Enabling Low Carbon Feedstocks for Gasification (FWP-FEAA437)

Jim Parks (parksjeii@ornl.gov), Charles Finney,
Costas Tsouris, Lawrence Anovitz,
Matthew Ryder, Vlad Lobodin, Stephen Purdy,
Samuel Sasser, Dipti Kamath, Ikenna Okeke
Oak Ridge National Laboratory

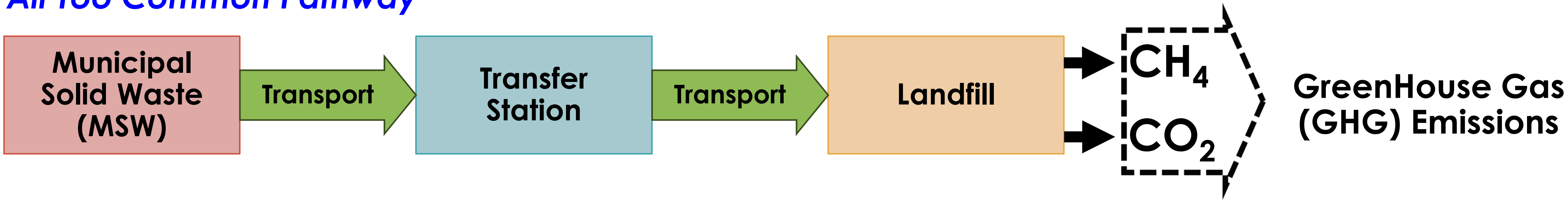
2024 FECM/NETL Spring R&D Project Review Meeting
April 23-25, 2024
Pittsburgh, PA

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

Thanks to Diane Madden (NETL), Jai-Woh Kim (DOE), Jonathan Leske (NETL), David Lyons (NETL), and the U.S. Department of Energy (DOE) Office of Fossil Energy and Carbon Management (FECM) for guidance and support of this project

Municipal Solid Waste (MSW) Pathways

All Too Common Pathway



Municipal Solid Waste (MSW) → **Transport** → **Transfer Station** → **Transport** → **Landfill** → CH_4, CO_2 → **GreenHouse Gas (GHG) Emissions**

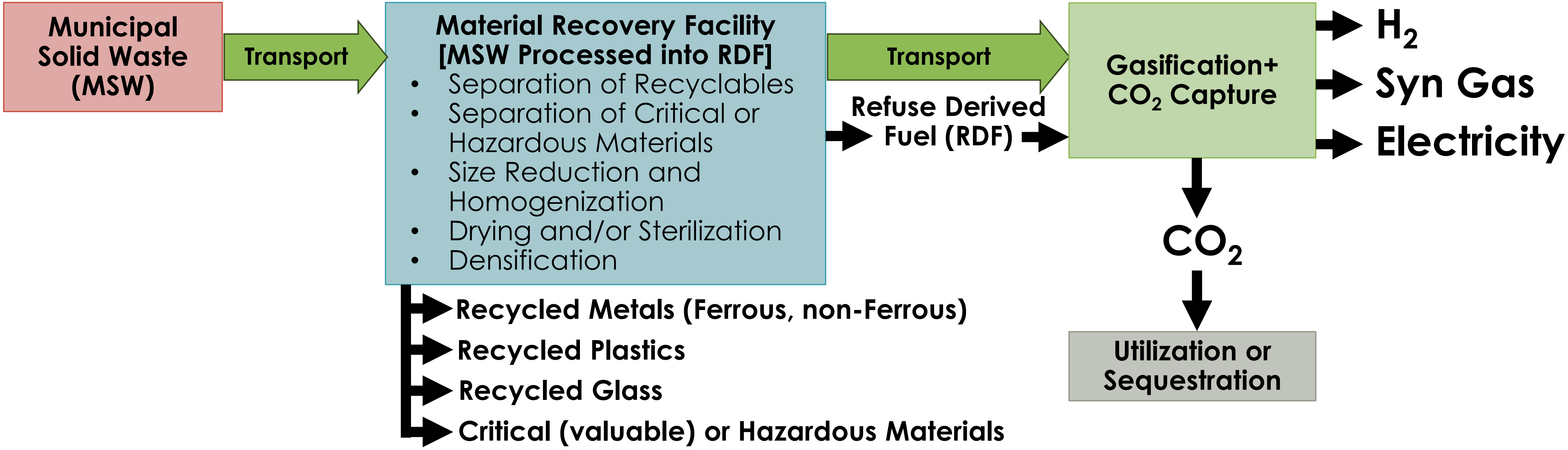
GreenHouse Gas	Global Warming Potential	Lifetime in Atmosphere
CO_2	1 (@100-year time-scale)	300-1000 years
CH_4	28 (@100-year time-scale)	7-12 years

14% of U.S. CH_4 emissions are from Landfills*

*www.epa.gov/lmop/basic-information-about-landfill-gas

Municipal Solid Waste (MSW) Pathways

Preferred Pathway with Material Valorization, CH_4 and CO_2 Avoidance, and Clean Energy Products



Municipal Solid Waste (MSW)

Transport

Material Recovery Facility [MSW Processed into RDF]

- Separation of Recyclables
- Separation of Critical or Hazardous Materials
- Size Reduction and Homogenization
- Drying and/or Sterilization
- Densification

Recycled Metals (Ferrous, non-Ferrous)

Recycled Plastics

Recycled Glass

Critical (valuable) or Hazardous Materials

Transport

Refuse Derived Fuel (RDF)

Gasification+ CO_2 Capture

H_2

Syn Gas

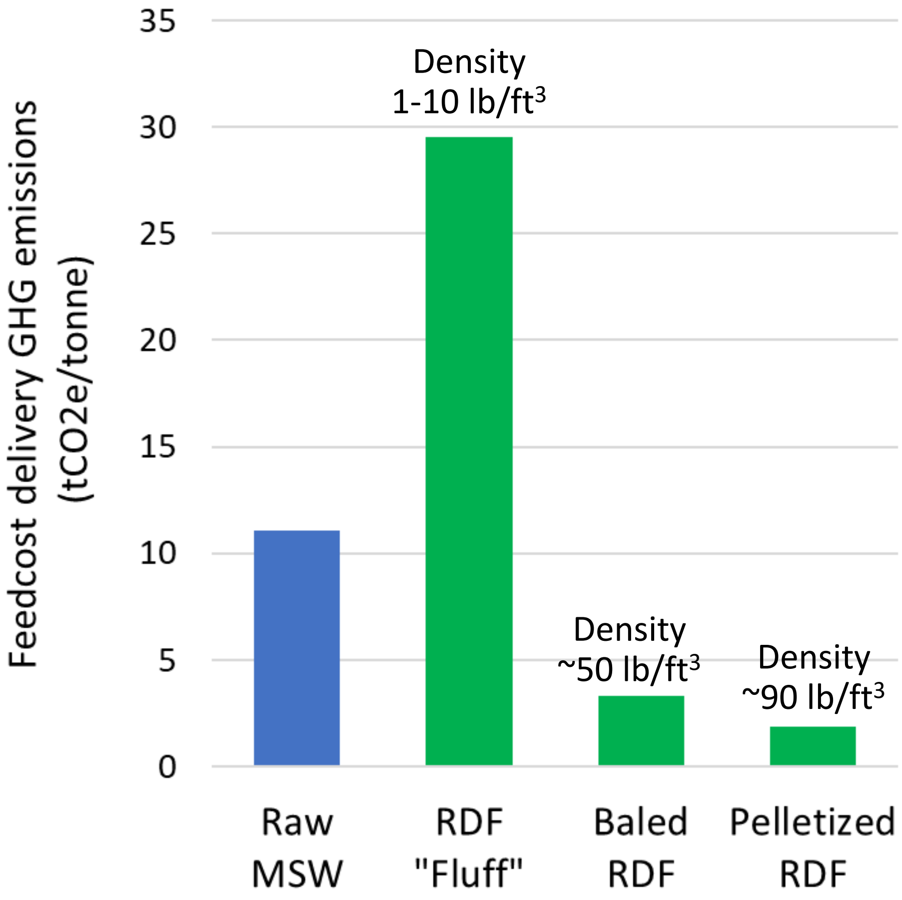
Electricity

CO_2

Utilization or Sequestration

Transport of MSW/RDF Affects Cost & Life Cycle Emissions

- Transportation (100-mile case shown) of MSW and RDF adds cost and GreenHouse Gas emissions
- Moisture content and density are primary factors
- Example analysis shown based on nominal values
  - MSW: 40-60% moisture
  - RDF: 5-15% moisture
- Analysis assumes natural gas for drying process



Analysis Details:

- The feedstock delivery emissions are associated with MSW drying, pelletization, and transportation operations.
- Drying GHG emissions are calculated using a natural gas emissions factor of 53.06 $kgCO_2e$/MMBTU.
- Energy use for pelletization was 12.1 MJ/ton assumed to be supplied via electricity.
  - An average U.S. grid emissions intensity of 0.37 $kgCO_2$/kWh was used.
- Transportation emissions are computed using the emissions factor of 1001 $kgCO_2e$/TEU-mi.

References:

www.epa.gov/system/files/documents/2023-03/ghg_emission_factors_hub.pdf
www.sciencedirect.com/science/article/pii/S0196890416000224
www.transportation.gov/sites/dot.gov/files/docs/emissions_analysis_of_freight.pdf

Industry Partner: Ekamor Resource Corporation

- A continuous process for treating (recycle separation & dewatering) MSW to create RDF
- 75+% less energy consumption vs. thermal-based processes
- MSW "dewatered" to RDF with <15% moisture content

Ekamor Facility in Cookeville, TN

ĒKAMOR RESOURCE CORPORATION

New Name in 2024

Novastus WASTE REDEFINED

RDF Fluff
(Processed MSW)

Baled RDF
(plastic wrap seal enables excellent long-term storage)

Vertical Shaft Impactor
(dewatering and size reduction unit operation)

Pelletized RDF
(easy to transport and feed)

Research of Feedstock Physical and Chemical Properties during Gasification Enables Improved Gasifier Design and Control

Feedstock Characterization with ORNL Materials Science Expertise including Neutron Science Facilities

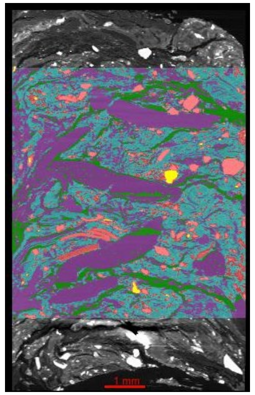
Critical Parameters, Validation Data, Design Guidance

Gasifier Reactor Modeling with NETL Computational Fluid Dynamics Expertise (MFiX)

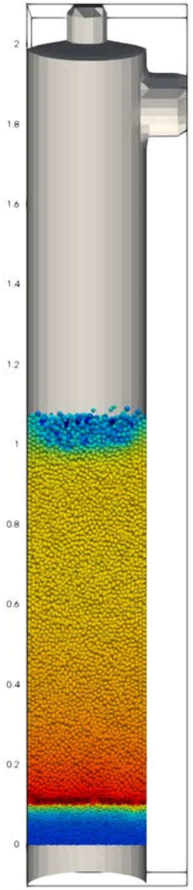
De-watered and pelletized RDF from Ekamor

Properties:
- Morphology
- Porosity
- Density
- Chemical composition
- Catalytic effects
- Ash effects

Low-carbon life-cycle feedstocks:
- Municipal Solid Waste (MSW) Sustainable Biomass
- Waste Plastics
- Food Waste
- Waste Coal

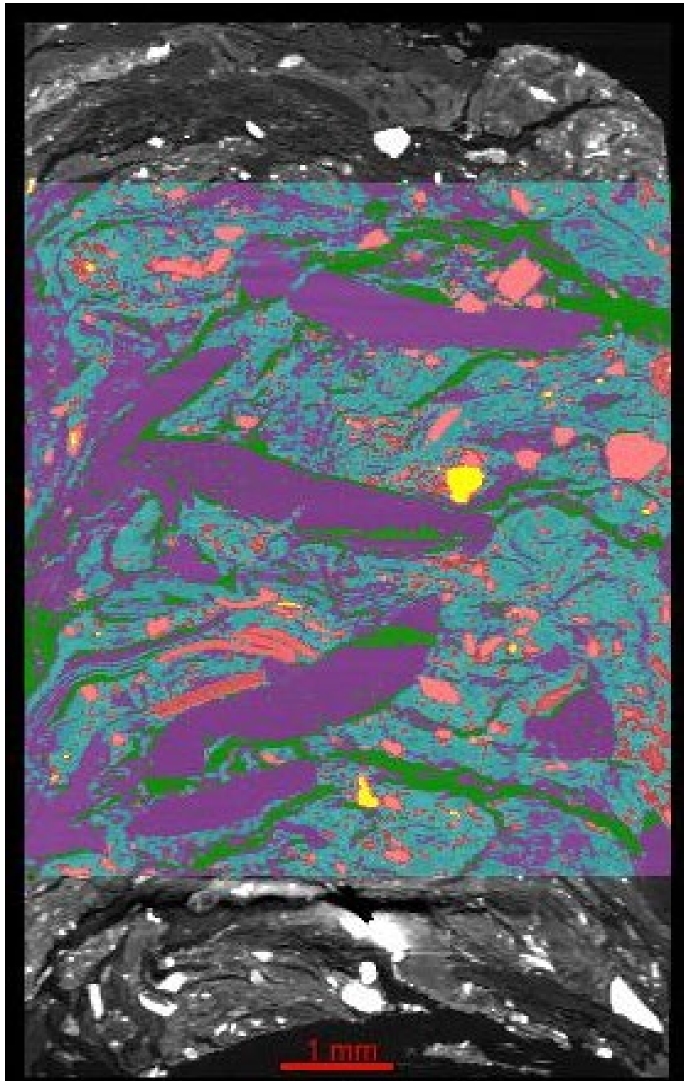


200 KW **5 MW** **22 MW**



MFiX models of a 200kw, 5MW and 22 MW modular moving bed gasifier at Sotacarbo [NETL graphics courtesy of Mehrdad Shahnam]

X-Ray Computational Tomography (XCT) of Engineered Refuse-Derived Fuel (ERDF)



Ekamor ERDF
Pellet Characteristics:

- 5-6 mm diameter
- Length varies (nominally 1 cm, but fractures shorten)
- Density: 1.1-1.2 g/cm^3 (nominally)
- Moisture Content: <15% (raw MSW typically 40-60%)
- Oxygen Content: 20% (nominally)
- Energy Content: ~15 M BTU/ton (for comparison, coal ~24 MBTU/ton)

Empty Space/Air: 9.40 vol.%
Low Absorption Solid: 42.36 vol.%
Medium Absorption Solid: 36.60 vol.%
Med-Hi Absorption Solid: 11.28 vol.%
High Absorption Solid: 0.36 vol.%

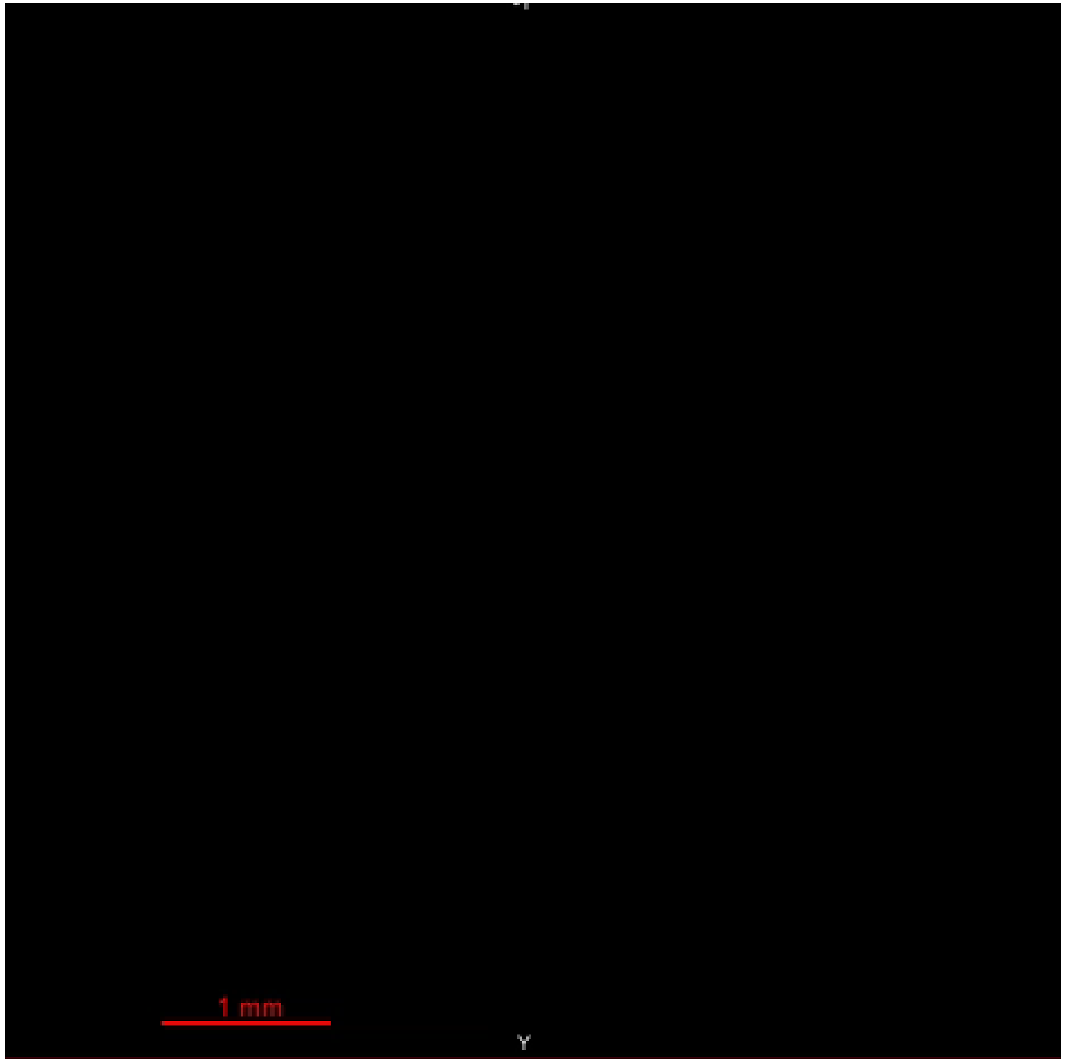
Engineered Refuse-Derived Fuel (ERDF): De-watered and Pelletized Municipal Solid Waste (MSW) from Ekamor

- *Most metal, glass, and large plastics are removed (for recycling) prior to drying and pelletization*
- *Size reduction of MSW components occurs during processing (homongeneity benefit)*

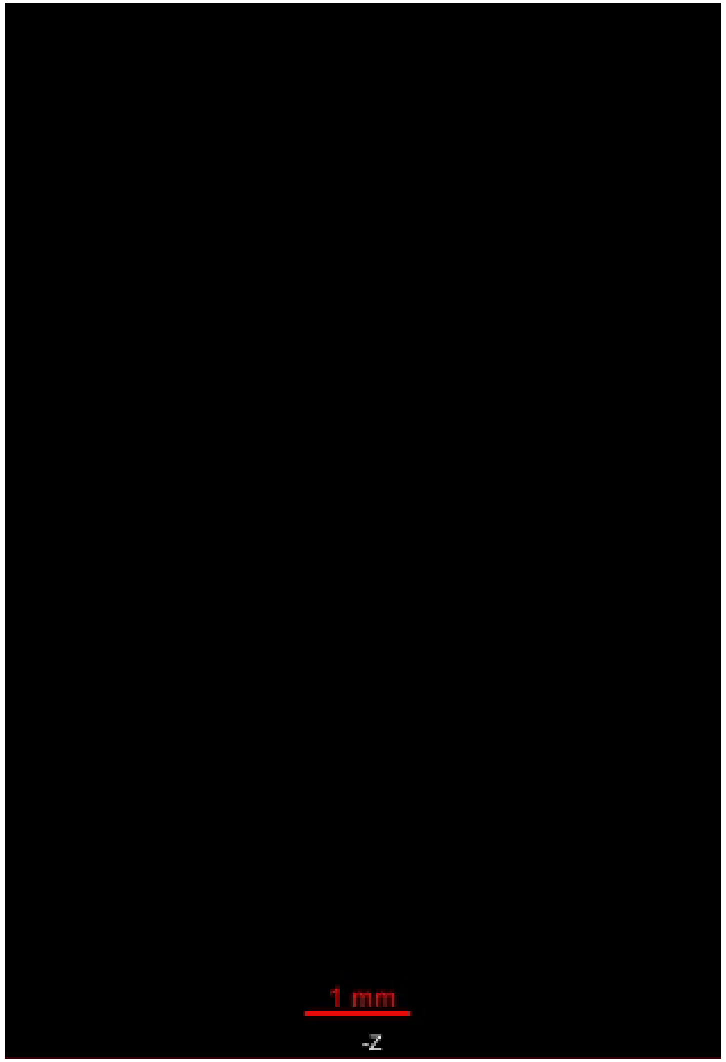
XCT data from Ercan Cakmak (ORNL)

XCT Movies of RDF Pellet

Horizontal Slice Movie



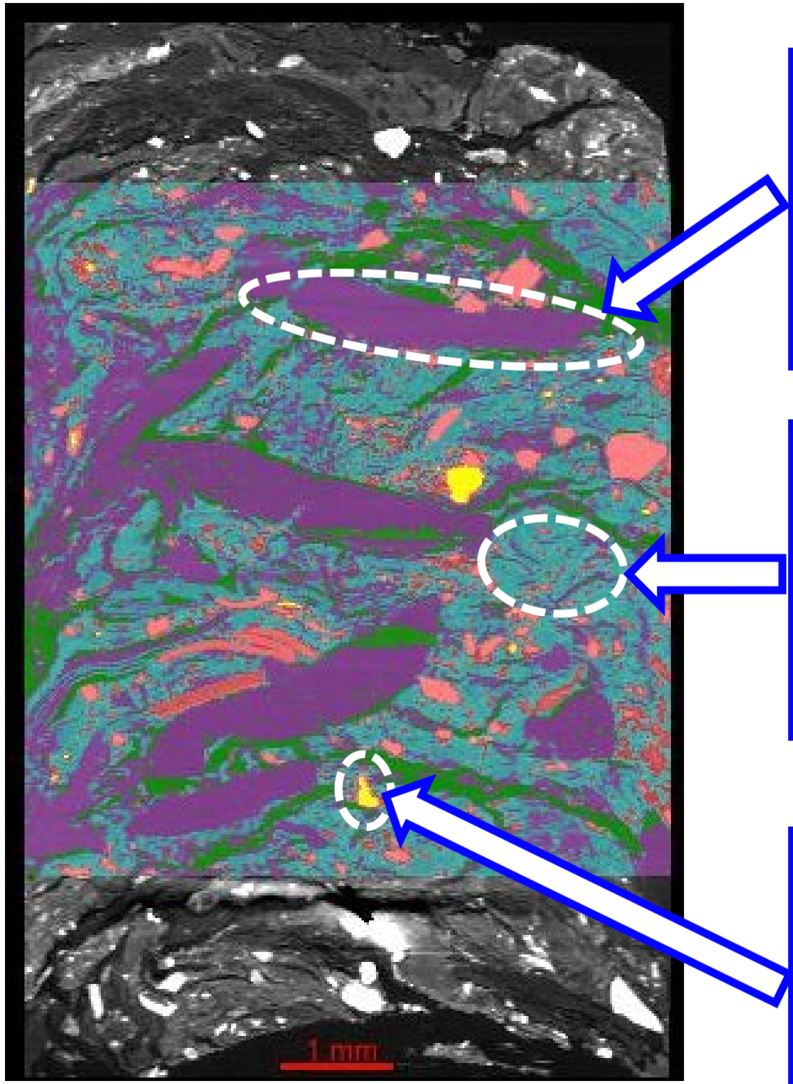
Vertical Slice Movie



In general, high absorption identified by brighter phases correspond to denser/heavier materials

XCT data from Ercan Cakmak (ORNL)

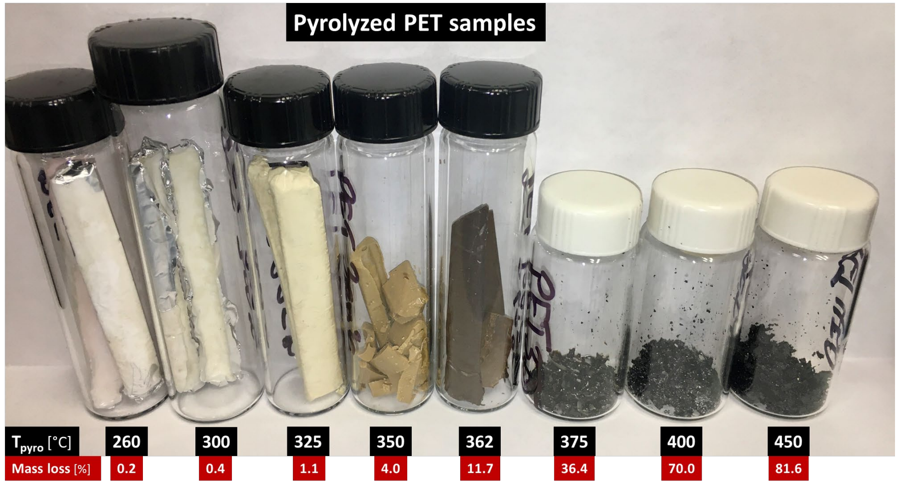
Project Goal: Characterize the physical and chemical transformation of feedstocks for gasification to enable reliable low-cost hydrogen (H_2) and power generation from low-carbon life-cycle and low-cost feedstocks.

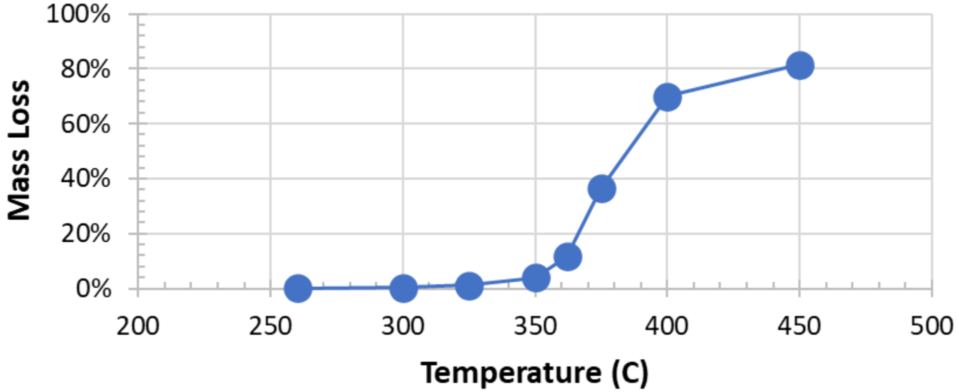


Plastics
- Long shreds of plastic bags (LDPE) are common
- Relatively low-density component
- Low permeability [e.g. LDPE: $2.89*10^{-7}$ kg/(m^2 Pa. days)]*

Cellulosic Materials
- Diverse sources: paper, cardboard, tissue paper, paper towels, food waste, fabrics
- High permeability [e.g. Kraft paper: $689*10^{-7}$ kg/(m^2 Pa. days)]*

Unknown Materials
- Diverse sources: sand, seeds/food shells, high-density plastics, metal fragments, etc.
- May lead to ash


Pyrolyzed PET samples



Morphology/Density vs. Temperature

Porosity/Permeability vs. Temperature

Chemistry vs. Temperature

---

*D. Lestari, Y. Elvina, M. T. A. P. Kresnowati, *J. Eng. Technol. Sci.* 2019, **51**, 64-82.

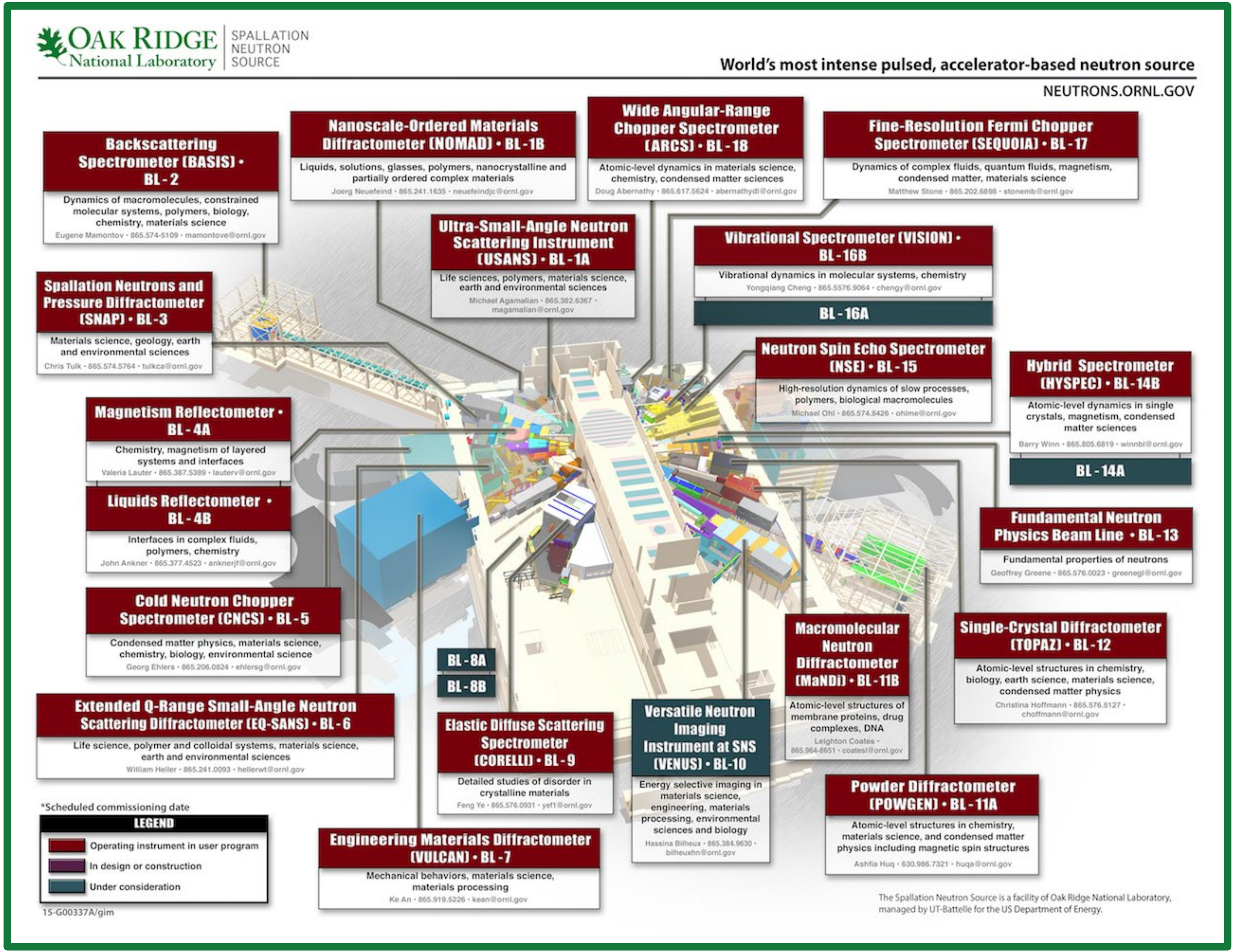
Neutron-Based Analysis of Gasification of Low C Feedstocks

- Neutron Imaging of Post-Pyrolyzed Samples
- In progress plans for future in situ R&D

Approach Utilizes Unique Office of Science Neutron User Facilities

Office of Science User Facilities:
- High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory (ORNL)
- Spallation Neutron Source (SNS) at Oak Ridge National Laboratory (ORNL)
- Center for Neutron Research (CNR) at the National Institute of Standards and Technology (NIST)

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



OAK RIDGE National Laboratory | SPALLATION NEUTRON SOURCE

World's most intense pulsed, accelerator-based neutron source

NEUTRONS.ORNL.GOV

Backscattering Spectrometer (BASIS) • BL-2
Dynamics of macromolecules, constrained molecular systems, polymers, biology, chemistry, materials science
Eugene Mamontov • 865.574-5109 • mamontove@ornl.gov

Nanoscale-Ordered Materials Diffractometer (NOMAD) • BL-1B
Liquids, solutions, glasses, polymers, nanocrystalline and partially ordered complex materials
Joerg Neuefeind • 865.241.1635 • neuefeindjc@ornl.gov

Wide Angular-Range Chopper Spectrometer (ARCS) • BL-18
Atomic-level dynamics in materials science, chemistry, condensed matter sciences
Doug Abernathy • 865.617.5624 • abernathydl@ornl.gov

Fine-Resolution Fermi Chopper Spectrometer (SEQUOIA) • BL-17
Dynamics of complex fluids, quantum fluids, magnetism, condensed matter, materials science
Matthew Stone • 865.202.6898 • stonemb@ornl.gov

Ultra-Small-Angle Neutron Scattering Instrument (USANS) • BL-1A
Life sciences, polymers, materials science, earth and environmental sciences
Michael Agamalian • 865.382.6367 • magamalian@ornl.gov

Vibrational Spectrometer (VISION) • BL-16B
Vibrational dynamics in molecular systems, chemistry
Yongqiang Cheng • 865.5576.9064 • chengy@ornl.gov

BL-16A

Spallation Neutrons and Pressure Diffractometer (SNAP) • BL-3
Materials science, geology, earth and environmental sciences
Chris Tulk • 865.574.5764 • tulkca@ornl.gov

Neutron Spin Echo Spectrometer (NSE) • BL-15
High-resolution dynamics of slow processes, polymers, biological macromolecules
Michael Ohl • 865.574.8426 • ohlme@ornl.gov

Hybrid Spectrometer (HYSPEC) • BL-14B
Atomic-level dynamics in single crystals, magnetism, condensed matter sciences
Barry Winn • 865.805.6819 • winnbl@ornl.gov

BL-14A

Magnetism Reflectometer • BL-4A
Chemistry, magnetism of layered systems and interfaces
Valeria Lauter • 865.387.5389 • lauterv@ornl.gov

Liquids Reflectometer • BL-4B
Interfaces in complex fluids, polymers, chemistry
John Ankner • 865.377.4523 • anknerjf@ornl.gov

Fundamental Neutron Physics Beam Line • BL-13
Fundamental properties of neutrons
Geoffrey Greene • 865.576.0023 • greenegl@ornl.gov

Cold Neutron Chopper Spectrometer (CNCS) • BL-5
Condensed matter physics, materials science, chemistry, biology, environmental science
Georg Ehlers • 865.206.0824 • ehlersg@ornl.gov

BL-8A

BL-8B

Macromolecular Neutron Diffractometer (MaNDi) • BL-11B
Atomic-level structures of membrane proteins, drug complexes, DNA
Leighton Coates • 865.964-8651 • coatesl@ornl.gov

Single-Crystal Diffractometer (TOPAZ) • BL-12
Atomic-level structures in chemistry, biology, earth science, materials science, condensed matter physics
Christina Hoffmann • 865.576.5127 • choffmann@ornl.gov

Extended Q-Range Small-Angle Neutron Scattering Diffractometer (EQ-SANS) • BL-6
Life science, polymer and colloidal systems, materials science, earth and environmental sciences
William Heller • 865.241.0093 • hellerwt@ornl.gov

Elastic Diffuse Scattering Spectrometer (CORELLI) • BL-9
Detailed studies of disorder in crystalline materials
Feng Ye • 865.576.0931 • yef1@ornl.gov

Versatile Neutron Imaging Instrument at SNS (VENUS) • BL-10
Energy selective imaging in materials science, engineering, materials processing, environmental sciences and biology
Hassina Bilheux • 865.384.9630 • bilheuxhn@ornl.gov

Powder Diffractometer (POWGEN) • BL-11A
Atomic-level structures in chemistry, materials science, and condensed matter physics including magnetic spin structures
Ashfia Huq • 630.986.7321 • huqa@ornl.gov

Engineering Materials Diffractometer (VULCAN) • BL-7
Mechanical behaviors, materials science, materials processing
Ke An • 865.919.5226 • kean@ornl.gov

*Scheduled commissioning date

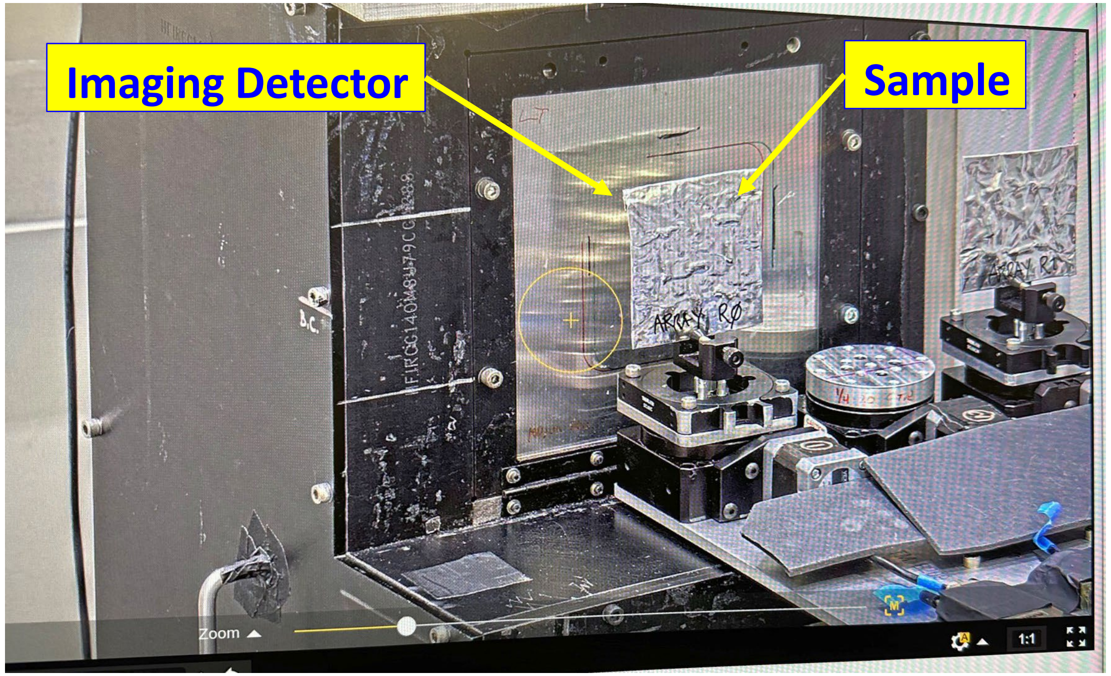
LEGEND	
🟥	Operating instrument in user program
🟪	In design or construction
🟦	Under consideration

15-G00337A/gim

The Spallation Neutron Source is a facility of Oak Ridge National Laboratory, managed by UT-Battelle for the US Department of Energy.

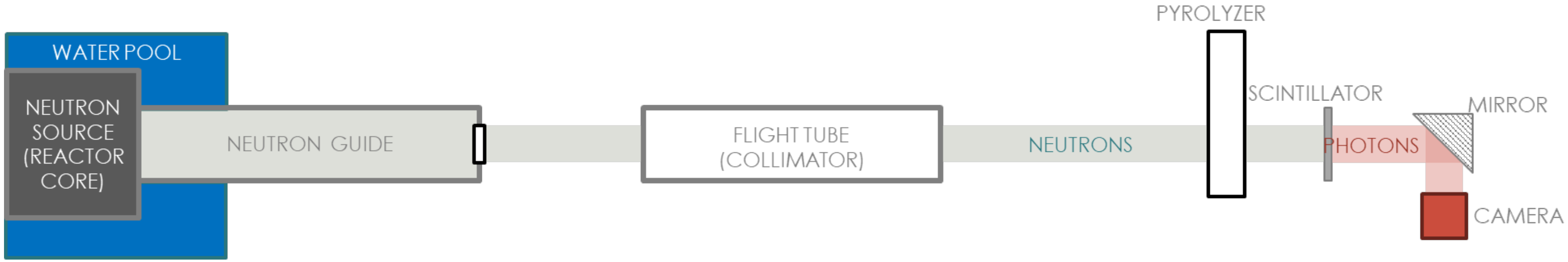
Neutron Science Techniques Utilized for Feedstock Characterization

Neutron Imaging
“Multimodal Advanced Radiography Station”
neutrons.ornl.gov/mars



Small Angle Neutron Scattering (SANS)
neutrons.ornl.gov/gpsans

Neutron Transmission of Engineered Refuse-Derived Fuel Pellets after Pyrolysis at Set Temperatures

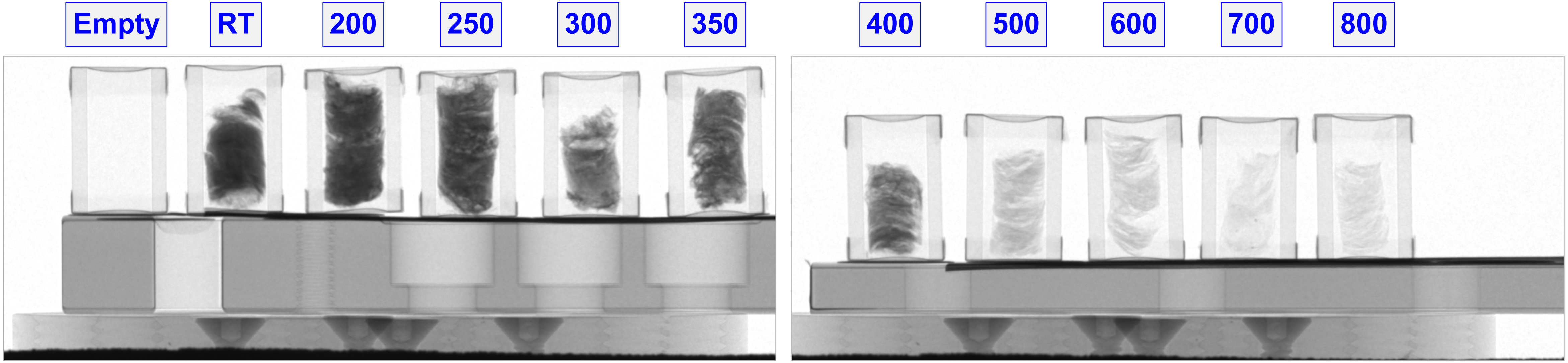


Elemental scattering cross-sections

Element *i*	**W_i** [g/mol]	**σ_i** [Barn]*
H	1.008	82.50
C	12.011	5.556
N	14.077	14.25
O	15.999	4.232
S	32.06	1.792
Al	26.982	1.837

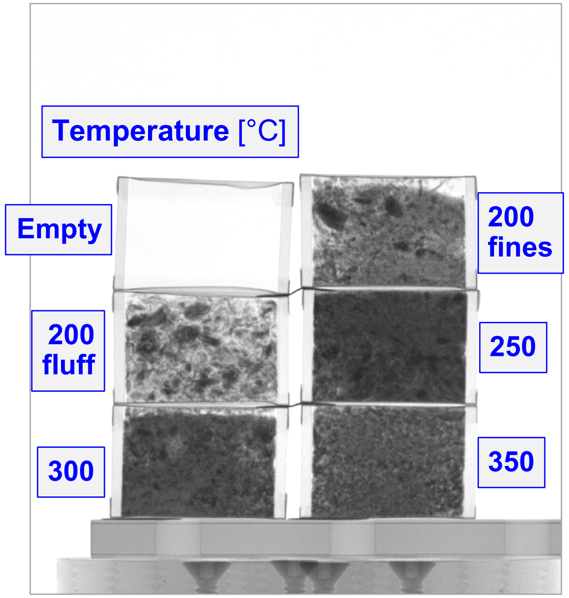
*1 Barn = 1 × 10^{-24} cm^2

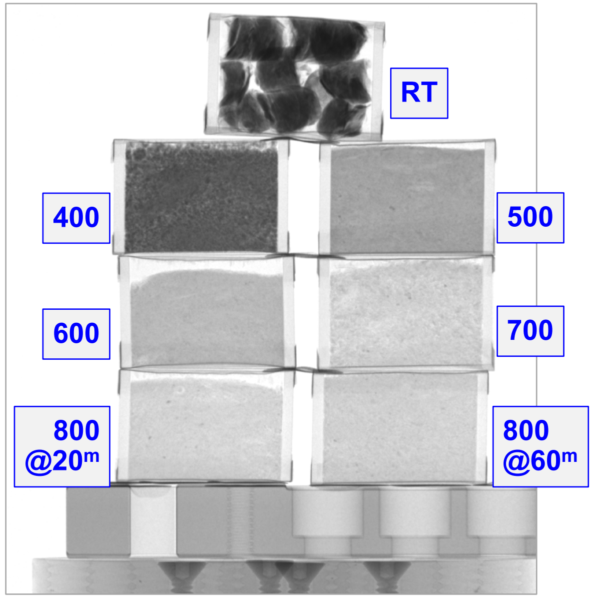
Temperature [°C]

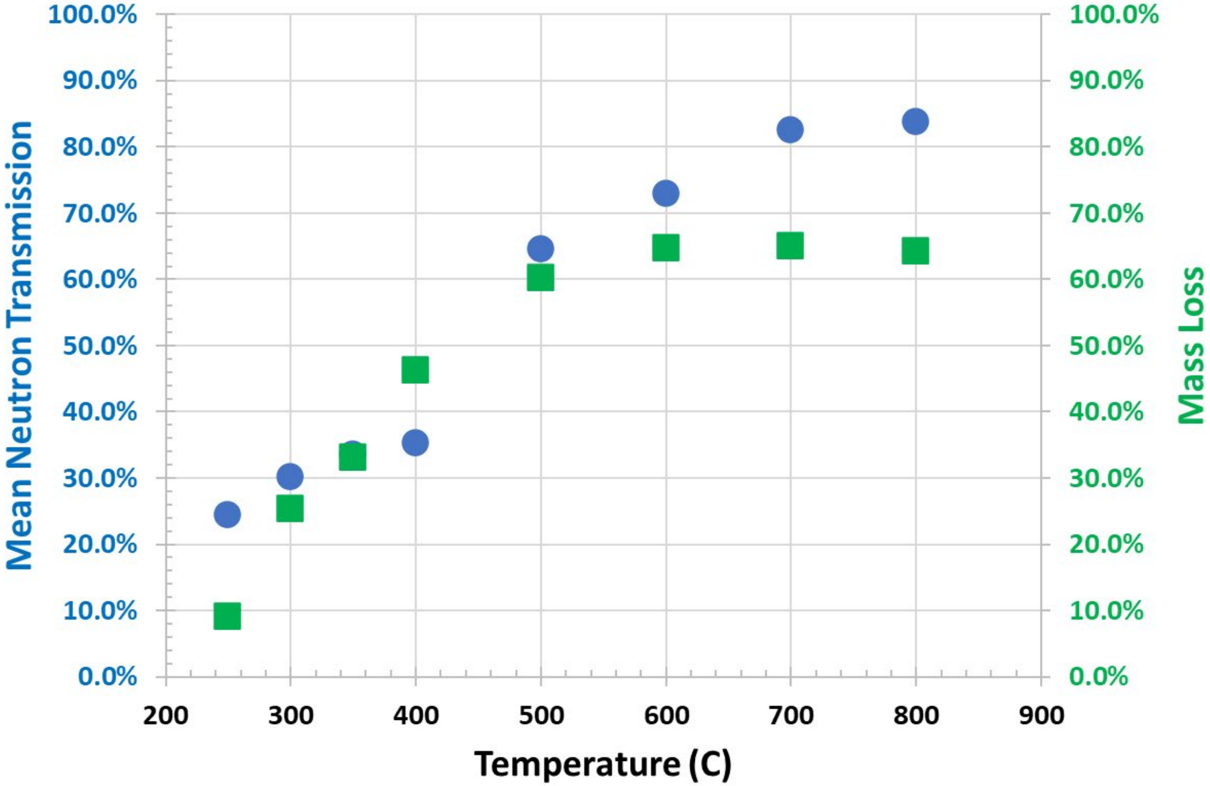


Darker images represent samples with higher Hydrogen content (H has highest neutron cross section)
Note: each sample is a different pellet

Neutron Transmission of Pulverized Engineered Refuse-Derived Fuel Pellets after Pyrolysis at Set Temperatures



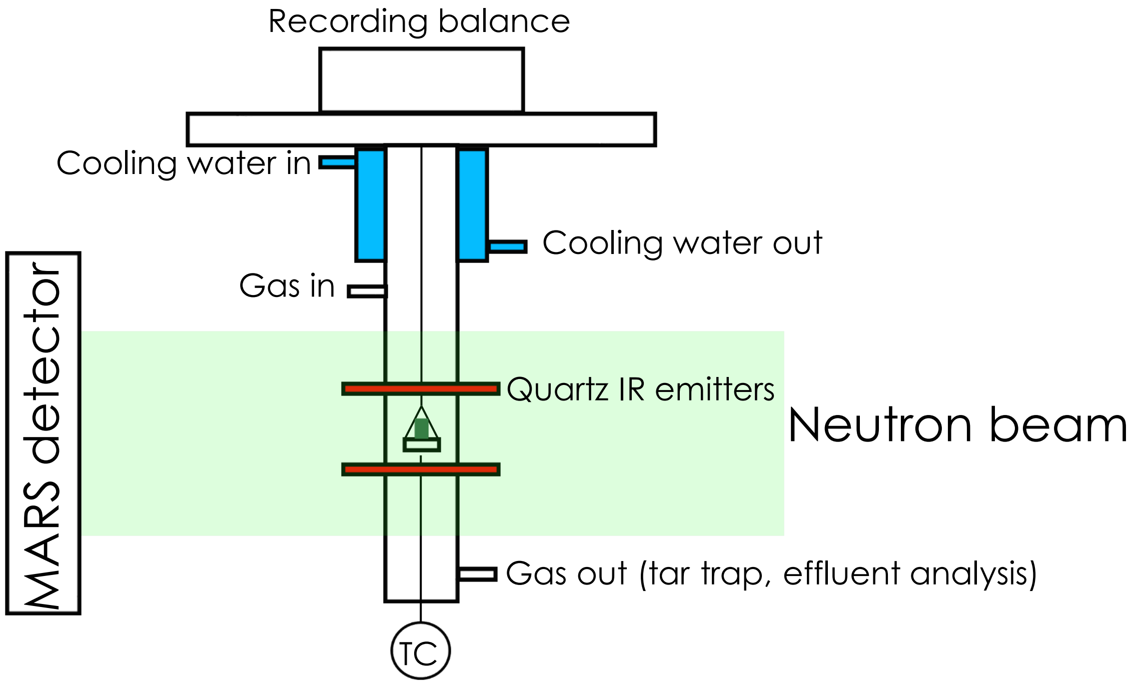




Darker images represent samples with higher Hydrogen content

Design & Construction of in-situ Reactor for Neutron Imaging R&D

- Construction of a dedicated in-situ reactor with thermogravimetric analyzer (TGA) functionality in progress
- Design specialized to enable neutron imaging R&D of pyrolysis and gasification reactions



Heraeus-NobleLight IR Heater

Schematic inset shows gold reflector to direct infrared (IR) radiation at a 45 degree angle to the emitter

Special thanks to Reinhard Seiser of NREL for helpful discussions in the design phase based on his experience building a custom TGA for biomass pyrolysis R&D

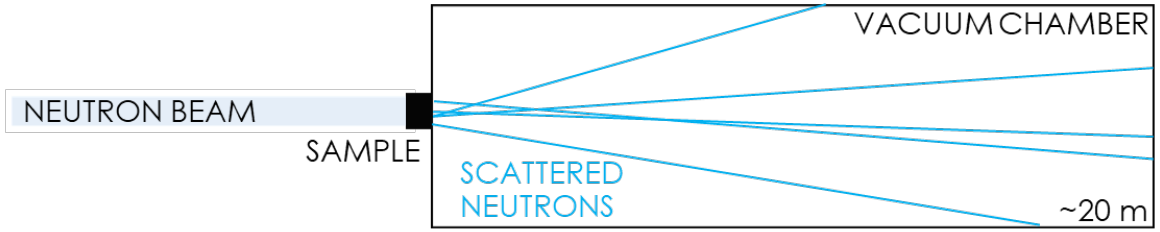
OAK RIDGE National Laboratory

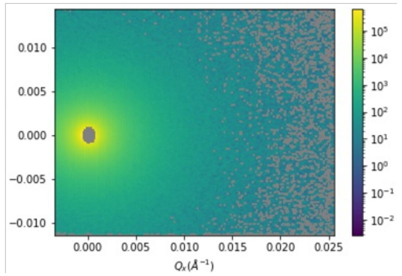
Analysis of Porosity and Permeability during Gasification of Low C Feedstocks

- Small Angle Neutron Scattering (SANS)
- Bench-Scale Permeability Measurement with Pressurized Gas Instrument

Small Angle Neutron Scattering (SANS) of MSW Components as a Function of Pyrolysis Temperature

Small Angle Neutron Scattering (SANS)

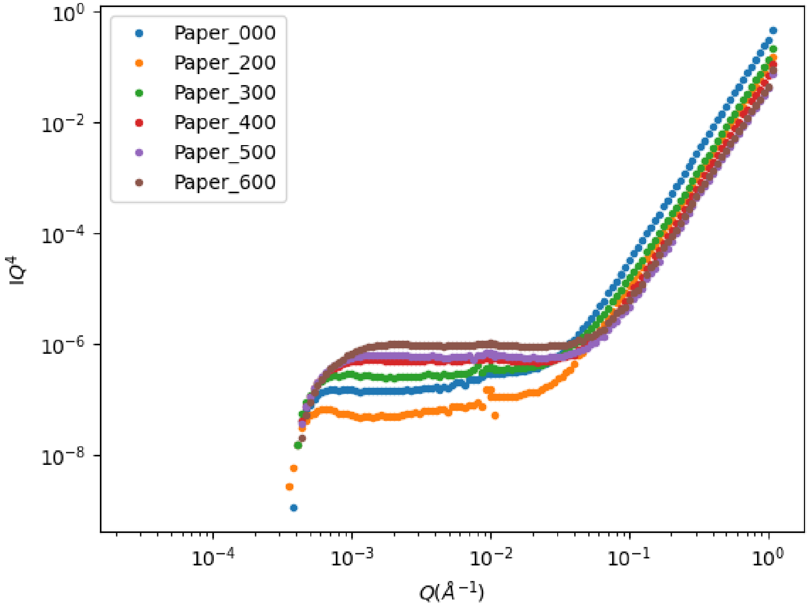




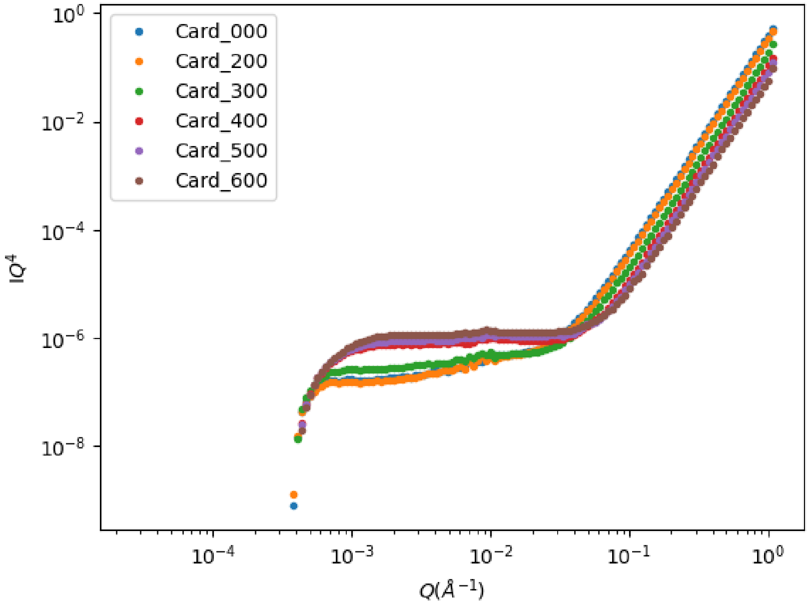
Momentum transfer (Q) is reciprocal of pore size

Q is derived from Bragg's law:
$|Q| = 4\pi \sin\theta/\lambda = 2\pi/d$

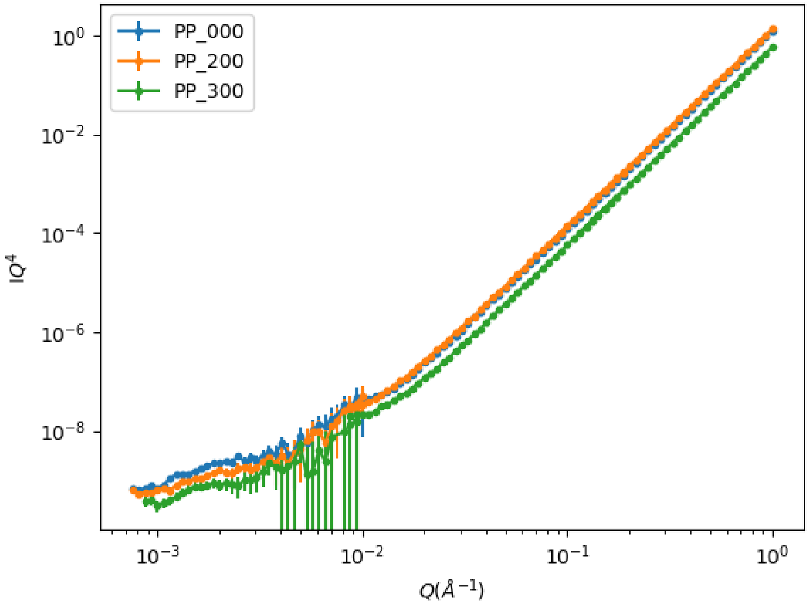
Paper Towel



Cardboard



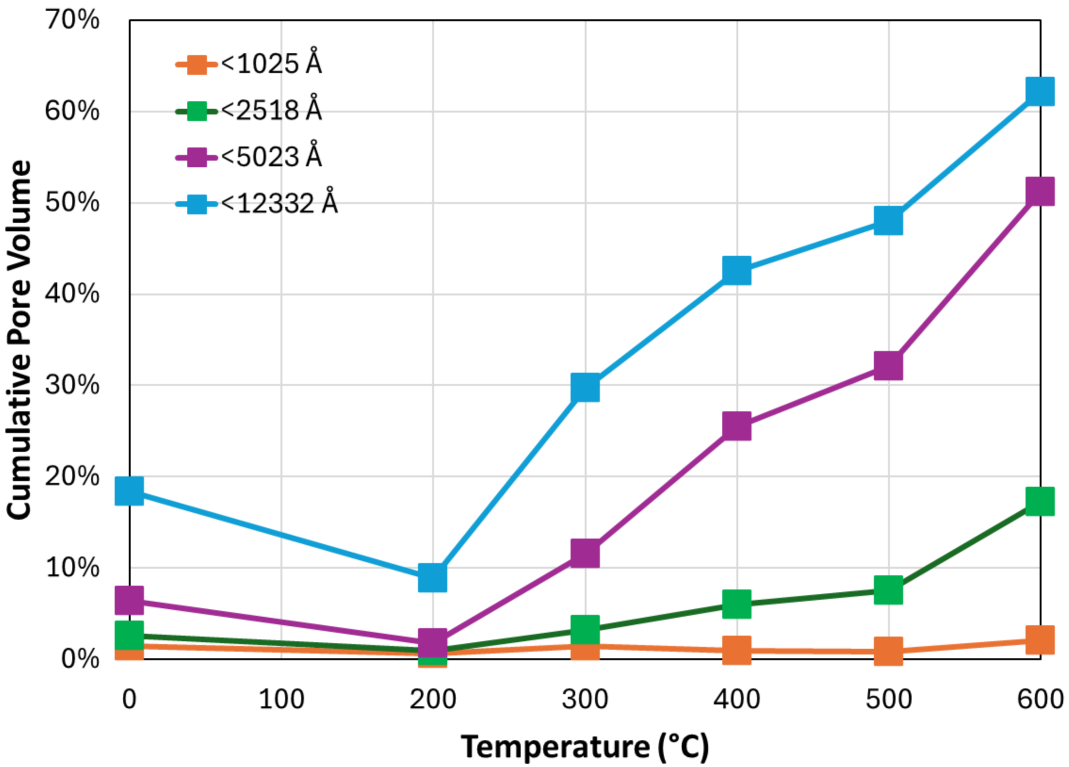
Plastic

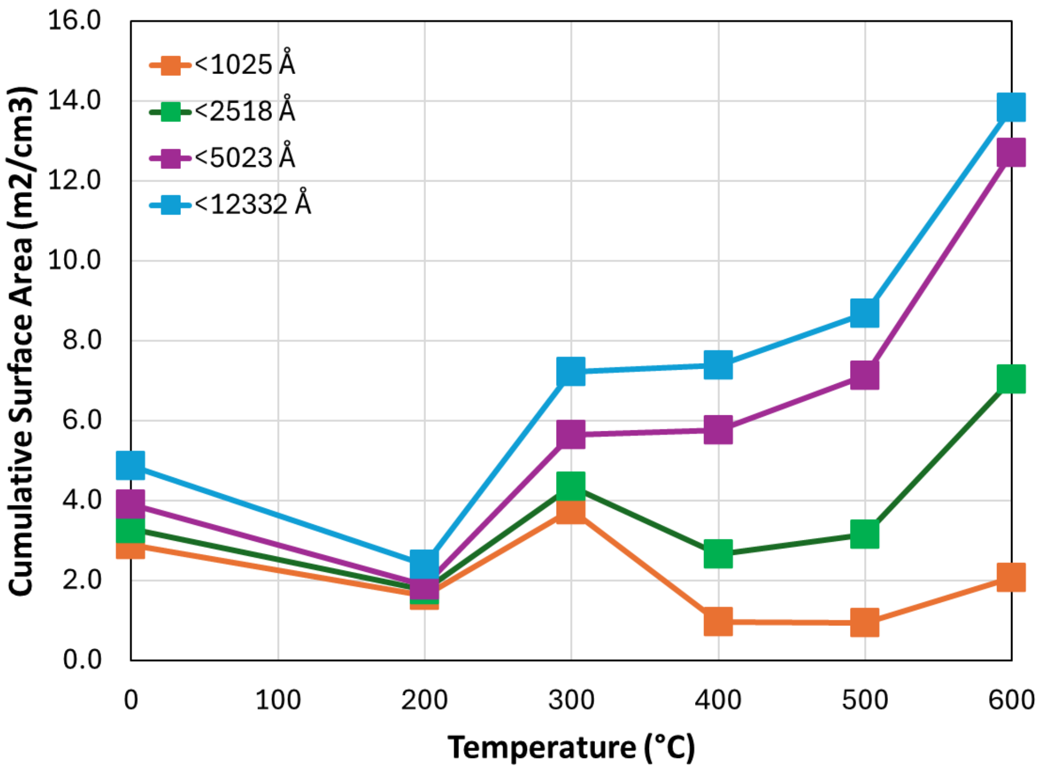


Analysis of these results give measurement of extremely small pores in feedstocks

Porosity and Surface Area Changes during Pyrolysis

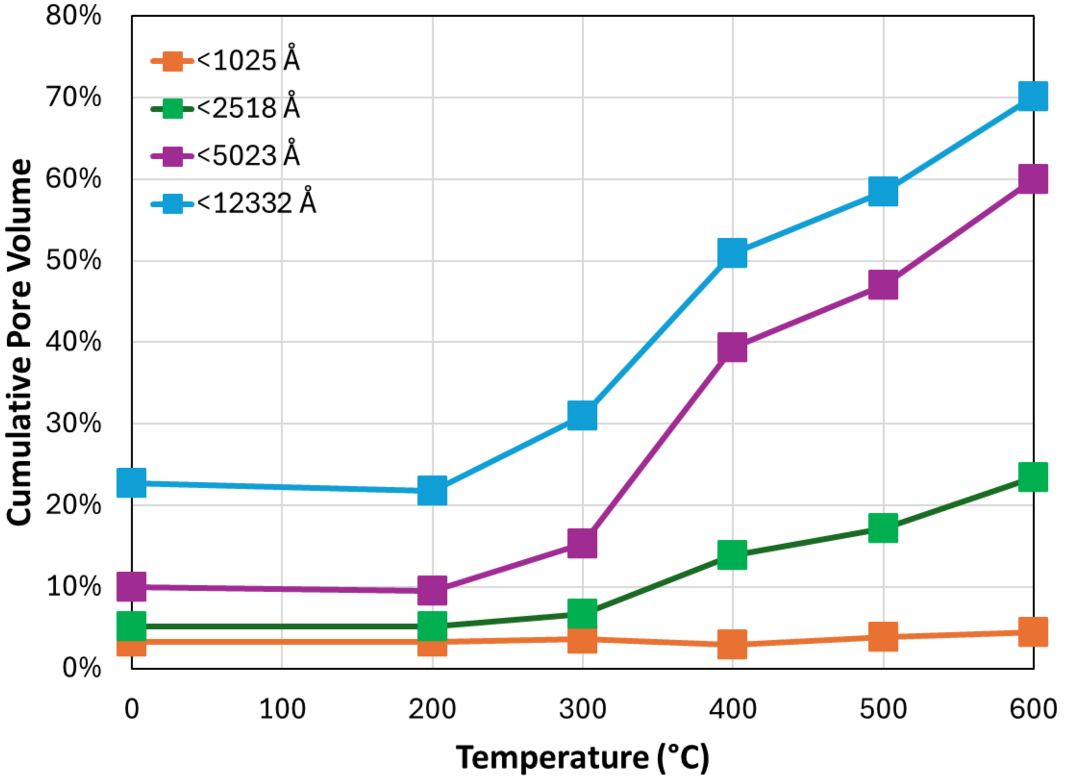
- Data for **paper towel** sample shown
- Overall, porosity and surface area increase with temperature
- For smaller (<250 nm) pores, there is constriction at intermediate temperatures (400-500°C)

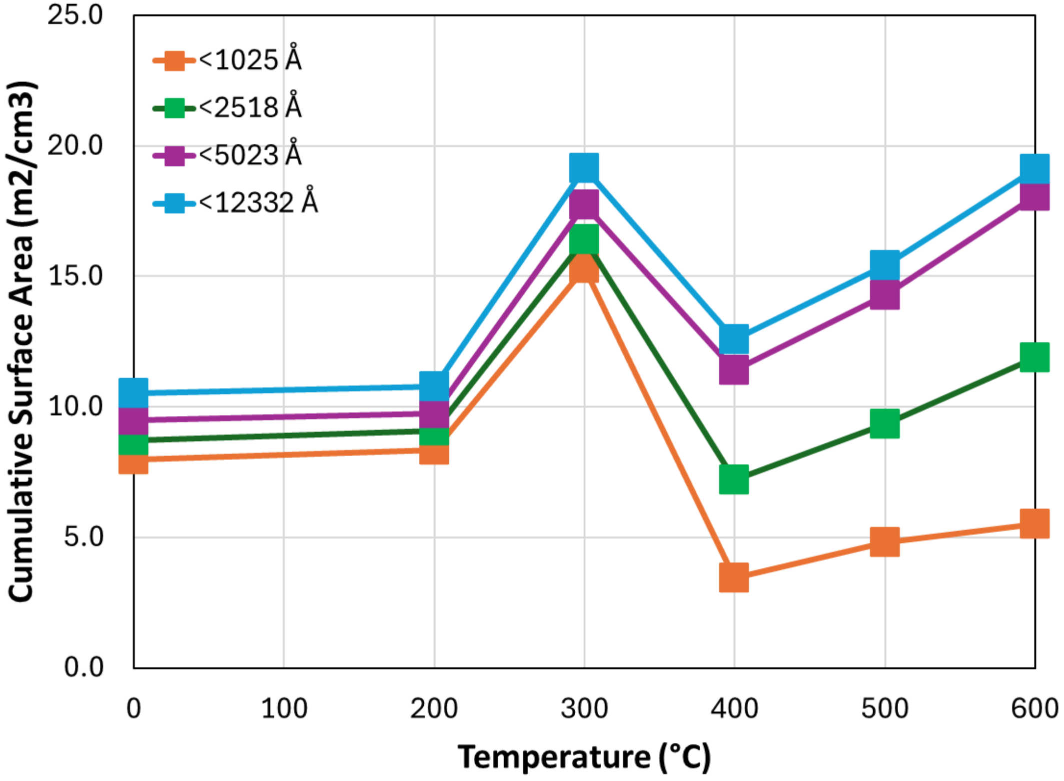




Porosity and Surface Area Changes during Pyrolysis

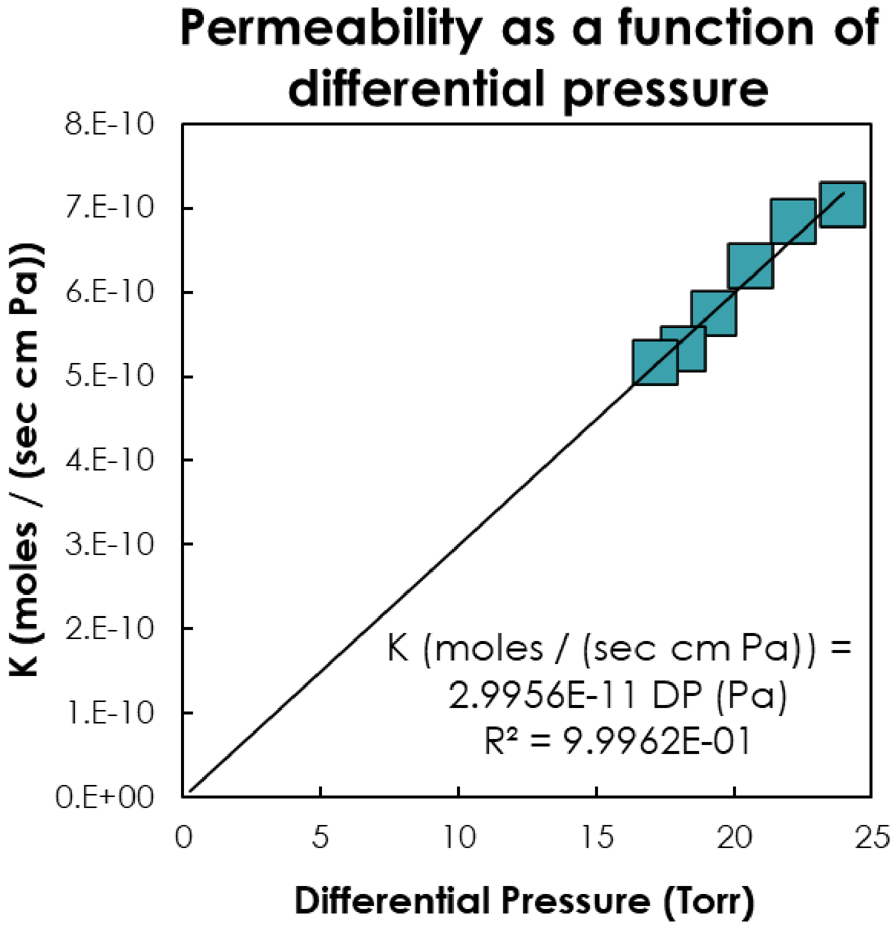
- Data for **cardboard** (corrugated) shown
- Overall, porosity increases with temperature
- Surface area changes are more prominent in 300 to 400°C transition



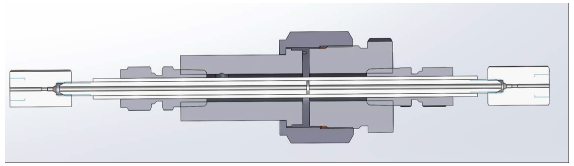


Customized Permeability Analyzer Enables Direct Measurement of Permeability Over Range of Pressures and Gases

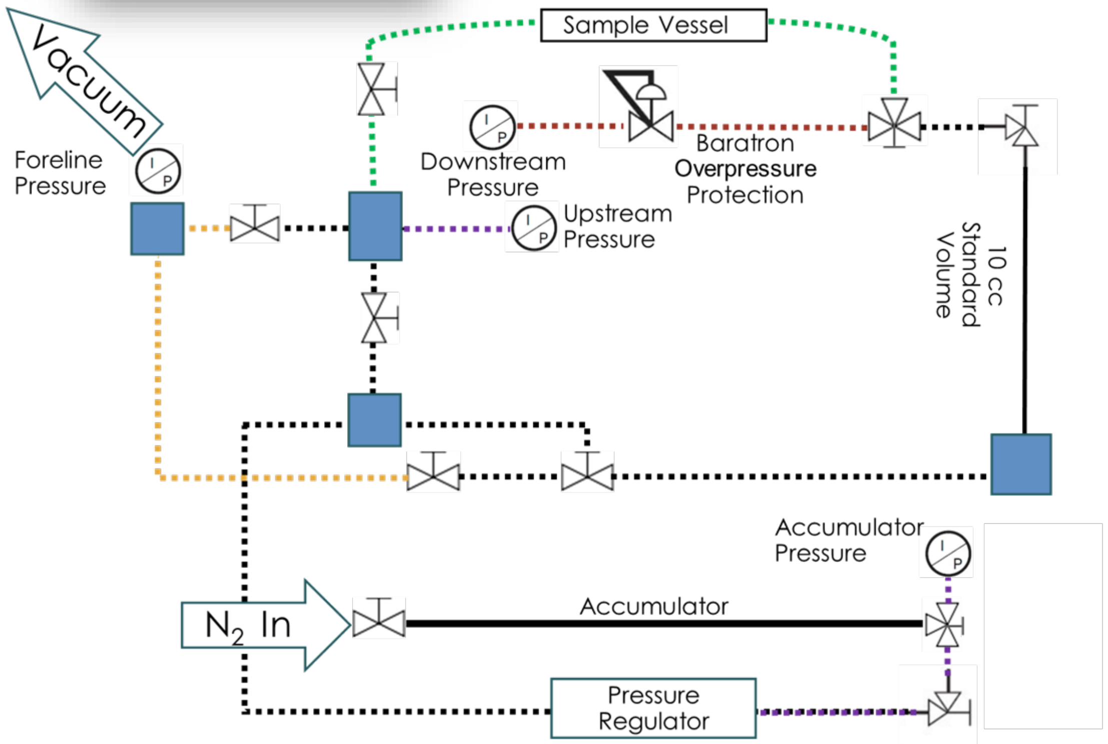
N_2 permeability through 0.32mm card stock



Custom Sample Holder Under Construction



Picture (left) and schematic (below) of Permeability Analyzer

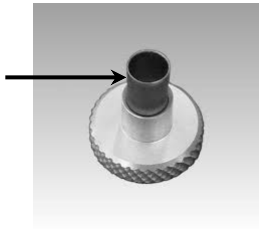


Investigation of Catalytic Effects on Gasification

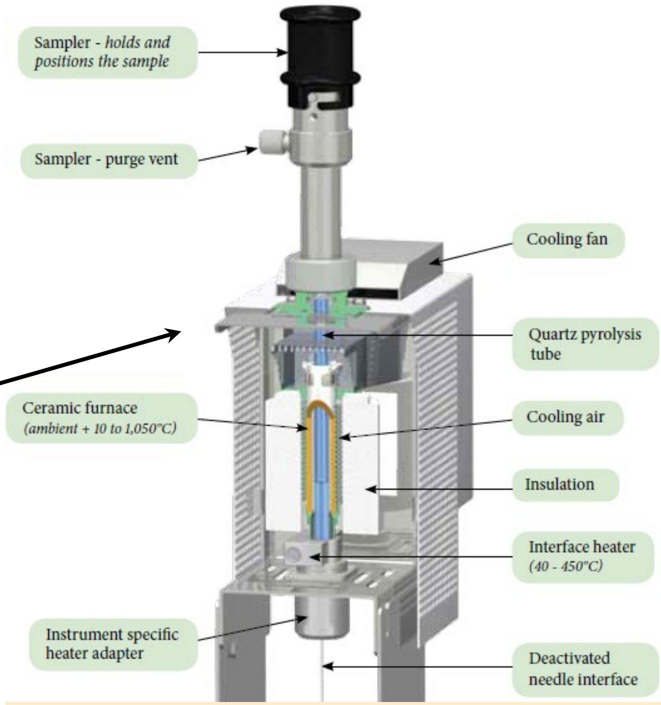
- Micro-Pyrolysis GC/MS
- Thermo-Gravimetric Analyzer (TGA)

Micro-Pyrolysis Gas Chromatography/Mass Spectrometry (GC/MS) Being Utilized to Study Catalytic Effects on Gasification

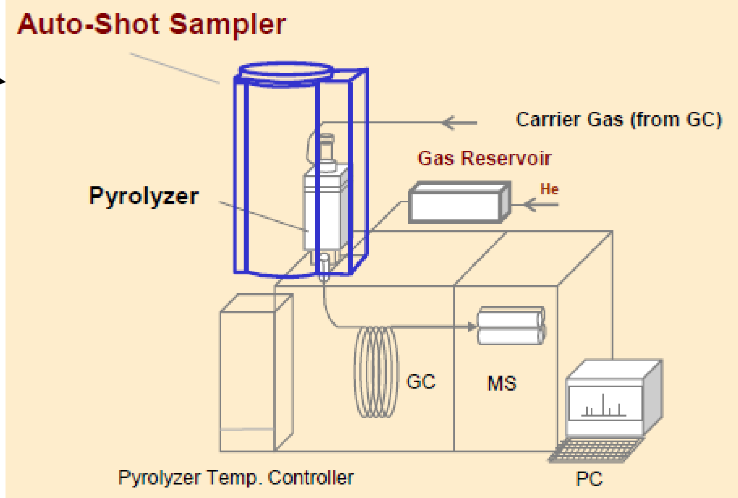
Sample cup



Micro-Pyrolyzer



Micro-Pyrolyzer Gas Products Feed Directly to GC/MS

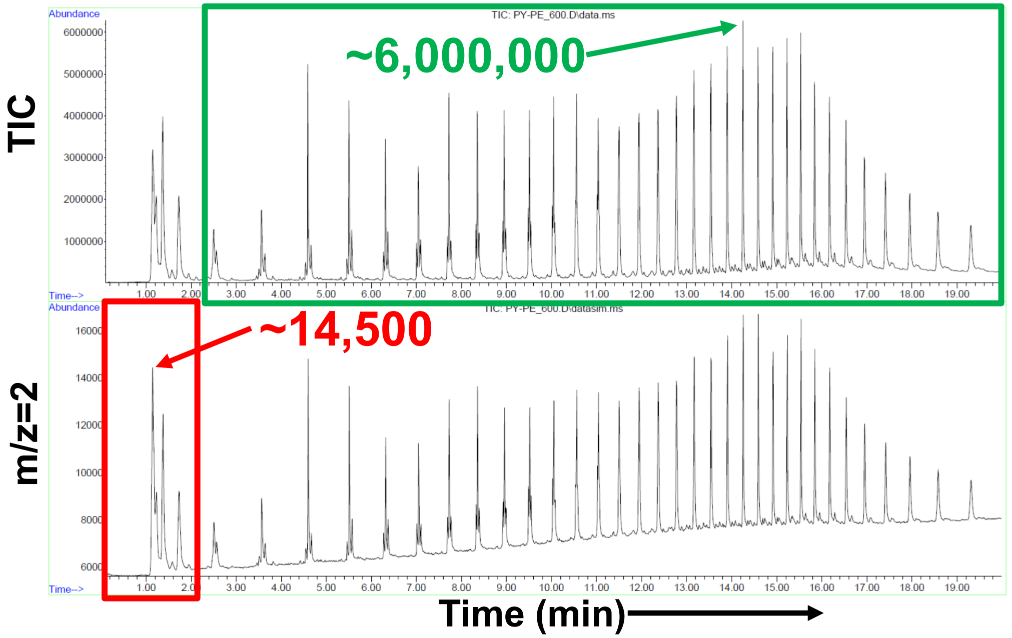


- Bench-scale studies with Micro-Pyrolyzer not directed at specific gasifier design
- Concept of staged pyrolysis and/or gasification may be optimal approach for catalytic strategy and is of particular interest for sustainable feedstocks:
  - S. Nilsson, A. Gomez-Barea, D. Fuentes-Cano, P. Ollero, *Fuel* 2012, **97**, 730-740
  - U. Henriksen, J. Ahrenfeldt, T. K. Jensen, B. Gobel, J. D. Bentzen, C. Hindsgaul, L. H. Sorensen, *Energy* 2006, **31**, 1542-1553
  - S. Heidenreich, P. U. Foscolo, *Progress in Energy and Combustion Science* 2015, **46**, 72-95
- Literature indicates significant interest in catalytic effects:
  - R. A. Arnold and J. M. Hill, *Sustainable Energy & Fuels* 2019, **3**, 656-672
  - Mandal et al., *Energy Fuels* 2019, **33**, 2453-2466
  - K. Tewari, S. Balyan, C. Jiang, B. Robinson, D. Bhattacharyya, J. Hu, *ACS Sustainable Chem. Eng.* 2024, **12**, 4718-4730.

Catalytic Effects on Pyrolysis (no O_2) of Polyethylene

- MicroPy-GC/MS preliminary data shows intended effects of catalyst:
  - HCs (tar) greatly reduced
  - H_2 increases (but difficult to quantify with column used)

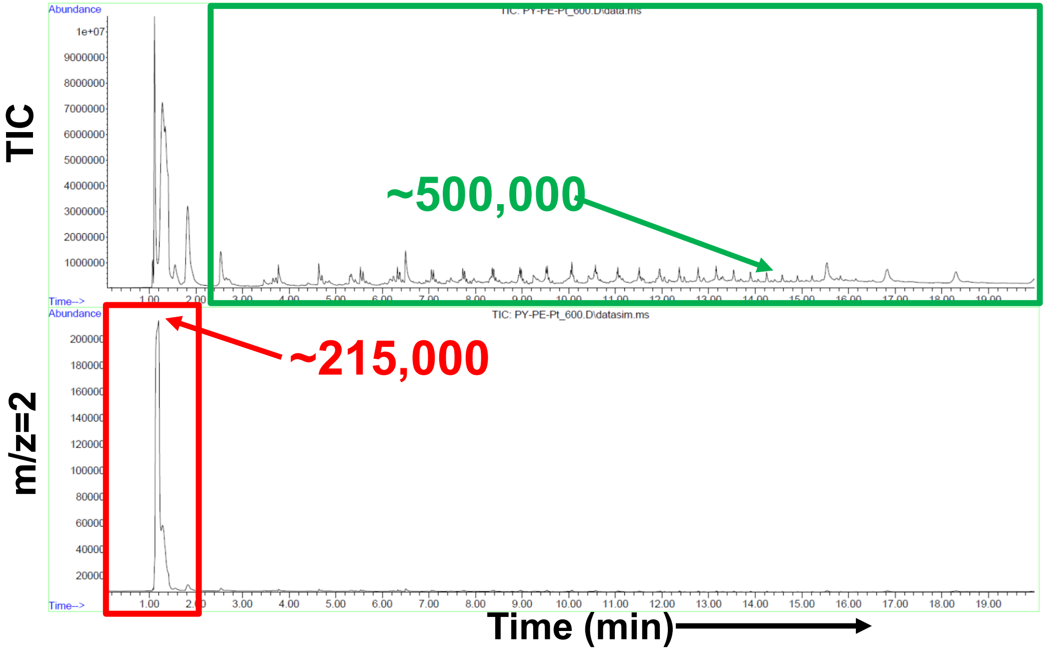
Pyrolysis@600ºC, 0% O_2 in He
No Catalyst



~6,000,000

~14,500

Pyrolysis@600ºC, 0% O_2 in He
1% Pt/Al_2O_3 Catalyst



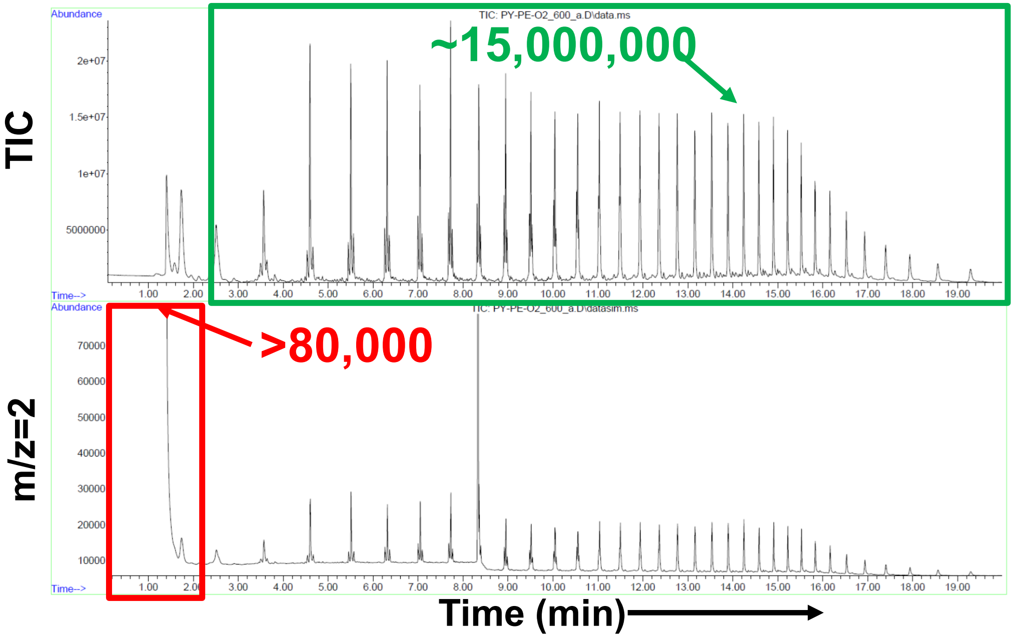
~500,000

~215,000

Catalytic Effects on Gasification (2% O_2) of Polyethylene

- MicroPy-GC/MS preliminary data shows intended effects of catalyst remains for gasification but with some open questions:
  - **HCs (tar) greatly reduced**
  - **H_2 difficult to quantify (and oxidation from 2% O_2 level may affect level)**

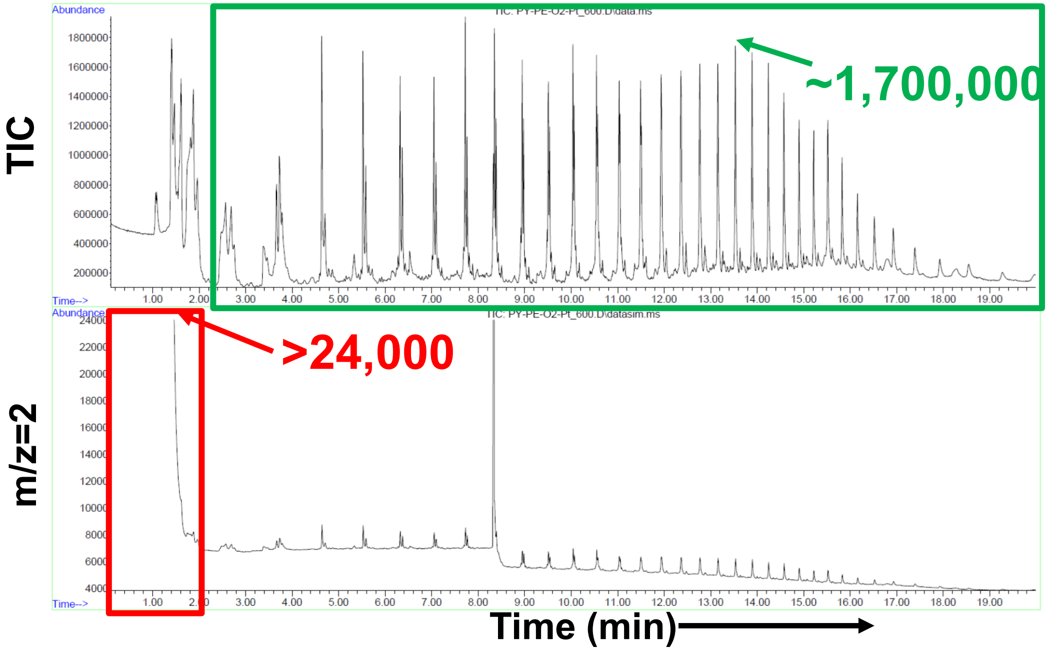
Gasification@600ºC, 2% O_2 in N_2
No Catalyst



~15,000,000

>80,000

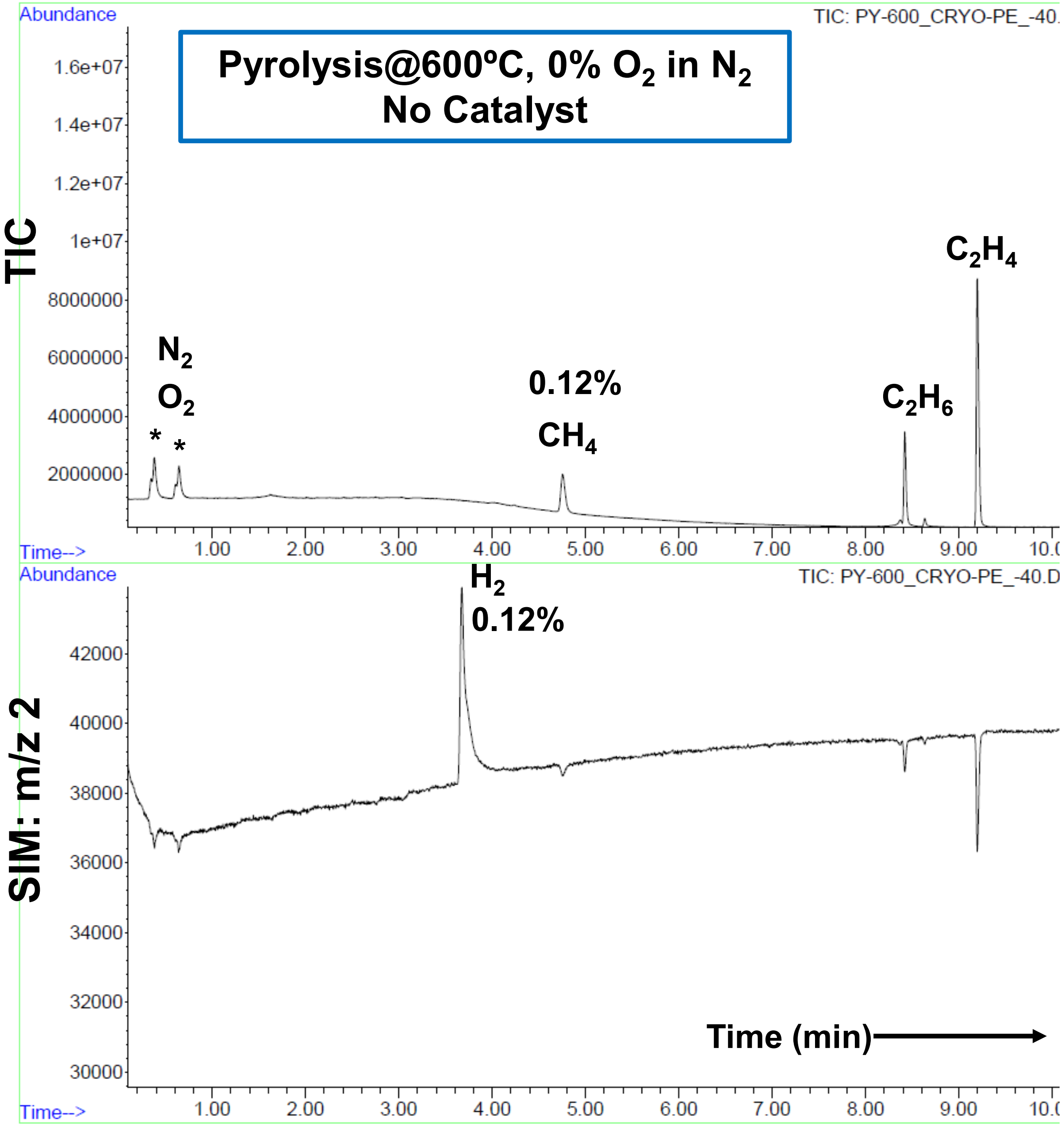
Gasification@600ºC, 2% O_2 in N_2
1% Pt/Al_2O_3 Catalyst



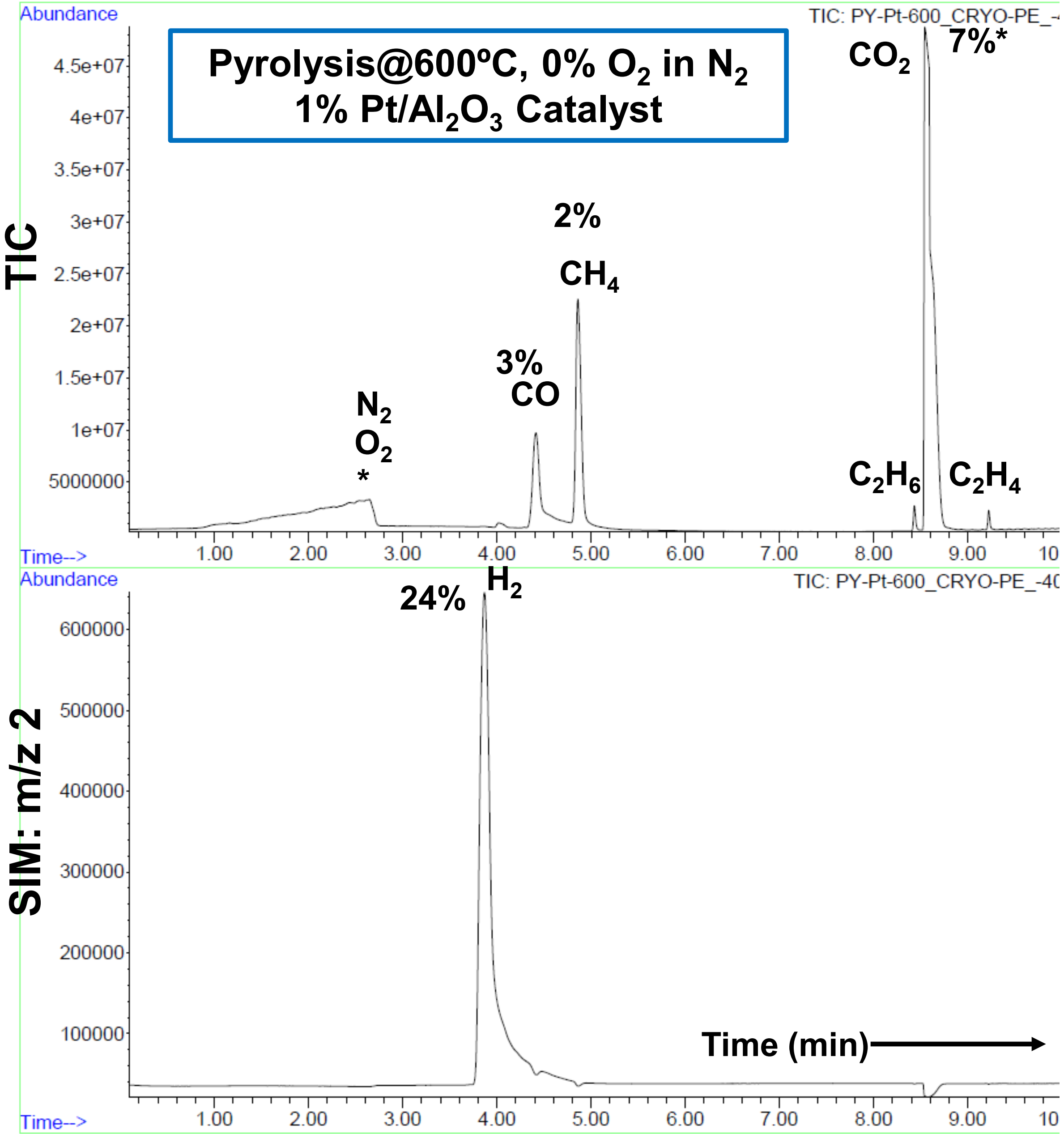
~1,700,000

>24,000

Optimized Analytical Method for Light Gases (Cyrogenic-GC/MS with H_2 Sensitive MS) Shows Catalyst Increases H_2 Substantially



Pyrolysis@600ºC, 0% O_2 in N_2
No Catalyst



Pyrolysis@600ºC, 0% O_2 in N_2
1% Pt/Al_2O_3 Catalyst

Catalyst Enables Tar Cracking and H_2 Production

- MicroPy-GC/MS preliminary data shows beneficial effects of catalyst for decreasing tar (hydrocarbons) and increasing H_2
  - Polyethylene feedstock and 1% Pt/Al_2O_3 catalyst
  - Benefits achieved at moderate temperatures (600°C) that have the potential to decrease cost for materials of construction of gasifier

Without Catalyst

Temperature	**H_2**	**CO**	**CH_4**	**CO_2**	**H_2:CO**
600°C	0.12%	0%	0.12%	0%	---
800°C	0.5%	1%	1%	0%	---
1000°C	2%	0%	2%	0%	---

With Catalyst (1% Pt/Al_2O_3)

Temperature	**H_2**	**CO**	**CH_4**	**CO_2**	**H_2:CO**
600°C	24%	3%	2%	7%	8
800°C	37%	9%	3%	12%	4.1
1000°C	36%	7%	3%	18%	5.1

Note: presence of H_2O observed desorbing from catalyst which is likely oxygen source for CO and CO_2 (water-gas shift reaction likely occurring)

Thermogravimetric Analysis (TGA) R&D of Catalytic Effects

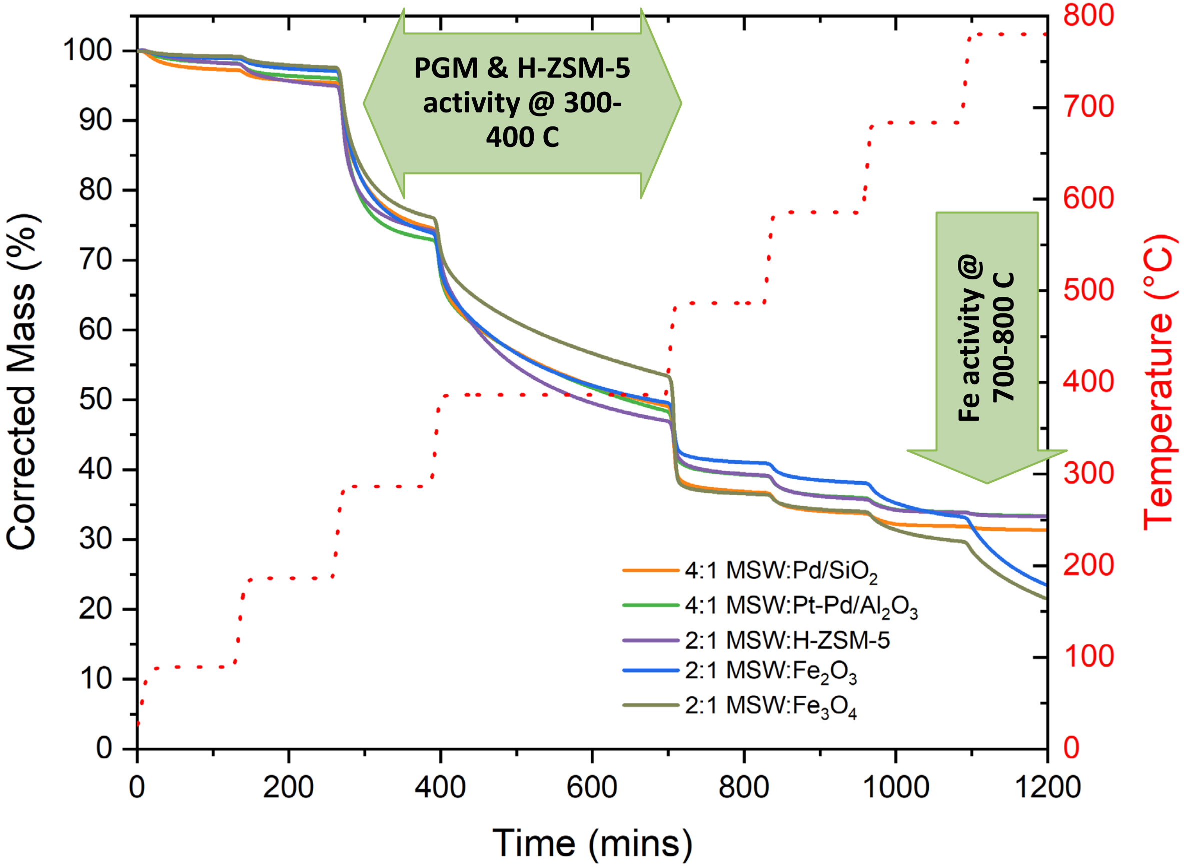
- TGA studies were conducted to investigate a variety of catalyst materials under pyrolysis (no O_2) and gasification (O_2 present) conditions
- The R&D is exploratory with intent to identify thermal regions of interest for accelerating pyrolysis or gasification processes
- Ultimately, there are many durability and coking issues that may occur with the catalysts
  - At this stage, the focus is on activity for different process conditions
- Relevant TGA study of pyrolysis or gasification of MSW/RDF feedstocks:
  - S. Aluri, A. Syed, D. W. Flick, J. D. Muzzy, C. Sievers, P. K. Agrawal, *Fuel Processing Technology* 2018, **179**, 154-166

Catalyst	Beneficial Properties	Limitations
H-ZSM-5	Strong acid sites, shape-selective	Susceptible to coking, requires regeneration
Fe_2O_3	Cost-effective, abundant	Less active than precious metals
Fe_3O_4	acid-base properties, typically stable under reducing conditions	Prone to reduction and structural changes
1.8% Pd/SiO_2	High selectivity, good hydrogenation activity	Expensive, sensitive to poisoning
2%Pt-1%Pd/Al_2O_3	Bimetallic synergy, high activity	Expensive, sensitive to poisoning

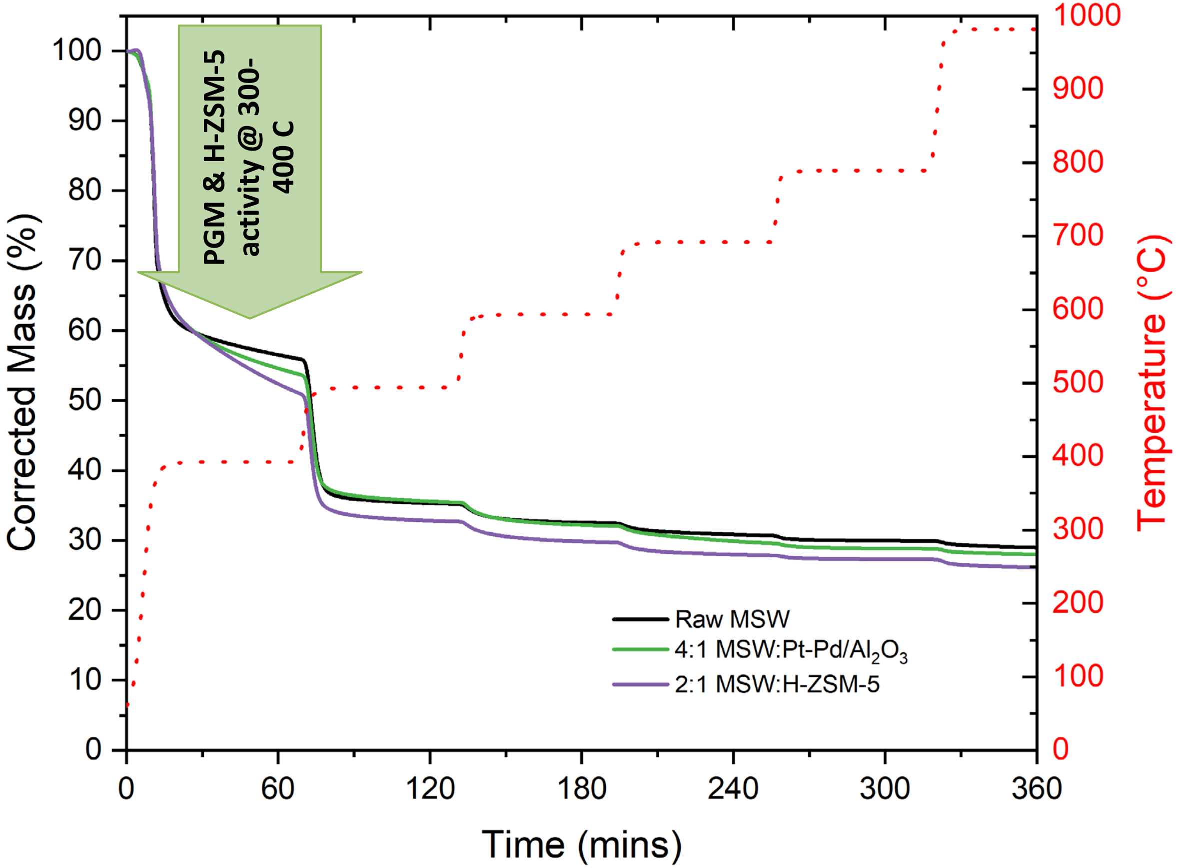
Stepwise Isothermal TGA with and without O_2

- Regions of activity observed by catalyst
- Overall, less effect on mass loss as compared with gas product changes in Py-GC/MS studies

Catalytic Pyrolysis under N_2



Catalytic Gasification under 4% O_2



Note: the masses have been corrected based on catalyst mass added and assuming the catalysts do not lose mass during the reactions.

Conclusions

- Sustainable feedstocks with low life-cycle GreenHouse Gas emissions offer economically viable fuels for gasification, but physical and chemical properties vary greatly.
  - Pelletized Refuse Derived Fuel from processing of Municipal Solid Waste offers a relatively more homogenous and transportable fuel option

- Findings to-date from feedstock characterization studies include:
  - H_2 evolution out of feedstock tracks well with mass loss measurements
  - Porosity and surface area vary greatly over the course of pyrolysis & gasification with small pores (observed via SANS technique) showing constriction at moderate (400-500°C) temperatures
  - Plastic and cellulosic (paper, cardboard) have dramatically different porosities resulting in large mass transfer differences during pyrolysis & gasification

- Preliminary catalytic effect studies show:
  - Gas product chemistry can be altered dramatically even at relatively low (e.g. 600°C) temperatures with much lower tar/HC gas products and high H_2 selectivity
  - The catalytic effects appear most dominant for gas chemistry, but some acceleration of solid mass loss was detected at different temperatures depending on catalyst material

Team Members

Jim Parks

Manufacturing Science Division

Spectroscopy;

Principal investigator

Larry Anovitz

Chemical Science Division

Geochemist, X-ray and neutron; Small angle neutron & X-ray scattering for porosity modeling

Dipti Kamath

Manufacturing Science Division

Techno-Economic Analysis;

Life-Cycle Analysis

Charles Finney

Buildings & Transportation Science Division

Combustion & fluidization diagnostics;

Pyrolysis; neutron imaging

Matthew Ryder

Materials Science & Technology Division

Neutron scattering & spectroscopy; Vibrational spectroscopy, neutron diffraction, and physical characterization

Ikenna Okeke

Manufacturing Science Division

Techno-Economic Analysis;

Life-Cycle Analysis

Costas Tsouris

Manufacturing Science Division

Chem. Eng.; Transport phenomena; Pyrolysis; sample preparation; neutron characterization

Vlad Lobodin

Buildings & Transportation Science Division

Analytical chemistry; Gas-phase analysis

Stephen Purdy

Manufacturing Science Division

Neutron scattering & spectroscopy; Vibrational spectroscopy, Catalysis

Novastus
WASTE REDEFINED

Capt. Samuel Sasser

Manufacturing Science Division

ORAU Intern transitioning from U.S. Marine Corp to Clean Energy career

NATIONAL ENERGY TECHNOLOGY LABORATORY