



Upgrading of bio-oil to boiler fuel by catalytic hydrotreatment and esterification in an efficient process



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ARTICLE INFO

Article history:

Received 4 September 2014

Received in revised form

11 December 2014

Accepted 13 February 2015

Available online 23 March 2015

Keywords:

Bio-oil

Esterification

Hydrotreatment

Ni/SiO₂-ZrO₂

Supercritical ethanol

ABSTRACT

Bio-oil can't be directly used as fuel due to its deteriorate properties. Here, an efficient catalytic upgrading process for the bio-oil, including esterification, hydrogenation, hydrodeoxygenation and depolymerization, is proposed with multifunctional catalyst Ni/SiO₂-ZrO₂ and biomass-derived solvent ethanol. Results showed that esters, alcohols, phenolics, and cyclo-ketones were the main components in the upgraded bio-oil while aldehydes were removed completely via catalytic hydrogenation and acids were removed by catalytic esterification with supercritical ethanol. The pH value of upgraded bio-oil rose drastically from 2.38 to 5.24, and the high heating value increased to 24.4 MJ kg⁻¹. Comparison characterization on the upgraded and crude bio-oil using FT-IR, GPC (Gel permeation chromatography) and ¹³C NMR (Nuclear Magnetic Resonance) demonstrated that lignin-derived oligomers contained in crude bio-oil were further depolymerized over Ni/SiO₂-ZrO₂ catalyst. The improved properties suggest that the upgraded bio-oil is more suitable to be used as boiler fuel. Furthermore, the loss of carbon is negligible because formation of coke is suppressed during the upgrading process.

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1. Introduction

Bio-oil derived from fast pyrolysis of biomass is complex mixtures, including more than hundreds of oxygenated compounds, such as carboxylic acids, ketones, aldehydes, alcohols, ethers, phenols, esters, furans, carbohydrates and lignin-derived oligomers [1,2]. The high oxygen content causes many deleterious properties, such as high viscosity, corrosion, low heating value, immiscibility with conventional fossil fuels, poor stability [3,4], which inhibit its application in engine fuels.

Catalytic hydrotreatment is considered an effective method for bio-oil upgrading [5–8]. For example, Fisk et al. [9] described a reaction of model bio-oil with in-situ hydrogen over Pt-based catalyst. The oxygen content of the model bio-oil decreased from 41.4 wt% to 2.8 wt% after hydrotreatment. Recently, an inexpensive novel Ni-based catalyst supported on SiO₂-ZrO₂ had been used for the efficient hydrotreatment of lignin-derived phenolic compounds,

showing a promising potential for the hydrotreatment of bio-oil [8]. Unfortunately, large amounts of cokes and tar were formed during the process of catalytic hydrotreatment, which can lead to the deactivation of catalyst [10]. And the acid content is still high after catalytic hydrotreatment [11]. To remove the organic acid, esterification of bio-oil with methanol/ethanol over solid catalyst was explored under mild conditions in previous work [12,13]. However, the variation of pH value is very small. Therefore, a new method for upgrading of bio-oil should be explored to reduce the acid content and prevent the formation of coke/tar during the upgrading process.

Supercritical fluid is considered to be an excellent reaction medium and a super solvent because of its complete miscibility with gas and liquid/vapor products, providing a single-phase environment for reactions. Ethanol, an environmentally benign solvent and can be obtained directly from the renewable lignocelluloses, is provided with relatively mild critical point (243.1 °C, 6.3 MPa) [14,15]. Also, it serves as a hydrogen donor solvent in supercritical condition [16]. It was reported that supercritical ethanol had been applied to the upgrading of bio-oil with HZSM-5 catalyst. The results showed that the acids contained in bio-oil can be efficiently converted into esters. However, large amounts of

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cokes were still formed during the upgrading process [17,18]. One of the alternatives to solve the issue of the coke is to find a suitable catalyst for the upgrading of bio-oil. It was reported that the bifunctional catalyst using amphoteric zirconium oxide as support exhibits excellent resistance against coking during the hydrodeoxygenation of phenolics [8,19,20].

In this work, upgrading of bio-oil was performed in supercritical ethanol using Ni/SiO₂-ZrO₂ as catalyst. The principal aim is to decrease the contents of acids, aldehydes and water with lower yield of coke. The compositions of the volatile fraction of crude and upgraded bio-oil were determined by GC-MS (Gas Chromatography-Mass Spectrometer) and the effects of process parameters on the changes of the main components were discussed. Besides, properties of the crude and upgraded bio-oils were also analyzed in detail by FT-IR, GPC (Gel permeation chromatography) and ¹³C NMR (Nuclear Magnetic Resonance).

2. Methods

2.1. Materials

The bio-oil used in this study was a viscous, dark brown liquid, which obtained from fast pyrolysis of rice husk provided according to the literature [21]. Bio-oil was filtered through the filter paper with mesh size of 45 μm to remove the colloids and waxy materials prior to the hydrotreatment experiment.

All chemicals employed in the study (with AR grade) were commercially available and used without further purification.

2.2. Catalyst preparation and characterization

The support of SiO₂-ZrO₂ with 3 of Si/Zr ratio was prepared according to the literature [8]. Supported Ni-based catalysts were prepared by incipient impregnation using Ni(NO₃)₂•6H₂O as precursor. After standing at room temperature for 6 h, the impregnated samples were dried in oven overnight at 120 °C and then calcined at 550 °C for 4 h. The catalyst was designated as xNi/SiO₂-ZrO₂ (x is the Ni loadings). Similarly, the 20Ni/HZSM-5(Si/Al = 38) was also prepared. These catalysts were reduced at 500 °C for 4 h in a flow of reducing gas (5% H₂ + 95% N₂) before use.

The BET (Brunauer-Emmett-Teller) surface area, average pore diameter and pore volume of the catalysts were determined by the N₂ adsorption-desorption isotherms recorded at -196 °C on a Quantachrome Corporation NOVA-2100 physical adsorption apparatus. All samples were degassed at 250 °C for 8 h prior to nitrogen adsorption. Pore size distributions were analyzed by the BJH method.

SEM (Scanning electron microscopy) image was recorded on a Hitachi S-4800 instrument operated at 20 kV. XRD (X-ray diffraction) measurements were carried out by an X'Pert Pro MPD diffractometer with Cu Kα monochromatized radiation (λ = 0.154 nm). The diffraction patterns were recorded at an angle range from 10° to 80°.

NH₃-TPD (NH₃-temperature programmed desorption) were carried out on a Quantachrome Corporation CPB-1 chemical adsorption apparatus with a TCD (thermal conductivity detector). The detailed procedure was reported elsewhere [8].

2.3. Upgrading of bio-oil

The typical schematic of the experimental procedure for the bio-oil upgrading was given in Fig. 1. Upgrading of bio-oil was performed in a 250 mL stainless steel autoclave equipped with an electromagnetic-driven stirrer. For each run, 50.0 g mixed reactants (bio-oil and ethanol) and 1.0 g catalyst were loaded into the reactor. After displacing air, the reactor was pressurized with H₂ to

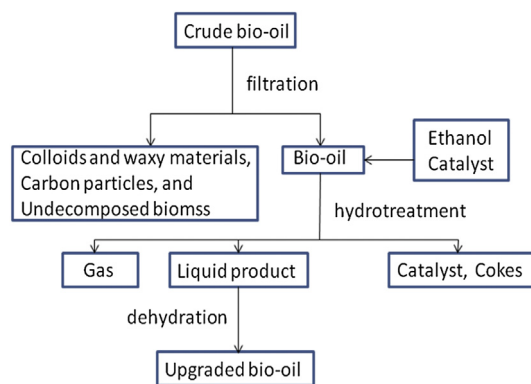


Fig. 1. Schematic of the experimental procedure for the bio-oil upgrading.

1.5 MPa. The reactor was heated to a desired temperature while the reagents were vigorously stirred at 800 rpm. After the pre-determined reaction time, the reactor was cooled to room temperature. The gas product was collected by vacuum bag for subsequent off-line analysis. The liquid product and solid residues (catalyst and cokes) were recovered from the reactor and separated through filtration. The collected sample of liquid product was dehydrated by anhydrous magnesium sulfate for subsequent off-line analysis. Solid residues were dried at 85 °C for 12 h and then weighed.

In order to assess the mass balance of the upgrading process, the collected liquid product was distilled carefully under atmospheric pressure to remove the solvent of ethanol, and then was weighed. The weight of gas product was determined based on the gas composition via calculation. The yield of gas, coke and upgraded bio-oil was calculated on the basis of the following formulas:

$$Y_{\text{gas}}(\%) = W_{\text{g}} / W_{\text{f}} \times 100\% \quad (1)$$

$$Y_{\text{coke}}(\%) = (W_{\text{s}} - W_{\text{catal}}) / W_{\text{f}} \times 100\% \quad (2)$$

$$Y_{\text{liquid}}(\%) = W_{\text{liquid}} / W_{\text{f}} \times 100\% \quad (3)$$

W_{g} : the weight of gas product; W_{s} : the weight of solid residues; W_{catal} : the weight of catalyst; W_{liquid} : the weight of liquid product in which the ethanol had been distilled out; W_{f} : the weight of fed crude bio-oil.

2.4. Products analysis

Gas product obtained from the upgrading process of bio-oil was analyzed on an Agilent 6890 GC (Gas Chromatogram) with a TCD (Thermal Conductivity Detector) and a FID (Flame Ionization Detector) using extranet standard method.

The compositions of the crude and upgraded bio-oils were determined on an Agilent 7890A-5975C GC-MS (Gas Chromatography-Mass Spectrometer) system equipped with a column of HP-5 MS (30 m × 0.25 mm × 0.25 μm). The contents of the main components contained in bio-oil were defined as the peak area of the identified component divided by the total area of all identifiable peaks. Herein, the peak area of solvent ethanol was deducted from the total area.

GPC (Gel permeation chromatography) analysis of the crude and upgraded bio-oils was performed using an Agilent HPLC 1100 system equipped with a refractive index detector. Three columns in

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