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Production of phenolic-rich bio-oil from catalytic fast pyrolysis of biomass using magnetic solid base catalyst

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ABSTRACT

A magnetic solid base catalyst (potassium phosphate/ferroferric oxide) was prepared and used for catalytic fast pyrolysis of poplar wood to selectively produce phenolic-rich bio-oil. Pyrolysis–gas chromatography/mass spectrometry experiments were conducted to investigate the effects of pyrolysis temperature and catalyst-to-biomass ratio on the product distribution. The actual yields of important pyrolytic products were quantitatively determined by the external standard method. Moreover, recycling experiments were performed to determine the re-utilization abilities of the catalyst. The results showed that the catalyst exhibited promising activity to selectively produce phenolic-rich bio-oil, due to its capability of promoting the decomposition of lignin to generate phenolic compounds and meanwhile inhibiting the devolatilization of holocellulose. The maximal phenolic yield was obtained at the pyrolysis temperature of 400 °C and catalyst-to-biomass ratio of 2. The concentration of the phenolic compounds increased monotonically along with the increasing of the catalyst-to-biomass ratio, with the peak area% value increasing from 28.1% in the non-catalytic process to as high as 68.5% at the catalyst-to-biomass ratio of 7. The maximal total actual yield of twelve quantified major phenolic compounds was 43.9 mg/g, compared with the value of 29.0 mg/g in the non-catalytic process. In addition, the catalyst could be easily recovered and possessed promising recycling properties.

1. Introduction

Fast pyrolysis of biomass is considered as one of the most promising ways for the clean and effective utilization of renewable biomass [1]. During the conventional fast pyrolysis process, a pyrolytic liquid product known as bio-oil will be obtained, which is a complex mixture of water and hundreds of organic compounds [2]. The yield and composition of the bio-oil will be affected by various factors, such as the pyrolysis temperature [3] and feedstock properties [4]. Conventional bio-oil is low-grade liquid fuel with low heating value, poor stability and high corrosiveness [5], due to the presence of many undesirable compounds such as water, acids, thermally unstable oxygenated compounds and non-volatile oligomers [6]. Hence, it can only be directly utilized in thermal devices such as boilers and kilns which have low requirements on the properties of the fuels. In addition, according to the chemical composition of bio-oil, there are many valuable chemicals, but most of them are in very low concentrations due to the poor selectivity during the conventional fast pyrolysis process [1]. Therefore, isolation of specific chemicals from conventional bio-oils is very difficult or economically unattractive [7]. In order to upgrade the bio-oil, one of the effective methods is to selectively control the biomass pyrolysis process, to directly obtain special bio-oils with improved fuel properties or enriched specific valuable compounds. Catalytic fast pyrolysis is the major way to achieve selective biomass pyrolysis process to produce target bio-oils [8].

The production of phenolic-rich bio-oil has gained some attention in recent years. Phenolic compounds are mainly derived from lignin. They are known to be the desirable compounds for the fuel properties of bio-oil since they significantly contribute to the heating value of bio-oil due to their low oxygen contents. Moreover, phenolic compounds also cover a wide application range for the production of energies, fine chemicals [9], food additives [10] and phenolic resins [11]. However, the phenolic content in conventional bio-oil is low because of the low lignin content in biomass and high tendency of char formation during lignin pyrolysis [9]. Lignin can be directly utilized as the feedstock for the production of phenolic-rich bio-oil [12], but this will be limited by the feedstock. Currently, two methods have been proposed to selectively produce phenolic-rich bio-oil directly from biomass. The first method was reported by Bu et al. who obtained phenolic-rich bio-oil via microwave catalytic pyrolysis of Douglas fir mechani-

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cally mixed with activated carbon [13]. They also investigated the effects of pyrolytic conditions [14] and different activated carbon catalysts [15] on the phenolic-rich bio-oil production. Under the optimum condition, the maximum content of total phenolic compounds was 66.9% (peak area% by GC/MS) [14]. By employing this catalytic method, phenolic-rich bio-oil was successfully produced from fruit bunch pellet [16], oil palm shell [17] and alkali lignin [18]. The phenol was usually the major phenolic compound in these cases. The second method was proposed by our research group to selectively produce phenolic-rich bio-oil from catalytic fast pyrolysis of biomass impregnated with K_3PO_4 [19] or K_2HPO_4 [20]. The maximal phenolics content reached 68.8% (peak area% by GC/MS) under the optimal reaction condition, and the composition of the phenolic compounds was mainly determined by the biomass type [19]. Nevertheless, despite the promising catalytic capabilities of the K_3PO_4 and K_2HPO_4 catalysts, there are several disadvantages for the utilization of this catalytic method. The K_3PO_4 or K_2HPO_4 should be impregnated on the biomass, which requires complex pretreatment process. Moreover, after the catalytic pyrolysis process, the catalysts would be retained in the pyrolytic char, bringing difficulties for catalyst recovery and char utilization. Therefore, it is vital to improve this selective pyrolysis technique or develop new catalysts for the phenolic-rich bio-oil production.

In this study, the magnetic solid base (potassium phosphate/ferroferric oxide, K_3PO_4/Fe_3O_4) catalyst will be displayed as another effective catalyst for the selective production of phenolic-rich bio-oil. Compared with the impregnation of the K_3PO_4 or K_2HPO_4 on biomass, the solid base catalyst will be very easy to utilize, by just mechanically mixing with biomass. Moreover, due to the magnetic nature of the catalyst, it can be easy to recover and recycle. These properties will offer significant advantages for the industrial application of this selective pyrolysis technique. Analytical pyrolysis–gas chromatography/mass spectrometry (Py–GC/MS) experiments were performed in this study, to investigate the effects of catalytic temperature and catalyst-to-biomass ratio on the distribution of the pyrolytic products. Major phenolic compounds and other important pyrolytic products were quantitatively determined using the external standard method. Moreover, recycling experiments were conducted by regeneration and re-utilization of the used catalyst, to reveal the recycling properties of the magnetic solid base catalyst.

2. Experiment

2.1. Materials

The biomass feedstock used in this study was poplar wood, collected from Beijing, China. Prior to experiments, it was ground and screened, and the detailed feedstock preparation can be found in our previous study [21]. Particles within 0.1–0.2 mm were selected and dried at 100 °C for 4 h before using. Its component composition was 49.8 wt% cellulose, 24.4 wt% hemicellulose, 23.3 wt% lignin, 2.2 wt% extractive and 0.3 wt% ash. Its elemental composition on the dry basis was 49.6 wt% C, 6.3 wt% H, 0.1 wt% N and 0.1 wt% S.

2.2. Catalyst preparation and characterization

Magnetic solid base catalyst (K_3PO_4/Fe_3O_4) was prepared using the incipient impregnation method. In a typical procedure, 3.8 g potassium phosphate trihydrate ($K_3PO_4 \cdot 3H_2O$, purchased from Aladdin) was firstly dissolved in specific volume of deionized water, followed by adding 4.0 g magnetic nanoparticle (Fe_3O_4, 99.5% metal basis, 20 nm, purchased from Aladdin) with ultrasonic treatment for 3 h. The mixture was then dried at 80 °C overnight and calcined at 450 °C for 4 h in air to get the final K_3PO_4/Fe_3O_4 catalyst.

X-ray diffraction (XRD) analysis of the fresh and regenerated K_3PO_4/Fe_3O_4 catalysts was conducted with a Rigaku Rotaflex diffractometer equipped with Cu Kα radiation ($\lambda = 0.15406$ nm). The data were recorded over the 2θ range of 10–80°. Crystalline phases were identified by comparison with the reference data from the International Center for Diffraction Data (ICDD) files.

Nitrogen adsorption/desorption isotherms at 77 K of the Fe_3O_4 and K_3PO_4/Fe_3O_4 catalysts were measured using an Autosorb-iQ-MP physisorption analyzer. The surface area was determined using the Brunauer–Emmett–Teller (BET) method.

The magnetic property (saturation magnetization) of the fresh and regenerated K_3PO_4/Fe_3O_4 catalysts was measured using a Lake-Shore 7407 series vibration sample magnetometer (VSM).

2.3. Analytical Py–GC/MS experiments

Fast pyrolysis experiments were conducted using the analytical Py–GC/MS instrument, including the CDS Pyroprobe 5200HP pyrolyser (Chemical Data Systems, USA) connected with the Perkin Elmer GC/MS (Clarus 560, USA). To prepare the experimental samples, the poplar wood and catalyst were mechanically mixed and filled in the middle of the quartz tube. Quartz wool was placed at both sides of the feedstock to prevent the escaping of the solid particles during pyrolysis process. The quartz tube containing the feedstock was placed in the pyrolyser, and could be quickly heated by the platinum wire to achieve fast pyrolysis. Detailed sample preparation can be seen elsewhere [22]. The quantity of the poplar wood was strict to be 0.30 mg in each sample, while the quantity of the catalyst was varied (0.30 mg, 0.60 mg, 0.90 mg, 1.50 mg, 2.10 mg) to achieve the catalyst-to-biomass ratios of 1, 2, 3, 5 and 7, respectively. Pure poplar wood samples (0.30 mg) without the catalyst were also prepared for experiments. An analytical balance with a readability of 0.01 mg was used for weighing.

Fast pyrolysis experiments were carried out at different temperatures (350 °C, 400 °C, 450 °C and 500 °C) for 20 s with the heating rate of 20 °C/ms. The pyrolysis vapors were directly transformed into GC/MS for analysis. The chromatographic separation was achieved by using an Elite-35MS capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness). Helium (99.999%) was the carrier gas with a constant flow rate of 1 mL/min at a 1:80 split ratio. The GC oven was heated from 40 °C (2 min) to 160 °C with the heating rate of 10 °C/min, and then to 280 °C (3 min) with the heating rate of 15 °C/min. Other detailed parameters for GC/MS analysis can be seen in our previous study [21]. The chromatographic peaks were identified according to the NIST library, Wiley library [23], and literature data of previous study [24].

For each sample, at least three independent experiments were conducted. For each identified product on the ion chromatograms, its average and standard deviation values of the peak area and peak area% were calculated for analysis. It is known that although analytical Py–GC/MS technique could not provide direct quantitative analysis of the compounds, the chromatographic peak area of a compound varies linearly with its quantity, and the peak area% varies linearly with its concentration among the detected pyrolytic products. Therefore, for each product, it is able to know its yield changes by comparing its average peak area values obtained under different reaction conditions, and to know the changes of its concentration among the detected products by comparing its peak area% values [25].

2.4. Quantitative determination of major pyrolytic products

In order to know the actual yields of the important pyrolytic products under different reaction conditions, a total of sixteen