Hydrotreatment of corn stover bio-oil using noble metal catalysts

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ABSTRACT

Hydrotreatment of corn stover bio-oil and its distilled fraction was performed using noble metal catalysts such as ruthenium and palladium on carbon support at 125 bar, 4 hour reaction time and 200 °C or 300 °C in a batch catalytic reactor. Results showed that ruthenium performed better at higher temperature (300 °C) and was more effective than palladium, giving about 25–26% deoxygenation. Higher yields (54–67 wt.%), higher H/C molar ratios (1.46–1.48) and lower O/C molar ratios (0.065–0.08) were obtained for the products from Ru-catalyzed processes at 300 °C. Analysis of the chemical composition of the products indicated that the major reactions involved hydrogenation of ketones to alcohols. Carbon dioxide, methane, ethylene and propane, were detected in the gas phase, indicating significant activity for this catalyst as compared to palladium. The hydrotreated product from the heavy distillate with ruthenium as catalyst at 300 °C had the lowest oxygen content (7.0 wt.%) and exhibited better product properties: lower moisture (2.6%), TAN (5.3 mg KOH/g sample), and the highest heating value (40.2 MJ/kg), making it a potential feedstock for co-processing with crude oils in existing refineries.

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1. Introduction

Alternative liquid fuel production from biomass involves the decomposition or conversion of the complex chemical structure of the biomass, especially the lignocellulosic ones, to produce a product that contains much simpler compounds that yield the same properties as those present in the currently used liquid fuels usually derived from petroleum [1,2]. The pyrolysis process meets this purpose as it yields a liquid product, bio-oil, which can be easily transported and stored [3] and has higher volumetric energy density than the original bio-mass [4]. However, major challenges that hinder the direct utilization of bio-oil as a petroleum fuel substitute include its high moisture content, acidic nature and instability, which can be attributed to the high oxygen content of the oil [4,5]. Thus, further processing of the bio-oil is necessary to produce a product with properties that render its potential use either directly as a liquid transportation fuel or as a potential feedstock for co-processing with petroleum feedstocks in existing refineries [1,5,6].

Current upgrading studies mainly focus on the removal of oxygen by applying conventional petroleum refining technologies such as catalytic hydrotreatment, which involves reacting the bio-oil with hydrogen in the presence of a catalyst at high temperature and pressure. Conventional petroleum hydrotreating catalysts have been used in bio-oil hydrotreatment, such as sulfided cobalt–molybdenum- (Co–Mo-) and nickel–molybdenum- (Ni–Mo-) based catalysts. However, these catalysts have the disadvantage of potential deactivation if sulfur is absent in the feed [1]. Several researchers have explored the effectiveness of noble metal catalysts such as palladium (Pd) and ruthenium (Ru) in bio-oil hydrotreatment [7–9]. Wildschut et al. [8] showed that both yields and the degree of deoxygenation were higher when noble metal catalysts were used instead of the traditional CoMo and NiMo catalysts. Hydrotreatment of chemical models like phenolic compounds has also been investigated by Elliot & Hart [10] and Zhao [11] to investigate the performance of these hydrotreating catalysts. Xiong et al. [12] also studied an in situ reduction treatment of bio-oil using Raney Ni and zeolites-supported noble metal catalysts (Pd and Ru) and formic acid as hydrogen source. Results showed that high activity of Raney Ni and Ru and improved properties of the upgraded bio-oil (lower oxygen content and viscosity, higher pH value and heating value) as the organic acids were converted into esters. Also, Sheu et al. [13] investigated the hydrotreatment of pine pyrolytic oil using the noble metal catalyst Pt as well as the conventional catalysts CoMo and Ni–Mo in alumina supports. They established two models for the oxygen removal and compositional changes in the hydrotreated oil, with oxygen removal being an empirical function of temperature and pressure.

In terms of catalyst support, alumina (Al_2O_3) suffers from possible conversion to boehmite (AlO(OH)) by the oxygen-containing compounds and the water formed in the hydrodeoxygenation reactions [14,15]. In addition, it has a relatively high acidity, which gives it high affinity for carbon formation [16]. Thus, carbon has been identified as a promising support due to its neutral nature and high surface area [9,14].

So far, the application of hydrotreatment by noble metal catalysts has not been applied to corn stover bio-oil upgrading. Thus, the

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upgrading of corn stover bio-oil by catalytic hydrotreatment using Pd and Ru catalysts on carbon support was explored in this study. The main objective was to investigate the effectiveness of hydrotreatment using noble metal catalysts in upgrading the corn stover bio-oil. The specific objectives of this study were: (a) to determine the effect of hydrotreatment by carbon-supported ruthenium and palladium catalysts on the properties of the bio-oil such as moisture, total acid number and higher heating value, and on the composition as well; (b) to evaluate the performance of the catalysts based on the degree of deoxygenation, product yield, hydrogen consumption and turnover frequency; (c) to assess the effect of temperature on ruthenium catalyst hydrotreatment based on the upgraded product properties and catalyst performance; and (d) to investigate the application of the better-performing catalyst on the hydrotreatment of distilled bio-oil fraction.

2. Materials and methods

2.1. Materials

The following catalysts were tested in this study and were obtained commercially: Ru/C and Pd/C, both with 5 wt.% metal loading (Sigma-Aldrich). Analytical grades of hydrogen and helium and technical grade of nitrogen were obtained from Airgas Distribution Inc. The bio-oil used in this study was produced from the batch pyrolysis of corn stover at 400 °C in a set-up described in a previous study [17]. A discussion of its characteristics can be found in another paper by the authors [18].

2.2. Experimental set-up

A 50-mL Micro Robinson-Mahoney catalytic reactor with a basket volume of 7.15 mL from Autoclave Engineers was used, which has a design pressure of 5000 psi at 650 °F (343 °C). Maximum temperature reaches as high as 1000 °F (538 °C). Fig. 1 shows the set-up used in this study.

The experiments were performed following a general factorial experimental design, as summarized in Table 1. The catalysts investigated were Pd/C and Ru/C at 5 wt.% loading and 100 bar initial hydrogen pressure. Initially, the temperature was varied between 200 and 300 °C for Ru/C hydrogenation then hydrotreatment using Pd/C was also done at the temperature where better Ru/C performance was

Table 1
Summary of experimental runs during catalytic hydrotreatment.

Experiment	Catalysts used	Operating temperature, °C
Effect of temperature	Ru/C	200, 300
Effect of catalyst	Ru/C and Pd/C	300
Effect of hydrotreatment feed	Ru/C	300

observed. Finally, the better-performing catalyst was used in heavy distillate hydrotreatment. Runs were made in triplicates.

Each hydrotreatment run was performed in batch and started by filling the reactor with about 7 g of bio-oil with the corresponding 5 wt.% of catalyst. Nitrogen gas was flushed through the reactor to remove as much air as possible, and then it was pressurized with 100 bar of hydrogen at room temperature. The reactor was then heated to the desired reaction temperature and maintained at that temperature for the intended reaction time of 4 h. In a typical run, the operating pressure reached 125 bar. After the reaction time has elapsed, the reactor was cooled to room temperature. Gas samples were obtained for analysis and the remaining gas was released from the reactor. The liquid product was obtained and filtered using a syringe filter. It was then characterized for its properties as discussed in the succeeding section.

2.3. Product analysis

The bio-oil and the hydrotreated products were analyzed for its properties and chemical composition. The moisture content was determined by the Karl-Fisher Titration method following the ASTM E203 standard and using Metrohm KF Titrino. The acid number was determined following ASTM D974. The elemental composition of the distillate samples was determined using Vario MICRO Elemental Analyzer (Elementar Analysensysteme GmbH, Germany). The chemical composition by GC–MS analysis was done using Shimadzu QP2010Plus, with the following parameters: column – DB5-MS (25 m, 0.25 μm film thickness, 0.25 mm i.d.); injection temperature of 250 °C; column oven temperature program: 40 °C (held for 4 min), then ramped to 160 °C (at 2.5 °C min^{-1}, held for 1.0 min), then ramped to 200 °C (at
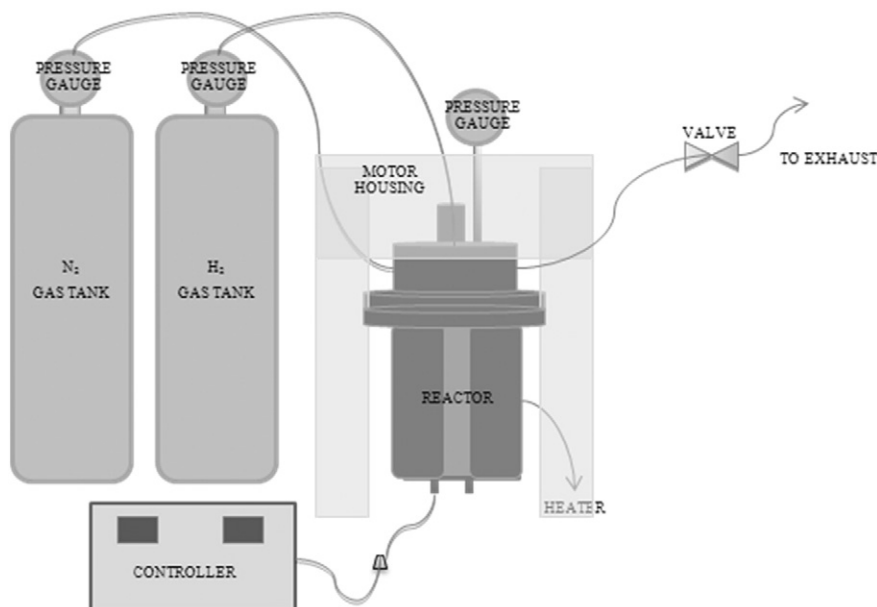

Fig. 1. Hydrotreatment set-up used in this study.