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Direct hydrocracking of oxidized bio-oil to hydrocarbons

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HIGHLIGHTS

- Direct hydrocracking of oxidized bio-oil to produce liquid hydrocarbons was tested.
- Hydrocarbon yield 36.6% higher than for raw bio-oil was achieved.
- GC–MS results showed 99.2 area% of hydrocarbon compounds in the produced product.
- The liquid hydrocarbons had 6.9% higher HHV than for HDO of raw bio-oil.

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ABSTRACT

Hydrodeoxygenation is considered a promising technology to convert bio-oils to liquid transportation fuels. Recently we tested a hydrodeoxygenation method to convert oxidized bio-oil to increase liquid fuel yield, reduce char and reduce required hydrogen. In this current study we tested direct hydrocracking of the oxidized bio-oil to produce high-energy liquid hydrocarbons. We tested various reaction conditions (reaction temperature, hydrogen pressure, time and catalyst type) on the hydrocracking of the oxidized bio-oil. Direct hydrocracking of the oxidized bio-oil produced 36.6% higher hydrocarbons yield compared to direct hydrocracking of the raw bio-oil. The hydrocarbons mixture produced had a higher heating value (HHV) of 43.6 MJ/kg. The oxygen content and acid value were 0.5 wt% and 0.3 mg KOH/g, respectively. Density and viscosity were considerably low at 0.9 g/ml and 1.8 cSt, respectively. pH value was 8.4. The hydrocarbon mixture was also analyzed by GC–MS, FTIR, NMR and DHA.

1. Introduction

Increasing energy demand and the approach of peak production of petroleum supply have led the world to search for renewable, sustainable and environmentally benign alternative fuels. According to the Renewable Fuels Standard the present use of renewable fuels is 14 billion gallons per year (BGY) and is projected to use 36 BGY by 2022 [1]. Woody biomass is one of the most important renewable energy resources for the production of sustainable liquid fuels [2]. Biomass as a renewable energy source will reduce dependency on conventional fuels and provides significant environmental advantages over fossil fuels. It is greenhouse gas neutral because the CO_2 emitted from the bio-fuels from which it is produced is recycled by photosynthesis [3,4]. The availability of biomass in the world is 220 billion dry tons per year and is the world's largest and most sustainable energy resource. These advantages make biomass a potential alternative energy source for fossil fuels.

Fast pyrolysis is one of the most promising thermal decomposition methods to produce pyrolysis oil (bio-oil) from lignocellulosic biomass [5]. Bio-oil produced from fast pyrolysis is a dark brown liquid with a pungent phenolic odor; its chemical properties vary with feedstock type and applied pyrolysis conditions [6]. As a fuel raw bio-oil has environmental advantages when compared to fossil fuels but its complex chemical composition contains numerous oxygenates such as carboxylic acids, aldehydes, ketones, alcohols, phenols and phenolic derivatives and others [7–9]. The high percentage of oxygenated compounds present in raw bio-oils results in a 40–50% oxygen content which causes negative properties such as low energy density, high acidity, immiscibility with petroleum products and viscosity increase with heating or over time [5,10]. It is universally agreed that bio-oils need to be significantly upgraded to allow their use to fuel internal combustion engines [4,11,12].

Hydrodeoxygenation (HDO) is a widely practiced method to produce hydrocarbons from pyrolysis oil [12–18]. Elliot and Baker [19] in U.S. Patent No. 4,795,841 disclosed a method to prevent bio-oil from polymerizing by practicing what they termed "mild hydrotreating" which consisted of utilizing a mild

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temperature regime in the range of 250–300 °C in the presence of hydrogen and a hydrotreating catalyst. It has now become traditional to apply this method to partially upgrade bio-oil prior to application of hydrocracking as a second stage to produce pure hydrocarbons. The utilization of a mild hydrotreating prevents polymerization of the bio-oil that would occur if direct hydrocracking were applied without this step [12,18,20,21].

Many researchers have practiced application of the hydrotreating step at mild temperatures (200–400 °C) to prevent bio-oil polymerization; typical hydrogen pressure applied for hydrotreating ranges from 4 to 10 MPa in the presence of a heterogeneous hydrotreating catalyst. The hydrocracking step is performed at more severe temperatures (300–500 °C) and also at higher pressures ranging from 10 to 20 MPa in the presence of a heterogeneous hydrocracking catalyst [15,19,22–24]. The general HDO reaction is shown as Scheme 1 [25].

Zhang et al. [22] studied the mechanism and reaction conditions of bio-oil deoxygenation in the presence of a sulfide cobalt molybdate catalyst and with addition of the hydrogen donor tetralin. The effects of reaction time, temperature, and hydrogen pressure on the single-stage deoxygenation were examined. Researchers performed several reactions by varying temperature and reaction times. They concluded that, as the temperature and reaction time increased, the deoxygenation of bio-oil also increased. However, higher temperature and longer reaction times also led to coke formation and catalyst deactivation. They also reported that hydrogen pressure had a significant effect on results by increasing the deoxygenation of the bio-oil [22].

Wildschut et al. [20] performed a two-stage HDO by which a hydrotreating 1st-stage was followed by a hydrocracking 2nd-stage on bio-oil with noble metal catalysts. Ru/Al_2O_3, Ru/C, Ru/TiO_2, Pd/C, Pt/C, CoMo/Al2O3, and sulfide $NiMo/Al_2O_3$ were tested. The hydrotreating 1st-stage was applied to bio-oil at a temperature of 250 °C and 100 bar hydrogen pressure and was followed by 2nd-stage hydrocracking at a temperature of 350 °C and 200 bar hydrogen pressure for 4 h in an autoclave reactor. The 1st-stage mildly deoxygenated hydrocarbon yields ranged between 21 and 58 wt% and the oxygen content ranged between 18.5 and 26.5 wt%. Pd/C was found to be the best choice for the 1st-stage hydrotreating process. The 2nd-stage hydrocracking process liquid hydrocarbon oil yields ranged between 25 and 65 wt% and oxygen content ranged between 6 and 11 wt% [20].

Wildschut et al. [15] performed a study to gain insight into catalyst stability of ruthenium on alumina (Ru/Al_2O_3), ruthenium on carbon (Ru/C) and platinum on carbon (Pt/C) catalysts for the direct HDO by single-stage treatment of fast pyrolysis oil at 350 °C and 200 bar hydrogen pressure for 4 h in a batch reactor set-up. Researchers concluded that ruthenium or platinum on carbon catalysts provided equally superior yield and deoxygenation compared to the Pt/C and Ru/Al_2O_3 catalysts. The highest upgraded oil yield obtained with Ru/C was 65 wt% with reduction of oxygen content from 40 to 6 wt%. They also concluded that prolonged reaction time led to decreased end-product yields and increased levels of oxygen content. Researchers hypothesized that these results may have been due to the gasification of the products and depolymerisation of solids. Complete deoxygenation of bio-oil by the applied method and catalysts was not achieved due to the mild temperature conditions applied in the single state of direct HDO applied [15].

McCall et al. [21] in U.S. Patent No. 8,329,969, B2 disclosed a method to produce fuel and fuel-blending components from biomass-derived pyrolysis oil. The process included the production of hydrocarbons by a two-stage deoxygenation of mixed-wood pyrolysis oil. In an example, researchers performed partial deoxygenation by pumping the pyrolysis oil through a fixed bed reactor loaded with a hydrotreating catalyst at a mild temperature between 250 and 340 °C and pressurized hydrogen at 1950–2010 psi. Once the hydrotreating was completed the oil fraction was isolated after separation and removal of water generated in the reaction. This partially deoxygenated oil was then fully deoxygenated by pumping through a full deoxygenation zone loaded with a hydrocracking catalyst and with the application of a more severe temperature between 405 and 407 °C in the presence of pressurized hydrogen between 1510 and 1525 psi [21].

$$\text{-}(CH_2O)\text{-} + H_2 \xrightarrow{\text{Catalyst}} \text{-}(CH_2)\text{-} + H_2O$$

Scheme 1.

Xu et al. [18] investigated two-stage catalytic HDO of fast pyrolysis oil to produce hydrocarbon liquid fuels. Researchers employed a first mild hydrotreating step to bio-oil to overcome coke formation using Ru/C noble catalyst at a temperature of 300 °C and 1500 psig hydrogen pressure. The hydrocracking step employed a more severe temperature of 400 °C and 1950 psig pressurized hydrogen using traditional $NiMo/Al_2O_3$ catalyst. Researchers reported that coke formation was effectively eliminated. The oxygen content of the hydrocarbon fuel decreased from 48.0 wt% rigidly contained in the bio-oil to 0.5 wt%. The HHV increased from 17.0 to 46.0 MJ/kg [18].

Tanneru et al. [17] developed a method to produce a fuel with increased yield, reduced coke formation and water content, and lower hydrogen pressure with lower hydrogen utilization following a two-stage hydrodeoxygenation (hydrotreating followed by hydrocracking) of oxidized bio-oil. Researchers applied a 1st-stage hydrotreating at a temperature of 360 °C and under 800 psig hydrogen pressure. The 2nd-stage hydrocracking of the hydrotreated product was performed at a higher temperature of 425 °C and under 1400 psig hydrogen pressure [17].

The objective of our current study was to produce liquid hydrocarbons by direct hydrocracking of oxidized bio-oil. The effect of the hydrocracking conditions of reaction time, temperature, hydrogen pressure and catalyst type were tested to determine the most effective reaction conditions.

2. Materials and methods

Nickel on silica–alumina (66 ± 5% Ni) catalyst powder was obtained from Alfa Aesar. Ru/C (5%, Ru), Ru/Al_2O_3 (5%, Ru) and Cu(II)O catalyst powder were obtained from Sigma–Aldrich. $Ni/SiO_2–Al_2O_3 + CuO$, Ru/C + CuO and $Ru/Al_2O_3 + CuO$ catalysts were prepared by physical mixing method. Bio-oil required for this research was produced from bark-free loblolly pine wood chips with a size of 1–3 mm and moisture content of 8–10% on dry-weight basis. Raw bio-oil (RBO) was produced by the fast pyrolysis process performed at a temperature of 450 °C with nitrogen carrier gas at a rate of 7-kg/h with the auger-feed pyrolysis reactor located in the Department of Sustainable Bioproducts, Mississippi State University (MSU). The MSU auger fast pyrolyzer produced 60–65 wt% of liquid product, 10–15% of non-condensable gases and 20–25% of char on a dry biomass weight basis.

2.1. RBO oxidation pretreatment

Bio-oil pretreatment by oxidation was performed in a stainless steel, high-pressure batch autoclave reactor equipped with an overhead magnetic stirrer, a pressure indicator with a maximum capacity of 5000 psig and a thermocouple for temperature monitoring in the range of 0–500 °C. The autoclave was equipped with an electrical heating and cooling system to control the temperature inside the reactor. The proprietary oxidative pretreatment applied