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Research paper

Effect of temperature and holding time on bamboo torrefaction

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ABSTRACT

Bamboo (*Phyllostachys sulphurea* (Carr.) A. et C. Riv.) was torrefied at temperatures ranging from 280 to 340 °C and holding times between 10 and 90 min. The changes of mass yield, high heating value, and energy yield were investigated. The variations of the chemical components were depicted in Ross diagram and the alterations of H/C and O/C were plotted in van Krevelen diagram. The structural changes of the torrefied bamboo were studied by Fourier transform infrared and nuclear magnetic resonance spectroscopies and the morphology was examined by scanning electron microscopy. Results indicated that a high temperature and long holding time produced the torrefied sample with low mass and energy yields. The lignin mass fraction increased due to the transformation of carbohydrate degradation products when the torrefaction severity increased. Only a minor amount of cellulose was detected (0.15%) when torrefied at 320 °C and a higher temperature of 340 °C resulted in the complete removal of carbohydrates. The torrefaction at 340 °C and holding time of 60 min produced solid products with H/C and O/C ratios lower than those of lignite. Less water and hydrogen bonding sites were presented in heavy torrefied bamboo resulted from the degradation of both cellulose and hemicelluloses. With the increase of temperature, aliphaticity decreased but aromaticity increased due to the deoxygenation and dehydration reactions. The mass fraction of absorbed moisture of bamboo decreased with the increase of torrefaction temperature and prolongation of holding time.

1. Introduction

To update lignocelluloses into valuable chemicals and biofuels, many thermo-chemical technologies, including carbonization, torrefaction, pyrolysis, and gasification, have been developed. Among them, torrefaction addresses most of the inherent issues and updates the feedstocks into products with higher quality and attractive properties [1]. As a relatively mild thermochemical treatment approach, torrefaction is generally conducted at low temperatures ranging from 200 to 350 °C under inert atmospheric conditions and heating rates below 50 °C min^{-1} [2,3].

In recent years, there are many studies on the torrefaction of lignocellulose. Aziz et al. reported that the chemical components of lignocellulose strongly affected the torrefaction of oil palm [4]. Among the main chemical component (cellulose, hemicelluloses, and lignin), only hemicelluloses were notably decomposed since they were less resistant to thermal degradation. The sample rich in lignin was difficult to decompose during torrefaction. Chen et al. [5] found that torrefaction at 230 °C showed only minor impact on the degradation of the major components of lignocellulose. A significant amount of hemicelluloses were degraded as temperature increased from 230 to 260 °C, and more hemicelluloses and cellulose were decomposed at 290 °C. Yan et al. studied the torrefaction of Loblolly pine and found that an increase of temperature resulted in a decrease of mass fraction and an increase of densification of torrefied lignocellulose, in which the produced solid had high C mass fraction but low O mass fraction [6]. During the torrefaction of rice straw and rape stalk [7], the mass yield of solid decreased while the mass yields of volatile products including liquid and non-condensable gases increased as the increase of temperature. It was found that hemicelluloses were influenced at relatively low temperature, whereas lignin and cellulose hardly degraded at temperatures lower than 240 °C [8]. Shoulaifar et al. found that two-thirds of anhydrous carbohydrates and most functional groups of hemicelluloses were degraded at 240 °C, whereas 300 °C was needed to decompose them completely [9].

Presently, most torrefaction studies focus on wood and agricultural residue and a few reports referring to bamboo. Bamboo, a grassy lignocellulose widely distributed in many Asian

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countries, is a promising feedstock for energy use due to its rapid growth rate, short renovation and easy propagation. Previously, the chemical components of bamboo have been investigated and the utilization of bamboo for fuels through enzymatic approach has been investigated [10,11]. As a continuing work of structural modification of lignin [12], the main aim of the present study was to evaluate the mass and energy yields of bamboo after torrefaction in nitrogen atmosphere under different conditions, and to characterize the physical and thermochemical properties of the solid char with advanced techniques. In this case, bamboo was torrefied at temperatures ranging from 280 to 340 °C and holding times between 10 and 90 min. The changes of mass yield, higher heating value, and energy yield were investigated. The variations of the chemical components, including cellulose, hemicelluloses, and lignin, were depicted in Ross diagram and the changes of H/C and O/C were plotted in van Krevelen diagram. The structural changes of the torrefied bamboo were studied by Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopies and morphology was examined by scanning electron microscopy (SEM). In addition, the capacity of moisture uptake was estimated by determining the mass fraction of absorbed moisture. The findings are beneficial for the utilization of bamboo in energy production as well as further thermochemical process.

2. Materials and methods

2.1. Materials

Bamboo (*Phyllostachys sulphurea* (Carr.) A. et C. Riv.) was cultivated in a farm in Yunnan province, China (N25°41′, E103°52′). The plants of 3 ages were harvested on 20 Feb, 2014 and then were dried at 25 °C for 15 d in a laboratory room. The air-dried culms with heights between 2 m and 4 m were collected by chopping and then were smashed by a micro plant grinding machine (FZ102, Tianjin Teste Co. Ltd). The powders with particle sizes between 0.180 mm and 0.850 mm were dewaxed with methylbenzene/ethanol (2/1, v/v) in a Soxhlet extractor under reflux for 8 h and then extracted with water at 80 °C for 6 h to remove starch before drying. The components of the lignocellulose were glucan 43.09%, xylan 28.10%, arabinan 0.82%, galacan 0.30%, lignin 27.41%, and ash 0.21%.

2.2. Torrefaction under nitrogen atmosphere

Bamboo powder (S0) was subjected to torrefaction in a horizontal tubular reactor (SK-G08123K, produced in Tianjin Zhonghuan Experimental Furnace Co. Ltd., China). The torrefaction was carried out at 280, 300, 320 and 340 °C with a holding time of 60 min, and at 300 °C with holding times of 10, 30, and 90 min, respectively. Take the experiment at 300 °C with a holding time of 60 min as example, 10 g of bamboo powder was added into a zirconium oxide boat (length: 60 mm, width: 51 mm, and height: 32 mm) which was placed in a quartz tube. The tube was flowed by an inert atmosphere of nitrogen (flow rate 100 cm^3 min^{-1}) and heated by a furnace from 25 °C to the target temperature of 300 °C at a heating rate of 5 K min^{-1}. After reaching the expected temperature, the system was kept for 60 min. Nitrogen was supplied in the furnace until the furnace was cooled externally by air to 100 °C. The boat was pulled out and the torrefied solid product was collected and weighted (Note: S-Temperature-time was used to denote the char obtained. e.g., S300–60 is indicative of the char torrefied at maximum temperature of 300 °C for retention time of 60 min).

2.3. Characterization of the products

The chemical components, including cellulose, hemicelluloses and lignin, were analyzed according to a previous report [13]. Monosaccharides and lignin mass fractions were determined by a Dionex chromatography HPAEC-PAD system [14]. The acid insoluble residue was reported as Klason lignin. The acid soluble lignin was determined on the hydrolyzed solution in a ultraviolet spectrometer (UV 2300, Shanghai Tianmei Science and Technology Corporation, China).

The elemental mass fractions (C, H, O, N and S mass fractions) were estimated using an elemental analyzer Vario EL III (Elementar, Germany). The atomic O/C and H/C ratios represent the ratio of atomic O to atomic C, and the ratio of atomic H to atomic C, respectively. HHV was estimated based on the elemental analysis data as the formula below:

$$\mathrm{HHV}\left(\mathrm{MJ\ kg^{-1}}\right) = 0.3383 Z_C + 1.422 (Z_H - Z_O/8);$$

where Z_C, Z_H, and Z_O are the mass fractions of C, H, and O, respectively (since no N and S mass fractions were detected and the calculation was conducted excluding the ash mass fraction) [15]. The mass and energy yields were calculated according to the equations below:

$$\text{Mass yield } (\%) = M_{\text{Torrefied bamboo}} \Big/ M_{\text{Original bamboo}} \times 100$$

$$\text{Energy yield } (\%) = \text{Mass yield} \times \mathrm{HHV}_{\text{Torrefied bamboo}} \Big/ \mathrm{HHV}_{\text{Original bamboo}} \times 100$$

where $M_{\text{Torrefied bamboo}}$ and $M_{\text{Original bamboo}}$ are the mass of bamboo after and before torrefaction on dry basis, and $\mathrm{HHV}_{\text{Torrefied bamboo}}$ and $\mathrm{HHV}_{\text{Original bamboo}}$ are the HHV of the bamboo after and before torrefaction, respectively.

FTIR and Solid CP/MAS ^{13}C NMR spectra were recorded according to the method in a previous report [10]. SEM images of the samples were taken at a scanning electron microscope (S–3400N, HITACHI, Japan) at acceleration voltages of 10 kV. The sample was coated with gold-palladium in a sputter coater (E–1010, HITACHI, Japan) before the experiment. The mass fraction of absorbed moisture of the sample at 6, 12, 24, 48, and 72 h was determined following the previous procedure evaluate the water absorption capacity [16].

3. Results and discussion

3.1. Change of the components of bamboo after torrefaction

A series of experiments was conducted to investigate the effect of torrefaction temperature and holding time on the treatment of bamboo. In the first set, bamboo was torrefied at 280, 300, 320, 340 °C with fixed holding time of 60 min, while in the other set, bamboo was torrefied at 300 °C with varied holding times of 10, 30 and 90 min, respectively. The data are given in Table S1 (in Supplementary data). The variation of the mass yield of the solid product defined as the mass ratio of dry solid to that of the original bamboo is plotted in Fig. 1(a). With the increase of temperature from 280 °C to 340 °C, the mass yield decreased from 84.08% to 41.93%. Clearly, a high temperature resulted in more release of bamboo mass. In addition, in the torrefaction at 300 °C, the prolongation of holding time from 10 min to 90 min also led to the decrease of the yield from 84.83% to 44.20%. The color of bamboo changed from light brown into dark brown and heavy black with