



Instrumental analyses of nanostructures and interactions with bound water of superheated steam treated plant materials

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ABSTRACT

Using multi-scale instrumental analyses, nanostructural changes due to superheated steam treatments were compared between Japanese cedar (*Cryptomeria japonica*) and bamboo (*Phyllostachys pubescens* Mazel). The lower amounts of aromatic carboxylic acids contained in lignin and hemicellulose/lignin in Japanese cedar suppressed not only the formation of pyrolysis products from hemicellulose but also fragmentation of cell walls. Variable temperature solid-state NMR spectra and relaxation time analyses were carried out on the nanostructures of the plant materials in order to examine molecular motions and interaction with bound water for the biomass constituents of the plant materials. The untreated and steam treated bamboos strongly interacted with bound water to change the ¹H spin-lattice relaxation time (T₁H) values depending on the content of bound water. Because the interaction between the biomass constituents and bound water in Japanese cedar was weaker than that in bamboo, the T₁H values of Japanese cedar were reduced less than those of bamboo in the humid conditions. The difference in the interaction with bound water between bamboo and Japanese cedar also affected the amount of the pyrolysis products and the decomposition rate of hemicellulose in the superheated steam treated materials. Furthermore, the pyrolysis products caused little change in the molecular mobility of Japanese cedar although they restrained that of bamboo.

1. Introduction

Sustainable industrial development demands the production of new biomass resources from plant materials. Steam treatments of plant materials are significant pre-treatment methods for bioconversions such as hydrolysis and fermentation to obtain biomasses and biofuels (Ramos, 2003; Kumar et al., 2009). Superheated steam, which is produced above the boiling point under atmospheric pressure, has recently been put to extensive use in various fields of bioresources. It is the basis of a convenient drying method; superheated steam drying has a high energy efficiency and high drying rate, and final products obtained are of high quality (Li et al., 2016). In the superheated steam treatment, the moisture content is an important parameter not only for manufacturing processes, but also for the properties of the materials obtained; several reports on the moisture content in superheated treated material have been published as follows. Changes in moisture content due to the use of superheated and saturated steams were examined by in situ weighing of specimens and measuring weight loss of wood substance (Ishikawa et al., 2004). The degree of compressive deformation caused by superheated steam was studied by the relative density change and

measurements of creep deformation. This study showed that higher temperature of compression resulted in a lower equilibrium moisture content for both superheated and the saturated steam (Kutnar and Kamke, 2012). The equilibrium moisture content in superheated steam depended on the activity of the superheated steam, the temperature, and the materials; these dependences showed the existence of absorbed water with different binding energies (Björk and Rasmuson, 1995). The sorption equilibrium was predicted during superheated steam drying over a wide range of temperatures and moisture contents (Pakowski et al., 2007). The treatment with superheated steam also brings about changes of chemical structures and compositions: useful bioresources, such as carbohydrate and furfurals, were extracted by superheated and pressurized steams (Karlsson et al., 2012). The superheated steam drying of bark chips formed several organic compounds as side-products, which was suppressed at low temperatures with a short drying time (Björk and Rasmuson, 1996). For the purpose of a biomass refinery, superheated steam pyrolysis of Japanese cedar (Sugi) provided useful organic compounds as same as isolated biomass constituents, such as cellulose and xylan (Sagehashi et al., 2006).

On the other hand, solid-state nuclear magnetic resonance (NMR)

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methods provide useful information about the chemical structure of woody materials without the separation of each biomass constituent (Maunu, 2002); several such studies on the changes of chemical structure due to steam treatment follow. Thermal modifications of hard- and soft-wood with steam treatment were studied by ^{13}C cross-polarization and magic angle spinning (CP-MAS) NMR and indicated an increase in the cellulose crystallinity by a degradation of less ordered carbohydrates (Wikberg and Maunu, 2004). With respect to steam explosion co-refining for production of wood plastic materials, an increase in the cellulose crystallinity was also confirmed by ^{13}C CP-MAS NMR (Rennecker et al., 2005). In the case of the steam drying of beech wood as a pre-treatment, the interaction of lignin and polysaccharides was examined by ^{13}C CP-MAS NMR and a relaxation time analysis to show the formation of lignin-cellulose complexes (Košíková et al., 1999). In a study of the steam explosion for vegetation, cellulose from degraded wheat straw was characterized by Fourier transform infrared spectroscopy (FT-IR) and ^{13}C CP-MAS NMR (Sun et al., 2005). Although chemical changes due to thermal processing have been revealed by composition analysis and mass balance (Zhang et al., 2015), solid-state NMR analysis has scarcely applied to chemical structural changes of biomass constituents in plant materials treated with the superheated steam.

In order to evaluate and improve the reliability of the superheated steam process for plant materials from the viewpoint of quality control, it is necessary to know details of the relationship of nanostructures to product characteristics. As shown below, we have reported multi-scale instrumental analyses for biomass constituents in plant materials, using solid-state NMR and FT-IR for molecular and nano-hierarchical levels, and scanning electron microscopy (SEM) for the micro-hierarchical level. For the superheated steam treatment of bamboo (*Phyllostachys pubescens* Mazel), the multi-scale instrumental analyses gave information on the nano-structural changes occurring in the biomass constituents (Nishida et al., 2017a). These analyses were also applied to several chemical removal processes of biomass constituents from bamboo to show the correlation between the deformation of cell walls and the nano-structural changes of the constituents (Nishida et al., 2014). Meanwhile, for the chemically modified Japanese cypress, the interactions between water molecules and biomass constituents, whose nano-structures were determined by multiscale instrumental analyses, were studied by a cycle of variable temperature ^1H MAS NMR and spin-lattice relaxation time analyses (Nishida et al., 2017b). Furthermore, we also revealed the impregnation process of phenol formaldehyde resin into Japanese cedar by the integrated analysis of solid-state NMR spectra and nuclear magnetic relaxation times (Nishida et al., 2017c).

In this paper, we focus on improving the reliability of the superheated steam process for plant materials by comparing the nano-structural changes occurring in woody and herbaceous plants; in particular, using our earlier study on untreated and superheated steam treated bamboos for reference (Nishida et al., 2017a), the Japanese cedar (Sugi) (*Cryptomeria japonica*) was examined using our multi-scale instrumental analyses, including solid-state NMR spectra and spin-lattice relaxation time analyses. Then, based on the nanostructures thus determined, the interactions between the biomass constituents and bound water for these superheated steam treated samples were examined by variable temperature ^1H MAS NMR and spin-lattice relaxation time analyses, which can analyze the interactions of biomass constituents in the modified Japanese cypresses (Nishida et al., 2017b). We will show how superheated steam changed the interfaces between the biomass constituents and the interactions between the biomass constituents and bound water/other constituents, targeting on the comparison between woody and herbaceous plants.

2. Experimental

2.1. Materials

A batch-type superheated steam apparatus consisting of a processing oven whose base had ports to introduce the superheated steam and whose cover connected to an exhaust port, as described in the previous report (Nishida et al., 2017a). Japanese cedar (*Cryptomeria japonica*) samples used in superheated steam process were derived from consecutive 2 mm thickness sapwood plates obtained in the Nara prefecture of Japan. The treatment of Japanese cedar with superheated steam was performed at 200 °C for 24 h and 220–260 °C for 2 h under ordinary pressure. Reference superheated steam-treated bamboo samples were derived from crushed eight-months-old Moso bamboo (*Phyllostachys pubescens* Mazel) obtained in the Toyama prefecture of Japan. The superheated steam treatment of bamboo was performed at 240 °C for 4 h under ordinary pressure as described in the previous report (Nishida et al., 2017a). For the instrumental analyses, the superheated steam-treated samples were cut to 2 mm long in the fiber direction and under 1 mm in thickness and then were stored in a desiccator at 20 °C and 35% relative humidity for 7 days, unless otherwise noted.

2.2. Scanning electron microscopy

Scanning electron microscopy (SEM) images were recorded with a JEOL JSM-5600ED (Tokyo, Japan) instrument at 1000-fold magnification at an acceleration voltage of 5 kV. The specimen was sliced along the longitudinal section and was coated via gold-sputtering in a vacuum using an ULVAC QUICK COATER VPS-020 (Chichibu, Japan). SEM images were taken from specimens, after their surfaces were smoothed with a microtome and fixed with an adhesive.

2.3. Infrared spectroscopy

Fourier transfer infrared (FT-IR) spectra were measured on a Thermo Scientific Nicolet 6700 FT-IR spectrometer (Waltham, MA) instrument with 4 cm^{-1} resolution using 32 scans in the range $550\text{--}4000\text{ cm}^{-1}$. The attenuated total reflection (ATR) data was collected using a Thermo Scientific SMART iTR single reflection diamond ATR attachment (Waltham, MA) at ambient temperature.

2.4. Thermogravimetric analysis

Thermogravimetric (TG) analysis curves were obtained on a Seiko instruments SII EXSTAR 6000 TG/DSC 6200 (Chiba, Japan) instrument. All analyses were performed with a 2–5 mg sample in a 5 mm diameter aluminum pans under a 250 ml/min N_2 flow condition between 30 and 600 °C at a 10 °C/min heating rate. The TG analysis repeated three times or more for each specimen and the TG curve was plotted using the average of three contiguous values.

2.5. Solid-state NMR measurement at ambient temperature

Solid-state nuclear magnetic resonance (NMR) spectra were measured on a Varian 400 NMR system spectrometer (Palo Alto, CA) with a Varian 4 mm double-resonance T3 solid probe. The cut samples were placed in a 4 mm ZrO_2 rotor (a normal rotor in an open system) spun at 15 kHz over a temperature range of 20–24 °C. A Varian liquid rotor (with an end cap for liquid samples) was also used for measuring NMR spectra in a closed system. Solid-state ^1H magic angle spinning (MAS) NMR spectra were measured at 399.88 MHz for the ^1H nuclei and were collected with a 2.9 μs $\pi/2$ pulse for the ^1H nuclei and 20 msec acquisition period over a 30.5 kHz spectral width in 16 transients, and a 3 s recycle delay. Solid-state ^{13}C MAS NMR spectra were measured at 100.56 MHz for the ^{13}C nuclei and were collected with a 40 msec acquisition period over a 30.7 kHz spectral width in 512–1024 transients.

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