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Comparative study of the pyrolysis of lignocellulose and its major components: Characterization and overall distribution of their biochars and volatiles

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HIGHLIGHTS

- Significant elemental difference was not found among biochars from different samples.
- Carbonyl compounds were the major volatiles of polysaccharide pyrolysis.
- Aromatic compounds were the major volatiles of lignin pyrolysis.
- Except lignin, lignocellulosic material pyrolysis was mainly occurred at 200–400 °C.

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ABSTRACT

In order to investigate the pyrolysis differences among lignocellulose and its major components, the biochars and volatiles of lignocellulose (bamboo), lignin, hemicellulose and holocellulose (from bamboo), and cellulose (from cotton linter) were studied using elemental analysis, FTIR, XRD, SEM, Py-GC/MS and TGA–FTIR. Result showed that the biochar yield of lignin (48.8%) was much higher than those of hemicellulose (21.1%), cellulose (8.3%), holocellulose (20.4%) and bamboo (15.1%), while no obvious elemental difference among these biochars was found. Results from Py-GC/MS indicated that carbonyl compounds, ethers and alcohols were the major volatiles of polysaccharide component pyrolysis, while aromatic compounds were the major volatiles of lignin pyrolysis. The pyrolysis of polysaccharide component mainly occurred at 200–400 °C, while the pyrolysis of lignin happened at 300–700 °C.

1. Introduction

As we known, fossil fuels are limited and nonrenewable, excessive consumption of which has caused serious environment and energy issues. Lignocellulose is the most abundant, green and renewable source in the world, the utilization of which has drawn worldwide attention. Because of the heterogeneity and macromolecular characteristics of lignocellulose, sustainable processing of lignocellulose into a spectrum of fuels, power, heat and value-added chemicals is the key for lignocellulose utilization (Gallezot, 2012).

Generally, lignocellulose is composed of varying amounts of cellulose (38–50%), hemicellulose (23–32%), lignin (15–25%) and small amounts of extractives (McKendry, 2002). In lignocellulose, cellulose and hemicellulose are chain polysaccharides, while lignin is a heterogeneous, cross-linked three-dimensional phenyl-propane polymer, which closely associates with cellulose and hemicellulose (Mussatto et al., 2008). In principle, lignocellulose can be converted into energy or small molecular chemicals in many ways, such as direct combustion, pyrolysis, hydrothermal conversion, hydrolysis, etc. Among these methods, pyrolysis is one of the promising thermochemical conversion routes. Like cracking heavy hydrocarbons into light hydrocarbons in petrochemical industry, lignocellulose pyrolysis is intended to upgrade the biopolymers in lignocellulose into small molecular syngas, chemicals, liquid fuels and/or high grade biochars. However, lignocellulose pyrolysis, which involves various condensation polymerization, dehydration, dehydrogenation, deoxygenation and decarboxylation reactions, is quite complex (Demirbaş, 2000). Furthermore, the structural differences among cellulose, hemicellulose and lignin greatly influence their pyrolysis. To better understand the pyrolysis mechanisms of lignocellulose, comparatively investigating the characteristics of lignocellulosic components pyrolysis is very essential. For decades, numerous works have been carried

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out to investigate the pyrolysis of the major components of lignocellulose (Qu et al., 2011; Shen and Gu, 2009; Couhert et al., 2009; Yang et al., 2006, 2007), their corresponding model compounds (Nowakowski and Jones, 2008; Raeisaenen et al., 2003) and lignocellulosic raw materials (Di, 2008; Carrier et al., 2013; Abnisa et al., 2013; Nanda et al., 2013). Generally, the pyrolysis products can be divided into volatiles and biochars. Volatiles are small compounds formed by decomposition of the lignocellulosic materials, while biochars are produced from the condensation polymerization of lignocellulosic materials. Previous studies have extensively investigated the pyrolysis volatiles, such as volatiles distributions, releasing profiles, reaction pathway and mechanisms, as well as chemical kinetics of lignocellulose (Di, 2008; Lv and Wu, 2012; Yang et al., 2007). The element, chemical structure, crystal and morphology of biochars from the pyrolysis of lignocellulose and their major components have been also studied (Abnisa et al., 2013; Nanda et al., 2013). However, since the characterizations of volatiles and biochars are significantly different, few works focus on exploring the characterization and overall distribution of both the volatiles and biochars from lignocellulose and its major components, which is essential for better understanding the pyrolysis path and optimizing the pyrolysis conditions of different lignocellulosic materials.

In the present study, the pyrolysis characteristics of lignin, hemicellulose, cellulose, holocellulose and lignocellulose, their pyrolysis volatile distributions and biochars characterization were studied comparatively by using pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS), thermogravimetric analyzer coupled with Fourier transform infrared spectroscopy (TGA-FTIR), elemental analysis, FTIR, XRD, and SEM. The objective of this work is to better understand the overall flows of these materials during pyrolysis, which is of interest for further studies on lignocellulose pyrolysis into energy and value-added chemicals.

2. Methods

2.1. Materials

Bamboo (*Dendrocalamus membranaceus* Munro) as a representative of lignocelluloses was kindly provided by a pulp and papermaking factory (Yunnan, China). Bamboo was first ground into a fine powder, and then the powder between 60 and 80 mesh was collected for subsequent experimentation. The bamboo powder was treated by refluxing in a Soxhlet apparatus with toluene–ethanol (2:1, v/v) for 6 h to remove fats and waxes. The extractive-free bamboo raw material (BRM), representing lignocellulose in this study, consisted of cellulose (39.9%), acid insoluble lignin (23.2%), and hemicelluloses (26.3%) according to the method of NREL (Sluiter et al., 2008). Holocellulose from bamboo was obtained by delignification of the extractive free bamboo with sodium chlorite in acidic solution (pH 3.7–4.0, adjusted by 10% acetic acid) at 75 °C for 2 h. Xylan-rich hemicellulose was extracted from the holocellulose by using 10% KOH at 25 °C for 10 h with a solid to liquid ratio of 1:20 (g/mL) (Peng et al., 2010). The acid insoluble lignin was obtained according to the method of NREL (Sluiter et al., 2008). Cotton linter was purchased from local markets and the degree of polymerization of the linter cellulose used in this study was 780, according to the method of ISO/FDIS 5351:2009. The ash contents of lignin, hemicellulose, cellulose, holocellulose and BRM were 12.8%, 1.6%, 0.2%, 6.6% and 5.5%, respectively, according to the method in previous work (Sluiter et al., 2005).

2.2. Methods

The lignocellulosic materials were charred in a tube furnace under nitrogen atmosphere. The heating rate was 45 °C/min, and it took about 20 min to reach 900 °C. The pyrolysis process was held at 900 °C for 2.0 h. Then the samples were cooled to room temperature naturally to yield black biochars.

Elemental analysis was performed on a Vario EL cube universal CHNOS elemental analyzer (Elementar, Germany).

FT-IR spectra of lignocellulosic materials and their biochars were recorded on a Bruker spectrophotometer in the range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1}. KBr disc containing 1% finely ground sample was used for measurement.

Wavelength-dispersive X-ray fluorescence spectrometer (WD-XRF) was used to determine the element concentrations in lignocellulosic materials. Lignocellulosic samples were first burned to ashes, and then the ash samples were analyzed by a PANalytical PW-4400 XRF.

X-ray diffraction patterns of lignocellulosic materials and their char were performed on a D8 Advance instrument (Bruker AXS, Germany) with Ni-filtered Cu Kα radiation (wavelength = 0.154 nm) from 5° to 60°.

Scanning electron microscope (SEM) images of these lignocellulosic materials and their biochar samples were carried out on a ZEISS EVO 18 (Germany) to compare the structure of these lignocellulosic materials and their biochars before and after pyrolysis. The accelerating voltage of the instrument was maintained at 10.00 kV.

Py-GC/MS was carried out using a CDS 5150 series pyrolyser. Trace sample was placed into the pyrolysis tube and heated to 900 °C at a heating rate of 20 °C/ms. The volatiles were on-line analyzed by GC/MS (QP2010Plus, Shimadzu, Japan). The injector temperature was kept at 280 °C. The oven temperature was programmed from 50 °C (hold 2 min) to 250 °C (hold 2 min) with a heating rate of 10 °C/min. Helium (99.999%) was used as the carrier gas with a constant column flow rate of 1 mL/min and a split ratio of 1:30. The ion source temperature and interface temperature was kept at 230 °C and 280 °C, respectively. The mass spectra were obtained from m/z 30 to 700. The chromatographic peaks were identified by comparison with the NIST library.

TGA-FTIR of lignocellulosic material was performed on a NETZSCH STA 449C apparatus (Germany). The sample was heated from room temperature to 900 °C at a constant heating rate of 20 °C/min under the purified nitrogen atmosphere (99.999%). The volatiles in TGA were immediately transferred into a gas cell and on-line detected using FTIR (Bruker, Tensor 27). The temperature of transfer line and gas cell was set to 230 °C to avoid volatiles condensation. The FTIR spectra were recorded every 5 s in the wavenumber range of 4000–650 cm^{-1}.

3. Results and discussion

3.1. Biochar yields

Table 1 shows the biochar yields of different lignocellulosic materials from tube furnace pyrolysis and TGA pyrolysis. It can be observed that lignin had much higher biochar yield (48.8–50.9%) than hemicellulose (21.1–24.3%) and cellulose (8.3–11.4%). The biochar yields of lignin, hemicellulose and cellulose were well in accordance with the biochar residues from TGA analysis reported by Yang et al. (Yang et al., 2006, 2007). The biochar yields of holocellulose and BRM were 20.4–27.9% and 15.1–20.1%, respectively. The biochar products from tube furnace showed lower yields than those from TGA, which were likely caused by the long pyrolysis time. In addition, without special instruction the biochars in this work refer to those from tube furnace pyrolysis.