DIRECT HYDROCRACKING OF OXIDIZED BIO-OIL TO HYDROCARBONS

Sathish K. Tanneru and Philip H. Steele*

Department of Sustainable Bioproducts, Mississippi State University, Mississippi State,
Starkville, MS, 39762

*Corresponding author: psteele@cfr.msstate.edu

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.

Keywords: Bio-oil, oxidation, hydrodeoxygenation, hydrocracking, HHV

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 CO₂ 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 to 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 (1989) [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 temperature regime in the range of 250 to 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. (2003) 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. (2009) 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/Al₂O₃, Ru/C, Ru/TiO₂, Pd/C, Pt/C, CoMo/Al₂O₃, and sulfide NiMo/Al₂O₃ were tested. The hydrotreating 1st-stage was applied to bio-oil at a temperature of 250 °C and 100 bar hydrogen pressure and was

70 followed by 2nd-stage hydrocracking at a temperature of 350 °C and 200 bar hydrogen pressure
71 for 4 h in an autoclave reactor. The 1st-stage mildly deoxygenated hydrocarbon yields ranged
72 between 21 to 58 wt% and the oxygen content ranged between 18.5 to 26.5 wt%. Pd/C was
73 found to be the best choice for the 1st-stage hydrotreating process. The 2nd-stage hydrocracking
74 process liquid hydrocarbon oil yields ranged between 25 to 65 wt% and oxygen content ranged
75 between 6 and 11 wt% [20].

76 Wildschut et al. (2010) performed a study to gain insight into catalyst stability of ruthenium
77 on alumina (Ru/Al₂O₃), ruthenium on carbon (Ru/C) and platinum on carbon (Pt/C) catalysts for
78 the direct HDO by single-stage treatment of fast pyrolysis oil at 350 °C and 200 bar hydrogen
79 pressure for 4 h in a batch reactor set-up. Researchers concluded that ruthenium or platinum on
80 carbon catalysts provided equally superior yield and deoxygenation compared to the Pt/C and
81 Ru/Al₂O₃ catalysts. The highest upgraded oil yield obtained with Ru/C was 65 wt% with
82 reduction of oxygen content from 40 to 6 wt%. They also concluded that prolonged reaction time
83 led to decreased end-product yields and increased levels of oxygen content. Researchers
84 hypothesized that these results may have been due to the gasification of the products and
85 depolymerisation of solids. Complete deoxygenation of bio-oil by the applied method and
86 catalysts was not achieved due to the mild temperature conditions applied in the single state of
87 direct HDO applied [15].

88 McCall et al. (2012) in U.S. Patent No. 8,329,969, B2 disclosed a method to produce fuel and
89 fuel-blending components from biomass-derived pyrolysis oil. The process included the
90 production of hydrocarbons by a two-stage deoxygenation of mixed-wood pyrolysis oil. In an
91 example, researchers performed partial deoxygenation by pumping the pyrolysis oil through a
92 fixed bed reactor loaded with a hydrotreating catalyst at a mild temperature between 250-340 °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 405-407 °C in the presence of pressurized hydrogen between 1510-1525 psi [21].

Xu et al. (2013) 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/Al₂O₃ 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. (2014) 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 ($66\pm 5\%$ Ni) catalyst powder was obtained from Alfa Aesar. Ru/C (5%, Ru), Ru/Al₂O₃ (5%, Ru) and Cu(II)O catalyst powder were obtained from Sigma-Aldrich. Ni/SiO₂-Al₂O₃ + CuO, Ru/C + CuO and Ru/Al₂O₃ + 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 significantly changed the RBO chemical composition. All pretreatment experiments were performed by adopting the procedure followed in Tanneru et al. (2014) [17]. Briefly, this procedure utilized a combination of both oxone (potassium peroxymonosulfate) and hydrogen peroxide to oxidize

RBO at room temperature and without pressure. In the remainder of this paper, for clarity of understanding, the pretreated RBO by oxidation will be termed *oxidized product*.

2.2. Hydrocracking of oxidized product

All hydrocracking experiments were performed in the same Parr batch autoclave described in section 2.1. Following the oxidative pretreatment of bio-oil direct hydrocracking was performed at temperatures of 375, 400 and 425 °C. The hydrogen pressures applied were 1000, 1200 and 1400 psig. Reaction times tested were 2.0, 2.5 and 3.0 h. The catalyst types tested were Ni/SiO₂-Al₂O₃, Ni/SiO₂-Al₂O₃+CuO, Ru/C+CuO and Ru/Al₂O₃+CuO. All catalysts were prepared by physical mixing method and catalysts were directly used without any further activation or purification. The best reaction condition was chosen based on the quality of the physical properties and yield of the hydrocarbons produced by hydrocracking the oxidized bio-oil. For the best reaction condition the hydrocracking of RBO was also performed as a control to compare hydrocracked RBO hydrocarbon properties and yield to those of the hydrocracked product produced from the oxidized product.

In each experiment, once the reaction was complete, the liquid products were cooled in the reactor. The liquid product was collected in test tubes and centrifuged for 2-4 h to separate the resulting aqueous and organic phases. Both phases were separated and weighed for mass balance computation. In this paper the products produced from hydrocracking the oxidized product and following its separation as an organic fraction will be referred to as the hydrocarbon mixture (HCM). The products produced from hydrocracking the RBO and following its separation as an organic fraction will be referred to as the hydrocarbon mixture from RBO (HCM-RBO). The byproducts produced in this process included water and off-gas.

3. Data analysis

The RBO, oxidized product, HCM and HCM-RBO were characterized with ASTM standard analysis methods. The HHVs were determined by Ika-5000 bomb calorimeter by ASTM D240. The acid values (AVs) were determined by dissolving 1 g of bio-oil in 50 ml of 35:65 ratio of isopropanol to water mixtures and titrating to a pH of 8.5 with 0.1N KOH solution according to ASTM D664. pH values were determined by addition of 1 g of bio-oil to 50 ml of 35% of isopropanol mixture by ASTM E70. Elemental carbon, hydrogen, and nitrogen were determined by EAI CE-440 elemental analyzer with oxygen content determined by difference according to ASTM D5291. Water content was determined by Karl-Fisher titration by ASTM E203. The densities were determined by Anton Parr DMA 35n portable density meter by ASTM D4052. Viscosities were determined by Ubbelohde capillary viscometer at 40 °C water bath temperature according to ASTM D445.

The GC-MS analysis of the RBO, HCM and HCM-RBO were performed with a Hewlett-Packard HP 5890-Series II GC equipped with a Hewlett-Packard HP 5971 series MS. FTIR spectra were obtained by Varian 3500 FTIR analyzer with standard potassium bromide disk technique and spectra were analyzed by Varian-Resolutions software. A mass balance for the mixed hydrocarbons produced by the best performing catalyst was calculated. A detailed hydrocarbon analysis (DHA) of HCM was performed by ASTM D6730-01. Nuclear magnetic resonance spectroscopy (NMR) spectra were collected using a Bruker 600 MHz spectrometer. Each sample was dissolved in chloroform-d (CDCl_3 as a solvent) and the proton (^1H) NMR spectra were obtained.

4. Results and discussion

4.1. Pretreatment of the raw bio-oil

The physical and chemical properties of the RBO and oxidized product are compared in Table 1. As shown in Table 1, following the oxidative pretreatment of RBO the oxidized product AV increased to 162.4 mg KOH/g from 90.2 mg KOH/g of RBO, an increase of 80.0%. The 15.8 MJ/kg HHV of RBO increased to 16.2 MJ/kg. The water content of the oxidized product increased to 33.3 wt% from the 30.6 wt% value of raw bio-oil. The pH of the oxidized product decreased to 2.6 from the 3.1 of RBO; the pH decrease was due to increase of acid value of the oxidized product. Oxidized product density decreased from 1.2 g/ml for RBO to 1.0 g/ml. The viscosity of the RBO at 12.2 cSt decreased to 9.4 cSt for the oxidized product.

4.2. Effect of the reaction temperature on hydrocracking of the oxidized product

Fig. 1 compares the HHVs, AVs, water contents, oxygen contents and HCM yields of the three hydrocracked oxidized product test samples at three tested reaction temperatures. As shown in Fig. 1, the HHVs of the HCMs produced at the reaction temperatures of 375, 400 and 425 °C were 39.5, 40.5 and 43.6 MJ/kg, respectively. The AVs of the HCMs produced at 375, 400 and 425 °C were 28.2, 12.8 and 0.3 mg KOH/g, respectively. The water contents of the HCMs produced were 1.4, 0.7 and 0.5 wt% for the respective treatment temperatures of 375, 400 and 425 °C. The oxygen content of the HCMs produced at 375, 400 and 425 °C were 11.4, 8.6, and 0.5 wt%, respectively. The HCM yields were 16.1, 30.4 and 23.5 wt% for the respective treatment temperatures of 375, 400 and 425 °C.

The HCM produced at the 425 °C treatment had a 10.4% higher HHV, 98.9% lower AV, 64.3% lower water content, 95.6% less oxygen content and 45.9% higher yield when compared to the 375 °C treatment. The HCM produced at 425 °C had 7.7% higher HHV, 97.6% lower AV, 28.6% lower water content, 94.2% less oxygen content and 22.7% higher yield when compared to the 400 °C treatment.

Among these three temperatures tested, the hydrocracking reaction performed at 400 °C produced a higher HCM yield (30.4 wt%) compared to the 375 °C (16.1 wt%) and 425 °C (23.5 wt%) treatments. However, the HCM physical and chemical properties produced at 425 °C (Fig 1) were of considerably higher quality compared to those for the 375 °C and 400 °C treatments. Therefore, hydrocracking performed at the reaction temperature of 425 °C was considered to be the best treatment.

4.3. Effect of the reaction hydrogen pressure and time on hydrocracking of the oxidized product

As shown in Table 2, effects of reaction hydrogen pressure and time were investigated by performing the hydrocracking reactions under pressurized hydrogen at 1000, 1200 and 1400 psig. The effect of reaction times of 2.0, 2.5 and 3.0 h were also tested. The temperature applied was 425 °C and was found to produce the best HCM properties as discussed above.

Table 2 results show that the HHVs of the HCM produced at the reaction pressures of 1000, 1200 and 1400 psig were 39.3, 41.9 and 43.6 MJ/kg, respectively. Therefore the HCM produced at the 1400 psig pressurized reaction had 10.9% and 4.1% higher HHV compared to those for 1000 and 1200 psig, respectively. The AVs of the HCMs produced at 1000, 1200 and 1400 psig were 3.7, 2.1 and 0.3 mg KOH/g, respectively. The reduction of AV for the HCM produced at 1400 psig was 91.9% and 85.7% more compared to the 1000 and 1200 psig treatments. The water content values for the HCMs were 1.8, 0.9 and 0.5 wt% for the respective treatment pressures of 1000, 1200 and 1400 psig. The oxygen contents of the HCMs produced at 1000, 1200 and 1400 psig were 8.7, 3.8 and 0.5 wt%, respectively. The HCM yields for the 1000, 1200 and 1400 psig treatments were approximately the same at 23.5, 24.0 and 23.5 wt%.

Among the three hydrogen pressure conditions tested, the HCM produced at 1400 psig had higher HHV, lower AV, lower water content and lower oxygen content compared to the 1000

and 1200 psig HCM products. Therefore, hydrocracking performed at 1400 psig hydrogen pressure was considered the best treatment.

The effects of the reaction time on the hydrocracking of the oxidized product were tested at the previously ascertained most-effective reaction temperature of 425 °C and 1400 psig hydrogen pressure. The HHVs of the HCMs produced at reaction times 2.0, 2.5 and 3.0 h were 42.8, 43.6 and 44.3 MJ/kg, respectively. The respective AVs of the HCMs produced at 2.0, 2.5 and 3.0 h were 3.2, 0.3 and 0.3 mg KOH/g. The water content values of the HCMs were 0.7, 0.5 and 0.4 wt% for the respective treatment times of 2.0, 2.5 and 3.0 h. The oxygen content values of the HCMs produced at 2.0, 2.5 and 3.0 h were 3.4, 0.5 and 0.4 wt%, respectively. The HCM yields were 19.0, 23.5 and 20.0 wt% for the respective treatment times of 2.0, 2.5 and 3.0 h.

Among the three reaction times tested, the HCM produced at the 2.5 h reaction time (yield of 23.5 wt%) had yields 23.7% and 14.9% higher compared to those for 2.0 (19.0 wt%) and 3.0 h (20.0 wt%), respectively. The AV of the HCM produced at 2.5 h (AV of 0.3 mg KOH/g) had the same AV as for the 3.0 h reaction (AV of 0.3 mg KOH/g) and was 90.6% lower compared to that of the 2.0 h reaction (AV of 3.2 mg KOH/g). The oxygen content of the HCM produced at 2.5 h (oxygen content of 0.5 wt%) was 85.3% lower compared to the 2.0 h reaction (oxygen content of 3.4 wt%); the HCM produced at 3.0 h had approximately the same oxygen content. Therefore, hydrocracking performed at the 2.5 h reaction time produced an HCM with the highest yield and best property qualities and was considered as the best treatment.

In summary, the hydrocracking of the oxidized product reaction performed at a reaction temperature of 425 °C under hydrogen pressurized of 1400 psig with a reaction time of 2.5 h was considered to be optimal. At these optimal reaction conditions the effects of the various

commercial catalysts were tested by following the hydrocracking procedure described in section 2.2.

4.4. Effect of catalyst type on hydrocracking of the oxidized product

The efficacy of the hydrocracking of the oxidized product at our selected optimal reaction conditions was tested by performing the reaction in the presence of various commercially available catalysts. Fig. 2 shows the comparison of the HHVs and AVs of the HCMs produced using Ni/SiO₂-Al₂O₃, Ni/SiO₂-Al₂O₃+CuO, Ru/C+CuO and Ru/Al₂O₃+CuO as catalysts via direct hydrocracking of the oxidized product. The HHVs of the HCMs produced using Ni/SiO₂-Al₂O₃, Ni/SiO₂-Al₂O₃+CuO, Ru/C+CuO and Ru/Al₂O₃+CuO were 43.8, 43.6, 42.6 and 36.2 MJ/kg, respectively. The AVs of the HCMs produced using Ni/SiO₂-Al₂O₃, Ni/SiO₂-Al₂O₃+CuO, Ru/C+CuO and Ru/Al₂O₃+CuO were 0.5, 0.3, 0.1 and 9.4 mg KOH/g, respectively.

Fig. 3 compares the HCM yield, oxygen content and water content of the hydrocracking of the oxidized product reaction performed using Ni/SiO₂-Al₂O₃, Ni/SiO₂-Al₂O₃+CuO, Ru/C+CuO and Ru/Al₂O₃+CuO as catalysts. As shown in Fig. 3, the HCM yields for the Ni/SiO₂-Al₂O₃, Ni/SiO₂-Al₂O₃+CuO, Ru/C+CuO and Ru/Al₂O₃+CuO as catalyst were 20.6, 23.5, 15.0 and 18.4 wt%, respectively. The oxygen contents were 0.2, 0.5, 6.3 and 11.3 wt% for the HCMs produced using the respective Ni/SiO₂-Al₂O₃, Ni/SiO₂-Al₂O₃+CuO, Ru/C+CuO and Ru/Al₂O₃+CuO catalysts. The water contents of the HCMs produced using Ni/SiO₂-Al₂O₃, Ni/SiO₂-Al₂O₃+CuO, Ru/C+CuO and Ru/Al₂O₃+CuO catalysts were 0.8, 0.5, 2.9 and 3.6 wt%, respectively. The HCM produced using Ni/SiO₂-Al₂O₃+CuO catalyst had 14.1%, 36.2% and 21.7% higher HCM yield

compared to the Ni/SiO₂-Al₂O₃, Ru/C+CuO and Ru/Al₂O₃+CuO catalysts, respectively. Therefore, the HCM produced using Ni/SiO₂-Al₂O₃+CuO as catalyst produced with better quality HCM fuel compared to the Ni/SiO₂-Al₂O₃, Ru/C+CuO and Ru/Al₂O₃+CuO as catalysts. The addition of CuO to Ni/SiO₂-Al₂O₃ increased fuel properties and yields compared to Ni/SiO₂-Al₂O₃ alone. It was well known Ni-based catalysts promote hydrogenation of bio-oil but here addition of CuO might have also promoted other decarboxylation or decarbonylation or deoxygenation type reactions along with hydrogenation. Therefore hydrocracking was taken place better than other catalysts and fuel properties were found best for this combination.

5. FTIR analysis

Fig. 4 shows the comparison of RBO and HCM FTIR spectra. These spectra analyze the functional groups present in the product types. Characteristic vibrational modes were observed at 3200-3600 cm⁻¹ (OH stretch), 2800-3050 cm⁻¹ (CH aliphatic stretch), 1600-1750 cm⁻¹ (C=O stretch), 1350-1470 cm⁻¹ (CH bending) and 1000-1250 cm⁻¹ (C-O stretch). As shown in Fig. 4, it is clear that the very broad OH stretching absorption peak present in the RBO spectrum completely disappeared in the HCM spectrum. The CH aliphatic stretch absorption band at 2800-3050 cm⁻¹ in the HCM spectrum dramatically increased compared to the RBO spectrum. The C=O absorption band of carbonyl functional group and the C-O absorption band of ether, alcohol functional groups were reduced in the HCM spectrum compared to the RBO spectrum. The change in the FTIR spectrum of HCM from RBO spectrum absorption bands indicated that the carboxylic acids, aldehydes and other oxygenated chemical compounds were converted into hydrocarbons.

6. GC-MS analysis

Table 3 shows the chemical composition of RBO and HCM identified by GC-MS. Approximately 50 major chemical compounds were analyzed by GC-MS in both samples. The chemical compound name and their area percentages are given in Table 3. The total area percentages of the major fifty compounds present in RBO and HCM were 100.0% and 99.9%, respectively. As shown in Table 3 there was a considerable change in the chemical composition and area% of the RBO as compared to the HCM produced by direct hydrocracking of the oxidized product at the selected optimum reaction conditions (reaction temperature of 425 °C, hydrogen pressure of 1400 psig, reaction time of 2.5 h, Ni/SiO₂-Al₂O₃+CuO as the catalyst). The 9.8 area% of carboxylic acids, 12.1 area% of esters-ethers, 35.9 area% of aldehydes-ketones, 38.3 area% of alcohols-phenols and 2.1 area% of other RBO compounds were nearly 100% converted to hydrocarbon compounds via direct hydrocracking of the oxidized product. The HCM was comprised of approximately 99.2 area% of hydrocarbon compounds.

7. DHA analysis

A DHA was performed by ASTM D6730-01 on the HCM produced at the optimum conditions. The DHA test is often referred to as the PIANO method (paraffins, iso-paraffins, aromatics, naphthenes and olefins) to classify the hydrocarbons present in the hydrocarbon mixture. The DHA results are given in Table 4. These results show that the hydrocarbon mixture contained n-paraffins of 0.6 mass%, iso-paraffins of 23.7 mass%, olefins of 26.1 mass%, naphthenes of 8.2 mass%, aromatics of 5.8 mass%, total C₁₄+ of 6.2 mass% and unknown compounds of 17.9 mass%. This DHA analysis also calculated the liquid hydrocarbon mixture octane number as 58.6 and average molecular weight was computed to be 110.75.

8. Direct hydrocracking of RBO and oxidized product

As a control, the RBO was also tested by application of the direct hydrocracking treatment at the optimal reaction conditions using Ni/SiO₂-Al₂O₃+CuO as catalyst and its HCM-RBO was compared with the HCM produced from the oxidized product. Fig. 5 compares the HHVs, AVs, water content, oxygen content and yields of both HCM and HCM-RBO. The HHVs of the HCM-RBO and HCM were 40.8 and 43.6 MJ/kg, respectively. The HCM had 6.9% higher HHV compared to the HCM-RBO. The AV of the HCM was 0.3 mg KOH/g compared to 1.4 mg KOH/g for the HCM-RBO, a reduction of 78.6%. The water content of the HCM-RBO and HCM were 0.9 and 0.7 wt%, respectively. The oxygen content of the HCM-RBO and HCM were 2.3 and 0.2 wt%, respectively. The HCM had 91.3% lower oxygen content compared to the HCM-RBO. The yield of HCM was 23.5 wt% compared to 17.2 wt% for the HCM-RBO. Hydrocracking of the oxidized product produced 36.6% higher HCM yield compared to the direct hydrocracking of the RBO. These results show that the oxidized product, when directly hydrocracked, produces both high quality and yields compared to RBO.

9. ¹H-NMR spectroscopic analysis

Proton (¹H) NMR spectra of the RBO (a), HCM-RBO (b) and HCM (c) are shown in Fig 6. As shown in Fig, 6 (a), (b) and (c) it is evident that there is a large difference between ¹H-NMR spectrum of the RBO, HCM-RBO and HCM. The RBO spectrum shown in Fig. 6(a) is very complex and consists of a large number of proton signals due to the presence of various oxygenated compounds with differing functional groups.

Comparison of the Fig. 6(a) spectra of RBO to the HCM-RBO in Fig. 6(b) shows that the oxygenated compounds' proton signals at a chemical shift of 2.0-2.8 ppm (acyl, benzylic and aliphatic hydroxyl functional groups) and proton signals with chemical shift from 3.2-5.2 ppm (esters, ethers, lignin derived methoxy phenols) were not completely eliminated. This indicates

that some of the oxygenated compounds present in the RBO were not deoxygenated or may not be fully converted to hydrocarbons during the hydrocracking of the RBO.

Comparing the Fig. 6(a) spectra of RBO and Fig. 6(c) spectra of HCM shows that the proton signals at a chemical shift of 2.0-2.8 and 3.2-5.2 ppm were reduced considerably due to the higher conversion of oxygenated compounds present in the oxidized product. In the HCM product spectra the aliphatic hydrocarbons' proton signals, with an up-field chemical shift of 0.8-1.9 ppm were higher than HCM-RBO. The HCM spectrum's number of proton signals reduced considerably compared to the HCM-RBO spectrum. This indicates that oxidation pretreatment followed by direct hydrocracking of the oxidized product resulted in conversion of a high percentage of oxygenated compounds to hydrocarbons compared to the direct hydrocracking of the RBO.

10. Conclusions

The direct hydrocracking of oxidized bio-oil produced liquid hydrocarbons of transportation fuel quality. The optimum reaction conditions were found to be a reaction temperature of 425 °C under hydrogen pressure of 1400 psig for 2.5 h. Ni/SiO₂-Al₂O₃+CuO was the best catalyst. Hydrocracking of the oxidized product produced 36.6% higher HCM yield compared to hydrocracking of the RBO. The HCM had 6.9% higher HHV compared to the HCM-RBO. The HCM had 91.3% lower oxygen content compared to the HCM-RBO. The AV of the HCM was 0.3 mg KOH/g compared to 1.4 mg KOH/g for the HCM-RBO, a reduction of 78.6%.

Acknowledgements

This research was performed based upon work funded through the Sustainable Energy Research Center at Mississippi State University (MSU) and is supported by the Department of Energy under Award Number DE-FG3606GO86025. We also thank B. K. Mitchell of the

Department of Forest Products, MSU, for his assistance in the production of bio-oil by fast pyrolysis.

Disclaimer

This report was prepared as an account of work sponsored by an agency of the United States government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

References

1. Perlack RD, Stokes, BJ. U.S. Billion-Ton Update: Biomass Supply for a Bioenergy and Bioproducts Industry. ORNL/TM-2011/224. U.S. Department of Energy. Oak Ridge National Laboratory, Oak Ridge, TN. 2011, 227p.
2. Yan J, Alvors P, Eidensten L. A future for biomass: Mechanical Engineering 1997;117, 94–98.
3. Mckendry P. Energy production from biomass (Part 1): Overview of biomass. Bioresour. Technol 2002;1, 37–46.
4. Huber GW, Iborra S, Corma A. Synthesis of transportation fuels from biomass: Chem. Catal. Eng. Chem. Rev 2006;106, 4044–4098.

5. Ingram Jr L, Mohan D, Bricka M, Steele PH, Strobel D, Crocker D, Mitchell B, Mohammad J, Cantrell K, Pittman Jr CU. Pyrolysis of wood and bark in an auger reactor: physical properties and chemical analysis of the produced bio-oils. *Energy Fuels* 2008;22, 614-625.
6. Mohan D, Pittman Jr CU, Steele PH. Pyrolysis of wood-biomass for bio-oil: a critical review. *Energy Fuels* 2006;20, 848-889.
7. Bridgwater AV, Meier D, Radlein D. An overview of fast pyrolysis of biomass. *Org. Geochem* 1999;30, 1479-1493.
8. Czernik S, Bridgwater AV. Overview of applications of biomass fast pyrolysis oil. *Energy Fuels* 2004;18, 590-598.
9. Oasmaa A, Elliott DC, Korhonen, J. Acidity of biomass fast pyrolysis bio-oils. *Energy Fuels* 2010;24, 6548-6554.
10. Peng J, Chen P, Lou H, Zheng X. Catalytic upgrading of bio-oil by HZSM-5 in sub- and super-critical ethanol. *Bioresour. Technol* 2009;100, 3415-3418.
11. Choudhary TV, Phillips CB. Renewable fuels via catalytic hydrodeoxygenation. *Appl. Catal. A: Gen* 2011;397, 1-12.
12. Elliott DC. Historical developments in hydroprocessing bio-oils. *Energy Fuels* 2007;21, 1792-1815.
13. Senol OI, Viljava TR, Krause AOI. Hydrodeoxygenation of methyl esters on sulphided NiMo/[gamma]-Al₂O₃ and CoMo/[gamma]-Al₂O₃ catalysts. *Catal. Today* 2005;100, 331-335.
14. Bu Q, Lei H, Zacher AH, Wang L, Ren S, Liang J, Wei Y, Liu Y, Tang J, Zhang Q, Ruan R. A review of catalytic hydrodeoxygenation of lignin-derived phenols from biomass

- pyrolysis. *Bioresour. Technol* 2012;124, 470-477.
15. Wildschut J, Melian CI, Heeres HJ. Catalyst studies on the hydrotreatment of fast pyrolysis oil. *Appl. Catal. B: Environ* 2010;99, 298-306.
16. De Miguel Mercader F, Groeneveld MJ, Kersten SRA, Way NWJ, Schaverien CJ, Hogendoorn JA. Production of advanced biofuels: Co-processing of upgraded pyrolysis oil in standard refinery units. *Appl. Catal. B: Environ* 2010;96, 57-66.
17. Tanneru SK, Steele PH. Pretreating bio-oil to increase yield and reduce char during hydrodeoxygenation to produce hydrocarbons. *Fuel* 2014;133, 326-331.
18. Xu X, Zhang YL, Zhai Y, Zhang R. Two-step catalytic hydrodeoxygenation of fast pyrolysis oil to hydrocarbon liquid fuels. *Chemosphere* 2013;93, 652-660.
19. Elliott DC, Baker EG. Process for upgrading biomass pyrolyzates. U.S. Pat. 4,795,841, 1989.
20. Wildschut J, Mahfud FH, Venderbosch RH, Heeres HJ. Hydrotreatment of fast pyrolysis oil using heterogeneous noble-metal catalysts. *Ind. Eng. Chem. Res* 2009;48, 10324-10334.
21. McCall MJ, Brandvold TA, Elliott DC. Fuel and fuel blending components from biomass derived pyrolysis oil. U.S. Pat. 8,329,969 B2, 2012.
22. Zhang SP, Yan YJ, Ren Z, Li T. Study of hydrodeoxygenation of bio-oil from the fast pyrolysis of biomass. *Energy Sources* 2003;3, 57-65
23. Elliott DC, Hart TR, Neuenschwander GG, Rotness L, Olarte MV, Zacher AH, Solantausta Y. Catalytic hydroprocessing of fast pyrolysis bio-oil from pine sawdust. *Energy Fuels* 2012;26, 3891-3896.
24. Steele PH, Tanneru SK, Gajjala SK. Composition and methods for improved fuel

435 production. U.S. Pat. 0291431 A1, 2013.

436 25. Ahmad MM, Fitrir M, Nordin R, Azizan MT. Upgrading of bio-oil into high-value

437 hydrocarbons via hydrodeoxygenation. Am. J. Appl. Sci 2010;7, 746-755.

438

439

Table 1. Comparison of the RBO and oxidized product physical and chemical properties.

Properties	RBO	Oxidized product
Acid value, mg KOH/g	90.2	162.4
HHV, MJ/kg	15.8	16.2
Water content, wt%	30.6	33.3
pH	3.1	2.6
Density, g/ml	1.2	1.0
Viscosity, cSt	12.2	9.4

Table 2. Comparison of the HCM HHVs, AVs, water content, oxygen content and yields at the reaction temperature of 425 °C for the three test hydrogen pressures.

TEST	HHV (MJ/kg)	AV (mg KOH/g)	Water content (wt%)	Oxygen content (wt%)	HCM (wt%)
Effect of pressure					
1000 Psig	39.3	3.7	1.8	8.7	23.5
1200 Psig	41.9	2.1	0.9	3.8	24.0
1400 Psig	43.6	0.3	0.5	0.5	23.5
Effect of time					
2.0 h	42.8	3.2	0.7	3.4	19.0
2.5 h	43.6	0.3	0.5	0.5	23.5
3.0 h	44.3	0.3	0.4	0.4	20.0

Table 3. RBO and HCM chemical composition analysis by GC-MS with area percentages.

Raw bio-oil		HCM	
Compound name	Area%	Compound name	Area %
Carboxylic acids	9.77	Hydrocarbons	99.2
Esters & Ethers	12.1	Other	0.79
Aldehydes & Ketones	35.86	Total	99.99
Alcohols	39.3		
Other	2.1		
Total	99.05		

Table 4. Hydrocarbon types and their mass% present in HCM results analyzed by DHA ASTM D6730-01.

Hydrocarbon type	Total mass%
Paraffins	0.6
Iso-paraffins	23.7
Olefins	26.1
Napthens	8.2
Aromatics	5.8
Total C14+	6.2
Unknowns	17.9
Octane number	58.6
Average molecular weight	110.7

Fig. 1. Comparison of HHVs, AVs, water content, oxygen content and HCM yields of the HCMs produced by the three hydrocracking runs at the reaction temperatures of 375, 400 and 425 °C.

Fig. 2. Comparison of the HHVs and AVs of the HCMs produced using Ni/SiO₂-Al₂O₃, Ni/SiO₂-Al₂O₃+CuO, Ru/C+CuO and Ru/Al₂O₃+CuO as catalysts via direct hydrocracking of the oxidized product reaction.

Fig. 3. HCM yield, oxygen content and water content comparison for Ni/SiO₂-Al₂O₃, Ni/SiO₂-Al₂O₃+CuO, Ru/C+CuO and Ru/Al₂O₃+CuO catalysts.

Fig. 4. FTIR spectra comparing raw bio-oil, pretreated-hydrotreated product and hydrocarbon mixture.

Fig. 5. Comparison of HHVs, AVs, water content, oxygen content and HCM and HCM-RBO yields of the direct hydrocracking of both RBO and oxidized product at the optimal reaction conditions using Ni/SiO₂-Al₂O₃+CuO as catalyst.

Fig. 6. ^1H -NMR spectra analysis of RBO (a), HCM-RBO (b) and HCM (c)