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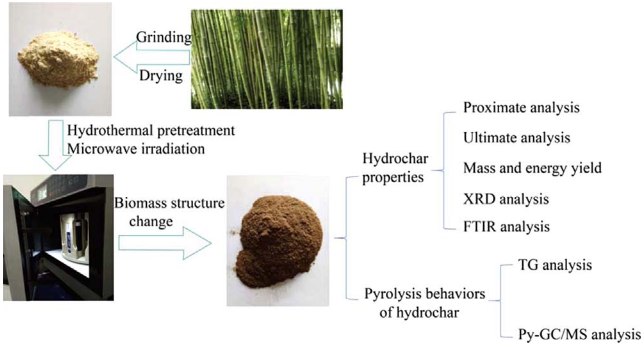
Hydrothermal pretreatment of bamboo sawdust using microwave irradiation

Leilei Dai[a,b], Chao He[d], Yunpu Wang[a,b,*], Yuhuan Liu[a,b], Roger Ruan[a,b,c], Zhenting Yu[a,b], Yue Zhou[a,b], Dengle Duan[a,b], Liangliang Fan[a,b,c], Yunfeng Zhao[a,b]

[a] *State Key Laboratory of Food Science and Technology, Nanchang University, Nanchang, Jiangxi 330047, China*
[b] *Engineering Research Center for Biomass Conversion, Ministry of Education, Nanchang University, Nanchang, Jiangxi 330047, China*
[c] *Center for Biorefining and Department of Bioproducts and Biosystems Engineering, University of Minnesota, 1390 Eckles Ave., St. Paul, MN 55108, USA*
[d] *School of Environmental Science and Engineering, Sun Yat-sen University, Guangzhou 510006, China*

GRAPHICAL ABSTRACT



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ABSTRACT

In the present study, the effect of temperature and residence time during microwave hydrothermal pretreatment (MHT) on hydrochar properties and pyrolysis behaviors was investigated. Experimental results indicated that higher heating value (HHV) and fixed carbon content gradually increased with increased pretreatment severity. Obvious reduction of oxygen content was found under MHT at 230 °C-15 min and 210 °C-35 min. Although lower mass yield was observed under severe conditions, corresponding energy yield was relatively higher. Crystallinity indexes of hydrochar demonstrated an upward trend with increased residence time. Unlike hydroxyl group, dissociation of acetyls was more favorable under prolonged residence time rather than increased temperature. Peaks in thermogravimetric and derivative thermogravimetric curves shifted to higher temperature region under severe conditions, indicating better thermal stability. Py-GC/MS analysis suggested that acids content was decreased but sugars increased with increased MHT severity. Moreover, compared to temperature, residence time was mainly responsible for acetic acid formation.

1. Introduction

The declining fossil fuels and deteriorating environment have spawned the development on green renewable energy (Doddapaneni et al., 2016; Nguyen et al., 2017). Biomass with the advantages of abundance, carbon neutral and low cost can be converted into desired fuels or chemicals. Therein, pyrolysis is a promising technology due to its eco-friendly and cost-effective characteristic, which can produce bio-

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[*] Corresponding author at: MOE, Engineering Research Center for Biomass Conversion, Nanchang University, 235 Nanjing East Road, Nanchang, Jiangxi 330047, China.
E-mail address: wangyunpu@ncu.edu.cn (Y. Wang).

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oil, gas and bio-char from biomass (Chen et al., 2016). However, the large-scale application of pyrolysis technology is hindered by the high oxygen content, chemical instability and corrosivity. According to the previous study by Chen et al. (2017a), the poor bio-oil quality is directly caused by low-quality raw material. In this way, biomass pretreatment before pyrolysis is very necessary to obtain appropriate pyrolysis substrate with high energy density, easily grinding and good fuel characteristics (Chen et al., 2017b; Zheng et al., 2015).

Hydrothermal pretreatment, also named wet torrefaction, is conducted in hot compressed water at the temperatures ranging from 150 °C to 260 °C, which has been considered as an effective biomass pretreatment technology. During the hydrothermal pretreatment, hemicellulose in biomass is decomposed into lightweight compounds, the lignin seal is broken, and the crystallized cellulose bundles remained in residue as the main component of solid product (Zheng et al., 2015). The effect of hydrothermal pretreatment on the physicochemical properties and thermal behaviors of biomass has been widely studied. Chang et al. (2013) found that hydrothermal pretreatment did not cause significant charring and carbonization of biomass constituents and the lower content of ketones and acids, higher content of levoglucosan in the pyrolysis oil were obtained. Zhang et al. (2017) evaluated the physicochemical properties and pyrolysis product properties of hydrochar from wet torrefied rice husk, confirming that wet torrefaction can achieve the improved fuel characteristics of rice husk and removal of minerals with the dual function of dry torrefaction and demineralization. In addition, the levoglucosan content in bio-oil was remarkably enhanced, and the obtained biochar can be used to produce nanosilica. It should be noted that the high levoglucosan content in the bio-oil from pyrolysis of wet torrefied biomass is attributed to the removal of alkali metals (Zheng et al., 2015). Also, wet torrefaction is recognized as a more promising pretreatment technology for biomass fast pyrolysis compared to dry torrefaction in terms of biomass structure and pyrolysis behaviors (Zheng et al., 2015). Le Roux et al. (2015) have reported that hydrothermal pretreatment improved the biomass grindability, which can reduce the grinding cost of fast pyrolysis process. The reduction of hydroxyl group and decomposition of some organic groups are conductive to improving the hydrophobicity and stability of biomass, enhancing biomass storage cycle (Zhang et al., 2016a).

However, few published literatures demonstrated the effect of microwave hydrothermal pretreatment on biomass structure and pyrolysis behaviors. Microwave is a high-frequency electromagnetic radiation (300 MHz–300 GHz) with the heating mechanisms of dipole rotation and ionic conduction (Wang et al., 2016). As an unique heating way, microwave heating has been universally applied in thermochemical conversion of biomass (Beneroso et al., 2017; Feng et al., 2016). In terms of the hydrothermal pretreatment process, microwave heating is more suitable for upgrading the quality of pyrolysis oil than conventional heating (Dai et al., 2017a). More importantly, microwave heating presents many advantages over conventional heating, such as higher energy recovery, less unit operations, selective heating mode and precise control (Beneroso et al., 2017; Dai et al., 2017b). In this regard, it is more promising to use microwave technology for industrial applications compared to conventional heating. In addition, hydrochar from microwave hydrothermal pretreatment produce more value-added products in the pyrolysis and less acid compounds, which can facilitate the development of hydrothermal pretreatment in the industrial applications. Therefore, microwave heating is more attractive for hydrothermal pretreatment during industrial applications.

According to our previous study, microwave heating can remove more oxygen content and enhance the calorific value of hydrochar over conventional heating. Moreover, microwave hydrothermal pretreatment is more suitable for upgrading the pyrolysis oil quality than conventional hydrothermal pretreatment (Dai et al., 2017a). Therefore, it has great significance to study the microwave hydrothermal pretreatment process and optimize the operation conditions. This study investigates the effect of MHT on hydrochar properties and its pyrolysis behaviors at different pretreatment temperatures and residence times. The hydrochar properties were determined by proximate and ultimate analysis, FTIR spectrum, XRD analysis. Thermogravimetric and Py/GC-MS analysis were conducted to evaluate the pyrolysis behaviors of hydrochar. This work will help to provide reference with a large-scale MHT process.

2. Materials and methods

2.1. Materials

The raw material, moso bamboo (*Phyllostachys heterocycla var pubscense*) sawdust, was from a bamboo processing mill in Jiangxi, China. The samples were sifted using a 60-mesh sieve. Then these obtained particles were dried in the absence of oxygen at 105 °C overnight before pretreatment.

2.2. MHT experiment

MHT was carried out at the temperatures ranging from 150 °C to 230 °C for the residence times varying from 5 min to 35 min in a microwave digestion system (MDS-6G, SINEO Microwave Chemistry Technology Co., Ltd.). In this study, the pressure in the reaction vessel achieved the maximum value (4.0 MPa) of this device at the temperature of 230 °C. In this way, the highest pretreatment temperature was selected as 230 °C. In a typical run, a mixture of bamboo sawdust and distilled water (bamboo sawdust: water = 1:10 w/w) were introduced into a 100 mL reaction vessel (Modified Teflon Material), and then the reaction vessel was sealed. Five reaction vessels was heated at the same time in the microwave digestion system at the microwave power of 800 W. The pressure during the pretreatments is absolutely caused by the augment of temperature. After hydrothermal pretreatment was completed, the reaction vessel was cooled to room temperature, and then bamboo sawdust and distilled water were separated by filtration under vacuum. The bamboo sawdust was washed three times with distilled water, and then dried in the absence of oxygen at 105 °C overnight for the subsequent analysis.

2.3. Characterization of raw sample and hydrochar

The proximate analysis of raw sample and hydrochar was conducted according to ASTM E870-82 (2013). The ultimate analysis were determined by an elemental analyzer (Vario EL III, Elementar, Germany). The high heating value (HHV) was measured by a calorimeter (DY-ZDHW-6, Hebi Daewoo Instrument Co., Ltd., China). Mass yield and energy yield were calculated based on the following Eqs. (1) and (2).

$$\text{Mass yield} = \frac{mass\ \ of\ \ pretreated\ \ samples}{mass\ \ of\ \ raw\ \ samples} \times 100\% \tag{1}$$

$$\text{Energy yield} = \text{mass yield} \times \frac{HHV\ \ of\ \ pretreated\ \ samples}{HHV\ \ of\ \ raw\ \ samples} \times 100\% \tag{2}$$

The cellulose crystallinity of raw sample and hydrochar was measured using a Bruker D8 ADVANCE X-ray diffractometer (XRD). The test conditions were as follow: Cu Kα radiation (1.5418 nm), the generator voltage of 40 kV, the generator current of 40 mA, the scanning range of 5–50°, the scanning rate of 2°/min with a step of 0.02°. The cellulose crystallinity index (CrI) was calculated according to Eq. (3).

$$\text{CrI} = \frac{I_{002}-I_{am}}{I_{002}} \times 100\% \tag{3}$$

where I_{002} is the intensity of the diffraction of (0 0 2) plane at $2\theta = \sim 22.5°$, and I_{am} is the intensity of amorphous region at $2\theta = \sim 18.7°$ (Segal et al., 1959).

FTIR analysis was conducted using a Fourier transform infrared