Neutron imaging of heterogeneous solid fuels under heating †

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Solid-fuel pyrolysis, gasification, and combustion continue to play an important role in the industrial and utility sectors. Behavior of heterogeneous fuels such as biomass (e.g., wood and grasses), municipal solid waste (MSW), and coal is less understood on the micro than the macro scales, particularly in relation to computational models which can assist reactor scale-up design and optimization. One limitation is understanding the complex processes of fuels as they degrade under heating, with counterflowing heat and mass fluxes.

Neutron imaging provides a unique means of peering into solid fuels during thermal degradation such as with pyrolysis and gasification/combustion. Neutrons interact strongly with hydrogen and weakly with most metals, meaning they can penetrate reactor walls and map the egress of hydrogenous compounds from fuels during heating. A better view inside of operating reactors is a major step in validating computational models.

We provide an overview of our neutron-imaging experiments of biomass and coals under various stages of thermal degradation. Experiments were conducted at the user facilities at the High Flux Isotope Reactor at Oak Ridge National Laboratory and at the Center for Neutron Research at the National Institute of Standards and Technology. We discuss the utility of such experiments in improving computational models of pyrolysis, gasification, and combustion and outline opportunities for the combustion industry using neutron sciences.

Overall objective‡

Our primary objective is to develop a technique to map the extent of solid-fuel pyrolysis, gasification, or combustion inside of an operating, laboratory-scale reactor to obtain better validation data for computational models. Because of the exposure times needed for neutron imaging (15–30 sec per frame), our first attempt will focus on moving-bed reactors with large particles because of their very low velocities and slow pyrolysis rates. If the methodology can be developed, then a next step is to focus on other types of reactors.

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Experimental apparatus

The experimental apparatus includes laboratory-scale pyrolyzers located at Oak Ridge National Laboratory (ORNL) and neutron and X-ray imaging facilities located at the High Flux Isotope Reactor (HFIR) at ORNL and the Center for Neutron Research at the National Institute of Standards and Technology (NCNR) in Gaithersburg, Maryland. Both of the neutron facilities maintain user programs where industry users are encouraged to apply for beam time and can be assisted by facility staff to conduct their experiments.

Pyrolyzers

ILL furnace: The first pyrolyzer is the ILL furnace maintained by the Spallation Neutron Source staff at ORNL. The ILL furnace pyrolyzes in vacuum and can control to 1100 °C (1373 K or 2012 °F) using a thermocouple placed near the samples. Samples are placed into a sample stick, which for high-temperature operation is an alumina tube of 2.54 cm (1 in) OD, 1.9 cm (0.75 in) ID, and 45 cm (18 in) long. The stick is inserted vertically into the furnace and evacuated, and 2–4 samples typically are stacked atop of each other to fit within the neutron field of view. Samples are typically individual wrapped in Al foil for pyrolysis up to 400 °C (673 K or 752 °F) or Nb foil for higher temperatures; both Al and Nb are relatively transparent to neutrons. Most of the ILL furnace is constructed of Al or Nb for that neutron transparency. The ILL furnace is used for real-time neutron imaging of pyrolysis. Off gases are collected in a vacuum collection chamber and allowed to deactivate (radiologically cool down) before later being released to the environment.

Tube furnace: The second pyrolyzer is a standard single-zone tube furnace within a 3.8 cm (1.5 in) ID horizontal quartz tube. A sweep gas of N_2 or Ar is typically used to remove pyrolysis gases from the vicinity of the samples. This furnace is intended for laboratory use only for off-line pyrolysis of samples to be analyzed later or imaged at a neutron beam.

In both furnaces, samples typically were heated from room temperature to the pyrolysis temperature at a specified rate and then held at the target temperature for a specified time period before being cooled at a slow rate by natural heat-transfer mechanisms; there was no ability to quench the reactions by rapid cooling. For the ILL furnace, the ramp rate was usually 1.5 or 5.0 K/min (2.7 or 9 °F/min), with a 5–15 min hold time, and for the tube furnace, 10.0 K/min (18 °F/min), with a 15-min hold time.

Neutron sources and imaging facilities

HFIR: The first neutron source used was the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory. HFIR is one of the highest-flux neutron sources for scientific use in the world; the reactor produces 85 MW_{th}. Some of the neutrons from nuclear fission are allowed to pass out of the reactor pool into a series of guides which direct neutrons to about two dozen scientific beamlines. The CG-1D Imaging beamline was used in this work, and Figure 1 shows a schematic of the setup.

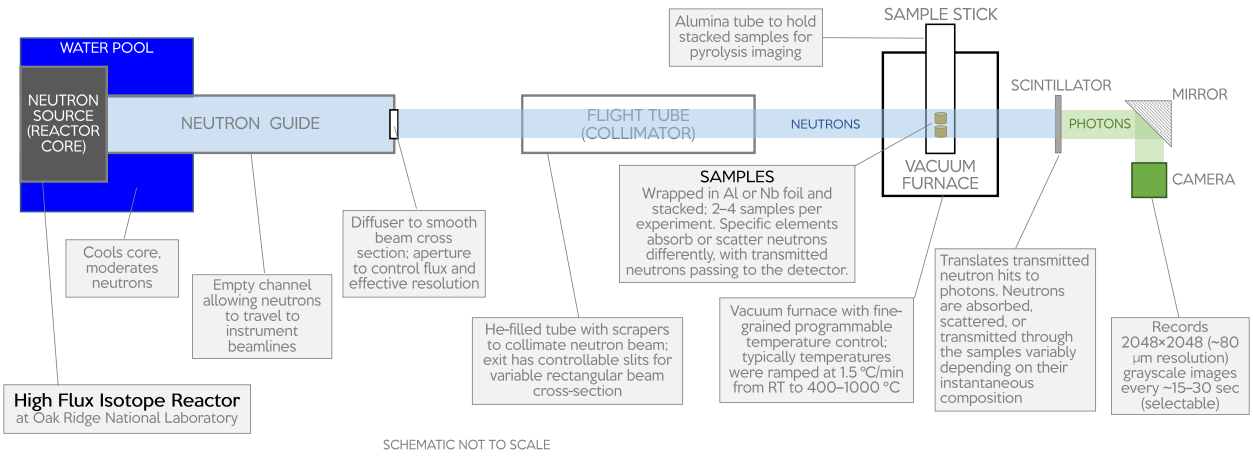

Figure 1. Schematic of the CG-1D Imaging beamline at HFIR.

NCNR: The second neutron source was the nuclear reactor located at the Center for Neutron Research at NIST in Gaithersburg, Maryland (NCNR). Like HFIR, NCNR supports dozens of instrument beamlines, and we used the BT-2 Neutron Imaging Facility. Although specific details differ, the general principle and setup for neutron imaging is similar to HFIR.

Samples

In this paper, we describe the pyrolysis of a variety of biomass, focusing on wood species of interest to the bioenergy sector, and different grades of coal.

Biomass

Our principal samples were the following:

- Beech – American Beech wood in dowel form, procured in Sweden at a retail shop
- Poplar – milled samples from two different trees from a reservation maintained by ORNL
- Cork – pelletized form from a Portuguese source
- Pine – pelletized form from a Portuguese source

In most cases, the samples were roughly cylinders of ~1cm (0.4 inch) diameter by ~1–1.5 cm high. Samples were weighed wet, then dried and weighed, and then pyrolyzed either to target temperatures (for NCNR imaging) or for continuous, *in situ* pyrolysis in the ILL furnace (for HFIR imaging).

Coal

Our samples were the following, with letter identifiers:

- A: Anthracite – consumer-grade coal of various sizes from Reading Coal Company in Pennsylvania.

- B: Bituminous – mine-provided samples of Blue Gem / Straight Creek coal from Pineville, Kentucky.
- C: Bituminous – Pittsburgh #8 provided by West Virginia University.
- D: Subbituminous – mine-provided Power River Basin, Monarch seam coal from Wyoming.
- E: Lignite – mine-provided samples from Center, North Dakota

Samples were prepared in similar dimensions and pyrolyzed as with the biomass. The biomass and coal studies were performed under different projects and times, so there were slight differences in the methodology, but not deemed to be significant.

Results

In this paper, we show the following:

- Neutron radiographs of samples at different pyrolysis temperatures.
- Neutron transmission relations in the samples as a function of pyrolysis temperature. Here it will be seen that the neutron transmission tracks with the mass loss during pyrolysis.
- Mass-loss relations in the samples as a function of pyrolysis temperature, weighed using a microbalance.
- Hydrogen-loss transmission relations in the samples as a function of pyrolysis temperature. Here it will be seen that "hydrogen gravimetry" based on neutron imaging tracks with the gross mass losses obtained using weighing with a microbalance.

This paper is meant to give a brief overview of the potential of neutron radiography, so comprehensive analysis is not included.

Neutron transmission

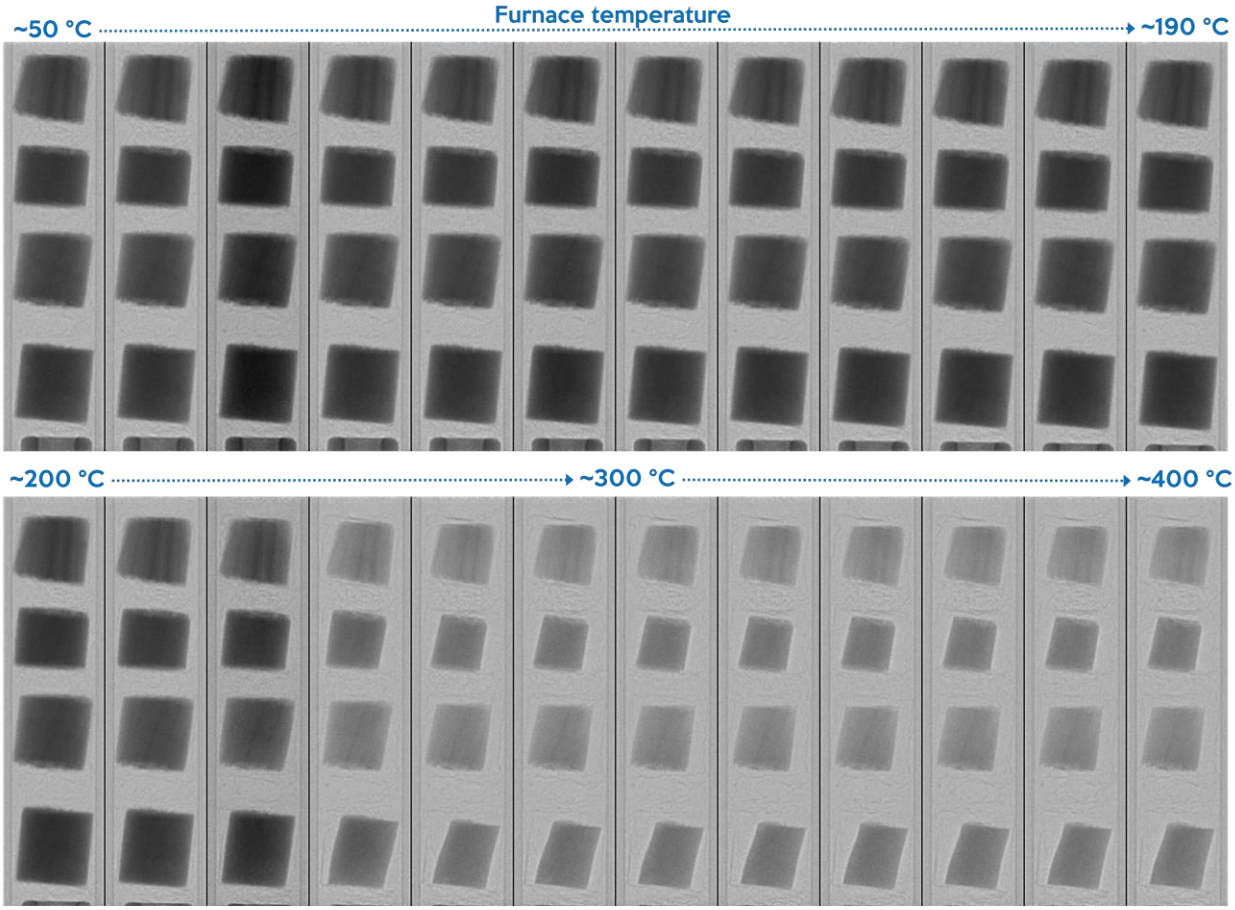

Figure 2. Sequence of neutron radiographs of poplar; each frame represents ~9-10 °C temperature increase.

In Figure 2, samples from two different trees of poplar, denoted A and B, are seen to shrink because of drying then pyrolysis as well as grow lighter as hydrogen if expelled from the wood. Figure 4 describes these samples and plots the neutron transmission through each sample as a function of temperature. These radiographs are analogous to X-rays, only that hydrogen scatters neutrons very effectively. In the radiographs, the more hydrogen in the sample, the darker the radiograph is. This sequence was recorded continuously, with 30-sec exposures and 6-sec latency between frames, at HFIR using the ILL furnace. The background is dark because the aluminum in the furnace attenuates neutrons.

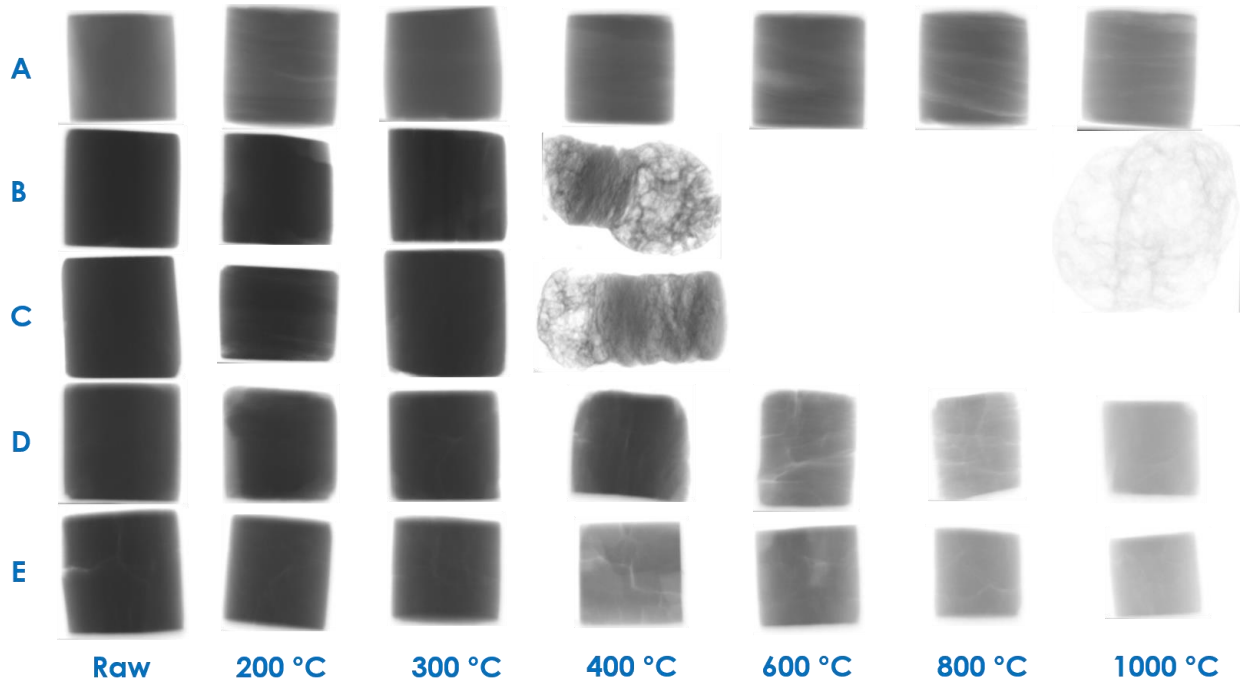

Figure 3. Radiographs of the five coal types as a function of pyrolysis temperature.

In Figure 3, samples from the five coal types are seen to shrink because of drying then pyrolysis as well as grow lighter as hydrogen if expelled from the coal. Figure 3 plots the neutron transmission through each sample as a function of temperature. This sequence was recorded in batches at NCNR using samples pyrolyzed earlier at ORNL. The background is white because the samples were in the open area, so almost all neutrons from the beam made it to the detector where there was not a sample of coal to interact with.

Above 400 °C, the bituminous samples expanded and bubbled, ending up like a very light foam. Because of the difficulties in handling samples B and C, they were omitted from the 600 and 800 °C. Despite these difficulties, bituminous coals are still of great interest for this research.

Neutron transmission

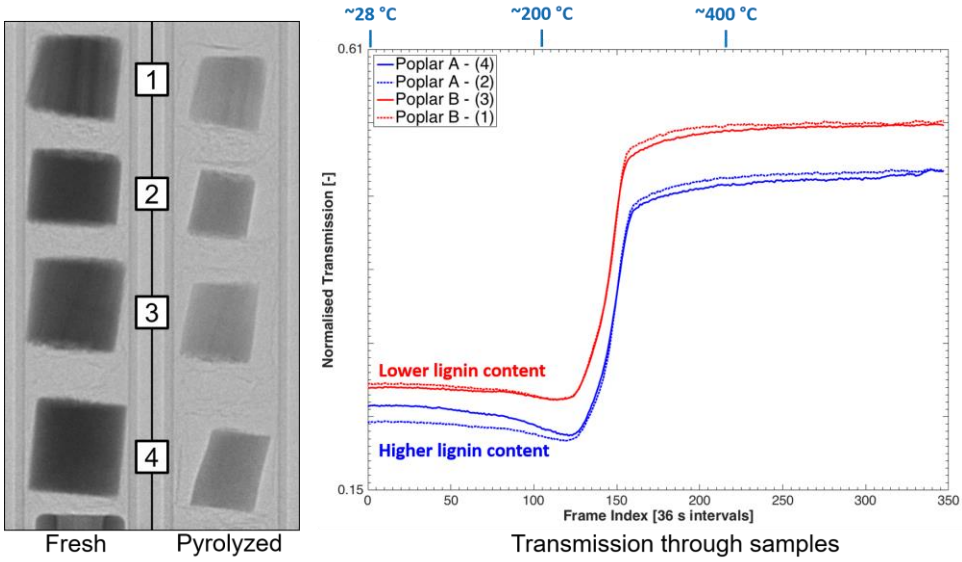

Figure 4. Identification of poplar samples in the radiographs as well as associated neutron transmission with furnace temperature.

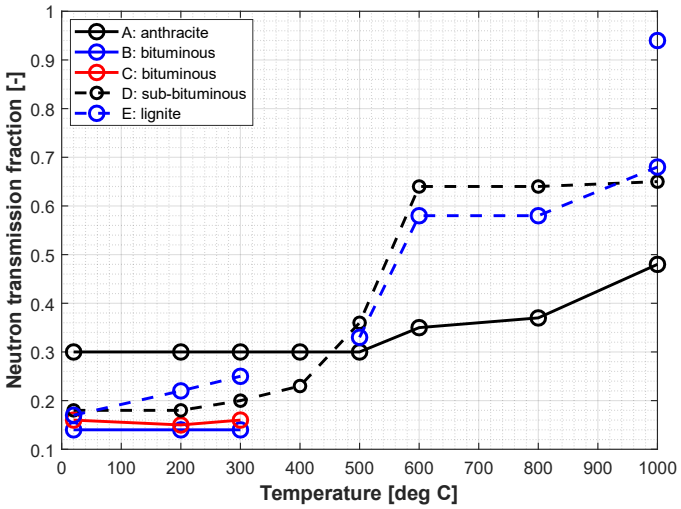

Figure 5. Neutron transmission through the coal samples per cm of material based on their pyrolysis temperatures.

As seen in Figure 4 and Figure 5, transmission of neutrons through the solid fuels increases as hydrogen leaves the samples during drying and pyrolysis. For unpyrolyzed wood, around 90% of the neutron interaction is due to hydrogen. Most woods that we have examined follow the rough relation as shown in Figure 4, as their composition is somewhat more homogenous compared with coal types. As seen in Figure 5, the sensitivity of neutron transmission to pyrolysis temperature varies by coal type, primarily because hydrogen content varies greatly between anthracite and lignite. For coal, the composition affects the ability to map pyrolysis based on neutron imaging, but this should be a tractable problem with other information.

Sample mass losses

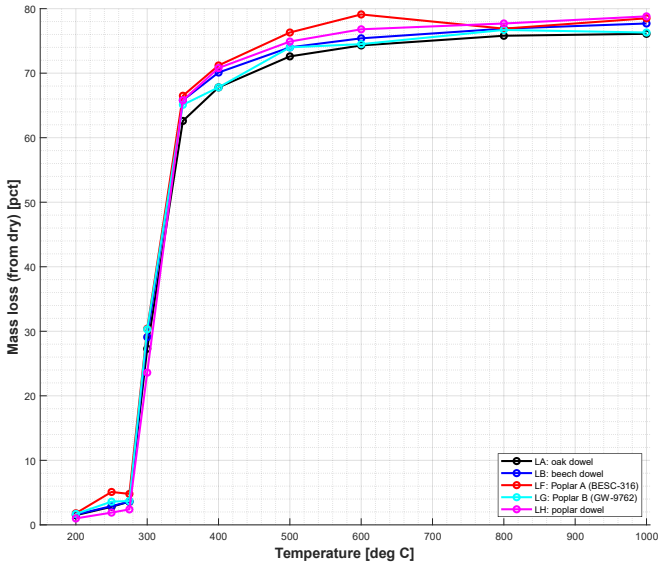

Figure 6. Mass losses of various wood samples as a function of pyrolysis temperature.

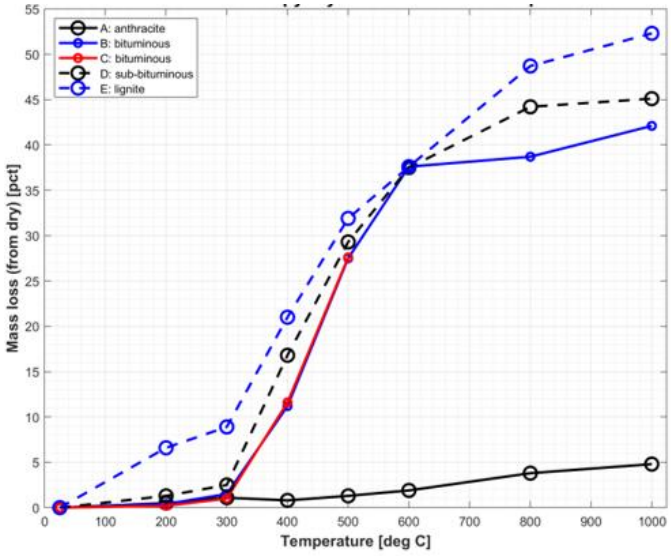

Figure 7. Mass losses of various coal samples as a function of pyrolysis temperature.

As seen in Figure 6 and Figure 7, mass loss tracks closely with neutron transmission, which verifies the expected behavior. As with the neutron transmission, biomass across various samples is more regular than coal with its wide range of hydrogen concentrations. However, with care, one can correlate the degree of pyrolysis with the transmission of neutrons through the samples.

Hydrogen gravimetry

Here, we reinforce the utility of neutron imaging to map hydrogen loss with pyrolysis. As seen in Figure 8, neutron radiography can map hydrogen loss in a fuel, guided by knowledge of the fuel's initial hydrogen concentration. This knowledge could be coupled with emissions measurements to map regions and extent of pyrolysis, gasification, and combustion in an operating, laboratory-scale reactor (laboratory scales are the limitation because of the limitation of neutrons to travel through large distances of hydrogenous materials – we anticipate using 2D reactors in future experiments).

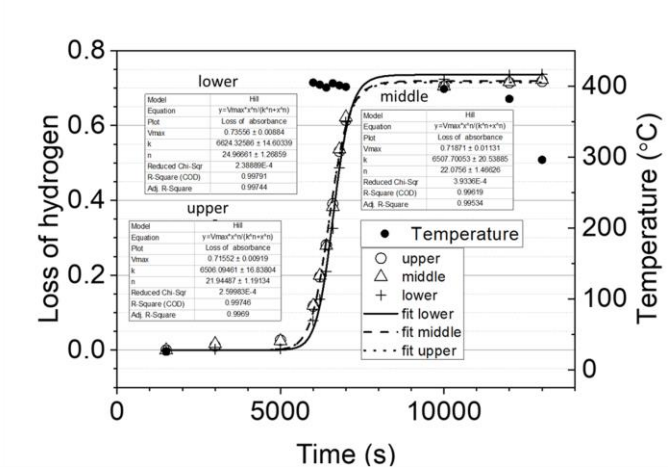

Figure 8. Loss of hydrogen in the beech sample with degree of pyrolysis.

Summary

Neutron imaging can track mass loss, primarily hydrogen, in solid fuels undergoing pyrolysis. The next stages of this work include real-time imaging of an operating pyrolyzer. This pyrolyzer will have a fixed fuel bed with a sweep gas percolating upwards through the bed, and as pyrolysis progresses, the neutron imaging will show the concentration gradients throughout the bed. Of critical importance will be temperature and gas-emissions measurements during pyrolysis. Observations will provide data to improve computational models of pyrolysis.

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