Experimental report

30/09/2022

Proposal: 1-05-84 **Council:** 4/2021

Title: Combined neutron and X-ray imagingof capillaries/pores, hydrogen andcarbon in pyrolyzing/combusting biomass/flour sticks

Research area: Physics

This proposal is a new proposal

Main proposer: **Frederik OSSLER**

Experimental team: Frederik OSSLER
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Local contacts: Alessandro TENGATTINI

Samples: Sample of combusted flour sticks
Samples of Wood pyrolyzed at different temperatures

Instrument	Requested days	Allocated days	From	To
NEXT	3	3	01/10/2021	04/10/2021

Abstract:

This project is aimed at using combined neutron and X-ray tomography (NCT and XCT) to study dynamics of hydrogen (H) and carbon (C) in thermochemical conversion (pyrolysis/carbonization) of wood and flour sticks (spaghetti). Cold neutrons show great sensitivity to H non-intrusively and have low sensitivity to carbon and heavier elements and thus complements very well X-rays, which show opposite sensitivity. Thus from combined NCT and XCT one can map out the abundance of H and C in 3D over the entire material during carbonization. In addition, the XCT and NCT at ILL, beamline D50 can be operated with high resolution, 10 micrometer or better. We study samples pyrolysis of wood samples that are of interest for production of biofuel, gas and chars and combustion/carbonization of solid flour sticks that are of interest for production of nanotubular structures for different technical applications related to energy and environment. They show quite different complex transformation schemes which include capillary and pore structures. These measurements will give important input to modelers that want to develop predictive models for energy and materials production and synthesis.

Experimental report 1-05-84: Combined neutron and X-ray imaging of capillaries/pores, hydrogen and carbon in pyrolyzing/combusting biomass/flour sticks

Main Proposer: Frederik Ossler, Co-proposers: Emanuel Larsson, Stephen Hall, Charles Finney

Local Contact: Cyrille Couture

Experimental date: 1/10 to 4/10 2021

Background and Scientific motivation

Lignocellulosic biomass is an important source for biofuel and hydrogen-rich gas. During thermochemical conversion the material undergoes complex multiscale changes, while hydrogen (H) separates from carbon (C) and oxygen (O) in the carbohydrates. It is a challenge to develop particle models that can predict the development of charring and can include changes in physical structure [1]. Cold neutron radiography (NR) and neutron tomography (NCT) show high sensitivity to H, but low sensitivity to C, O and heavier elements found in wood. Conversely, corresponding X-ray imaging techniques, X-ray radiography (XR) and X-ray microtomography (XCT) show low sensitivity to H but high sensitivity to C, O and heavier elements (see, e.g., [2]). Combining NCT and XCT would thus give the possibility to follow the dynamics of separation of H from C, with attendant structural changes, in carbonization processes in thermochemical conversion processes of both wood pyrolysis that causes contraction and milled flour-based solid products that causes expansion and nanotubular structures (studied by electron microscopy-based techniques) [3]. The aim is to resolve the question of how pore and capillary systems develop and affect how H separates from C and O in thermochemical processes. The purpose of this project is to utilize combined XCT and NCT with high spatial resolution available at ILL, beamline D50 and study pore-evolution dynamics for thermochemical conversion and carbonization processes to produce 3D maps of H and C (together with heavier elements) and how they relate to pore and capillary structure. An additional aim is to gain experience to further develop the technique for in-situ measurement sample environment involving combined XCT/NCT.

Experimental procedures and results

Samples of beech and pinewood were subjected to fast pyrolysis in hot nitrogen gas flow into carbonization. Samples were also partially burnt (heating from one end) once wrapped in aluminum foil using a torch cigarette lighter so that gradual carbonization was achieved. Samples of small twigs of beechwood and pinewood were also selected in the study as well as partially burnt spaghetti.

In this report we show the results from a more detailed analysis on fully carbonized and partially carbonized samples of beechwood and pinewood dowels that were presented at the 2022 CARBON Conference [1]. XCT and NCT scans of the samples were performed sequentially for every sample, so that the same alignment (with main wood fiber direction along the rotation axis) was maintained on the rotation stage. The partially and fully pyrolyzed samples were glued together so that transition regions from fresh to partially burnt material, as well as the fully pyrolyzed sample could be scanned at the same time.

An overview of NCT and XCT from beechwood of the fully pyrolyzed and partially burnt samples is shown in **Fig.** 1. The glue shown in this figure was a polymer-based glue, rich in hydrogen (H). We found that the pristine wood appears brighter, but with lower resolution and contrast in the NCT scan compared to the XCT scan. This could be due to the high concentrations of H that yields increased (probably diffuse) scattering in the NCT. The fact that the capillaries appear brighter for NCT could be from H in moisture contained inside and will be investigated further. We also observe that the glue appears very bright in NCT, due to its high H content. In principle this will allow us to do a more

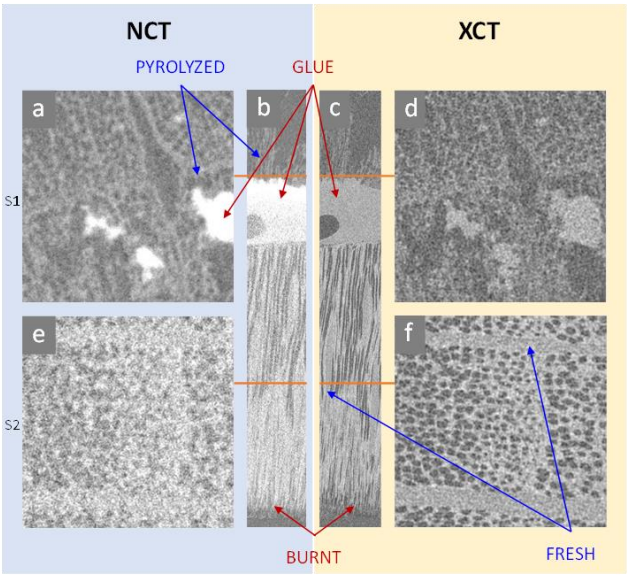

Fig. 1 *Overview panel of NCT and XCT (raw data images) of a fully pyrolyzed beechwood sample a) and d) showing corresponding horizontal sheets. b) and c) show axial sheets including the glued regions (white patches in NCT). d) and f) show parts from the pristine region of the partially burnt*

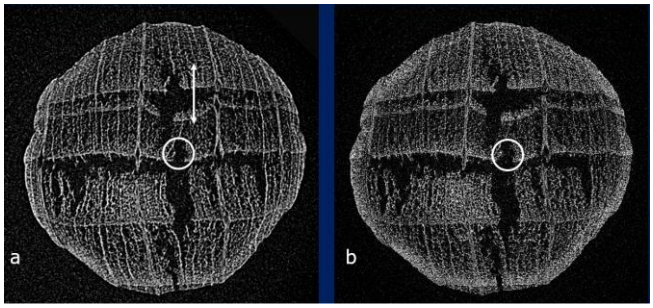

Fig. 2 *(a) NCT, b) XCT of fully pyrolyzed beech wood dowels. Images are brightness/contrast adjusted for comparison.*

performed at a Lund University laboratory are also shown for comparison. The brighter spots in NCT seem to be combined with line junctions/branching in the observed slices. This could mean that the water moisture is absorbed to the carbon structure and that it is more attracted to corners of the 3D carbonized biomass structure. A more extended image analysis over the sample in 3D will allow us to study the details further and hopefully obtain a clearer understanding of the nature of these features. During the carbonization process it is expected that H will detach from carbon (C) diffuse out of the wood material and leave a carbon-based skeleton, as discussed in a previous work based on in-situ radiography and comparing pre- and post-pyrolysis NCT results [2]. In this study we have combined NCT and XCT, with higher spatial resolution, better than 10 μm/voxel on partially burnt regions of wood where qualitative analysis, once the isotopic composition of the glue is determined. This will enable us to make qualitative estimates of the relative H/C in pyrolyzed regions of the wood (where oxygen concentrations are expected to be relatively low). For the fully pyrolyzed sample material (a), and (b) the levels of contrast levels of NCT and XCT are more similar, however, the line structure appears to be more distinct and slightly wider for the NCT compared to the XCT. This is in contrast with what was observed for the glue, see e.g. (a) and (d), where the patches are considerably similar in shape and border structure. This suggests that hydrogen is localized to the surface of the carbon structure material, possibly due to the moisture.

A slice from both NCT and XCT is shown in **Fig. 2**. They have been brightness/contrast adjusted to facilitate the comparison. The white line with arrows shows the direction of rupture during the fast pyrolysis. The white circles indicate the region of interest chosen for analyzing the details of the lines structures. These parts of the pictures have been magnified in **Fig. 3**. From **Fig. 3** we observe that the higher contrast areas in the NCT follow the lines' structure of the material more than the corresponding XCT. Post experiment XCT

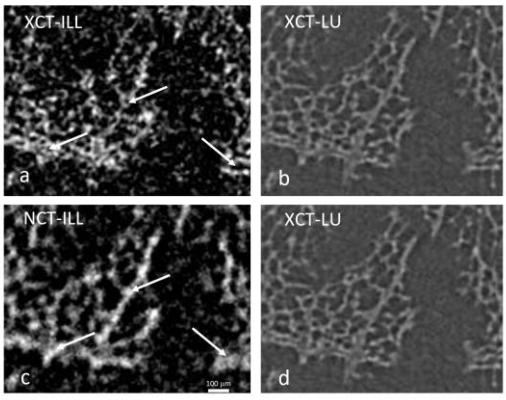

Fig. 3 *a) NCT from ILL, b) XCT post experiment (ca. 6 months after) measured at Lund University, c) XCT from ILL, d) same XCT as in b). Arrows indicate some reference regions.*

one can capture regions of different degrees of carbonization on the same NCT and XCT image. As an example of partially burnt regions we report partially burnt pinewood dowels of the same diameters as for the beech samples previously discussed.

Figure 4 shows an example of the differences in contrast between NCT and XCT at corresponding sample positions. In **Fig. 4a** and **Fig. 4b** one can observe the bright regions of late wood in the ring structure aligned in the horizontal direction. On the right side of the sample, at the edge, we observe the regions that have been partially carbonized. After heating the aluminum foil was removed. The sample was then glued onto the fully pyrolyzed sample and scanned using NCT and XCT. The region of interest in this study has been marked out and magnified in **Figs. 4c** and **4d**. If we compare the NCT and XCT, we see that the areas highlighted by the arrows in d) show a bright region (A). This area is narrower than the corresponding one in **Fig. 4c** from NCT. Since NCT is mostly sensitive to H while XCT to C and O, it appears that H has diffused out of the of the carbon structure to its outer surface. In Region B it appears that H has diffused out of the lower part of the void. In general, the experiments have provided interesting new results, however, there is a strong desire to increase the signal-to-noise levels, so that a more detailed evaluation can be performed.

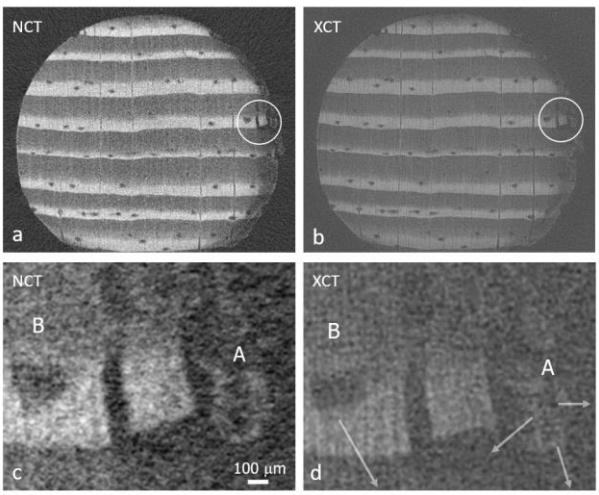

Fig. 4: *Tomographic slices of raw data images: a) and b) cut planes of NCT and XCT, respectively. c) and d) show the regions marked in a) and b) zoomed in*.

The images from spaghetti sticks at different levels of carbonization have been obtained by NCT and XCT, but data analysis is still ongoing, and we intend to present and publish results at a later occasion.

Conclusions

Results from the experiments are promising and they have been presented at the CARBON conference in London this year. The next steps are to proceed with a full 3D evaluation, including quantitative image analysis and 3D rendering. When we have determined the isotope composition of the glue, we should be able to evaluate the H/(C+O) composition more in detail. New measurements are strongly desired to improve signal-to-noise ratio in future Biomass pyrolysis investigations.

References:

1. Anca-Couce, A., et al., Progr. Energy Combust. Sci. 53 (2016) 41-79; https://doi.org/10.1016/jpecs.2015.10.002.
2. Ossler, F., et al., Carbon 176 (2021) 511-529; https://doi.org/10.1016/j.carbon.2020.11.060
3. Ossler, F.; Hetherington, C.J.D., C 2019, 5, 21; https://doi.org/10.3390/c5020021
4. Ossler, F.; Larsson, E.; Hall, S.; Couture, C.; Tengattini, A.; Finney, C.E.A., "Combined Neutron and X-ray Microtomography for Tracking Local Hydrogen and Carbon + Oxygen Distribution in Biomass Pyrolysis", presented at CARBON 2022, World Conference on Carbon, London 3-8 July, 2022 (DOI number is soon to be generated).