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Research article

Catalytic upgrading of bio-oil by simultaneous esterification and alkylation with azeotropic water removal

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ABSTRACT

Due to the negative effects of acids and aldehydes, crude bio-oil has to be upgraded before its application as a high-graded fuel. A novel method for bio-oil upgrading by simultaneous catalytic esterification and alkylation with azeotropic water removal using n-butanol and 2-methylfuran was investigated in this work. Under the optimum upgrading conditions, water content was evidently decreased from 27.82% to 3.21%, and acid number was reduced from 41.12 mg NaOH/g to 6.17 mg NaOH/g. High heating value of upgraded bio-oil was more than 2 times higher than crude bio-oil and the other properties were also improved significantly. GC-MS analysis indicated that labile acids, aldehydes, ketones and lower alcohols were transformed to stable target products. The introduction of 2-methylfuran effectively suppressed acetalization reactions and the yields of more stable alkylation products were higher than acetals. In addition, oxygenated liquid fuel and sugars and their derivatives could be effectively separated from upgraded bio-oil by H_2O/CH_2Cl_2 extraction. The main product in crude sugars part was butyl-β-D-glucopyranoside, which was formed by means of hydrolysis of levoglucosan and the following glycosidation.

1. Introduction

Concerns about the environment pollution and energy shortage have promoted academics to exploit fossil fuel alternatives, such as biomass. Fast pyrolysis of biomass is a thermal degradation process that transforms biomass into liquid bio-oil in the absence of oxygen and has been developed recently [1]. Presently, there are many laboratories trying to advance pyrolysis technologies using different reactors such as fluidized beds [2,3], spouted beds [4,5], ablative reactors [6,7] and auger reactors [8,9]. In addition, bio-oil has significant environmental advantages over fossil fuels as a green fuel [10] and the yield can be as high as 60 ~ 70 wt.% based on dry feed under the conditions of short residence time (0.5 ~ 2 s), moderate temperature (400 ~ 500 °C) and rapid condensation [11]. However, the compositions of bio-oil are more than 400 organic compounds, including acids, ketones, aldehydes, esters, ethers, alcohols, phenols, as well as carbohydrates, and the other oxygenated organics [12,13]. Bio-oil also has many fatal drawbacks with high oxygen content and water content, high corrosiveness, high viscosity, poor stability, lower heating value [14]. These poor properties can reduce the storage stability and limit the application as high-grade liquid fuels. Therefore, more and more researchers have paid attention to upgrade bio-oil.

At present, most researchers set the target to reduce the oxygen content of bio-oil mainly in order to obtain hydrocarbon products or hydrogen, and the refining processes include steam reforming [15,16], hydrodeoxygenation [17–19], catalytic cracking [20,21]. These methods not only consume large amounts of energy, but also need complex operation process, even lead to coke formation and catalyst deactivation [22], therefore greatly restrict mass production of upgraded bio-oil. What's more, stable oxygenated liquid compounds themselves are very good fuels and can be added to fossil fuels, so there is no need for oxygen removal. Compared to the above methods, catalytic esterification can lower the acidic value and improve the stability of bio-oil by adding alcohols at more moderate reaction conditions [23]. Esterification of crude bio-oil over solid acid catalysts can neutralize organic acids and aging test showed the stability of upgraded bio-oil improved positively [24,25]. Moreover, simultaneous esterification and acetalization with alcohols was reported to convert acids and aldehydes to esters and acetals, respectively [26,27]. But the water in crude bio-oil as well as the water produced by upgrading reactions creates obstacles that cannot drive the equilibria to the right side by the reason of closed reaction devices. Xu et al. [28] reported bio-oil upgrading by means of ozone oxidation and esterification in azeotropic distillation system, the results indicated water content was reduced from 44.75% to 2.38%, while high heating value was increased from 9.5 MJ/kg to 25.0 MJ/kg. A number of studies have also focused on simultaneous esterification and azeotropic water removal to convert almost all of the acids and

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aldehydes in crude bio-oil to the corresponding esters and acetals and to get an upgraded bio-oil with a lower water content, lower acid number, lower viscosity and a higher heating value [29–31]. Nevertheless, some acetals would decompose at high catalyst loadings and high operating temperatures during those upgrading processes [32]. To overcome this problem, the other organics should be introduced to transform aldehydes to more stable components. Although bio-oil upgrading by catalytic esterification has been frequently investigated and some significant results have been found out, most studies have only focused on improvement of properties and few of them have reported to separate high value-added products from upgraded bio-oil. For example, sugars obtained from pyrolysis of cellulose exhibits great potential as a valuable byproduct.

Therefore, it was logical to infer that modified esterification and convenient separation processes were necessary to improve the certain properties of bio-oil. In this work, we used the commercial solid acid catalyst Amberlyst-36, which has higher concentration of acidic sites (≥5.40 eq/kg) than Amberlyst ion-exchange resins used in previous literature [24,33]. We also adopted a novel method for bio-oil upgrading by simultaneous catalytic esterification and alkylation with azeotropic water removal using n-butanol and 2-methylfuran, which can be produced by the fermentation of biomass and selective hydrogenation of furfural, respectively, and can be directly added to gasoline as fuels [34]. The main reactions happened in upgrading process were shown in Fig. 1. Thus, the major objectives are as follows: (1) converting active reactants such as acids, aldehydes, ketones and lower alcohols to stable esters and ethers, which were stable target products and could be applied as high-graded liquid fuels; (2) removing water from bio-oil through azeotropic distillation to abolish the inhibitory effects of esterification and acetalization and improve the calorific value and combustion performance of bio-oil; (3) obtaining water-insoluble upgraded bio-oil, which had a higher boiling point and a longer carbon chain, and separating oxygenated liquid fuel and sugars and their derivatives from upgraded bio-oil by H_2O/CH_2Cl_2 extraction.

2. Experimental section

2.1. Chemicals and materials

The crude bio-oil, provided by the Devotion Corporation (Guangzhou, China), was produced from fast pyrolysis of saw dust in a circulating fluidized bed. The specific operation conditions were moderate temperature (600 ~ 700 °C), high heating rate (1000 °C/s), short residence time (1 ~ 2 s), meanwhile the yield and capacity of bio-oil were about 70 wt.% and 20,000 tons/year, respectively. Methanol (>99.5), n-butanol (>99.5), 2-methylfuran (>99) and dichloromethane (>99.8) were purchased from J&K Scientific Co., Ltd. The commercial solid acid catalyst Amberlyst-36 (Aladdin Reagent Co., Ltd) is a macroporous cation exchange resin with the concentration of acidic sites ≥5.40 eq/kg. The surface area, pore volume and average pore diameter of Amberlyst-36 are 33 m^2/g, 0.2 cm^3/g and 240 Å, respectively.

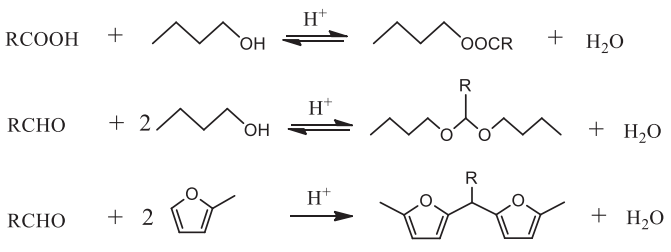

Fig. 1. Main Reactions of catalytic upgrading bio-oil by simultaneous esterification and alkylation.

2.2. Upgrading procedure

The effects of catalyst loading (weight percent of crude bio-oil), mass ratio of n-butanol to bio-oil and 2-methylfuran dosage were investigated to explore the optimum upgrading conditions. Firstly, a total amount of 50.00 g of crude bio-oil and n-butanol with 1.5 of mass ratio, 10.00 g of 2-methylfuran and different loading dosages of Amberlyst-36 (6 ~ 18 wt.%) were charged into a 150 mL three-neck flask, which was equipped with a Dean-Stark trap consisted of a reflux condenser and a glass-stem thermometer monitored temperature of the reactants. The flask was heated in a silicon oil bath with a magnetic mixing heating set under vigorous stirring and the temperature in the flask was remained about 100 °C. In order to make the upper layer fraction in Dean-Stark trap back to the flask, some water was added in Dean-Stark trap below the neck inlet in advance. When an experiment was performed and a continuous distillation was maintained, a two-phase liquid was formed and the upper layer was returned to the flask while the lower liquid surface was become closer to the neck inlet. Then the lower liquid was collected from plug value of Dean-Stark trap until no more water was separated, the reaction was typically carried out for about 4 h. Secondly, to investigate the influence of mass ratio of n-butanol to bio-oil in this reaction system, the experiments were performed with 12 wt.% of catalyst loading and 10.00 g of 2-methylfuran by varying the mass ratio of n-butanol to bio-oil 0.5 to 2. And subsequently a series of experiments were conducted with 2-methylfuran dosage in the range of 0 ~ 15.00 g at the fixed catalyst loading and mass ratio of crude bio-oil to n-butanol selected from the previous experiments. After the reaction, all of the products were cooled to room temperature quickly and the vacuum filtration was used to separate upgraded bio-oil from catalyst.

2.3. Separation procedure

Water/dichloromethane (H_2O/CH_2Cl_2, mass ratio of 1:1) was used to separate sugars and their derivatives from upgraded bio-oil. A total of 25.00 g of upgraded bio-oil and 50.00 g of H_2O/CH_2Cl_2 were sufficiently mixed in a 150 mL round-bottom flask under vigorous stirring, then the mixture was transferred to a 150 mL separatory funnel and let stand for 1 h, it was obviously separated into H_2O-soluble phase and CH_2Cl_2-soluble phase. H_2O-soluble phase was concentrated by rotary evaporation at the conditions of 70 °C, 100 mbar until droplet did not outflow. The residual products in the bottle were crude sugars part. CH_2Cl_2-soluble phase was distilled in a flask at 40 °C to recycle CH_2Cl_2 and obtain oxygenated liquid fuel.

2.4. Analytical methods

The crude bio-oil and products were analyzed by gas chromatography–mass spectrometry (GC-MS) using a Shimadzu QP 2010 Plus system equipped with an Rxi®-5 ms column (length: 30 m, internal diameter: 0.25 mm, film thickness: 0.25 μm). The flow rate of helium carrier gas was 2.15 mL/min. Methanol solutions containing 10 vol.% of the samples were injected into the injection port set at 260 °C with a split ratio of 10:1 and the solvent delay time was 1.5 min. The column was maintained at 35 °C for 10 min before being heated to 180 °C at a rate of 5 °C/min, then heated to 270 °C at 10 °C/min and held for 10 min. The identification of all compounds was achieved by means of the NIST08 and NIST08s mass spectral data library. For compounds without standard substances, the quantification was done by area normalization method.

Functional group analysis of bio-oil was performed using Nexus 670 Fourier transform infrared (FTIR) spectrometer. Spectra were collected from 4000 cm^{-1} to 400 cm^{-1} with a resolution of 4 cm^{-1}, using an oil liquid membrane on KBr pellets with a 5 μm spacer. Thermogravimetric analysis (TG/DTG) was conducted using a TA Instruments Q50 to analyze the qualitative changes of bio-oil. About 10 mg of samples