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Comparison of the effect of wet and dry torrefaction on chemical structure and pyrolysis behavior of corncobs

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HIGHLIGHTS

- Both wet and dry torrefaction removed hemicellulose from corncobs.
- Dry torrefaction caused more significant structural change than wet torrefaction.
- Wet torrefaction dramatically improved levoglucosan yield from fast pyrolysis.

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ABSTRACT

Wet and dry torrefaction of corncobs was conducted in high-pressure reactor and tube-type reactor, respectively. Effect of wet and dry torrefaction on chemical structure and pyrolysis behavior of corncobs was compared. The results showed that hemicellulose could be effectively removed from corncobs by torrefaction. However, dry torrefaction caused severe degradation of cellulose and the cross-linking and charring of corncobs. X-ray diffraction analysis revealed that crystallinity degree of corncobs was evidently enhanced during wet torrefaction, but reduced during dry torrefaction as raising treatment temperature. In thermogravimetric analysis, wet torrefied corncobs produced less carbonaceous residues than raw corncobs, while dry torrefied corncobs gave much more residues owing to increased content of acid insoluble lignin. Pyrolysis–gas chromatography/mass spectroscopy analysis indicated that wet torrefaction significantly promoted levoglucosan yield owing to the removal of alkali metals. Therefore, wet torrefaction can be considered as a more effective pretreatment method for fast pyrolysis of biomass.

1. Introduction

The negative impact of the increasing use of limited fossil fuels on environment and energy security has urged the development of green renewable energy sources (Demirbas, 2009a). Biomass has been considered as an important renewable resource for the future, which can be converted into fuels and chemical feedstock by various technologies (Demirbas, 2009b). Owing to the structural heterogeneity and low volumetric energy density of biomass, pretreatment is usually needed to improve the efficiency of its conversion into end products (Chew and Doshi, 2011). Among all kinds of pretreatment technologies including thermal, physical, chemical methods or the combination of them, thermal pretreatment is a promising pretreatment method for thermochemical conversion of biomass. Dry torrefaction as one of thermal pretreatment technologies is generally performed at temperatures varying from 200 °C to 300 °C in the absence of oxygen. By the process, a uniform solid product spoken of as torrefied biomass with low moisture content, high energy density, enhanced grindability and hydrophobic properties is obtained (Bridgeman et al., 2008; Shang et al., 2012). The torrefied biomass is generally used as a feedstock for combustion or gasification. Compared to raw biomass, torrefied biomass is more reactive, and thus the efficiency of combustion and gasification can be improved (Chen et al., 2012; Couhert et al., 2009). In addition, the chemical composition of biomass is altered due to the typically thermal degradation of hemicellulose, and the volatiles consisting of plenty of water, organic acids and other lightweight compounds are released from biomass during dry torrefaction (Chang et al., 2012; Prins et al., 2006). It is well known that the poor quality of bio-oil from fast pyrolysis of biomass is mainly attributed to the existence of plenty of water and lightweight compounds. This suggests that dry torrefaction can be used as a pretreatment method prior to fast pyrolysis to produce high quality bio-oil. Some research studies on torrefaction-aided pyrolysis have been conducted, and it has been

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found that there were some positive influences of dry torrefaction on properties of bio-oil. More stable bio-oil with reduced concentration of water and organic acids and increased concentration of phenols and anhydrosugars has been obtained from fast pyrolysis of torrefied biomass (Meng et al., 2012; Zheng et al., 2012).

Wet torrefaction, another thermal pretreatment method, which is also known as hydrothermal pretreatment, is carried out in hot compressed water where the chemical structure of biomass is disturbed and the resulting solid product is facilitated to subsequent conversion (Holopainen-Mantila et al., 2013). Compared to dry torrefaction, the reaction temperature used for wet torrefaction is relatively lower, and the pressure is the saturated water vapor pressure. In wet torrefaction process, hemicellulose in biomass can be completely solubilized into aqueous compounds, the lignin seal is broken, and cellulose is almost entirely preserved in the solid product. Cellulose in the wet torrefied biomass is more readily accessible to enzyme, and the enzymatic digestibility of cellulose is enhanced. Thus wet torrefaction is considered as an effective pretreatment technology for subsequent enzymatic hydrolysis of cellulose (Cybulska et al., 2012; Rohowsky et al., 2013; Yu et al., 2011). As a result of the remarkable reduction in reactive hemicellulose of wet torrefied biomass, wet torrefaction may be also a potential pretreatment method prior to fast pyrolysis to improve quality of bio-oil through decreasing the formation of water and lightweight compounds mainly derived from reactive hemicellulose.

Although some similar changes in properties of biomass are observed in dry and wet torrefaction, there may be some differences in chemical structure of dry and wet torrefied biomass, which will contribute to divergences of pyrolysis behavior between them. A comparison of pyrolysis behavior of dry and wet torrefied biomass with the same mass yield will help to make a choice between two pretreatment methods for pyrolysis. However, reviewing recent literatures indicates that no such a study has been reported. In the present work, wet torrefaction of corncobs was carried out in a high-pressure batch reactor (autoclave) in the temperature range of 175–185 °C for 5 min, while dry torrefaction of corncobs was performed in a tube-type reactor at 245 and 265 °C for 20 min. Chemical structure and pyrolysis behavior of wet and dry torrefied corncobs were respectively examined. A comparative study was made to clarify different effects of wet and dry torrefaction on pyrolysis behavior of corncobs.

2. Methods

2.1. Material preparation

The corncobs were purchased from Baodi feed mill in Tianjin, China. The samples were ground to pass a BS 40-mesh sieve and retained on a BS 60-mesh sieve. Then these selected particles were oven-dried at 105 °C for 6 h before torrefaction.

2.2. Torrefaction experiment

Wet torrefaction of corncobs was carried out at 175, 185, and 195 °C in a high-pressure batch reactor detailed in a previous paper (Chang et al., 2013). A mixture of corncobs and water (corncobs:water = 1:9 w/w) was put into the reactor, and then the reactor was sealed. Before heating the reactor, nitrogen gas was passed through it at a flow rate of 1 L/min for 20 min to eliminate the presence of oxygen. Then the reactor with magnetic agitator operating at 600 rpm was heated using an electric furnace up to the target temperatures within 10–15 min. When the reactor reached the reaction temperature, the electric furnace was moved away. After maintaining the reaction temperature for 5 min, the reactor was cooled quickly to <100 °C using a coolant box filled with cooling water. The wet torrefied corncobs were obtained by filtrating the reaction products including solid residue and liquid product, and washed carefully with water for several times. The solid residue was weighed after it was oven-dried at 105 °C for about 15 h.

Dry torrefaction of corncobs was conducted in a tube-type reactor made of quartz. About 2 g of samples were placed in a porcelain boat, and the loaded boat was then pushed into the center of the reactor at room temperature. The center of reactor was heated using a ribbon heater at a heating rate of 10 °C/min under the inert environment up to the desired temperature (245 and 265 °C). After 20 min of torrefaction, the boat was moved to the end of reactor for cooling the samples to the ambient temperature. Then the dry torrefied samples were recovered and weighed. The mass yield of torrefied corncobs was calculated as the dry weight of original corncobs divided by the dry weight of torrefied corncobs. Three parallel experiments were performed for each reaction temperature, and all of experimental results were found to be highly reproducible. Torrefied corncobs were kept in the airtight sample bags and stored in a desiccator for characterization of chemical structure and pyrolysis behavior later.

2.3. Chemical composition analysis of solid samples

The contents of hemicellulose, cellulose, and acid insoluble lignin in solid samples consisting of raw and torrefied corncobs were determined by the National Renewable Energy Laboratory (NREL) method (Sluiter et al., 2008b). Firstly, the extractives in the sample were removed by exhaustive water and ethanol extraction. Then approximately 0.15 g of the extractives-free sample was weighed and treated with 72% H_2SO_4 for 1 h. Subsequently, the mixture was diluted with water of 42 ml and further hydrolyzed in an autoclave at 121 °C for 1 h. The hydrolysis solution was filtered by crucibles to separate the filtrate and residue. The sugars in the filtrate were analyzed by high performance liquid chromatography (HPLC). Conversion factors were used to convert monose concentrations into the contents of cellulose and hemicellulose in the sample. The residue was dried at 105 °C for 8 h, and the residue exclusive of ash was expressed as acid insoluble lignin in the sample. The reported results of composition analysis were the average of duplicate analysis. To investigate the decomposition degree of chemical component in torrefaction, a recovery rate of chemical component in torrefied corncobs is defined as follows:

$$\text{Recovery rate } (\%) = \frac{\text{component content in torrefied corncobs}}{\text{component content in raw corncobs}} \times \text{torrefied corncobs yield} \quad (1)$$

2.4. Elemental analysis

The contents of organic elements including carbon, hydrogen, nitrogen, and sulfur in solid samples were determined in an elemental analyzer (Vario EL cube, elementar, Germany). The ash content of the sample was determined by NREL method (Sluiter et al., 2008a). The oxygen content on dry basis was calculated from subtracting a hundred percentage with contents of ash, carbon, hydrogen, nitrogen and sulfur.

The analyses of main metal elements in solid samples were conducted by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) (Optima 8000, PerkinElmer, U.S.A.). For ICP-OES analysis, the sample of about 0.15 g was digested for about 6 h in the 4 ml mixed acids of concentrated HNO_3 and $HClO_4$ (3:1, v/v). Then the digested sample was diluted to 10 ml with