ESRF	**Experiment title:** Thermal degradation of wood and microstructure of biocarbon: Simultaneous XRD and SAXS investigation during *in-situ* pyrolysis of wood.	**Experiment number**: ME549
Beamline: ID13	**Date of experiment**: from: 11/07/2003 to: 15/07/2003	**Date of report**: 26/02/2004
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Report:

Thermal treatment of wood in a non-oxidising atmosphere for manufacturing of carbon char is a matter of increasing interest for the use as biocarbon templates in advanced ceramics manufacturing. A major question is, if wood can be transformed into a carbon replica that is structurally pseudomorphous to the original tissue at the nanometre scale. It might be expected, for instance, that the nanometre sized, oriented crystalline cellulose fibrils in wood are converted into textured carbon, similarly as in the well-known transformation of cellulose fibres into carbon fibres with high preferred orientation. The present experiment aimed at a detailed *in-situ* study of softwood pyrolysis by applying simultaneously X-ray diffraction (XRD) and small-angle X-ray scattering (SAXS) using microbeam synchrotron radiation. The kinetics of cellulose degradation and the kinetics of carbon formation were investigated at different temperatures.

For the study of *in-situ* wood pyrolysis a heating cell was developed by the applicants in collaboration with the ID13 beamline staff to fit the requirements of the beamline instruments. Sample heating was performed by mirror heaters which focus the energy of a tungsten halogen lamp (Osram Xenophot) to a small spot at the sample. A thermocouple (Type K) attached to the samples for temperature control (Eurotherm 2404) was used at the same time as a specimen holder. Thin wood foils (thickness between 40 and 150 μm) were sandwiched between two TEM-grids that were glued with a ceramic glue onto the thermocouple weld. In this way, the specimens could be heated in a controlled manner while measuring 2D-XRD/SAXS patterns in transmission geometry. Since wood pyrolysis has to be

performed in an inert atmosphere, a closed sample container with continuous flow of nitrogen was constructed, and sapphire single crystal windows (250 μm) transmission of both, X-rays and heating light, were used. The development and implementation of the in-situ furnace was one of the technical challenges of the experiment, and it may be utilisable for other medium-term planed projects in the future.

A beamline setup with an X-ray beam at the sample position of approximately 5 μm from a KB mirror setup, a small beamstop with a diameter of 200 μm and a short specimen-to-detector distance of 130 mm provided medium resolution measurements for simultaneous XRD/SAXS, using the 16-bit MAR-CCD currently available at the beamline. For fast *in-situ* experiments a binning of the detector pixels gave readout times as low as 2 s, being a sufficient time resolution. By using a monochromatic X-ray beam with an energy of 13 keV in combination with short exposure times the radiation damage at the cellulose fibrils was hoped to be rather low. Figure 1 shows a photograph of the experimental setup. The setup was tested offline first, however, three shifts of beamtime had to be used for online testing and alignment. At higher temperatures protection for detector, collimation system and other heat sensitive instruments against radiated heat from the mirror furnace were needed. Metallised foils proved to be sufficient to protect these instruments. For temperatures higher than 400°C, however, the long-time stability of the whole setup must be improved for future experiments (drift of guard pinhole and beamstop).

For *in-situ* pyrolysis, radial cross sections of spruce wood were prepared, since this allows one to scan several annual rings (earlywood and latewood) in a single measurement. Native, dry wood samples as well as samples pre-heated in nitrogen atmosphere in a temperature range between 200 and 250°C were investigated. The pre-heating considers the fact that in this temperature range no cellulose degradation is expected, while partial degradation of lignin and hemicellulose should take place. The samples were scanned across the beam by mesh scans of approximate size of 100×100 μm^2, in order to cover data from annual rings consisting of latewood (thick cell walls) and earlywood (thin cell walls). Furthermore the scanning of the sample provides the advantage of keeping the radiation damage at one position low. It turned out, that at least for low temperatures ($T < 300$°C) radiation damage causes similar changes in the diffraction patterns, as sample heating does. Figure 2 shows a typical mesh scan with a step size of 10 μm at a temperature of 250°C over a region including an latewood (Figure 2, left) - earlywood (Figure 2, right) transition. The axial direction of the wood and therefore the fibre orientation was vertical. Various measurements in one column of the scanning mesh can be compared in terms of kinetics studies, because it can be presumed that they belong to the same wood cell, being only minimal influenced by radiation damage.

The two-dimensional scattering patterns were normalised with respect to primary intensity, corrected for background scattering and than azimuthally averaged using the Software Fit2D. Figure 3 shows a typical series of scattering profiles as function of scattering vector q. The length of the scattering vector q is given by $q = 4\pi (\sin\theta) / \lambda$ (λ is the wavelength and 2θ is the scattering angle). The scattering profiles belong to the marked column in Figure 2. The cellulose reflections diminish with time at a fixed temperature, whereas the position of the peaks stays constant and does not shift nor considerably broaden with heating time at 250°C. These changes of the scattering profiles as a function of pyrolysis time at a constant temperature give first insight into the kinetics of cellulose degradation. Further data evaluation is currently still in progress.

In summary, this first *in-situ* experiment on wood pyrolysis demonstrated the feasibility of *in-situ* sample heating in combination with microbeam scanning diffraction.

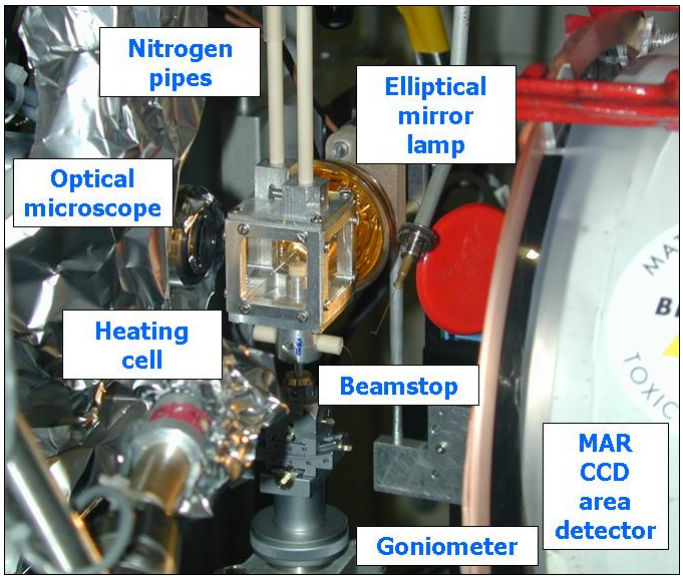

Figure 1: *Photograph of the experimental setup with the in-situ heating cell at the ESRF microfocus beamline ID13.*

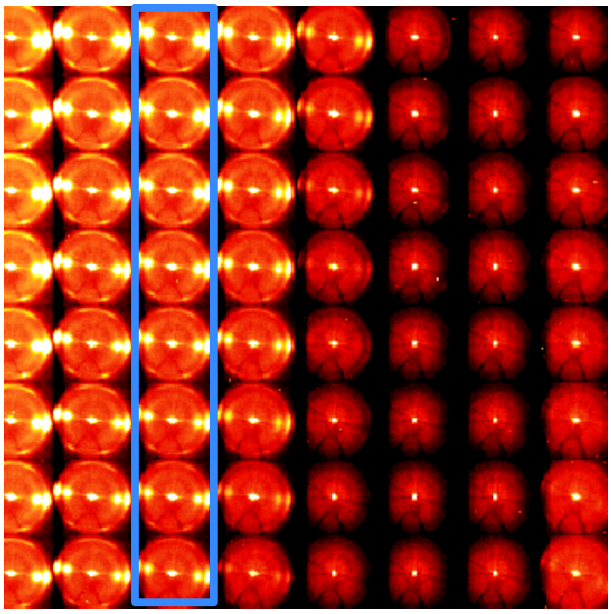

Figure 2: *Part of a scanning mesh of 2D diffraction patterns from a thin wood section at a temperature of 250°C, beam size: ~5 µm, step: 10 µm. The scan started at the left upper and ended at the right lower corner of the figure by successively scanning line by line. The time between two succeeding frames in a vertical row is 150 s.*

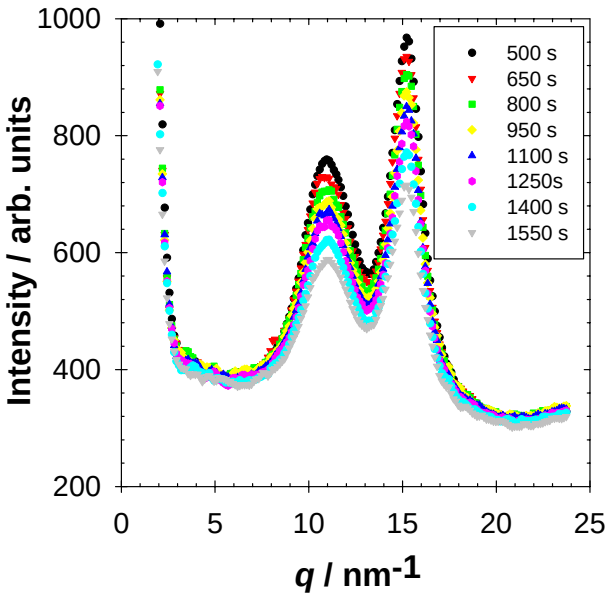

Figure 3: *Series of scattering profiles of wood at a temperature of 250°C. The data correspond to the third row in Figure 2 and are chosen to separate radiation damage effects due to specimen heating (every frame has suffered the same time of illumination by the X-ray beam, but an increasing time at T=250°C.*