Upgrading of fast pyrolysis oil via catalytic hydrodeoxygenation: Effects of type of solvents

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A B S T R A C T

Effects of type of solvents (hydro-treated bio-oil and ethanol) and temperature (300 and 350 °C) on hydrodeoxygenation (HDO) of fast pyrolysis oil (PO) were studied. The presence of a solvent effectively reduced self-polymerization of the intermediates during the bio-oil HDO process. HDO of PO using hydro-treated oil as the solvent produced higher yields of oil fraction (OF) and consumed more H_2 than those with ethanol. While the OF yields from all the HDO experiments ranged from 60 to 90 wt%, the highest OF yield was obtained using hydro-treated bio-oil as the solvent. Nevertheless, HDO of PO in ethanol is more promising as it improves the HHV (higher heating value) of the bio-oil substantially (from 21 to 38 MJ/kg), reduces the molecular weight of bio-oil, and the resulted OFs have the lowest O/C value (0.08). HDO upgrading of bio-oil in ethanol has similar effects as HDO operation at a higher temperature (350 °C) without solvent with respect to molar mass reduction for the bio-oil.

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1. Introduction

With an increasing emphasis on energy saving and global warming, renewable and environmental friendly energy resources have attracted many researchers [1—3]. Biomass is a renewable, immense and readily available resource which has been regarded as a promising alternative to fossil resources [4—6].

Different technologies have been established to convert biomass into a variety of energy and chemical products, depending to the feedstock's characteristics and the form of desired energy/chemicals. A wide range of conversion processes have been developed, among which thermochemical conversion is believed to be a viable route to producing liquid fuels and chemical feedstock from various biomass feedstocks [5]. Among all thermochemical processes, fast pyrolysis is by far the only industrially realized technology for conversion of lignocellulosic biomass and waste materials into liquid oils (i.e., fast pyrolysis oils). Fast pyrolysis oils can be a renewable energy source for the production of bio-energy, bio-fuels and bio-based chemicals. However, fast pyrolysis oils need to be upgraded due to many detrimental properties of the oils such as a high water content, high viscosity, large molecular weight, low stability, high oxygen content, etc. The high oxygen content of a pyrolysis oil leads to low stability and a lower caloric value of the oil whose lower heating value (LHV) is 15—20 MJ/kg, approximately half that of a conventional hydrocarbon fuel [7—9].

The large molecular weight and high oxygen contents of pyrolysis oils also makes them immiscible with conventional hydrocarbon fuels, and unstable related to self-polymerization of the oils during storage and processing due to the presence of some reactive oxygen-containing functional groups (such as hydroxyaldehydes, hydroxyketones, carboxylic acids, sugars and phenolics). Thus, reducing molecular weight and removing oxygen from pyrolysis oils are essential to enhance their thermal stability, miscibility with fossil fuel and heating values [10,11]. On the other hand, reducing molecular weight and removing oxygen are also needed in order to prevent from self-polymerization of the oils during processing and hence avoid reactor plugging and catalyst deactivation.

Fast pyrolysis oils can be effectively upgraded by catalytic cracking [12,13], steam reforming [14,15], emulsification [16], esterification [17], and hydrodeoxygenation (HDO) [18—23]. Among these routes for upgrading of bio-oils, HDO was believed to be more advantageous as it could lead to high quality oil products containing less oxygen with lower molecular weights. For example, very recently the author's group [24] has published a research work

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investigating the effects of stabilizing fast pyrolysis oil (PO) with glycerol via catalytic glycerol pretreatment on upgrading via HDO over Ru/C catalyst. It was found that HDO decreases the molecular weight of PO.

Over the past 20 years, there have been extensive efforts reported in the literature on the HDO of biomass-derived oils using high pressure hydrogen and/or in the presence of a hydrogen donor solvent (such as tetralin) and a conventional petroleum hydro-treating catalyst, e.g., sulfided CoMo and NiMo supported on γ-alumina [25,26]. Xu and his group were successful in developing a novel series of sulfided CoMo catalysts supported on MgO with phosphorus as a catalyst promoter for HDO of bio crude using phenol as a model compound in supercritical hexane at temperatures of 300—450 °C under 5.0 MPa hydrogen, and CoMoP/MgO catalyst led to a product consisting of 65 wt% benzene and more than 10 wt% cyclohexyl-compounds at 450 °C [27]. Supercritical fluids as bio-oil HDO solvents have drawn increasing attention due to their unique properties such as faster rates of mass and heat transfer, liquid-like density and enhanced dissolving power, gas-like higher diffusivity and lower viscosity [28]. Recently, sub- or super-critical ethanol (240—300 °C) was used for HDO of pyrolysis bio-oil using HZSM-5 as a catalyst [29,30] and 5%Pt/SO$_4^{2-}$/ZrO$_2$/SBA-15 as a bi-functional catalyst [2]. It was found that the acidic catalyst (HZSM-5) catalyzed esterification of the bio-oil in super-critical ethanol to convert the bio-oil-containing carboxylic acids into different types of esters. Increasing the mass ratio of ethanol to bio-oil increased desired products formation and the heating value of the oil product and a reduced coke yield. The results also showed that higher initial hydrogen pressure inhibited coke formation as expected.

It is thus clear that the type and composition of solvent (and the amount of solvent used in relation to the bio-oil in the HDO treatment) played an important role in the performance of a catalyst during the bio-oil HDO process. Hydrogen donor solvents such as tetralin are effective but expensive. In this work, for the first time, hydro-treated or upgraded pyrolysis oil was used as a solvent for HDO of wood-derived pyrolysis oil in a batch reactor using a commercially obtained Ru/C catalyst. For comparison, supercritical ethanol was also tested for HDO of the same pyrolysis oil. The present research aimed to examine the effects of type of solvents (hydro-treated pyrolysis oil vs. ethanol) on bio-oil HDO process.

2. Material and methods

2.1. Materials

Fast pyrolysis oil (PO) used for this research was obtained from Biomass Technology Group (BTG) in the Netherlands. It had a higher heating value (HHV) of 21.48 MJ/kg and a water content of 27.92 wt%. The PO was derived from hardwood sawdust via a fast pyrolysis process at 450—600 °C. A commercial catalyst, Ru/C, was obtained from Sigma/Aldrich. The catalyst has a Ru loading of 5 wt %, BET surface area of 780.91 m^2/g, Langmuir surface area of 1042.44 m^2/g, pore diameter of 34 Å, and was used without any pre-treatment. Pure (anhydrous) ethanol was obtained from Commercial Alcohols (density 0.7885 g/mL, and water content < 0.1 wt %). Acetone used was ACS reagent grade solvent, obtained from Sigma/Aldrich and used as received.

2.2. Apparatus and experimental procedure

A Parr stirred autoclave with a nominal reactor volume of 500 mL was used for HDO upgrading of the PO in this study. This setup as illustrated in Fig. 1 can operate in both batch and semi-batch modes of hydrogen, while it operated in batch mode in this work.

All experimental conditions tested in this study are shown in Table 1. In the first 3 replicate runs, UO1, typically 150 g PO was loaded to the reactor and Ru/C was added as the catalyst at 3.3 wt% of the feed (on wet liquid basis). These replicate runs were performed to obtain sufficient amount of upgraded oil that was then used as a HDO solvent for next runs.

In UO2, 120 g upgraded oil (as the solvent, denoted as HDO$_1$ obtained from UO1), and 30 g PO were loaded to the reactor and, Ru/C at 3.3 wt% of the PO feed (on wet liquid basis) was added to the liquid mixture. From UO3 to UO6, the amount of solvent obtained from the previous run was decreased to 100 g and amount of PO was increased to 50 g to make a total feed of 150 g. In UO7 and UO8, (100 g ethanol+50 g PO) and (50 g ethanol+100 g PO) were charged into the reactor, respectively. Experimental condition of UO9 was the same as UO1 except that the temperature of UO9 was 350 °C, compared with UO1 at 300 °C. Then, the reactor was sealed and a leak test was carried out at 150 bar g of hydrogen for 30 min. If no
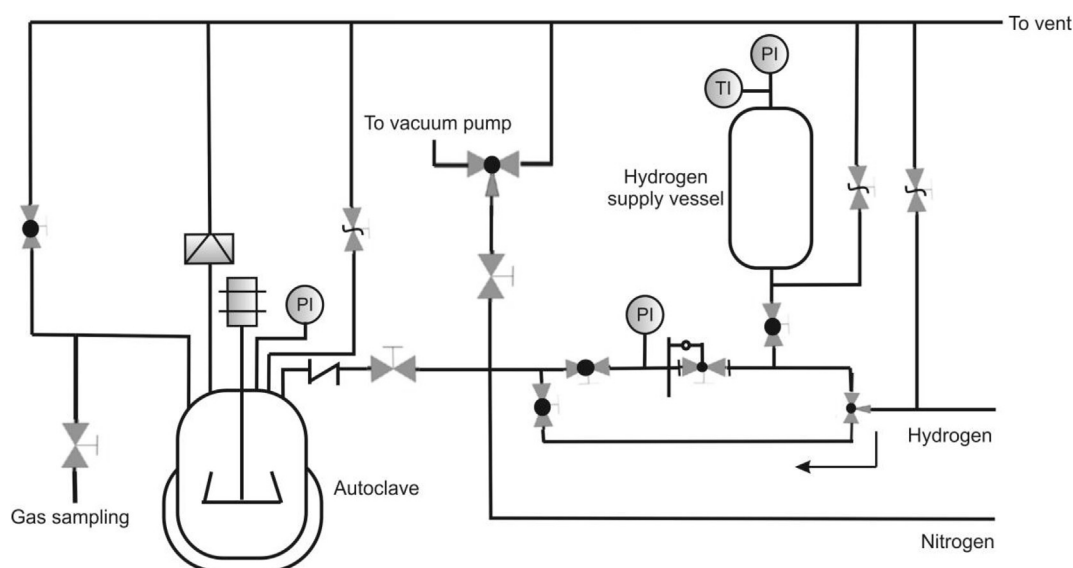

Fig. 1. Schematic diagram of the experimental setup.