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Study on the hydrodeoxygenative upgrading of crude bio-oil produced from woody biomass by fast pyrolysis

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ABSTRACT

Crude bio-oil produced from fast pyrolysis of yellow poplar wood was subjected to HDO (hydrodeoxygenation) for the purpose of reducing water content as well as increasing heating value. HDO was performed in an autoclave reactor at three different reaction factors: temperature (250–370 °C), reaction time (40–120 min), and Pd/C catalyst loading (0–6 wt%) under hydrogen atmosphere. After completion of HDO, gas, char, and two immiscible liquid products (light oil and heavy oil) were obtained. Liquid products were less acidic and contained less water than crude bio-oil. Water content of heavy oil was ranged between 0.4 wt% and 1.9 wt%. Heating values of heavy oil were estimated between 28.7 and 37.4 MJ/kg, which was about twice higher than that of crude bio-oil. Elemental analysis revealed that heavy oil had a lower O/C ratio (0.17–0.36) than crude bio-oil (0.71). H/C ratio of heavy oil decreased from 1.50 to 1.32 with an increase of temperature from 250 °C to 350 °C, respectively.

1. Introduction

Energy security, environmental concerns, foreign exchange savings, and rural-sector socioeconomic issues support biofuels as a relevant technologies [1]. Among the various conversion technologies, fast pyrolysis is a thermal decomposition process that occurs at moderate temperatures (around 500 °C) with a short residence time of hot vapor (1–2 s) in the absence of oxygen [2]. This technique can produce 50–75% of liquid bio-oil from renewable resources such as lignocellulosic biomass [3]. The bio-oil has the potential to replace the traditional liquid fossil fuels and chemical [2].

However, bio-oil has unsuitable properties for internal combustion engines, such as high viscosity, high water content, corrosiveness, and high oxygen content, preventing its widespread application. High water content lowers the heating value and flame temperature. Actually, the calorific value of bio-oil (17 MJ/kg) [4] is lower than that of fossil oil (40 MJ/kg). Therefore, the better performance and ignition of bio-oil was achieved by lowering the water content in bio-oil. Furthermore, bio-oil has low thermal stability, limiting its use in commercial applications. In a previous study, we reported that the viscosity and average molecular weight of bio-oil increased considerably with increasing storage duration. Moreover, distinguishable changes such as an increase in yield of pyrolytic lignin and a decrease in oxygenated functional groups in pyrolytic lignin were also observed [5]. Therefore, a process to reduce the oxygen content of bio-oil is required before it can be used commercially. Recently, various upgrading techniques have been reported, including HDO (hydrodeoxygenation), esterification, catalytic cracking of pyrolysis vapors, and emulsification [6]. Hydrodeoxygenation is a hydrotreatment process in which hydrogen gas and suitable catalysts are used to reduce the oxygen content in bio-oil [7]. This well-known process not only removes the oxygen in the bio-oil, but also improves its stability by converting aldehydes and unsaturated compounds into more stable compounds [8]. However, extreme conditions (200–400 °C and 100–200 bar) are required, so this process is neither economical nor energy efficient [9]. Esterification is an effective method for converting organic acids in bio-oil to the corresponding esters by reacting them with alcohol under milder conditions [10]. Moreover, supercritical alcohols such as ethanol (Tc = 243 °C, Pc = 6.38 MPa) are expected to readily dissolve relatively high molecular weight products from cellulose, hemicelluloses, and lignin due to lower dielectric constants when compared with that of water [11–13]. Thus, supercritical ethanol might also be applied to upgrade oligomers in bio-oil both as a reaction medium and reactant.

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Whatever the bio-oil upgrading process is used, suitable catalysts are critical. These catalysts should ideally be active, remove the oxygen in bio-oil effectively with high yield, and not produce coke. In general, most hydrodeoxygenation studies have been performed using NiMo and CoMo as suitable carriers [14,15]. In addition, noble metal catalysts such as Ru/C, Ru/γ-Al_2O_3, Ru/TiO_2, Pt/C, Pd/Al_2O_3, and Pd/C have also been tested and shown to result in higher yields and levels of hydrodeoxygenation than the classical hydrotreatment catalysts [8,16–19]. Most of previous research about HDO of bio-oil was mainly carried out to evaluate the effect of different catalysts. Little work has been done on investigating the influence of reaction conditions on HDO products.

On the basis of the above considerations, we focused primarily on improving the properties of bio-oil by establishing an HDO process under supercritical conditions and studying the effects of various process conditions. Moreover, experiments were conducted to investigate the influence of process conditions on the yields and properties of HDO products. We performed a hydrotreatment reaction of bio-oil in supercritical ethanol, which can function as both a reaction medium and reactant for esterification of organic acids in bio-oil. We chose palladium on carbon (Pd/C) as a catalyst due to its high level of deoxygenation [16]. We performed the process under different temperature ranges, reaction times, and catalyst loadings using an autoclave reactor. After the reaction, mass balances were constructed and the resulting liquid products were characterized using several analytical techniques including elemental analysis and GPC (gel permeation chromatography).

2. Materials and methods

2.1. Performance of fast pyrolysis to produce bio-oil

Air-dry condition xylem tissues of yellow poplar wood (*Liriodendron tulipifera*) which moisture content estimated ca. 8 wt% wet basis were utilized for raw materials to produce crude bio-oil in a lab-scale fast pyrolysis system (200 g/h) equipped with a fluidized-bed type pyrolyzer. They were finely ground through 40 meshes screens to sort them by the particle size and then fed into the pyrolyzer. Fast pyrolysis was conducted using fluidized bed type reactor (Fig. 1) under a nitrogen atmosphere at 500 °C and the residence time of pyrolytic vapors was set to ca. 2 s based on the nitrogen flow rate. The volatile pyrolytic products were passed through a cyclone, two coolers maintained at 0 °C, and an electrostatic precipitator ($-7 \sim -8$ kV) in which the product vapors were cooled and condensed to a crude bio-oil with a yield of ca. 63 wt% based on the dry weight of yellow poplar wood [20].

2.2. HDO (hydrodeoxygenation) of bio-oil

Crude bio-oil was hydrotreated in a 150-ml batch autoclave reactor. The temperature of this system was controlled using an electric heating mantle combined with a cooling coil using water. This device also included a mechanically driven stirrer, gas inlet, and gas outlet.

The reactor was filled with bio-oil (40 g), anhydrous ethanol (10 g) and Pd/C (0, 2, 4 or 6 wt% on the basis of total reactant), and flushed with nitrogen gas. The anhydrous ethanol and noble metal catalyst Pd/C was obtained from Sigma Aldrich and contained 5 wt% active metal. After the air was displaced with nitrogen, hydrogen gas was injected into the reactor up to 30 bar. The reactor was heated to the reaction temperature (250, 300, 350, or 370 °C) and maintained at this temperature for the duration of the reaction (40, 60, 90, or 120 min). The reaction mixture was stirred at 350 rpm with a mechanical impeller. For comparison, a reaction without ethanol (only 50 g of bio-oil) was also conducted with HDO conditions of 300 °C, 40 min of reaction time and 4 wt% of catalyst. After completion of the experiment, the reactor was cooled to ambient temperature. The liquid product (HDO-treated oil), consisting of an aqueous phase and organic phase, was weighed. The upper aqueous phase (light oil) was recovered from the reactor using a separating funnel. Subsequently, the reactor was rinsed with ethanol (50 g). The combined ethanol fractions containing the organic phase and suspended solids were filtered. The filtrate was evaporated to recover the organic phase (heavy oil). The gas yield was determined by difference. All experiments were conducted in duplicate.

2.3. Characterization of raw bio-oil and HDO oil

2.3.1. Physical properties

The water content of the crude bio-oil and HDO-treated oil was determined by Karl-Fischer titration with Hydranal® composite 5 solutions. A pre-weighed sample was injected into the sample solvent (dried methanol) and the water was titrated using a

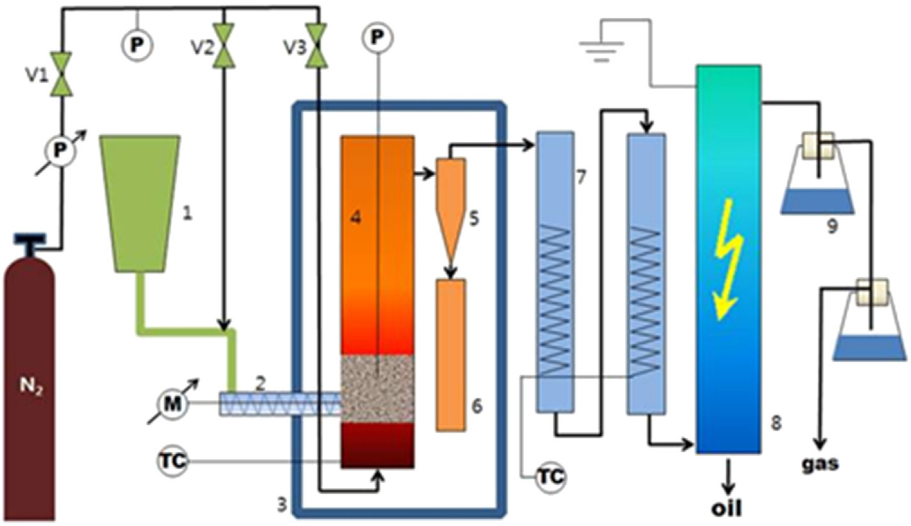

Fig. 1. Schematic diagram of fast pyrolysis system (1: feeder; 2:screw feeder; 3: isolation; 5: cyclone; 6: char collector; 7: cooler; 8: electrostatic precipitator; 9: filter).