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Combined different dehydration pretreatments and torrefaction to upgrade fuel properties of hybrid pennisetum (*Pennisetum americanum* × *P. purpureum*)

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ABSTRACT

Different dehydrating methods combined with torrefaction were investigated to find the underlying mechanism that how dehydration process influence the degree of hornification. Hybrid pennisetum was selected as the experiment material. Oven-dried sample (ODS), crushed dried sample (CDS), and sun-cured dried sample (SDS) were torrefied under the temperature of 275 °C and 300 °C with the duration time of 60 min. The results showed that, changes in elevated carbon content and higher heating value (HHV) and reduced oxygen content of SDS were the most obvious under identical torrefaction conditions. Fuel ratio of SDS was enhanced most under 300 °C. It also had the highest devolatilization index (D_i). The combination of sun-cured dried with torrefaction under 300 °C caused lowest degree of irreversible hornification happened during dehydrating process, and different hornification degrees caused by different dehydrating methods effect the enhancement of fuel properties of lignocellulosic biomass material.

1. Introduction

With increasing global population and rising living standards, the demand for energy has grown significantly over the past few years (Chen et al., 2015a). The limited stockpile of traditional fossil fuel and increasing concerns of the climate change caused by greenhouse gas emission make energy usage become an increasingly important topic worldwide (Chen et al., 2014). That draws researchers more attention to sustainable and renewable energy sources (Gu et al., 2014). Among popular renewable energy sources, biomass is a promising renewable energy to replace fossil fuels (Huang et al., 2017).

Biomass can be transformed into combustible gases by gasification and liquid fuels by pyrolysis, transesterification, fermentation, and saccharification (e.g. Erlich and Fransson, 2011). It can also be utilized as a solid fuel and burned directly to generate of heat and power (Kinoshita et al., 2010; Zhang et al., 2015). However, biomass always has high moisture content, heterogeneity of material, poor biological stability, and low energy density. These drawbacks make it difficult to use and increase processing, transportation and storage costs. Pretreatment is a good way to overcome these issues (Arias et al., 2008; Toscano et al., 2015). There are many pretreatment methods such as drying, acid hydrolysis, torrefaction, etc. Torrefaction is a mild thermochemical pyrolysis process within the temperature window of 200–300 °C. Pretreatment of biomass in an inert atmosphere without presence of oxygen has been employed to improve fuel properties of solid biomass and has received more and more attention in recent years (Tran et al., 2013). During torrefaction, the biomass loses moisture and a proportion of the volatile content and then becomes dry, darker, and brittle. The main benefits of torrefaction include higher energy density and hydrophobicity, higher calorific value, lower atomic O/C and H/C ratios, and better grindability and reactivity (Yan et al., 2010). Temperature, residence time and particle size are top three factors that affect the torrefaction. Bridgeman et al. (2010) found that the effect of temperature was the most significant, duration was the second, , and particle size was the least. In previous research, the temperature selected was between 200 °C and 300 °C, and duration time was controlled within 1 h considering energy efficiency and results (Chew and Doshi, 2011). Previous study showed that the internal diffusion of vapors generated inside particles affected the rate of torrefaction (Peng et al., 2012), and this influence decreased when particle size was smaller than 1 mm.

Many studies have been done to detect the effectiveness of the combination of pretreatment methods. A combination of aqueous phase bio-oil washing and torrefaction was investigated (Chen et al., 2017).

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Combining acid washing and torrefaction pretreatment to improve the fuel characteristics also was proposed (Ukaew et al., 2017). However, acids and ionic liquids washing are chemical pretreatment methods which are toxic, high-cost, and corrosive. Thus, the usage of chemical pretreatment methods is limited (Bai et al., 2017). On the contrary, dehydration is an environmentally friendly method and widely used in storage and process of agricultural products. However, it was barely used as a pretreatment method, and no dehydrating-torrefaction combination pretreatment was studied. Furthermore, irreversible hornification is widespread during dehydration process that caused changes on fiber structure of the cell wall. That will lead the differences in many aspects of fuel properties such as HHV, element contents and devolatilization ability. Thus, as the perennial C4 plant with high photosynthetic rate, which has the similar hemicellulose and cellulose contents as common hardwood (Bridgeman et al., 2008), hybrid pennisetum was selected as the experimental material based on its potential to be a renewable energy resource.

The objectives of this research were to examine the underlying mechanism and to understand how the dehydration process influences the degree of hornification. Hybrid pennisetum samples processed with different dehydrating methods were torrefied and then characterized from chemical and physical points of view in order to evaluate the effects of different pretreatment methods on its physicochemical properties. Torrefection temperatures were 275 °C, and 300 °C with a residence time of 60 min. Physical and chemical characterizations were performed for raw and torrefied biomass through proximate and ultimate analysis, mass yield and energy yield, HHV, and devolatilization ability under the nitrogen atmosphere.

2. Materials and methods

2.1. Raw materials

Raw hybrid pennisetum was harvested and obtained from Guangdong Province, China in 2017. Crop samples were harvested at different growing stages. Crop heights were 1.2 m, 1.8 m, 2.5 m, and 4.0 m (the mature crop height), respectively, when they were harvested. Harvested crops were collected and then cut into 10–15 cm length. The initial moisture contents of the raw hybrid pennisetum were 89.4%, 86.2%, 80.2%, and 76.61% (wet basis), respectively. Crop sample from each growing stage was divided into three groups. Then, these groups were oven-dried, crushed dried, and sun-cured dried, respectively. . For the oven-dried method, samples were dried in the oven (DHG-9240A, China) at 105 °C for 24 h. For the crushed-dried method, crops were crushed with a universal testing machine (SUNS UTM5504X, China) before sun cure. Stems were laid flat on the test platform and crushed down to 50% of their diameters. All samples were milled to 1 mm using a hammer mill (TRF-70) after the moisture contents were under 15%. Processed samples were stored in ziplock plastic bags and kept refrigerated during experiments.

2.2. Torrefaction experiments

The torrefaction experiments were done in a fixed-bed tubular rector (SK-G08123K; Tianjin Zhonghuan Experimental Furnace Co. Ltd., China), which consisted of a tubular unit, gas supply, and an electric heater. The reactor was preheated to the set temperature before torrefaction. The biomass material was carried by a moving quartz ark and heated with a flow of nitrogen (99.99%, 0.5 L/min) to prevent oxidation. The setting torrefaction conditions were 275 °C and 300 °C with the duration time of 60 min. Each experiment was repeated twice.

2.3. Characterization of biomass sample

2.3.1. Ultimate and proximate analysis

The carbon, hydrogen, sulfur, and nitrogen contents of both raw and torrefied samples were measured with an Elementar Vario EL II (Vario Macro, Germany), while the oxygen content was calculated by difference. Proximate analysis was performed according to standard analysis methods including ASTM D3174-04 for analyzing ash content and ASTM D3175-89 for volatile matter (VM) analysis. The fixed carbon (FC) was calculated by difference.

Fuel ratio was used to evaluate the combustibility of coal and biochar after torrefaction. It is a crucial indicator to compare the similarity of biochar and coal. It was calculated by Eq. (1) (Huang et al., 2017).

$$\textit{Fuel ratio} = \textit{Fixed carbon content}/\textit{Volatile matter content} \tag{1}$$

2.3.2. Torrefaction yield

Mass yield, energy yield, and energy density were calculated to explore torrefaction yield and energy density. Mass yield, energy yield, and energy density were calculated with Eqs. (2), (3), and (4), respectively (Bridgeman et al., 2008). HHV was calculated by Eqs. (5) proposed by Friedl et al. (2005).

$$\textit{Mass yield}\ (YM) = \textit{Mass of torrefied biomass}/\textit{Mass of raw biomass} \times 100\% \tag{2}$$

$$\textit{Energy yield}\ (YE) = \textit{HHV of torrefied biomass}/\textit{HHV of raw biomass} \times YM \tag{3}$$

$$\textit{Energy density} = \textit{energy yield}/\textit{mass yield} \tag{4}$$

$$HHV = 232{\cdot}C^2 - 232{\cdot}C - 2230{\cdot}H + 51.2{\cdot}C{\cdot}H + 131{\cdot}N + 20600,\ \ \text{kj/kg} \tag{5}$$

2.3.3. X-ray diffraction (XRD) analysis

XRD experiments were conducted with a D8 ADVANCE X-ray diffractometer (Bruker, Germany) using Cu-K at 40 kV, 40 mA and 2 kW in the scanning range of 5–40° at the rate of 2°/min with 0.02° increments. Crystallinity Index (*CrI*) was used to characterize the crystallinity of the raw and torrefied cellulose based on the diffracted intensity, as shown in Eq. (6):

$$CrI\,(\%) = (I_{002} - I_{am})/I_{002} \times 100\% \tag{6}$$

where I_{002} was the 002 diffraction peak intensity located at the 2θ around 22°, which was a representative of crystal part of the sample, and I_{am} was the lowest intensity at the 2θ around 18°, used to define the amorphous part (Wang et al., 2017b).

2.3.4. Morphology analysis

Scanning electron microscopy (SEM) and specific surface area (SSA) were used to evaluate morphology changes of samples. SEM (JSM-6700F, JEOL) was used to record electron micrographs. All samples were dried at 40 °C for 48 h before test. ASAP 2010 instrument (Micromeritics instrument Co., Ltd, Norcross, GA, USA) was used to determine the relationships between the equilibrium adsorption pressure and the amount of adsorbed gas. Samples were placed in a liquid nitrogen environment to make nitrogen be adsorbed and desorbed. The SSA was calculated by fitting the adsorption curve according to the BET sorption process.

2.3.5. Fourier-transform infrared (FTIR) spectrometer analysis

FTIR (Spectrum100, ONE, Two, RX1, RX-I, 2000, USA) was used to characterize the changes of the typical functional groups in samples during torrefaction. The samples were mixed with KBr at a mass ratio of 1:100 and were ground to 160–200 mesh. Then, the mixture was loaded into a diffuse reflectance sampling head and kept flat. The spectra were recorded between 4000 and 400 cm^{-1} with a resolution of 4 cm^{-1} and the scan rate of 128 min^{-1}.

2.3.6. Thermogravimetric (TG) analysis

TG experiments for samples were carried out using a DTG-60