



Efficient upgrading process for production of low quality fuel from bio-oil



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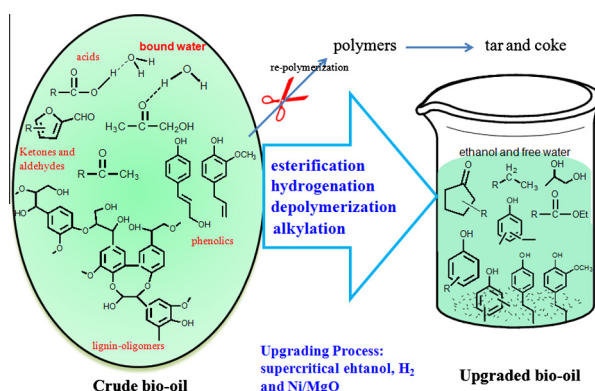
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HIGHLIGHTS

- Upgraded bio-oil with higher HHV and weaker acidity was obtained.
- Acids and aldehydes were converted efficiently during the upgrading process.
- Cleavage of aryl ether bond was facilitated by Ni/MgO catalyst.
- Lignin-derived oligomers were further depolymerized during the upgrading process.
- Alkylation of aromatic ring took place during the upgrading process.

GRAPHICAL ABSTRACT

An efficient catalytic process for upgrading of bio-oil was proposed with pristine Ni/MgO catalyst and ethanol solvent. Esterification, hydrogenation, depolymerization and alkylation of aromatic ring took place simultaneously during the upgrading process, obtaining an upgraded bio-oil with higher HHV and weaker acidity.



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ABSTRACT

To improve the quality of fast pyrolysis bio-oil, an efficient catalytic upgrading process is proposed with pristine Ni/MgO catalyst and ethanol. Esterification, hydrogenation, alkylation of aromatic ring and depolymerization of lignin-derived pyrolytic oligomers simultaneously occurred in the upgrading process. Esters, ketones and alkyl-substituted aromatic compounds were found to be the main components in the volatile fraction of the upgraded bio-oil. Under the optimal conditions, pH value and HHV (high heating value) of the upgraded bio-oil were 5.01 and 24.9 MJ kg⁻¹, respectively. This result suggested that the properties of bio-oil could be effectively improved by the catalytic upgrading process. Moreover, carbon efficiency of this upgrading process was relatively high because that formation of coke is suppressed in the upgrading process.

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1. Introduction

Bio-oil can be efficiently obtained by fast pyrolysis of biomass [1,2]. However, bio-oil cannot be used as high grade fuels directly due to its deteriorated properties, such as the lower heating value, strong acidity and instability. The deteriorated

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properties were mainly caused by the high content of water, acid and unstable components such as furfurals, oligomers [3]. Thus, the qualities of bio-oil need to be improved by partial or total elimination of the water, acid and unstable components contained in bio-oil.

Catalytic hydrotreatment is found to be an effective method for bio-oil upgrading [4–6]. It was reported that the bio-oil (model compounds) had been converted into hydrocarbons via hydrodeoxygenation [6]. For example, Fisk et al. [7] 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. Unfortunately, large amounts of cokes and tar were formed when crude bio-oil was used as feedstocks in the process of catalytic hydrotreatment [8,9]. Hydrocarbons can hardly be obtained because the catalyst deactivated swiftly at the initial stage of the hydrotreatment due to the formation of cokes and tar. In addition, the pH value is still lower after hydrotreatment [10]. A major reason is that organic acids are hardly to be reduced during the process of catalytic hydrotreatment.

Theoretically, it is feasible that the properties of bio-oil can be improved by converting acids to esters. At first, the esterification of bio-oil was explored in mild condition (atmosphere, $T \leq 80$ °C) to avoid the formation of coke and/or tar [11–13]. However, the variation of pH value is still minor. Recently, esterification of bio-oil with methanol/ethanol was carried out with solid acid catalyst in supercritical condition, and the acids contained in bio-oil were efficiently converted into esters [14,15]. It was also reported that the esterification process was performed with H_2 over bifunctional (metal/acid) catalyst [16,17]. The results showed that furfurals contained in the bio-oil were converted with the formation of cyclopentanone and substituted cyclopentanones as well as the efficient conversion of acid by esterification. This is attractive for the improvement of bio-oil stability and acidity.

However, large amounts of cokes were still formed during the upgrading process of bio-oil. An alternative to solve the issue of the coke is to find a suitable catalyst. It was reported that the hydrogenation catalyst using solid-base as support exhibits excellent resistance against coking during the upgrading process of bio-oil [18–20]. For example, Yang et al. [21] reported that only about 8–10 wt.% of coke was deposited on the spent catalysts of CoMo/MgO and CoMoP/MgO after hydrotreatment.

In this work, the upgrading process for bio-oil was carried out in supercritical ethanol over the Ni-based catalyst supported on solid base (MgO, MgO–Al₂O₃ and MgO/SBA-15). The principal aim is to obtain low grade fuel with lower corrosive and higher heating value. In the upgrading process, esterification, hydrogenation, decarboxylation, and depolymerization of lignin-derived oligomers can be simultaneously completed in “one pot”. And the properties of bio-oil were efficiently improved. Moreover, the carbon efficiency of this upgrading process is relatively high because of the lower yield of coke.

2. Experimental

2.1. Materials

The crude bio-oil used in this work was obtained via fast pyrolysis of rice husk according to the literature [22]. Rice husk had been dried by exposure to the sun light. The feed rate was about 10 kg/h while the fluidized gas (N_2) was 12 Nm³/h. Pyrolysis temperature was set at 520 °C. To remove the carbon granules and colloids prior to the hydrotreatment experiment, crude bio-oil was filtered through the filter paper with mesh size of 45 μm. The filtered crude bio-oil can be completely dissolved in ethanol.

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

2.2. Preparation of catalyst

MgO: support material MgO was prepared by homogenous precipitation. With continuously stirring, the solution of Mg(NO₃)₂ was dropped gradually into the solution of ammonia until the pH of the solution reached an approximate value of 8.0. The obtained precipitate was aged for 3 h at 60 °C. Subsequently, the precipitate was filtered and washed with deionized water to remove impurities. The obtained solid was dried overnight at 110 °C and then calcined at 550 °C for 3 h, by which the support MgO was prepared.

MgO–Al₂O₃: mixed oxide MgO–Al₂O₃ (mole ratio of Mg/Al is 2) was prepared by homogenous co-precipitation using Mg(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O and NaOH as materials, and calcined at 550 °C for 3 h.

MgO/SBA-15: support material MgO/SBA-15 with 10 wt.% Mg loadings were prepared by incipient-wetness impregnation method, and calcined at 550 °C for 3 h.

Ni-based catalyst: Ni-based catalysts with 10, 15 and 20 wt.% Ni loadings were prepared by an incipient-wetness impregnation method. The catalysts were calcined at 550 °C for 6 h and reduced at 750 °C for 2 h in a flow H_2 before use.

2.3. Characterization of catalyst

The BET (Brunauer–Emmett–Teller) specific surface area, average pore diameter and pore volume of the catalysts were determined by N_2 isothermal (77 K) adsorption using QUADRASORB SI analyzer equipped with QuadraWin software system. Samples were pretreated at 250 °C for 8 h under vacuum before N_2 adsorption.

The Catalysts were also characterized by X-ray diffraction (XRD) (X'Pert Pro MPD with Cu $K\alpha$ ($\lambda = 0.154$) radiation, Philips).

SEM (Scanning electron microscopy) images of catalysts were obtained on a Hitachi S-4800 instrument operated at 20 kV.

CO₂-TPD (CO₂-temperature programmed desorption) of catalysts were carried out a Quantachrome Corporation CPB-1 chemical adsorption apparatus with a thermal conductivity detector (TCD). Similar procedure had been reported in literature [23].

2.4. Hydrotreatments of bio-oil

The hydrotreatment of bio-oil was performed in a 250 ml stainless autoclave equipped with an electromagnetic driven agitator blade (Fig. S1 in Supplementary data). 50.0 g mixed reactants (bio-oil 15.0 g and 35.0 g ethanol) as well as 1.0 g catalyst were loaded into the autoclave. The autoclave was pressurized with H_2 to 1.5 MPa after the air was replaced. Then the autoclave was heated to a desired reaction temperature while the reagents were stirred at a rate of 800 rpm. The time of heat-up and cool-down were excluded from the recorded reaction time. The pressure of autoclave in the reactor after the reaction (measured in room temperature) was recorded, and gas product was collected by vacuum bag for subsequent off-line analysis when the reaction was completed. Liquid product was filtered and weighed. The solid residues were weighed, then dried overnight at 85 °C and weighed again. The weight difference was added to the liquid product. The amount of coke formed during the hydrotreatment process was determined by subtracting the weight of initial catalyst from the weight of dried solid residues. The yields of gas, coke and oil were calculated based on the following formulas:

$$Y_{\text{gas}} = \frac{W_g}{W_f} \times 100\% \quad (1)$$

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