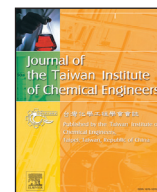




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Hydrodeoxygenation upgrading of pine sawdust bio-oil using zinc metal with zero valency

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ABSTRACT

Hydrodeoxygenation (HDO) is an effective method for bio-oil upgrading. However, the high hydrogen consumption resulted in high bio-oil upgrading cost. In this study, a novel method of hydrogen generation from water for bio-oil HDO was reported. Zinc metal with zero valency was used to generate hydrogen through zinc hydrolysis reaction in the bio-oil HDO process. The effects of different temperatures (20 °C, 250 °C, 300 °C, 350 °C, 400 °C) on in situ bio-oil HDO was investigated. The results showed that high temperatures resulted in high hydrogen yield that led to promoted HDO activity over zinc metal-based materials. Although 20 °C bio-oil HDO process generated the highest oil phase yield at 14.07%, 400 °C bio-oil upgrading process produced upgraded bio-oil with highest hydrocarbons content at 68.95%. Physicochemical properties of raw bio-oil improved significantly after bio-oil HDO upgrading at higher temperatures (250 °C, 300 °C, 350 °C and 400 °C). The pH of upgraded bio-oils (5.70–6.49) increased significantly compared to raw bio-oil (3.24). The higher heating value of upgraded bio-oils (28.67–33.43 MJ/kg) increased significantly compared to raw bio-oil (15.54 MJ/kg), and valuable hydrocarbons content improved significantly from 16.94% in raw bio-oil to 37.86%–68.95% in upgraded bio-oils.

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1. Introduction

A predicted shortage of fossil fuels and environmental issues of global warming resulted from massive fossil fuel consumption led to great interest in the research of developing renewable resources such as biomass to partly replace fossil fuels [1]. Fast pyrolysis is an effective method to convert biomass to bio-oil, which has the potential to be used as transportation fuel [2]. However, the raw bio-oil product has high oxygen contents (35–40 wt.%), which was due to the presence of water and organic compounds such as aldehydes, ketones, carboxylic acids, ethers and esters in raw bio-oil [3]. As a result, the bio-oil has a strong acidity (pH values of around 3) and a low energy density (lower than 19 MJ/kg) compared to conventional petroleum-derived fuels (43 MJ/kg), hindering its direct use as fuels [4,5]. The quality of bio-oil can be improved by the partial elimination of the oxygenated components. HDO is effective for bio-oil upgrading, and it involves the stabilization and selective removal of oxygen from raw bio-oil through

its catalytic reaction with hydrogen [6]. The high hydrogen pressure (7.5–30 MPa), temperature (250–450 °C) and metal catalysts such as Pt/C, Ru/C, Pd/C, Rh/ZrO₂, Ni-Mo/Al₂O₃ and Co-Mo/Al₂O₃ were commonly used for bio-oil HDO [7–14]. However, the harsh operation conditions resulted in the high hydrogen consumption and severe design standard of HDO reactors, which led to unfavorable economic evaluation of bio-oil HDO [15]. Besides, the availability and high cost of noble metals (Pt, Ru, Pd and Rh) are main challenges for their application and the sulfided catalysts (Ni-MoS₂/Al₂O₃ and Co-MoS₂/Al₂O₃) are less suitable for bio-oil HDO due to the economic factors of using sulfur and product contamination. In order to avoid these disadvantages, more economical and effective catalyst and operation condition should be established to upgrade bio-oil.

Recently, zinc metal with zero valency were used to upgrade bio-oil at atmospheric pressure and room temperature due to its reaction with organic acids in bio-oil to generate active hydrogen [16]. This method significantly reduced operation cost of bio-oil HDO process. However, the catalytic effect of bio-oil upgrading is limited (heating value of bio-oil increased slightly from 12.5 to 13.4 MJ/kg), which might be due to the low hydrogen pressure in the study. On the other hand, the hydrolysis of metal was a

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promising approach for large-scale production of hydrogen [17]. For instance, the hydrogen can be produced from the cheap and available water via zinc metal hydrolysis reaction, which can be presented as follows: $\text{Zn} + \text{H}_2\text{O} = \text{ZnO} + \text{H}_2$ [18]. The reaction was found to start at about 250 °C. Bio-oil has a content of water as high as 15–30 wt.% [4], so it can be used to generate hydrogen for bio-oil HDO from zinc hydrolysis. Besides, the generated zinc oxide (ZnO) can be used as an effective catalyst for acetic acid (bio-oil model compound) HDO in the presence of hydrogen [19]. To the best of our knowledge, few studies have been reported to use in-situ hydrogen generation from zinc hydrolysis for real bio-oil HDO process.

In this work, the zinc hydrolysis reaction coupled with the catalytic effect of zinc oxide were used for pine sawdust bio-oil hydrodeoxygenation. Emphasis was put on the effect of temperatures on the yield and quality of upgraded bio-oil (water content, pH, higher heating value and chemical compositions) over zinc metal-based material.

2. Materials and method

2.1. Materials

The zinc metal with zero valency and zinc oxide were purchased from Fisher Scientific and used as received. Anhydrous methanol was purchased from Sigma Aldrich and used as received. The pine sawdust (PSD) bio-oil was produced in a proprietary pyrolysis pilot reactor in the Advanced Biofuel Development Lab at South Dakota State University [20].

2.2. Method

The batch bio-oil HDO experiments were performed in a 500 ml Parr 4575 autoclave reactor. The stirrer mixing speed used in the experiment was 1000 rpm.

Water is an excellent solvent in upgrading of pyrolysis bio-oil [21], and it can also be used to promote zinc hydrolysis reaction for hydrogen generation. In this study, 6 g zinc metal with zero valency, 60 g PSD bio-oil and 100 g deionized water were firstly loaded into the autoclave vessel. In the control experiment, The vessel with reactant was installed and flushed with nitrogen (0.34 MPa) for 3 times to remove the inside air. Then the vessel was heated up to the targeted temperature at 250 °C, 300 °C, 350 °C and 400 °C by a furnace at a heating rate of 5 °C/min. The room temperature (20 °C) control experiment was conducted without heating. In the control 1 treatment, 6 g zinc metal with zero valency, 60 g PSD bio-oil and 100 g anhydrous methanol were loaded into the autoclave vessel, the nitrogen (0.34 MPa) was used to remove the inside air, and the vessel was heated to the targeted 300 °C. In the control 2 treatment, 6 g zinc oxide (ZnO), 60 g PSD bio-oil and 100 g deionized water was loaded into the autoclave vessel. Hydrogen (0.34 MPa) was used to remove the inside air and then pressurized to 3.45 MPa before bio-oil HDO test, and then the vessel was heated to the targeted 300 °C. The designed temperature was kept stable for 5 h. After the reaction, the furnace was removed and the vessel was quickly cooled to room temperature by a cooling fan. Non-condensable gas (NCG) products were collected in sample bags. The upgraded bio-oil product included two phases: aqueous phase (AP) and targeted oil phase (OP). The two bio-oil phases were separated by a separating funnel. The suspended zinc material with coke product in aqueous phase and oil phase were separated by filtration (using 0.2 μm PTFE filter), washed with ethanol and then dried at 110 °C for 3 h in air in a drying oven. The used zinc material with coke product left in the vessel was filtrated, washed with ethanol and then dried at 110 °C in air for 3 h. The following abbreviations were defined

to determine products (gas, aqueous phase, oil phase and coke) yields: Solid 1 (S1) is fresh zinc metal with zero valency for 20 °C, 250 °C, 300 °C, 350 °C, 400 °C and control 1 treatment or ZnO for control 2 treatment. Solid 2 (S2) is used zinc material with coke in aqueous phase, Solid 3 (S3) is used zinc material with coke in oil phase. Solid 4 (S4) is used zinc material with coke left in the vessel. Liquid (L) is defined as raw bio-oil and used solvent (water for 20 °C, 250 °C, 300 °C, 350 °C, 400 °C and control 2 treatment, or methanol for control 1 treatment). Aqueous phase (AP) is defined as aqueous phase after filtration. Oil phase (OP) is defined as oil phase after filtration. Gas (G) is defined as gas product. Coke (C) is defined as coke product. The yields of products including gas (Y_G), aqueous phase (Y_{AP}), oil phase (Y_{OP}) and coke (Y_C) were calculated based on the following equations:

$$Y_G(\text{wt.}\%) = (M_L + M_{S1} - M_{AP} - M_{OP} - M_{S2} - M_{S3} - M_{S4})/M_L \times 100\% \quad (1)$$

$$Y_{AP}(\text{wt.}\%) = M_{AP}/M_L \times 100\% \quad (2)$$

$$Y_{OP}(\text{wt.}\%) = M_{OP}/M_L \times 100\% \quad (3)$$

$$Y_C(\text{wt.}\%) = (1 - Y_G - Y_{AP} - Y_{OP}) \times 100\% \quad (4)$$

where M_L , M_{S1} , M_{AP} , M_{OP} , M_{S2} , M_{S3} , M_{S4} were the mass of Liquid, Solid 1, Aqueous phase, Oil phase, Solid 2, Solid 3 and Solid 4, respectively.

2.3. Zinc-based material characterization

X-ray Diffractometer (XRD, MiniFlex, Rigaku Corporation) was used to determine zinc crystallinity. The filtered Cu-K α radiation was employed in the XRD analysis. The X-ray tube was set as 30 kV (tube voltage) and 15 mA (tube current). The scan range of X-ray pattern was 30–90° (2 theta) and the scan speed was 2°/min. The step size of X-ray pattern was 0.02° (2 theta).

Transmission electron microscope (JEOL, JEM-2100 LaB6) was used at 200 kV to determine zinc based material morphology. EDS (Energy Dispersive X-Ray Spectroscopy) data of elemental composition for fresh and used zinc based material samples were acquired in the TEM using an Oxford Inca energy-dispersive silicon-drift X-ray (EDX) spectrometer [18].

The XPS measurements of zinc sample were performed on a PHI Versa Probe III XPS system (ULVAC-PHI) using a monochromated Al K α X-ray source (1486.6 eV). The zinc sample was mounted on a stainless steel holder using a piece of carbon sticking tape. The sample was conductive and no charge neutralization was needed. The X-ray spot size was 0.1 × 0.1 mm² with a power of 25 W. The high resolution spectra were collected using 0.05 eV/step and a pass energy of 13 eV for Zn 2p peaks and 26 eV for O 1s elements.

2.4. Product characterization

Physicochemical properties of bio-oils such as water content, pH, higher heating value (HHV) and chemical compositions were determined. Water content was determined by a Karl Fischer Titrator V20 (Mettler Toledo Company) based on ASTM E1064. Bio-oil pH value was analyzed by a pH meter (AB15, Accumet Company). HHV was tested by a Calorimeter System (C2000, IKA-Works) in accord with ASTM D4809 [22,23].

The major components of bio-oil products (oil phase) were analyzed by gas chromatography–mass spectrometry (GC–MS) [24]. The used gas chromatography was Agilent GC-7890A (Agilent DB column: 30 m × 0.25 mm × 0.25 μm) and the used mass spectrometry was Agilent 5975C (electron ionization at 70 eV, mass range

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