Neutron imaging-based investigations of carbon and hydrogenous gas-release dynamics and interactions during pyrolysis and combustion of woody biomass

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Hard X-rays and neutrons are able to resolve structural details across multiple scales down to the atomic level due to their short nm to sub-nm wavelengths. Neutrons in particular can penetrate through heterogeneous and dense materials (e.g., enclosed cells, reactors, and/or combustion devices) that are difficult to assess with the longer wavelength of lasers. This opens up new possibilities to study different complex nonlinear phenomena in connection to phase transitions, particle formation, as well as hydrogen dynamics in materials, where theoretical modeling is limited and needs input and verification from realistic-scale experiments.

In this presentation we summarize some of the results obtained from studies on the dynamics of elemental hydrogen in biomass pyrolysis and the hydrogenous gases methane and ethane in porous, soot-based carbon materials. This presentation includes work in progress of the investigations from collaborative work by the Swedish group from Combustion Physics, Lund University, Lund, Sweden, and research groups at the Oak Ridge National Laboratory (ORNL), Oak Ridge TN USA. The experimental neutron-based activities/measurements have been performed at ORNL, using the CG-1D imaging beamline at the High Flux Isotope Reactor (HFIR), and the VISION vibrational spectrometer beamline at the Spallation Neutron Source (SNS).

X-ray and neutrons for scattering and imaging

X-ray radiation with a wavelength on the order of interatomic distances (typically between 1 and 2 Å) is able to resolve structure and size of molecules, clusters, nanoparticles and materials. X-ray scattering analysis can describe and retrieve structural information based on the atomic spatial distribution, and the atomic scattering cross section of each atom [1,2], where the electrons are the basic scattering centers. Consequently, the higher the atomic number, the stronger is the scattering contribution from each atom. The size and structural information is then obtained from the angular scattering pattern as the intensity distribution of the superposition of wave amplitudes from the individual scattering centers, basically the electron cloud of each atom. The attenuation of the X-ray beam is determined by the scattering of photons from the beam and absorption, which usually is connected to photo-ionization.

Neutrons interact mainly with the nucleus of the atom dependent on the isotope number, i.e., combination of protons and neutrons in the nucleus, and therefore show a more irregular

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pattern with isotope number. Generally, for thermal [3] and cold neutrons interaction is particularly high for the proton or the hydrogen atom (compare attenuation cross sections of ≈82 b for H and 5.6 b for C) since the mass of the proton and neutron are similar and have a high efficiency of momentum transfer in classical thermal physics where the neutron and the atom are conceptualized as hard spheres. Light elements generally show high neutron-scattering cross sections. Metals show limited attenuation except for some particularly strong absorbers such as Cd and Gd.

The complementary sensitivities of hard X-rays and neutrons can be of great relevance for structural studies in biomass where the main elements are H, C, and O. For instance, the spatial composition of the H-to-C ratio (H/C) can be obtained from imaging experiments, which primarily include quantitative radiography (2D imaging) and computer aided tomography (3D imaging) for both neutron and X-ray irradiation (NCT and XCT, respectively).

Biomass pyrolysis studies

Biomass for cleaner and more efficient bioenergy production requires multi-disciplinary understanding and research collaborations among experts in different fields such as physics, chemistry, biology, mathematics, and computing. Important tasks are mapping what happens inside the biomass during the pyrolysis or burning process and then correlating it to events at the surface and the surrounding atmosphere.

In the last year, we have used a novel approach to determine hydrogen content in burning biomass using neutron imaging. A diagnostic method was developed to map hydrogen inside pyrolyzing biomass [4]. This method is foreseen to support one of the most difficult challenges in biofuels production: Understanding and control of thermochemical conversion of hydrogen from the biomass into bio-gas.

In the pyrolysis experiments it was possible to follow the changes of biomass structure and hydrogen content during pyrolysis that were monitored with considerably high precision and accuracy by neutron radiography. Methods of high-resolution XCT and NCT are being developed to determine carbon and hydrogen distributions or relative H/C throughout the entire framework structure of charred material of the pyrolyzed biomass.

These neutron experiments will be complemented with concurrent gas-phase analysis to monitor gas composition during the pyrolysis. Mass spectrometry and laser-spectral analysis are two primary methods of interest to develop a complete picture of the correlations between bulk, surface, and gas-phase dynamics of pyrolyzing/burning biomass.

Combustion generated carbon materials

Combustion is able to produce carbon structures of different kinds, for instance, graphene-like components [5]. These may be found as components in carbon soot, one of the most common and unwanted by-products from incomplete combustion. Carbon soot and nanoparticles from combustion are normally considered to have a negative effect on human health, the environment, and climate change, but they can also have positive aspects if they can be harnessed for clean energy conversion. We have been investigating the interesting material properties of soot including low density and fractal structure utilizing *in-situ* synchrotron X-ray scattering during formation [6-9] and by sample analysis utilizing high-resolution electron microscopy energy dispersive techniques.

Since 2015 we have been performing neutron-based imaging [10] and more recently also spectroscopy on soot-based materials (work in progress). We have used a novel approach based on neutron radiography to determine storage and interaction of hydrogen-rich fuels in

porous materials. We developed a method to determine the adsorption/absorption properties of heterogeneous porous carbon materials, in our first cases represented by flame soot. We were able to monitor *in-situ* methane in the materials at pressures up to 100 bar (1 bar = 10^5 Pa) at room temperature [10]. Figure 1 shows a graphical abstract of our first results utilizing a stainless-steel pressurized container. It becomes clear that methane gas has sufficient contrast using neutron imaging in both the soot and reference cells inside the container.

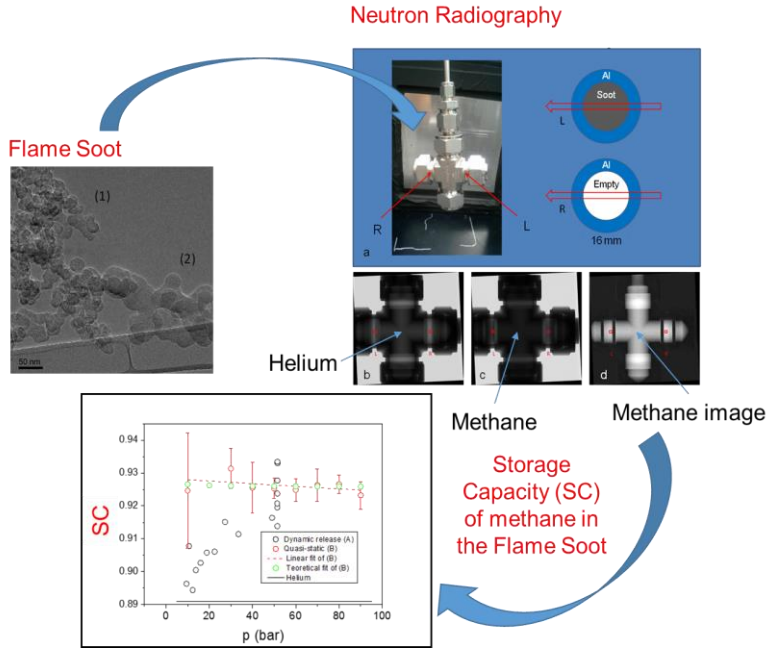

Fig.1. Flame-soot porous material was collected and analyzed in a high-pressure stainless-steel cell system. The neutron absorbance of the sample (L) vs. reference (R) was determined for methane between (10–90 bar) under both dynamic and steady-state pressure conditions [10]. The storage capacity (SC) in (L) relative to (R) was determined in situ *for the different conditions corresponding to fuel storage and delivery. Figure adapted from [10].*

In our ongoing development, we have been able to introduce a new setup and cell system yielding improved signal-to-noise ratio that enable measurements of pressure up to 100 bar and temperatures from room temperature down to cryogenic temperatures. We have obtained interesting results concerning static and dynamic gas behavior for methane gas, potentially of interest for real operation in fuel tanks. We have also investigated the properties of ethane and found that we could collect and store more than 60% in the soot material with respect to the clean reference cell at room temperature. We have introduced studies on condensation and evaporation of methane and ethane at different points in the phase diagram crossing the phase transition lines for pure gases and the effect of compression on the porous carbon material. We are also introducing new materials such as chemically modified soot and char from biomass pyrolysis.

We find from our results that collection efficiency and storage capacity can be determined with considerably high precision and accuracy with the neutron radiography method. The diagnostic technique is not limited to carbon materials but in principle can be adapted with relative ease to other heterogeneous and complex materials such as metallo-organic frameworks. The technique can support research and development of new materials for clean energy storage.

During the last year we have also introduced neutron-based neutron inelastic scattering studies, mainly by vibrational analysis, to investigate the way different gases interact with the

combustion-produced materials. The work is in progress, and we have included species such as H_2, H_2O, CH_4, C_2H_6, and CO_2.

Our results are useful, since they do provide a structural density map of elemental hydrogen inside the biomass during the entire pyrolysis or burning process. Of particular of interest is to correlate these changes with the release of different gases. In this way, quite unique multiscale information is provided that can make clean energy conversion better understood and more efficiently applied.

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