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Pyrolysis characteristics of poplar sawdust by pretreatment of anaerobic fermentation

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ABSTRACT

Pyrolysis characteristics of poplar sawdust (PS) pretreated by anaerobic fermentation were investigated by means of thermogravimetric analysis (TGA) and pyrolysis-gas chromatograph/mass spectrometry (Py-GC/MS) analysis. Results indicated that with an increase of pretreatment time from 0 to 20 days, the contents of cellulose and hemicellulose decreased from 54.05 and 17.96 wt. % to 51.29 and 12.61wt. % and the contents of the extractives and lignin increased from 1.41 and 26.58 wt. % to 7.31and 28.19 wt. %, respectively. The bio-pretreatment enhanced the starting pyrolysis temperature and increased the remains at 700 °C. Distinct weight loss of cellulose between 250–350 °C were observed at the TGA curves of P5, P10 and P20. Activation energy increased from 87.90 to 103.21 kJ mol^{-1}. The bio-oil yield and product distributions also changed. Sugars content firstly increased from 7.64 to 16.73% and then decreased to 13.70%. The content of linear carbonyls initially decreased from 12.40 to 8.64% and then increased to 14.39%. Phenols show similar changing pattern. Its content changed from 24.72 to 22.54 and then 25.03%. The contents of linear acids, linear ketones and furans decreased. The contents of laevoglucose, hydroxyl acetaldehyde and 1, 2-benzenediol in the bio-oil increased from 4.54, 10.78 and 3.07% to 12.30, 13.30 and 5.44%, respectively. This indicated the pyrolysis selectivity of PS was improved. Effects of anaerobic fermentation on wood pyrolysis behaviors were remarkably different not only from straw biomass but from that of white- and brown-rot fungi.

1. Introduction

The growing utilization of fossil fuels has resulted in some devastating problems such as global warming, environmental pollution and energy supply security. This has led to an increasing interest in the use of biomass due to abundant nature, wild-spread and renewable for different aims. The biomass can be converted into bio-char, bio-oil, biogas and even high-valued chemicals by a thermochemical or biochemical technology (Wang et al., 2009). As an important thermochemical technology, pyrolysis of biomass has been studied in past decades. Some fast pyrolysis reactors including fluidized bed (Heidari et al., 2014), rotating cone (Saleem and Nadeem, 2015) and spouted beds (Maria et al., 2018) have also been developed. The pyrolysis products and distributions were affected by the biomass composition, pyrolysis temperature, dwell time, particle size, reactors and so on. The chemical composition of biomass is very complex including cellulose, hemicellulose, lignin, extractives and minerals. Besides, the chemical composition of different kinds of biomass varies greatly. This is one of the main reasons for complex composition of bio-oil. Hundreds of organic compounds have been identified in the bio-oil. In order to improve the pyrolysis selectivity of biomass, biomass pretreatment technology was needed.

Biomass could be degraded into small molecular compounds such as bio-gas, bioethanol by microorganism. In this process, biomass chemical compositions were changed and physical structures were destroyed by the microorganism, which were contributed to promoting the pyrolysis reactions and changing the pyrolysis behaviors (Darshan and Akshaya, 2017; Vinciguerra et al., 2007; Gao et al., 2016; Yang et al., 2010). In our previous study (Wang et al., 2017), the pyrolysis characteristics of poplar wood (PW) during natural decay were researched. The results indicated that with an increase of decay degree from 0% to 60%, the contents of lignin and extractives increased from 23.9 and 7.51 wt. % to 39.85 and 26.06 wt. %, respectively; the decayed PW have better pyrolysis selectivity to phenols, which content significantly increased from 22.52% to 35.97%.

Various microorganism digested different chemical parts of biomass. Brown-rot fungi mainly degrade the cellulose, hemicellulose and extractives (Gao et al., 2016); white-rot fungi are considered to be the most efficient microorganism to degrade the lignin (Popescu et al., 2016); as the most important microorganism in the anaerobic

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fermentation, methanogen mainly degrade the extractives, cellulose and hemicellulose (Nualsri et al., 2016). In the previous researches (Pezzolla et al., 2017; Provenzano et al., 2014; Cavallo et al., 2018), anaerobic fermentation technology has often been used to dispose the organic matters with high holocellulose (cellulose + hemicellulose) content, high starch content or high organic acid content and so on. As the brown- and white-rot fungi, the methanogen should also have the good potential to pretreat the biomass for improving pyrolysis behaviors. In fact, our previous study had also confirmed that anaerobic fermentation pretreatment changed chemical compositions of corn stalk and improved its pyrolysis selectivity (Wang et al., 2014a, 2014b). Phenols content increased from 42.25 to 79.32% and 4-vinyl phenol (4-VP) content increased from 28.6 to 60.9% at 250 °C.

As one of the most important wood resources, pyrolysis characteristics of PW were studied widely by some research projects (Agblevor et al., 2010; Chen et al., 2016; Gu et al., 2014; Hwang et al., 2013; Kim et al., 2011; Makibar et al., 2015; Wang et al., 2018). However, improving the pyrolysis behaviors and enhancing pyrolysis selectivity are still a focus of this area now. Anaerobic fermentation pretreatment could be an effective method to obtain high-value products from PW by pyrolysis. So, to explore the effects of anaerobic fermentation on pyrolysis behaviors of PW, poplar sawdust (PS) was fermented in anaerobic conditions and then the pyrolysis characteristics were studied by means of chemical analysis, TGA and Py-GC/MS.

2. Materials and methods

2.1. Biologic pretreatment of PS and chemical analysis

PS was collected from Taian city, Shandong province in 2016. After drying in the sun, the PS was stored in plastic bags. Only the fractions 0.2–0.3 mm were used for the anaerobic fermentation. The biogas slurry of cattle manure from a cattle farm at Qing County (Hebei province) was used to conduct the biological pretreatment experiments. Compared with pig waste and chicken waste, the biogas slurry of cattle manure could include more microorganisms degrading cellulose and hemicellulose. The PS 50 g and the biogas slurry 400 ml were sealed in a reactor (1000 ml) and its pH value was accurately adjusted to 7.0 by use of 1.0 mol/l sodium hydrocarbonate solution. After being fermented for 0, 5, 10 and 20 days respectively, the residue was filtered and then washed with deionized water until the filtrate was colorless. According to the anaerobic fermentation time, the samples were named P0, P5, P10 and P20. The fermentation conditions were: fermentation temperature 37 °C and C/N 25:1. The pretreated samples were dried and stored in a valve bag before use. The weights of the samples were 50 g (P0), 47.75 g (P5), 46 g (P10) and 45 g (P20).

The chemical components and proximate analysis of the samples were analyzed according to ASTM E1758-01 and GB/T 28731-2012, respectively. And the content of extractives was obtained by difference.

2.2. FT-IR analysis

Nicolet iS10 Fourier transform infrared spectroscopy (FT-IR, USA) was used for identification of functional groups on the sample surface. About oven-dried sample 5 mg was mixed completely with about 100 mg KBr powder. The FT-IR spectrum scope was in the range of 4000–500cm^{-1} at a scanning rate of 32 with the step size of 4 cm^{-1}.

2.3. TGA analysis

The pyrolysis progresses of the samples were conducted in a Thermo-Gravimetric Analyzer (TGA, TA Q500, USA) from 30 to 700 °C at a heating rate of 10 °C/min under nitrogen environment (99.999%) at a flow rate of 50 ml/min, respectively. The experiment was repeated for 3 times.

2.4. Pyrolysis kinetic analysis (the activation energy)

Referring the literature (Wang et al., 2017), the activation energy E of samples were obtained. The kinetic equation is described as follows:

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \quad (1)$$

where T is the reaction temperature, K; A is the frequency factor; E is the activation energy, kJ mol^{-1}; β is the heating rate, °C/min; α is the fractional weight loss %, which is computed as follows:

$$\alpha = \frac{w_{oi} - w_{ij}}{w_{oi} - w_{fi}} \quad (2)$$

Where w_{oi} is the initial weight of sample, w_{ij} is the sample weight for the reaction i at time j, and w_{fi} is the final mass of the sample in the reaction.

Due to

$$\ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right] \approx \ln\left(\frac{AR}{\beta E}\right),$$

so the Eq. 1 is changed:

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln\frac{AR}{\beta E} - \frac{E}{RT} \quad (3)$$

E is calculated according to the slope from Eq. 3.

2.5. Py-GC/MS analysis

Referring our previous study (Wang et al., 2014a), the fast pyrolysis experiments were conducted with a CDS Pyroprobe 5200HP pyrolyser (Chemical Data Systems) connected with a GC/MS (Perkin Elmer, Clarus 560). In experiment, sample 0.3 mg was filled in a pyrolysis tube and then was pyrolyzed at 500 °C for 20 s with a heating rate of 20 °C/ms. The volatile products were analyzed online by GC/MS. The temperatures of transfer line and injector were kept at 280 °C A TR-35MS capillary column (30m*0.25 mm i.d., 0.25 μm film thickness) was used to separate the volatile products. As carrier gas, helium (99.999%) was with a flow rate of 1 ml/min and a split ratio of 1:80. During analysis, the GC oven was heated from 40 °C to 180 °C with a heating rate of 10 °C/min for 2 min, and then to 280 °C with a heating rate of 15 °C/min for 2 min. The MS was operated in EI mode at 70ev and the GC/MS interface was held at 280 °C. The NIST library, Wiley library and other literatures were used to identify the pyrolytic products.

3. Results and discussions

3.1. Properties of samples

From Table 1, anaerobic fermentation pretreatment changed remarkably the chemical compositions of PS. With an increase of pretreatment time from 0 to 20 days, the contents of cellulose and hemicellulose decreased from 54.05 and 17.96 wt. % to 51.29 (P20) and 12.61 (P10) wt.%, respectively. However, the lignin content increased from 26.58 to 28.19 wt. %. The extractive compounds included protein, amino acids, pectin and so on. The extractives content increased significantly from 1.41 to 7.31 wt. %. Its content was obtained by difference, 1-cellulose content- hemicellulose content - lignin content. The ash and fixed carbon contents increased from 0.91 and 17.57 wt. % to 1.52 and 18.51 wt. %, respectively. The volatiles content decreased from 78.93 to 76.21 wt. %.

In the anaerobic fermentation, methanogen is the main microorganism. It is well known that the methanogen mainly degrade the cellulose, hemicellulose and the extractives (Nualsri et al., 2016). In the plant cell, the hemicellulose, cellulose and lignin formed a complex structure by various covalent bonds, and the extractives are the fillers.

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