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Comparative study on microwave and conventional hydrothermal pretreatment of bamboo sawdust: Hydrochar properties and its pyrolysis behaviors

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ABSTRACT

Comparative study on microwave and conventional hydrothermal pretreatment of bamboo sawdust was carried out in this study. Microwave and conventional hydrothermal pretreatment both improved the hydrochar properties and its pyrolysis behaviors. Proximate and elemental analyses show that the properties of hydrochar from microwave hydrothermal pretreatment are better than conventional hydrothermal pretreatment in terms of calorific value and oxygen content except for 150 °C. Microwave hydrothermal pretreatment removes more acetyl groups in hemicellulose compared to conventional hydrothermal pretreatment, which may be attributed to the hot spot effect of microwave irradiation. The peaks of thermogravimetric and derivative thermogravimetric curves of pretreated samples always shifted to higher temperature region. Also, the conventional hydrothermal pretreated samples are more thermally stable than those by microwave heating. In addition, the glucopyranose content in pyrolysis vapors of microwave hydrothermal pretreated bamboo sawdust (190 °C) was 9.82% higher than that from conventional hydrothermal pretreated bamboo sawdust. However, the acids content from microwave hydrothermal pretreated bamboo sawdust (150 °C) was 4.12% lower. In this regard, microwave hydrothermal pretreatment is more suitable for upgrading the pyrolysis oil quality than conventional hydrothermal pretreatment.

1. Introduction

Lignocellulosic biomass has been recognized as an important renewable feedstock for chemicals and fuels, especially when the excessive consumption of fossil fuels caused severe environmental pollution and energy crisis [1,2]. Pyrolysis as an eco-friendly and commercially viable manner to produce biomass-derived bio-oil attracted much attention in recent years [3,4]. However, the low quality of biomass feedstock including low heating value and energy density, high oxygen and water content brought the obtained bio-oil a series of drawbacks, which limited the application of pyrolysis technology [5]. The presence of minerals in biomass also influence the quality of pyrolysis oil [6]. In consequence, pretreatment prior to pyrolysis is needed to improve biomass characteristics for high-quality bio-oil production.

Hydrothermal pretreatment, otherwise known as wet torrefaction, is a promising thermochemical pretreatment technology to enhance the fuel characteristics of biomass and bio-oil quality [7,8]. After pretreatment, the grindability and hydrophobicity of biomass are improved, reducing the cost of grinding and storage in the biomass utilization process [5]. In this regard, the cost of biomass pretreatment is offset partly, which enhances the economic feasibility of this process. Many literatures have reported the effects of wet torrefaction on the physicochemical properties and pyrolysis products of biomass. Zhang et al. [9] studied the changes of fuel characteristics of duckweed after wet torrefaction, finding that wet torrefaction resulted in the significant decrease of oxygen

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content by dehydration and decarboxylation and the increase of fixed carbon and high heating value (HHV). It is confirmed by them 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 [10]. Chao et al. [11] demonstrated that higher bio-oil yield and lower contents of ketones and acids were obtained by hydrothermal pretreatment compared to untreated samples. In addition, hydrothermal pretreatment can remarkably increase the content of levoglucosan in bio-oil and improve the fuel quality of bio-oil. Bach et al. [12] pointed out that wet torrefaction make biomass feedstock more homogeneous to use the common parameters for pyrolysis kinetic model of different biomass. Feng et al. [13] reported that formic acid pretreatment of biomass under irradiation enhanced the content of aromatics and suppressed the formation of coke in the pyrolysis process.

Bamboo is an abundant plant with the advantage of high growing rate, strong ability to reproduce, updating easily [14]. Bamboo sawdust produced from bamboo treating process is usually used to burn for heating or discard carelessly. Hence, there is the very vital significance to take full advantage of bamboo sawdust for renewable energy production by pyrolysis. From the perspective of the heating way, microwave-assisted heating is very different from other heating methods considering the principle of heating. Microwave is a high-frequency electromagnetic radiation (300 MHz–300 GHz) with the heating mechanisms of dipole rotation and ionic conduction [15]. Conventional hydrothermal pretreatment has been widely investigated, but the study on the microwave hydrothermal pretreatment was reported seldomly. A comparison of the effect of microwave and conventional hydrothermal pretreatment on hydrochar characteristics and its pyrolysis behaviors is presented in this work for the first time.

In this study, microwave and conventional hydrothermal pretreatment were used to improve the hydrochar properties and its pyrolysis behaviors. Herein, microwave and conventional hydrothermal pretreatment with the temperature varying from 150 °C to 230 °C for 30 min were conducted. Proximate and elemental analysis, mass and energy yield analysis and FTIR analysis were used to evaluate the hydrochar properties and raw sample. TG analysis and Py/GC–MS analysis were carried out to evaluate the pyrolysis behavior of hydrochar and raw sample. The differences in the hydrochar properties by microwave and conventional hydrothermal pretreatment were investigated. Comparison between pyrolysis behaviors of hydrochars from different heating ways can guide the optimization of pretreatment process to upgrade pyrolysis oil.

2. Materials and methods

2.1. Materials

Bamboo sawdust of moso bamboo (*Phyllostachys heterocycla var pubscense*) from a bamboo processing mill in Jiangxi of China was selected as raw material in this study. The samples were dried in the absence of oxygen at 105 °C for 12 h prior to hydrothermal pretreatment.

2.2. Microwave and conventional hydrothermal pretreatment

Microwave hydrothermal pretreatment (MHP) was carried out in a microwave digestion system (MDS-6G, SINEO Microwave Chemistry Technology Co., Ltd.). In a typical run, 5 g of bamboo sawdust samples and 50 mL of distilled water were introduced into a 100 mL reaction vessel (Modified Teflon Material). Thereafter the reaction vessel was placed in the microwave digestion system to heat at the microwave power of 800 W. Five reaction vessels were disposed at the same time. Conventional hydrothermal pretreatment (CHP) was conducted in an autoclave reactor (4566, Parr Instrument Company). 15 g of bamboo sawdust samples and distilled water (the same ratio with microwave hydrothermal pretreatment) were placed in the reactor, which was heated by the heater outside the reactor with the average heating rate of 10 °C/min. The two pretreatments by microwave and conventional heating was achieved at the temperatures of 150 °C, 190 °C, 230 °C for 30 min, and the pressure during the pretreatments is absolutely caused by the augment of temperature. After hydrothermal pretreatment (HP) was completed, 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. All experiments were conducted in triplicated.

2.3. Characterization of the raw sample and hydrochar properties

The ash content, fixed carbon content and volatile content of raw sample hydrochar were measured according to ASTM E870-82 (2013). The C, H, N and O contents were determined using an elemental analyzer (Vario EL III, Elementar, Germany). High heating value (HHV) was measured using a calorimeter (DY-ZDHW-6, Hebi Daewoo Instrument Co., Ltd., China). All experiments were conducted in triplicated to assure experimental reproducibility. Mass yield and energy yield were calculated based on the following equations:

$$Energy\ yield = mass\ yield \times \frac{HHV\ of\ pretreated\ samples}{HHV\ of\ raw\ samples} \times 100\% \quad (1)$$

$$\text{Mass}\ yield = \frac{\text{mass}\ of\ pretreated\ samples}{\text{mass}\ of\ raw\ samples} \times 100\% \quad (2)$$

FTIR spectra was obtained using a fourier transform infrared spectrometer (Nicolet iS5, Thermo, USA) in the wave number range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1} and 32 scans. It is presented in FTIR spectra that the chemical structure was changed as a function of temperature and heating ways.

2.4. TG analysis of raw sample and hydrochar

TG analysis of raw sample and hydrochar was performed to understand the thermal behavior of biomass using a thermogravimetric analyzer (TGA 4000, PerkinElmer, USA). Prior to TG analysis, all samples were dried in the absence of oxygen at 105 °C to constant weight. For a typical experiment, 4 mg samples with the particle size of 200 mesh were used to conduct TG and DTG analysis. A high-purity N_2 was applied to provide the pyrolysis experiment with an inert atmosphere at a flow rate of 100 mL/min. The experiment started from room temperature, and samples were heated from 30 °C to 800 °C at a constant heating rate of 10 °C/min.

2.5. Py-GC/MS analysis of raw sample and hydrochar

Pyrolysis experiments were conducted at 550 °C in a double-shot pyrolyzer (PY-2020iD, Binder, Germany). In each run, approximately 0.5 mg samples with the particle size of 200 mesh was introduced into quartz reactor. High-purity helium was used as the carrier gas to maintain an inert atmosphere with a constant flow rate of 1 mL/min. Then the samples were heated rapidly to desired temperature at a heating rate of 20 °C/ms and maintained for 30 s. The pyrolysis vapors were directly swept into a gas chromatography/mass spectrometry (GC/MS) equipped with the