

Visualization of Internal Structural Changes during Transient Pyrolysis of Wood Containing Ammonium Nitrate

Tadafumi Daitoku, Takashi Tsuruda, Toma Kinugasa
Akita Prefectural University
Yurihonjo, Akita, Japan

1 Introduction

Wood is widely used in various fields because of its relatively low cost, availability, and light weight. Recently, biomass power generation using wood fuel as a sustainable energy resource has increased significantly. However, the use of wood carries the risks of fires and explosions. For example, on September 26, 2016, a fire at a wood chip factory in Coity, Bridgend, caused significant damage [1]. Therefore, it is important to understand the pyrolysis phenomenon of wood not only when it is used as a fuel but also from the perspective of disaster prevention.

Wood is a porous material that absorbs moisture easily. Therefore, highly deliquescent solids can dissolve in water and penetrate wood. Ammonium nitrate is a deliquescent substance used worldwide as a fertilizer. Ammonium nitrate melts at 170 °C and decomposes at 210 °C to produce oxygen. On August 4, 2020, a large explosion occurred in a warehouse in Beirut, Lebanon [2], where ammonium nitrate was stored, causing extensive damage.

The pyrolysis rate of combustible solids is an important property in solid combustion. The pyrolysis rate and composition of polymers have been measured using thermogravimetric analysis and differential thermal analysis [3–8]. However, determining the condition of the interior of a sample is difficult; in particular, the changing internal structure is unclear.

In this study, microscopic visualization of the pyrolysis of wood biomass was conducted using the BL20B2 beamline at “Spring-8,” a large synchrotron radiation facility. X-ray computed tomography (CT) imaging was used to observe the differences in the internal structures of wood caused by thermal pyrolysis. To measure the sample using high-speed X-ray CT, an ultrahigh-speed CT of less than 10 s per CT was performed.

In X-ray CT, X-rays are incident on an object to obtain the spatial distribution of the linear absorption coefficient. In CT, time is required to obtain a transmitted image of a sample in multiple directions. If the sample changes while the images are captured, it cannot be reconstructed successfully; hence, capturing images when the sample is in motion is difficult. However, when synchrotron radiation is used for X-ray CT, a high flux can be obtained, even in a short time, making it possible to perform high-speed

imaging, unlike with industrial X-ray CT apparatuses. Hence, the time evolution of a three-dimensional structure can be monitored by continuously capturing images.

In this study, wood impregnated with ammonium nitrate was heated under a high heat flux, and its pyrolysis behavior and changes in its internal structure were observed. The objectives of this study were to gain insight into the pyrolysis mechanism of wood and investigate the impact of its interaction with ammonium nitrate on the pyrolysis of wood in detail.

2 Experimental Setup and Procedure

The synchrotron X-rays used in this experiment were characterized by parallel light with high luminance and high directivity. Using a beam with high synchrotron radiation directivity, the refraction of X-rays by a substance can be processed; thus, the technique is effective for samples with small differences in the absorption coefficient.

The large synchrotron radiation facility SPring-8 BL20B2 beamline uses a bending electromagnet as the light source [9]. “SPring-8” is an abbreviation of “super photon ring-8 GeV,” where 8 GeV is the power output of the ring. To obtain a high spatial resolution with parallel light synchrotron radiation, the transmitted X-ray image is converted to a visible light image using a thin-film fluorescent plate (scintillator), magnified by an optical lens system, and projected onto a complementary metal–oxide–semiconductor camera.

Figure 1 shows an overview of the experimental apparatus. The sample installed in the apparatus receives radiation heating on its surface using a radiation heater. The experimental apparatus is installed on a rotating stage between the X-ray irradiation unit and the scintillator in the experimental hatch of the SPring-8 beamline. The sample is placed on the sample stage and inserted into the apparatus. In addition, because the rotation stage with the apparatus and the sample stage are independent, X-ray CT measurements are possible during heating. Polyimide sheets are used in the X-ray transmission windows. Heating is performed using a radiation heater in the direction perpendicular to the X-ray irradiation direction. At that time, the sample is rotated using a rotating stage; thus, it can be heated all around. The inside of the device is an inert nitrogen atmosphere. To remove moisture from wood, it is irradiated its center by a radiant heater for 10 min at an output of 100 °C, followed by irradiation for 5 min at an output of 40 W for pyrolysis. The heating conditions are listed in Table 1.

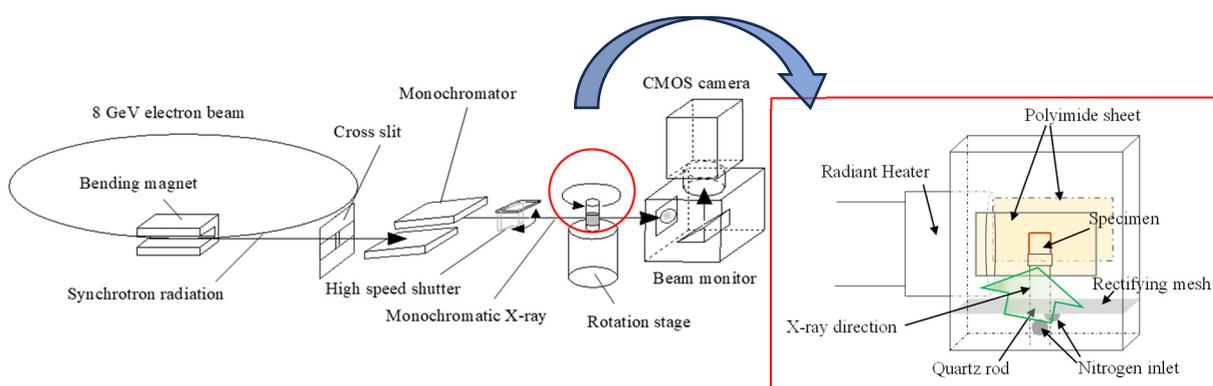


Figure 1: Projection tomographic X-ray system at BL20B2 of SPring-8.

Table 1: Heating condition.

Condition ID	(a)	(b)
processing	non	AN
Output (W)	40	40
Atmosphere	N ₂	N ₂
Moisture removal time (min)	10	10
Pyrolysis time (min)	5	5
Number of CTs	114	114

Table 2: Experimental conditions used in X-ray CT.

Energy (keV)	15
Pixel size ($\mu\text{m}/\text{pixel}$)	6.6
Exposure time (ms)	8
Number of projection (/ 180°)	600 / 180

AN: ammonium nitrate

In the experiment, X-ray CT was performed continuously for 15 min using a radiant heater. Japanese cypress was used as the specimen. Before pyrolysis, the specimens were circular columns (height: 5 mm; diameter: 5 mm). Untreated cypress wood and cypress wood impregnated with ammonium nitrate were prepared. The X-ray source direction and radiant heating direction were in the radial direction of the specimen, as shown in Figure 1. The heat flux was extremely high owing to the thermally thick conditions. The specimen had a temperature distribution and was deformed under the condition of a large Biot number. The projection conditions are listed in Table 2. The time required for one CT scan was approximately 7.8 s. The energy value of the X-rays was 15 keV for the target carbon, which is the main element in wood. As the spatial resolution of the detector, a pixel size of 6.6 μm was used for imaging.

3 Results and Discussion

Figure 2 show examples of real-time X-ray CT images of a specimen during transient pyrolysis by radiant heating. Figures 2(a) and (b) correspond to the IDs in Table 1 of the heating conditions. Figures 2(a) and (b) show the cross section at the center position (the slice numbers are 416 and 430, respectively) in the height direction of initial specimen. The numbers in the figure represent CT numbers. For these CT images, the light regions in the images correspond to regions where X-rays are absorbed, and the dark regions correspond to regions from which they are transmitted. In Figures 2(a) and (b), grains of wood and the structure of the tracheid can be clearly identified in the 001- and 073-CT image. In the pyrolysis experiment of standard cypress wood shown in Figure 2(a), the moisture removal process continues until CT number 074. During this time, the grain and tracheids can be observed clearly. After drying for 10 min, when the output of radiant heater was set to 40 W, the wood began to deform rapidly. Approximately 60 s after the heater output was increased to 40 W, pyrolysis proceeded rapidly, and the outer edge of the wood could not be reconstructed. This is because the specimen was moving. This indicates that the pyrolysis was progressing, and the outer part of the specimen was being deformed. However, tracheid structures are visible up to CT number 079. In other words, no structural changes resulting from pyrolysis had occurred near the center of the specimen at this point.

As shown by CT number 075 in Figure 2(b), for the cypress wood impregnated with ammonium nitrate, the outer periphery of the sample could not be reconstructed. However, after CT number 077, shrinkage of the specimen was observed, and cracks and cavity formation occurred in some areas; however, the grain and tracheid structure were maintained until the end of the experiment.

Figure 3 shows X-ray transmission images of the specimens in Figure 2. In contrast to the CT image, the dark regions absorbed X-rays. Figure 3(a) clearly shows that X-rays first become more easily transmitted through the outer periphery of the untreated cypress wood owing to radiant heating, and, as time passes, it becomes easier to transmit X-rays through the center as well. For example, the dark area in the transmission image of CT number 077 appears to be the area where the tracheid structure remains, based on its correspondence to Figure 2(a). As Figure 3(b) shows, the distribution of luminance values observed in the untreated cypress wood does not appear in the cypress wood impregnated with

ammonium nitrate. After the radiant heater was set to 40 W, the luminance of the entire sample quickly becomes uniform.

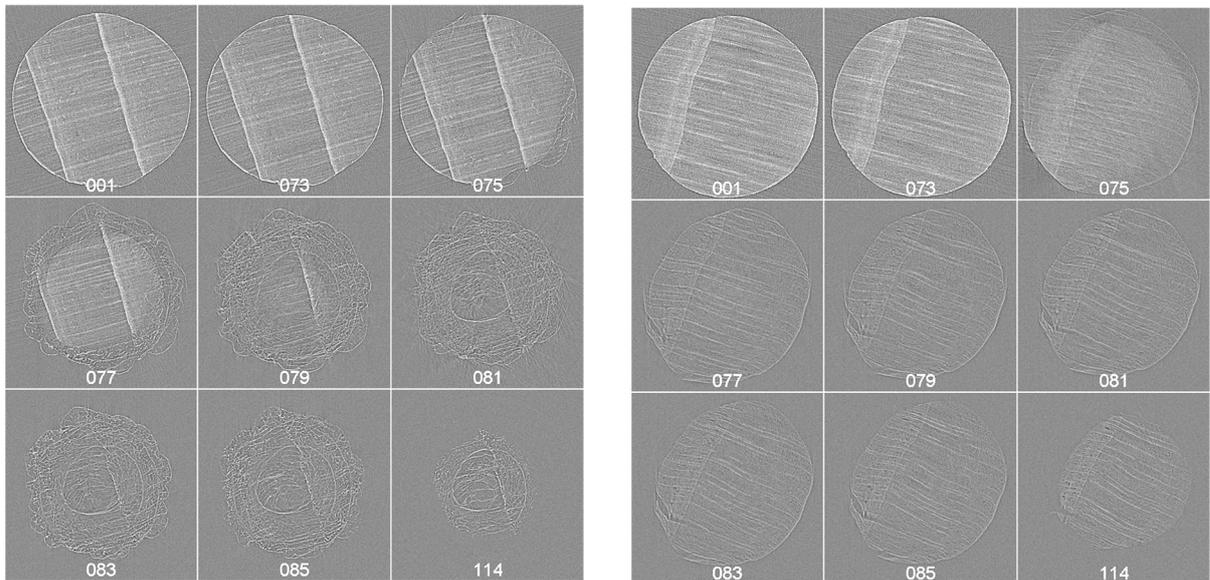


Figure 2: Real-time X-ray CT images of a specimen during transient pyrolysis by radiant heating. Left:(a) Untreated cypress wood. Right:(b) The cypress wood impregnated with ammonium nitrate.

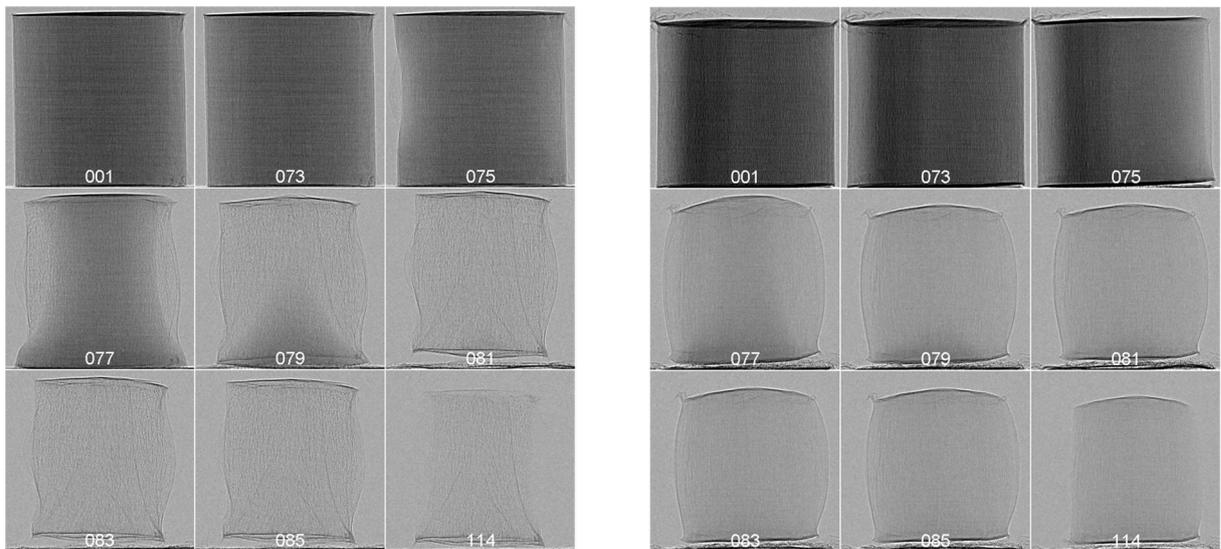


Figure 3: X-ray transmission images during transient pyrolysis of the specimen shown in Figure 2. Left:(a) Untreated cypress wood. Right:(b) The cypress wood impregnated with ammonium nitrate.

Figure 4 shows the transition of the average luminance values for the transmitted images of all CTs scans. Figure 4(a) shows the change in the luminance value of the untreated cypress wood, and Figure 4(b) shows the change in the luminance value of the cypress wood impregnated with ammonium nitrate. The difference in the luminance values at the beginning occurred because the specimen sizes were not the same. Under both conditions, the luminance values slowly increased during the drying process, and the moisture was removed gradually. In Figures 4(a) and (b), the luminance values increase rapidly, which clearly indicates that the pyrolysis proceeded when the heater output was 40 W. In both cases, the change in the luminance value exhibited an easy gradient within 60 s after the start of heating at 40

W. The average luminance value shown in Figure 4(b) is larger than that in Figure 4(a). This is thought to be because the ammonium nitrate that penetrated into the cypress wood easily absorbed the X-rays.

The results of this study show that, in cypress wood impregnated with ammonium nitrate, the change in luminance was fast all the way to the center of the specimen. This is thought to be because the melting of ammonium nitrate promoted heat transfer to the interior. In addition, the tracheid structure was maintained until the end of the experiment, which was significantly different from the results obtained with the untreated cypress wood. The thermal decomposition temperature of ammonium nitrate is 210 °C, which is close to the pyrolysis temperature of wood. An endothermic reaction occurs as ammonium nitrate decomposes thermally. This endothermic reaction hinders the progression of cypress pyrolysis. Therefore, it is believed that the cypress was carbonized while the tracheid structure remained.

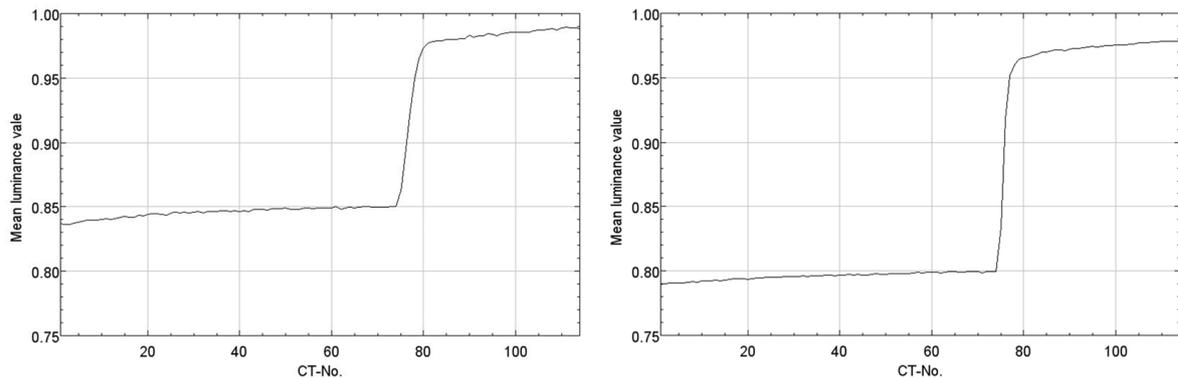


Figure 4: Transition of average luminance value during transient pyrolysis. Left:(a) Untreated cypress wood. Right:(b) The cypress wood impregnated with ammonium nitrate.

4 Conclusions

Wood impregnated with ammonium nitrate was heated under high heat flux, and its pyrolysis behavior and changes in its internal structure were observed using ultrahigh-speed X-ray CT imaging. The results are summarized as follows.

- 1) During the rapid progression of pyrolysis, the outer edge of the wood could not be reconstructed.
- 2) The change in luminance value has an easy gradient within 60 s after the start of heating at 40 W. In particular, the results show that, in cypress wood impregnated with ammonium nitrate, the change in luminance was fast all the way to the center of the specimen.
- 3) In the cypress wood impregnated with ammonium nitrate, cracks and cavities formed, but the grain and the tracheid structure were maintained until the end of the experiment.

Acknowledgments

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