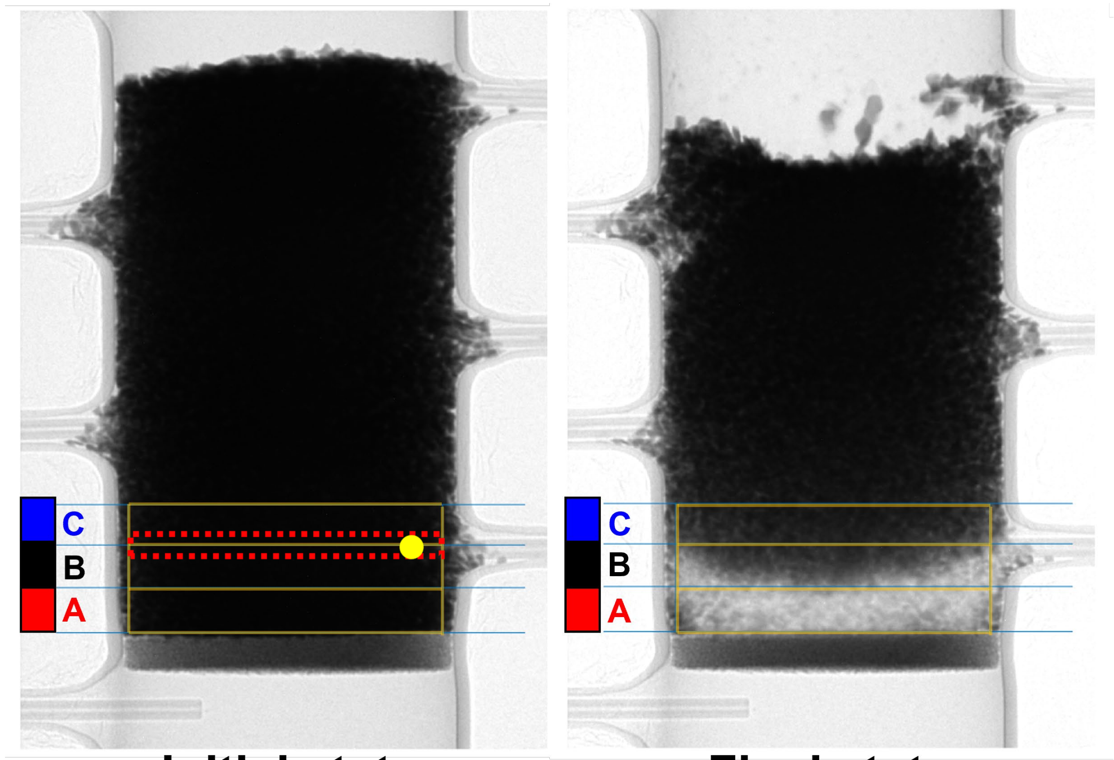
Sintered quartz frit for heated N_2 or N_2+air

Schematic of neutron imaging beamline at the High Flux Isotope Reactor at ORNL

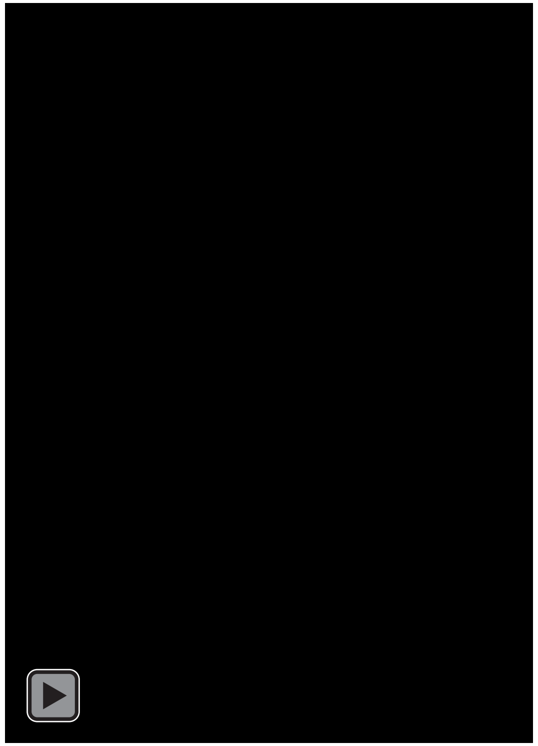


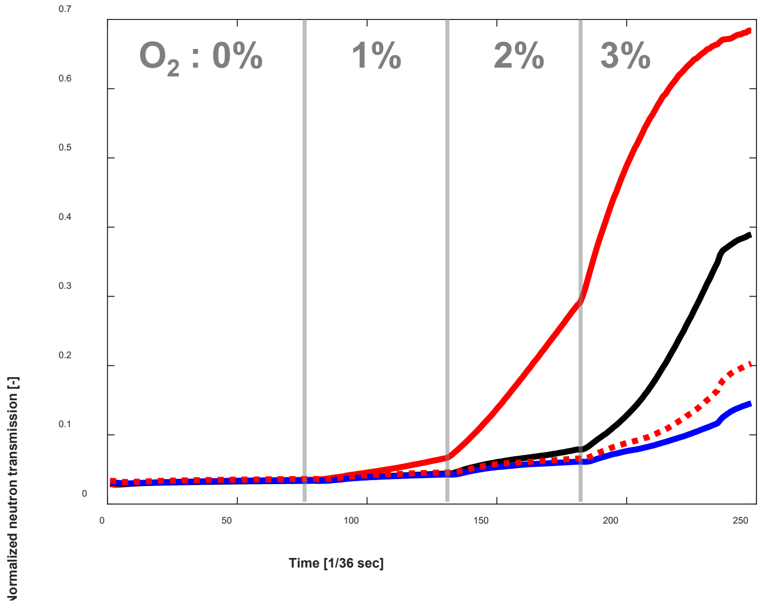
Neutron imaging shows H_2 content during coal gasification

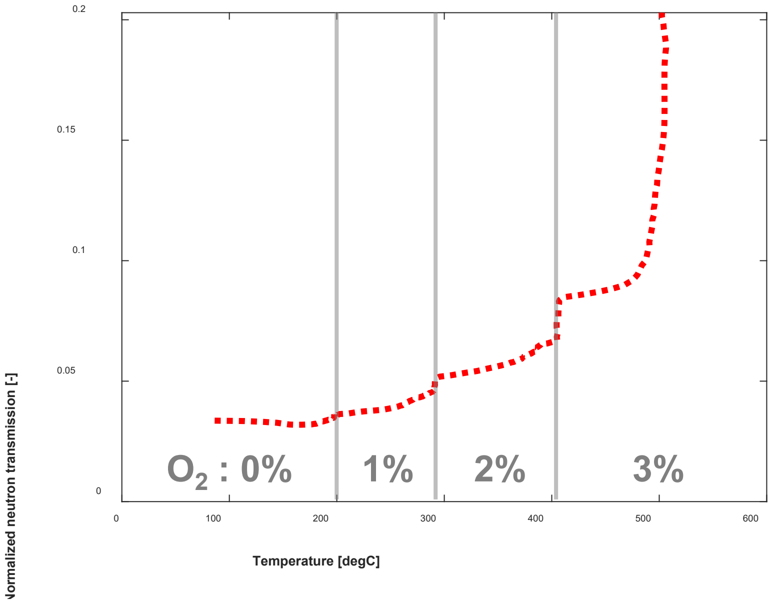
Neutron radiographs



Initial state **Final state**







Thermocouple location in Yellow

- Staged O_2 introduction allows for time required (30 sec exposure) for neutron imaging while capturing various states of gasification
- Neutron attenuation greatly reduced (H_2 content reduction) in sample area where gasification is complete
- Sample densifies as gasification occurs (bed shifts down in reactor)

X-ray scattering of Usibelli coal shows pore structure changes

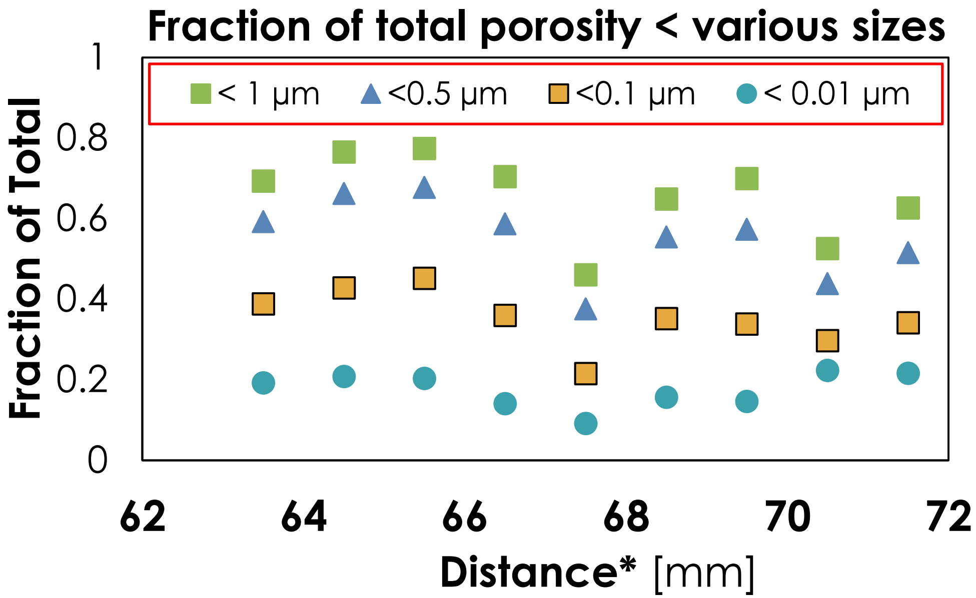
INITIAL STATE

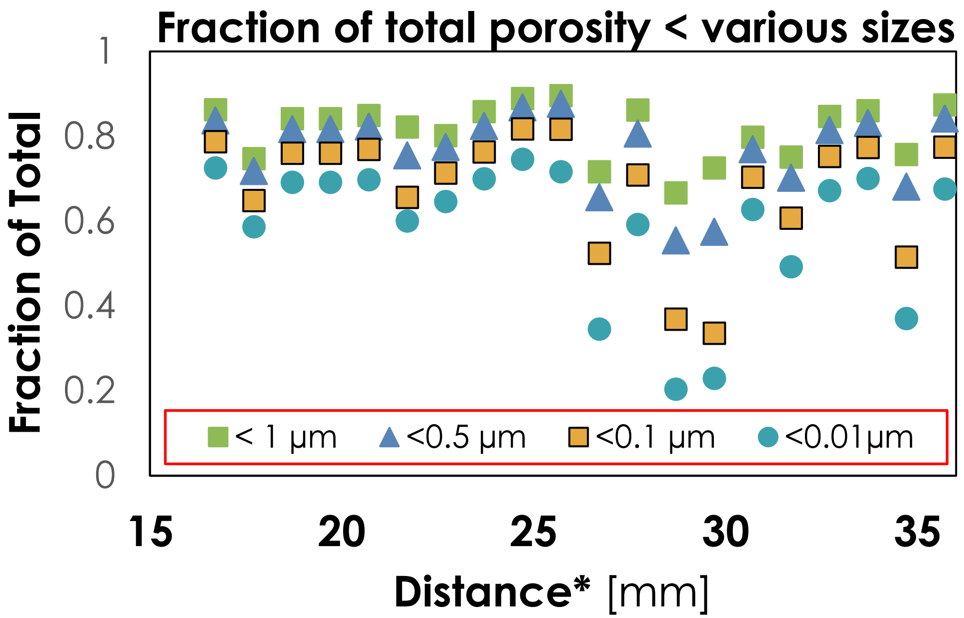
Mean Pore Fraction 0.015
(pores ≤ 6.04 μm)

900°C PYROLYZED

Mean Pore Fraction 0.143
(pores ≤ 6.04 μm)

- As pyrolysis occurs, pore fraction for <6 μm pores increases as devolatilization leads to pore access and more surface area for pyrolysis and gasification
- In addition to total porosity increase, the fraction of <0.01 μm pores increases dramatically





*Distance across samples (constant scattering length density)

Gasification of Municipal Solid Waste (MSW)

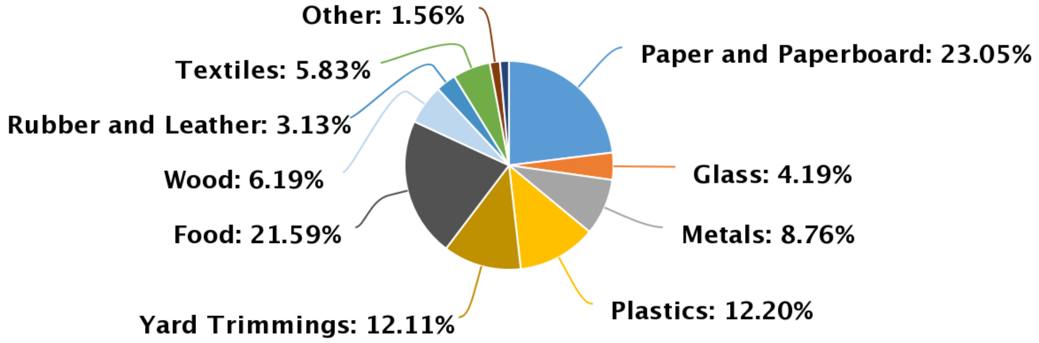
- Bench-scale pyrolysis
- Micro-Pyrolysis GC–MS
- Spallation Neutron Source (SNS) at Oak Ridge National Laboratory
  – Beamline BL-16B (VISION): Vibrational Spectroscopy

Municipal Solid Waste (MSW)

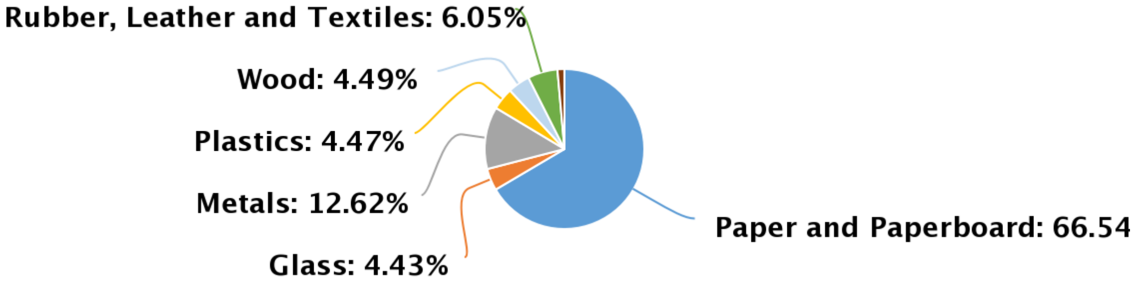
- MSW composition varies greatly and is a complex mixture
- Material macro structure varies greatly too
- EPA data shows total composition mixtures
- Recycling is the preferred processing step, but the overall rate low
- Our focus on plastics; wood & biomass studied early in the project

1	PET or PETE	Polyethylene Terephthalate
2	HDPE	High-Density Polyethylene
3	PVC	Polyvinyl Chloride
4	LDPE	Low-Density Polyethylene
5	PP	Polypropylene
6	PS	Polystyrene
7	Other	

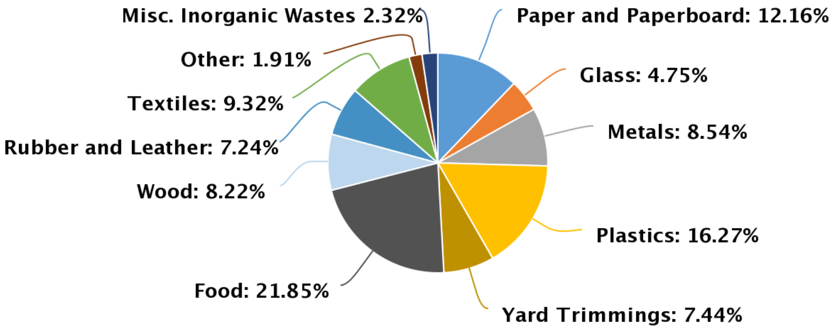
Total MSW Generated (2018)
292.4 million tons



Total MSW Recycling (2018)
69.1 million tons



Total MSW Combusted (2018)
34.6 million tons

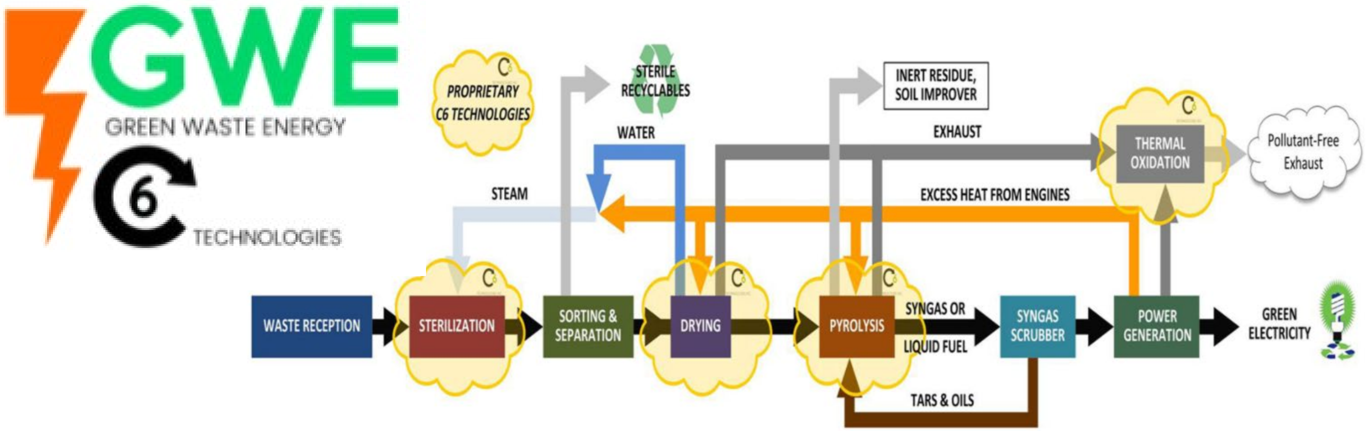


https://www.epa.gov/facts-and-figures-about-materials-waste-and-recycling/national-overview-facts-and-figures-materials

U.S. Companies Sanitizing and Homogenizing Municipal Solid Waste (MSW)

- WastAway (Morrison, TN)
  - A continuous process for treating (recycle separation & sanitation) MSW
  - Fluff® product can be compressed into fuel pellets
  - Focused on MSW-to-fuel process; fuel sent to power producers for demonstration
  - www.wastawayfuel.com
    - Images at right from WastAway website

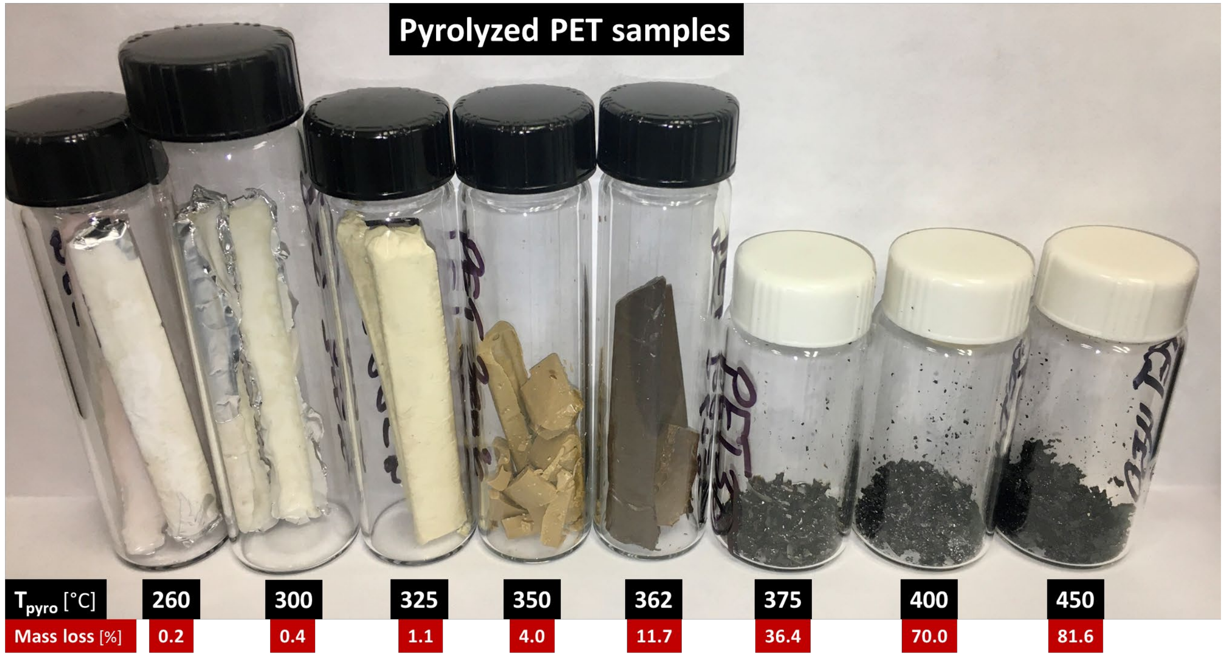
- Green Waste Energy (Greenwich, CT)
  - A batch process for treating (recycle separation & sanitation) MSW
  - Green Waste Energy "C6" technologies span entire process from MSW to power production
  - greenwasteenergy.com
    - Images at right from Green Waste Energy website

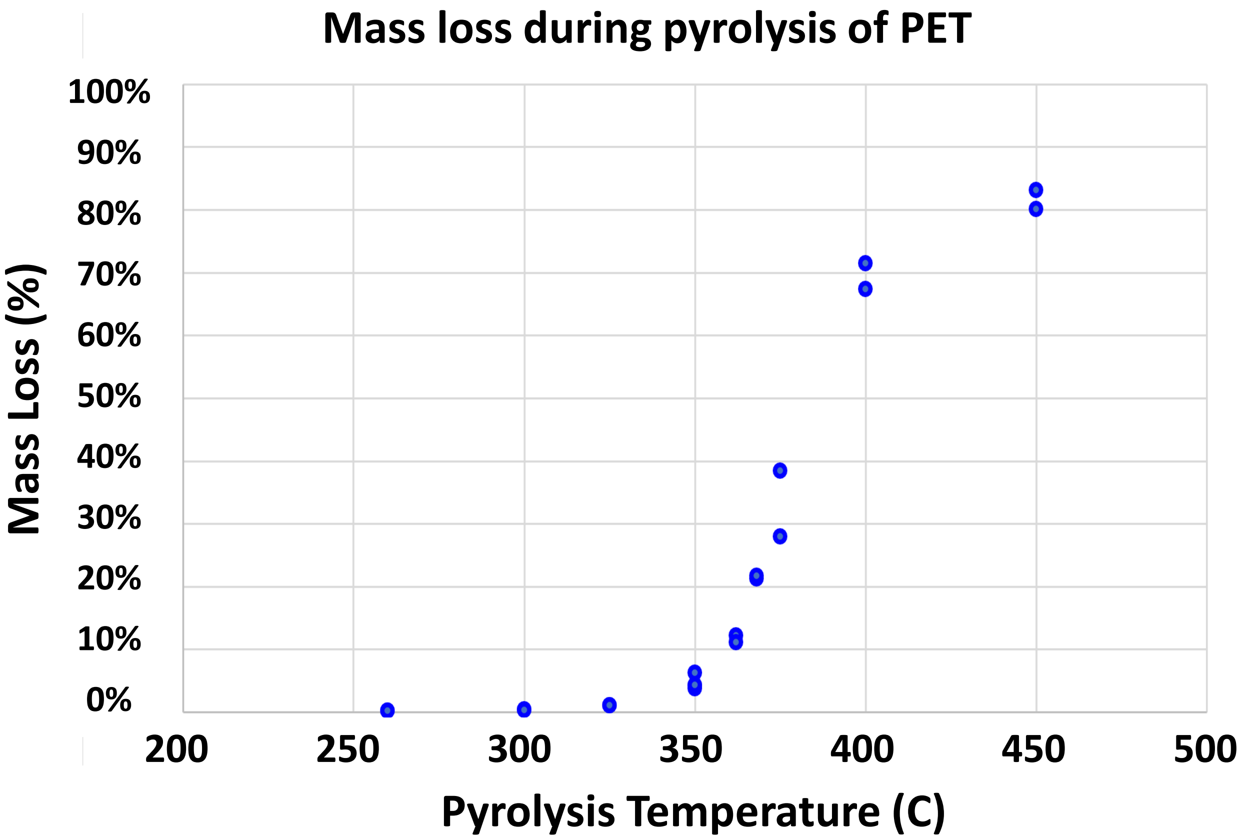


C6 ADVANCED RECYCLING & ENERGY CONVERSION (AREC) SYSTEM

Pyrolysis of plastic shows mass loss and morphology changes

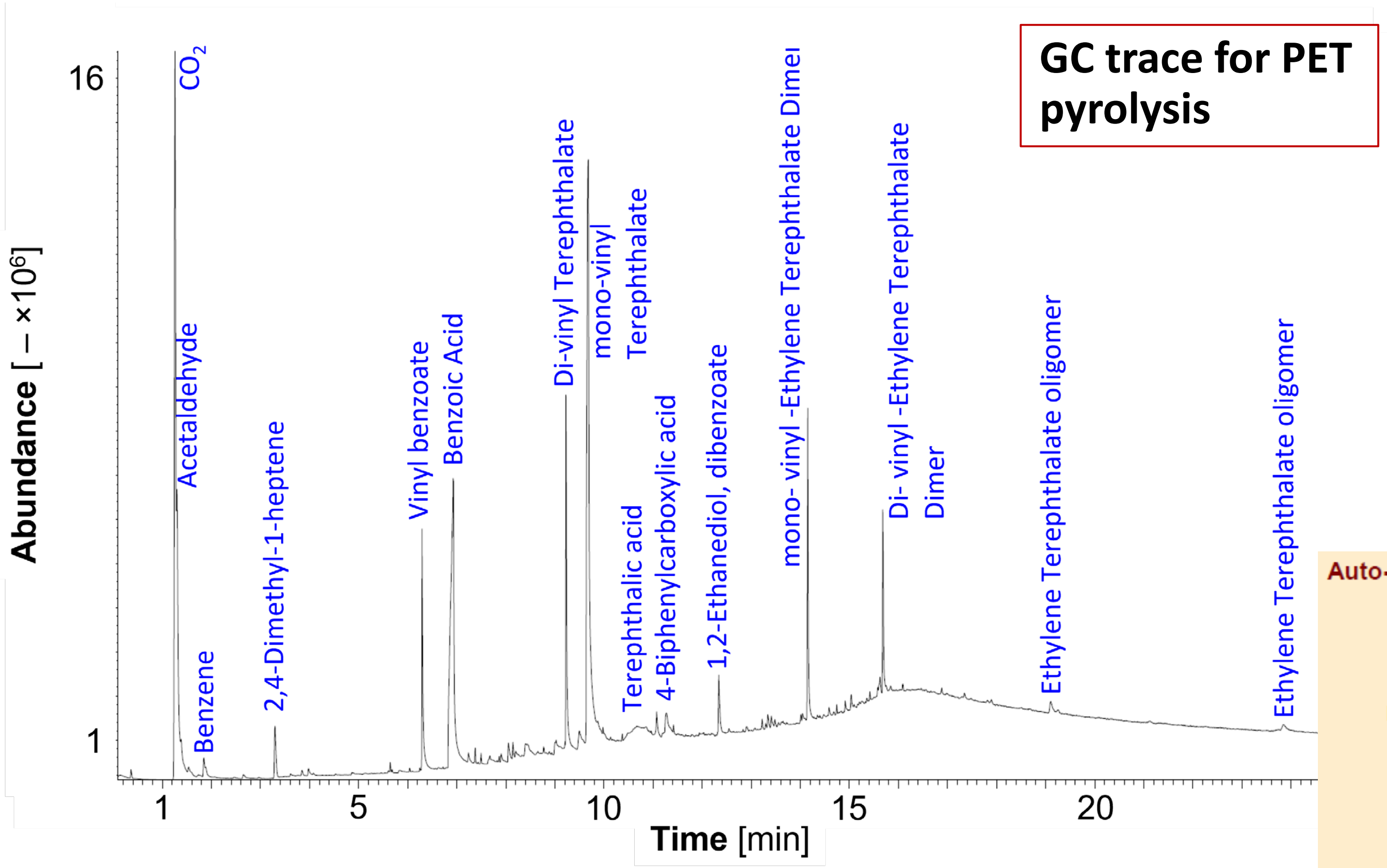
- Lab bench-top experiments of pyrolysis of plastic
- Polyethylene terephthalate (PET) samples shown
- Morphology changes significant

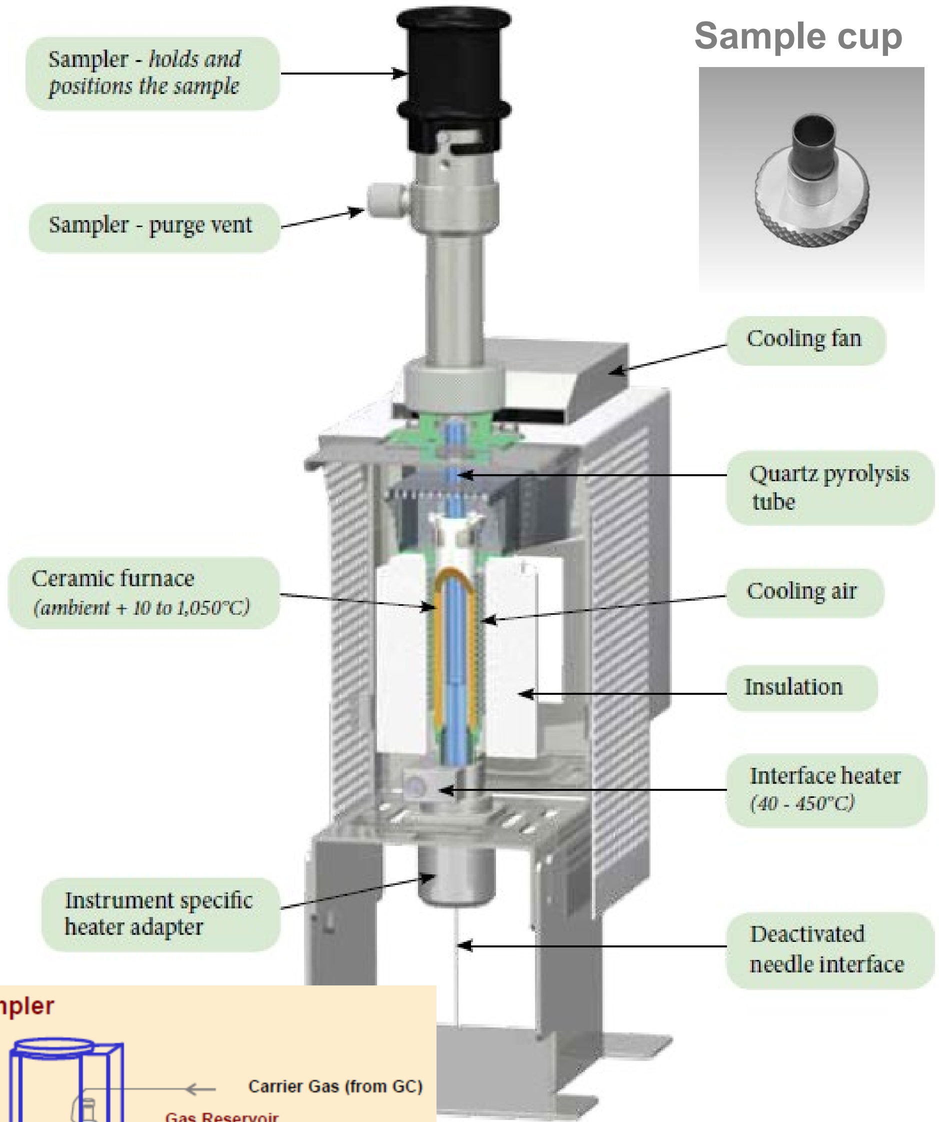


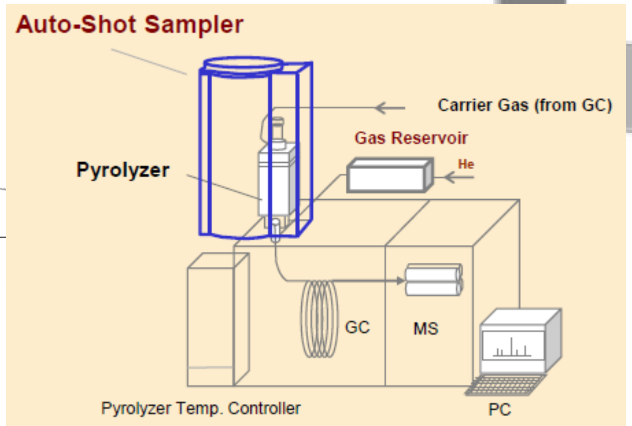


Gas-phase pyrolysis products can be characterized by Micro-Pyrolysis GC–MS

- Micro-furnace with ceramic heater and programmable temperature and heating rate
- Pyrolysis Temperature: 600 °C; Interface Temperature: 300 °C



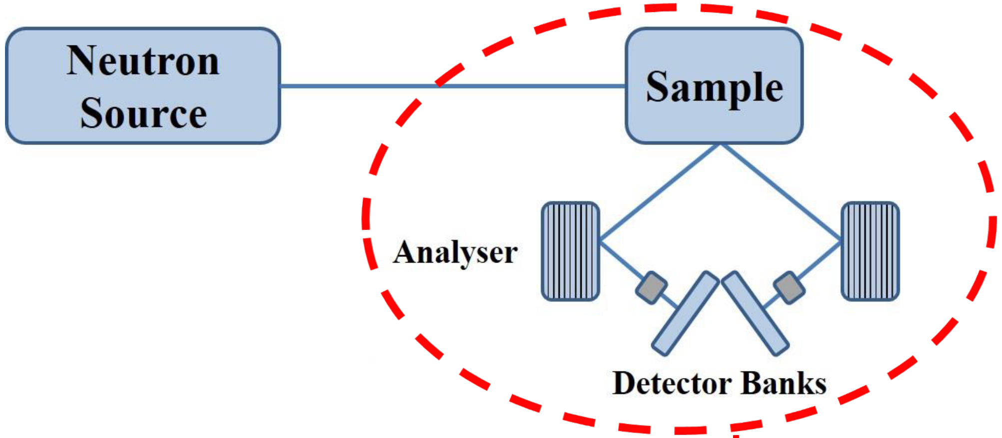


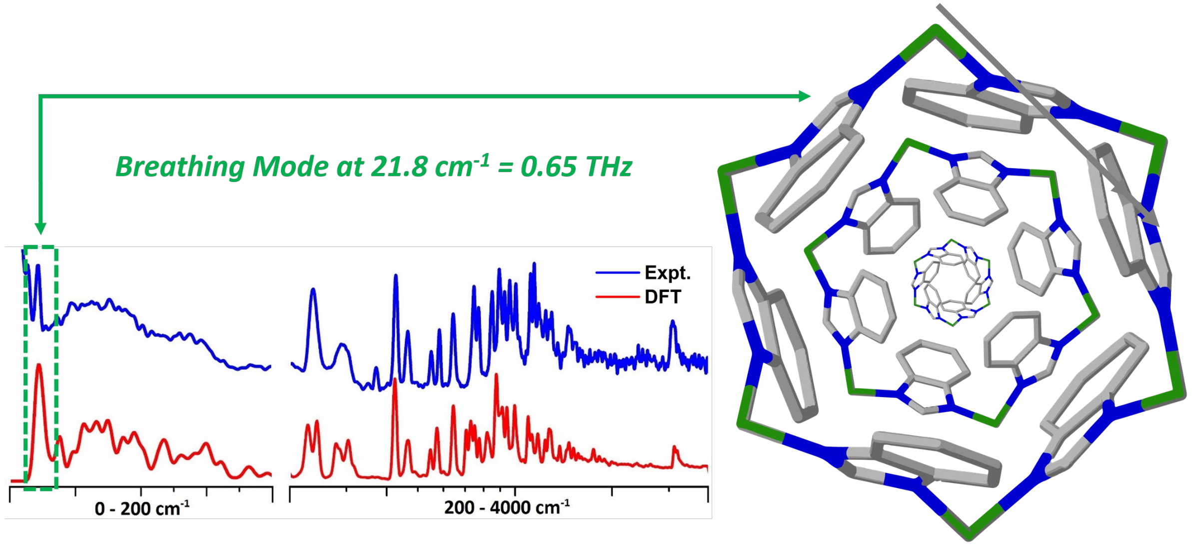


Frontier Lab EGA/PY-3030

Inelastic Neutron Scattering (INS): Vibrational Spectroscopy

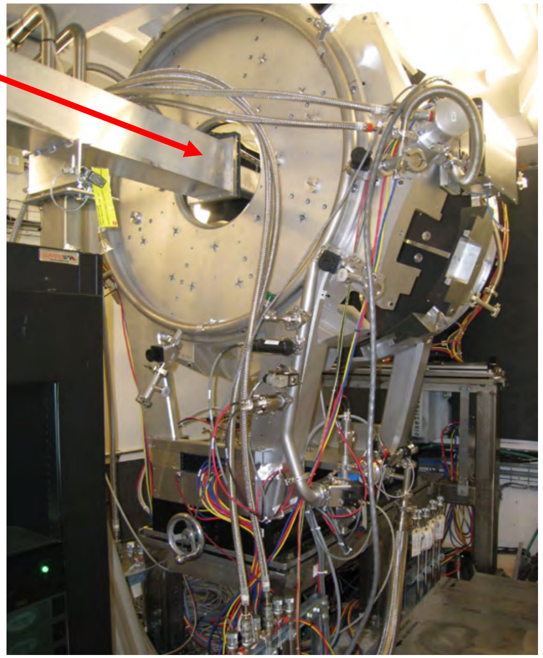
- INS data from Beamline 16-B (VISION) is the neutron analog of Raman and infrared spectroscopy with an affinity for hydrogen-containing materials.
- ***The measurements encompass the bulk sample***, not only surface effects, and are not restricted by optical selection rules.





Example of vibrational mode assignment in a crystalline porous material.

Neutron beam



Outside view of the spectrometer chassis, facing upstream.
https://neutrons.ornl.gov/sites/default/files/VISION_spec_sheet.pdf

For more information:
Ryder *et al., Phys. Rev. Lett.*, 113, 215502 (2014)
Armstrong *et al., J. Phys. Commun.*, 4, 072001 (2020)

Inelastic Neutron Scattering provides the chemistry for a range of plastics

2800–3400 cm^{-1}

- ▶ C–H stretching

950–1700 cm^{-1}

- ▶ C–C and C–O stretching
- ▶ C–H bending

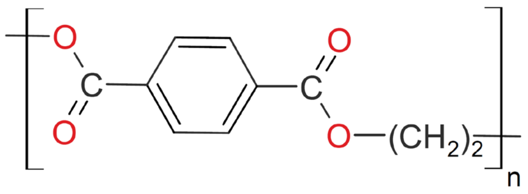
350–950 cm^{-1}

- ▶ Aromatic ring deformations

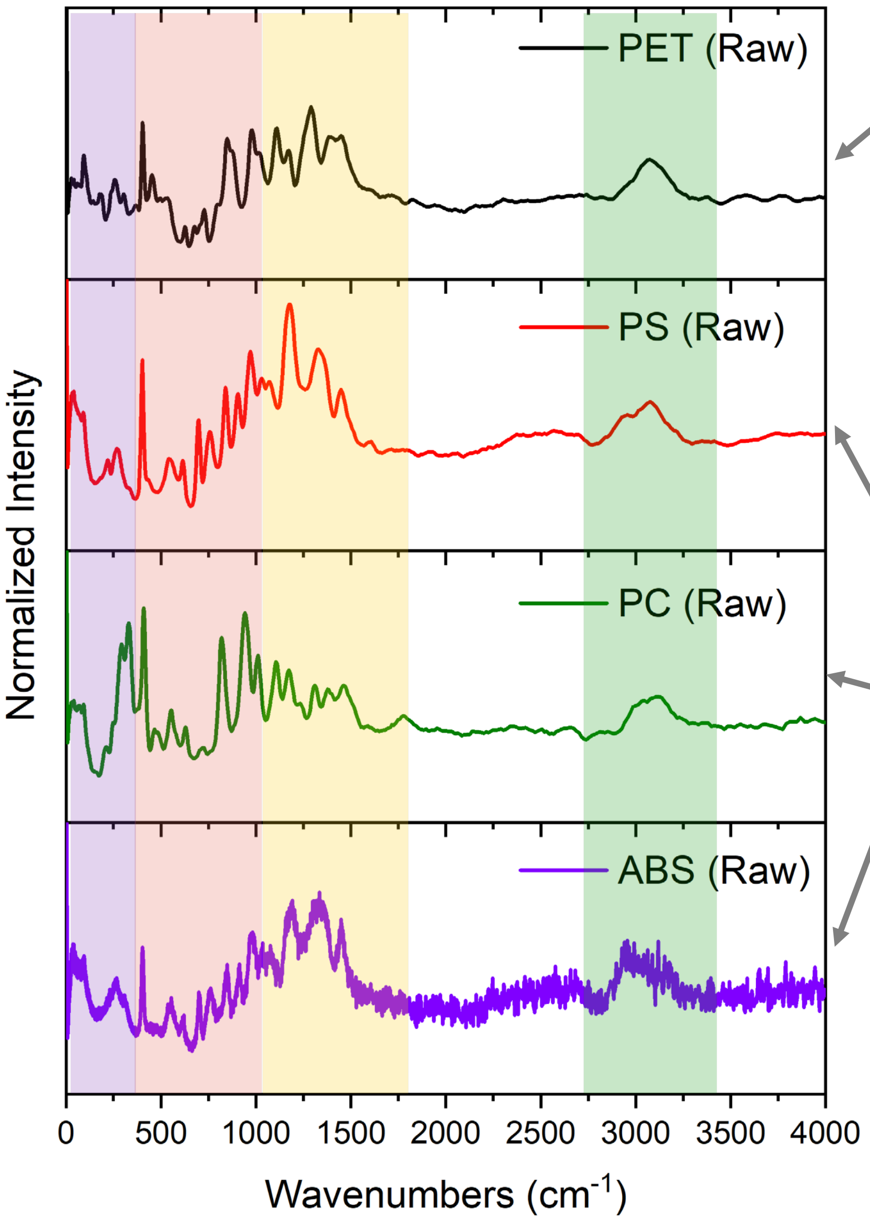
0–330 cm^{-1} – Phonon (THz) modes

- ▶ Collective dynamics
- ▶ Polymer chain deformations

Polyethylene terephthalate (PET)



Other plastics investigated:
- Polystyrene (PS)
- Polycarbonate (PC)
- ABS



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4	LDPE	Low-Density Polyethylene
5	PP	Polypropylene
6	PS	Polystyrene
7	Other	

Note: Spectra normalized to the elastic line.

Inelastic Neutron Scattering shows chemical breakdown during pyrolysis

2800–3400 cm^{-1}

- ► C–H stretching

950–1700 cm^{-1}

- ► C–C and C–O stretching
- ► C–H bending

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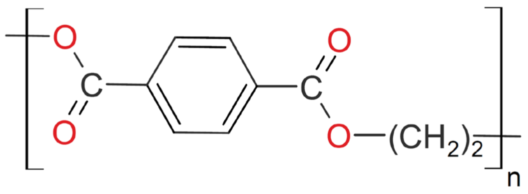

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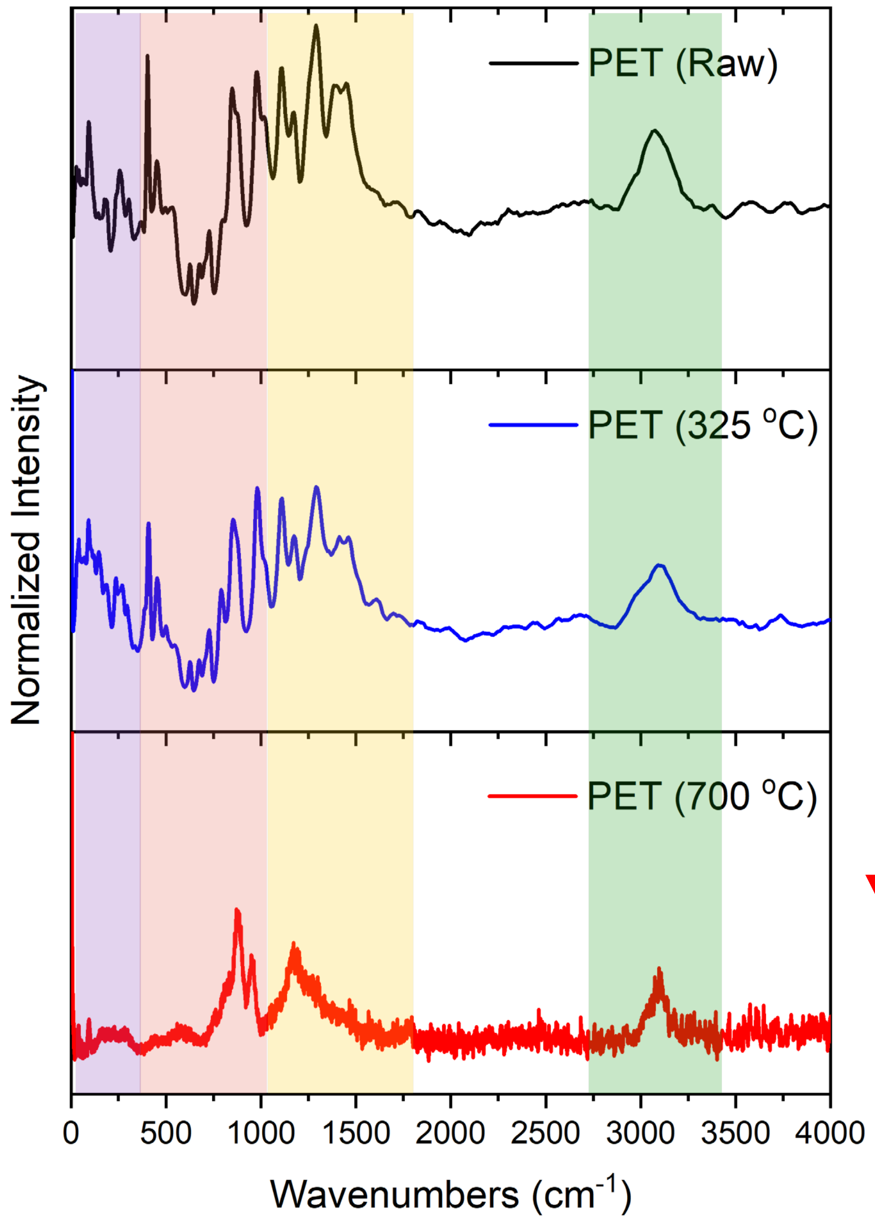

1	PET or PETE	Polyethylene Terephthalate

Minimal structural changes before pyrolysis temperatures.

Pyrolysis breaks polymer chains and reduces structural complexity.

Remaining spectral features like those seen for pyrolyzed coal (graphitic).

Note: Spectra normalized to the elastic line.

Summary: Feedstock Gasification Characterization with Neutron Techniques

Coal

- 6 different coals (over 4 ranks) studied
- Dynamic *in situ* neutron imaging of gasification studies with coal capture complex stages of the process
- Porosity changes, including a fraction of < 0.01 μm pores captured with neutron scattering

Municipal Solid Waste

- Cellulosic component: pyrolysis of biomass studied in early stages of the project
- Plastic component: 4 different plastics studied
- A combination of inelastic neutron scattering studies (bulk chemistry) and micro-pyrolyzer GC-MS (devolatilized gas chemistry) captures chemical changes

Publications (in process)

- Finney CEA, Tsouris C, Smith DB, Parks JE *et al.* (2022). Neutron imaging of *operando* biomass and coal pyrolysis.
- Ryder MR *et al.* (2022). Investigating pyrolysis dynamics of coal gasification using neutron spectroscopy
- Anovitz LM *et al.* (2022). Pore-size evolution of pyrolyzed coal using SANS and SAXS.

Plastic (PET)

Coal (Sub-Bituminous)