1 **Hydrocarbon bio-oil production from pyrolysis bio-oil using non-sulfide**

2 **Ni-Zn/Al₂O₃ catalyst**

3 Shouyun Cheng,^a Lin Wei,^{a*} James Julson,^a Kasiviswanathan Muthukumarappan,^a Parashu Ram Kharel,
4 ^a Eric Boakye

5 ^a Department of Agricultural & Biosystems Engineering, South Dakota State University, 1400 North
6 Campus Drive, Brookings, South Dakota 57007, USA

7 ^b Department of Physics, South Dakota State University, 1400 North Campus Drive, Brookings, South
8 Dakota 57007, USA

9 ^c Department of Chemistry & Biochemistry, South Dakota State University, 1400 North Campus Drive,
10 Brookings, South Dakota 57007, USA

11 Corresponding author: Lin Wei Tel.: +1 605 688 4179; fax: +1 605 688 6764; E-mail:

12 lin.wei@sdstate.edu; Address: Department of Agricultural and Biosystems Engineering, South Dakota
13 State University, Brookings, South Dakota 57007, USA

14 **Abstract:** Upgraded bio-oil can partly replace fossil fuels to reduce the environmental issues caused by
15 the massive consumption of fossil fuels. Hydrodeoxygenation is a promising route for upgraded bio-oil
16 production from pyrolysis bio-oil. Non-sulfide catalysts are effective in bio-oil hydrodeoxygenation due
17 to low cost and high activity. Ni-Zn/Al₂O₃ catalysts were first used to selectively produce hydrocarbon
18 upgraded bio-oil through bio-oil hydrodeoxygenation. Upgrading pine sawdust bio-oil to upgraded
19 hydrocarbon bio-oil was performed using a series of Ni and/or Zn loaded Al₂O₃ catalysts. The crystalline
20 structure of Al₂O₃ was maintained after Ni and/or Zn loading, but BET surface area and total pore
21 volume of Ni-Zn/Al₂O₃ catalysts decreased significantly compared to Al₂O₃ support. Bimetallic
22 Ni-Zn/Al₂O₃ catalysts were more effective than monometallic Ni/Al₂O₃ or Zn/Al₂O₃ catalyst. Bimetallic
23 15%Ni-5%Zn/Al₂O₃ catalyst generated the highest upgraded bio-oil yield at 44.64 wt.% and produced
24 the upgraded bio-oil with the highest hydrocarbon content at 50.12%. Physicochemical properties of
25 upgraded bio-oils including heating value, water content and pH were significantly improved in

comparison with raw bio-oil. The improved catalytic performance of bimetallic Ni-Zn/Al₂O₃ catalyst was associated with the synergistic effect of Ni and Zn on Al₂O₃ support.

Keywords: upgraded bio-oil; Hydrodeoxygenation; Ni-Zn/Al₂O₃; Catalysis; Bio-oil; Pyrolysis

1.Introduction

Increased energy demand and diminishing fossil fuels concerns, and the related environmental issues including air pollution and global warming, have sparked great interest in the use of biomass as a partial fossil fuel alternative resources [1]. Liquid upgraded bio-oils derived from renewable biomass sources are an attractive substitute for fossil-derived fuels[2]. Pyrolysis is an effective technology for the conversion of biomass into liquid bio-oil. Pyrolysis involves the rapid heating of biomass to the temperature range of 400–600 °C in an oxygen-free atmosphere [3]. Bio-oil cannot be used directly as a transportation fuel for high-speed combustion engines due to the high oxygen content (35–40 wt.% dry basis), high water content (up to 30 wt.%) and the presence of corrosive organic acids compounds (up to 10 wt.%) [2,4]. Bio-oil upgrading is required before it can be used as fuel (upgraded bio-oil). The upgraded bio-oil (biofuel) is defined as bio-oil with higher quality (lower water content, improved pH and carbon content, higher heating value and improved hydrocarbons content).

Hydrodeoxygenation (HDO) is a promising bio-oil upgrading technology [5]. This technique selectively removes oxygen from pyrolysis bio-oil through a catalytic reaction using hydrogen in the presence of a heterogeneous catalyst [6]. Catalysts play a significant role in bio-oil HDO. Many catalysts with different active phases, promoters and supports have been studied on bio-oil HDO. For instance, noble metal catalysts including Ru/C, Ru/TiO₂, Ru/Al₂O₃, Pt/C and Pd/C have been widely tested for bio-oil HDO processes [7-11]. However, scarcity and the high price of noble metals are the main problems for industrial scale application. Conventional hydrodesulfurization (HDS) catalysts such as sulfided NiMo/Al₂O₃ and CoMo/Al₂O₃ were also tested for bio-oil HDO [12,13]. However, the sulfided catalysts have problems of sulfur usage and product contamination [14]. Therefore, non-sulfided Ni based catalysts including MoNi/Al₂O₃, NiCu/Al₂O₃ and NiFe/Al₂O₃, have attracted great interest because of their excellent catalytic activities for HDO of pyrolysis bio-oil [15-17]. Xu et al.

found that MoNi/Al₂O₃ catalysts considerably improved the upgraded bio-oil properties. These improvements included hydrogen content (increased from 6.25 wt.% to 6.95 wt.%) and acidity (pH increased from 2.33 to 2.77). The addition of Mo metal promoted the dispersion of nickel species and inhibited NiAl₂O₄ spinel formation on the MoNi/Al₂O₃ catalysts [15]. Bimetallic Ni-Cu/Al₂O₃ catalysts were more active than monometallic Ni/Al₂O₃ catalyst for anisole and pyrolysis bio-oil HDO [16]. Leng et al. demonstrated that NiFe/Al₂O₃ improved the bio-oil heating value from 37.8 MJkg⁻¹ to 43.9 MJkg⁻¹, and the main involved reaction pathway was C-O cleavage rather than C-C cleavage during the bio-oil HDO process [17].

Zinc, a transition metal present in ZnCl₂, is cost effective and can be used to improve the catalytic performance of zeolite during upgrading vegetable bio-oil to hydrocarbon fuel [18-20]. Recently, the study of Zhao et al. indicated that Zn modified Mo-Zn/Al₂O₃ catalyst exhibited an excellent catalytic activity and stability for the conversion of oxygenated compounds in vegetable oil to hydrocarbons. This was due to its acidity and coke resistance properties [21]. To the best of our knowledge, few studies have been performed using non-sulfided Zn promoted Ni-Zn/Al₂O₃ catalysts for HDO of pyrolysis bio-oil.

The purpose of this study was to investigate the effects of Ni-Zn synergy during HDO of pine sawdust bio-oil during the production of hydrocarbon upgraded bio-oil using Ni-Zn/Al₂O₃ catalysts with different Ni and Zn loading ratios at a temperature of 250 °C and pressure of 500 psig. The catalytic effect of different Ni-Zn/Al₂O₃ catalysts on upgraded bio-oil yield and physicochemical properties (water content, pH, higher heating value and chemical compositions) were determined. The catalysts were characterized by BET, XRD, NH₃-TPD and TEM. The compositions of produced gases were analyzed by GC.

2. Material and methods

74 2.1. Feedstock

75 The raw pine sawdust (PSD) bio-oil was produced using a proprietary pyrolysis pilot reactor in our lab
76 [22].The sawdust was ground into powder with screen of 1 mm using a hammer mill.The sawdust
77 powder was then screened by 200-250 mesh sieve.The average particle size of pine sawdust feedstock
78 was 0.06 mm[23].The reactor is consisted of a screw feeder, a reaction chamber and a condenser. The
79 feeding rate of PSD through the screw feeder into the reactor was 1.36 kg h^{-1} , and the residence time of
80 PSD in the reactor was approximately 1 s. The temperature of the reaction chamber and the condenser
81 were 538°C and -10°C , respectively.

82 2.2. Catalyst preparation

83 Nickel nitrate hexahydrate and aluminum oxide were provided by Sigma-Aldrich and used as
84 received. Zinc chloride was provided by Fisher Scientific and used as received. A series of
85 Ni-Zn/ Al_2O_3 catalysts with differing Ni and/or Zn mass loading ratios (20%Ni/ Al_2O_3 ,
86 15%Ni-5%Zn/ Al_2O_3 , 10%Ni-10%Zn/ Al_2O_3 , 5%Ni-15%Zn/ Al_2O_3 and 20%Zn/ Al_2O_3) were prepared
87 using a wet impregnation method. The aluminum oxide support was impregnated with a given amount
88 of nickel nitrate hexahydrate and zinc chloride aqueous solution at 20°C . The prepared catalysts were
89 then dried at 120°C for 5 h in static air and calcined at 600°C for 4 h in static air [24].

90 2.3. Catalysts characterization

91 A X-ray Diffractometer (XRD, MiniFlex, Rigaku Corporation) was used to determine catalyst
92 crystallinity. The filtered Cu-K α radiation was employed during the XRD analysis. The X-ray tube was
93 set at 30 kV (tube voltage) and 15 mA (tube current). The scan range of the X-ray pattern was $10-90^{\circ}$ (2
94 theta) and the scan speed was 2°min^{-1} . The step size of X-ray pattern was 0.02° (2 theta).

95 A transmission electron microscope (JEOL JEM-2100 LaB6) was used at 200 kV to determine TEM
96 images of catalysts. Isopropyl alcohol (0.5–1.0 mL) was employed to disperse the catalyst samples
97 (several micrograms). The dispersed suspension was then mixed using an ultrasonic for 2 minutes. A
98 few suspension droplets were placed on a copper grid (200-mesh, carbon-coated) and dried before
99 testing. EDS (Energy Dispersive X-Ray Spectroscopy) data of elemental composition for catalysts
100 samples were obtained in the TEM using an Oxford Inca energy-dispersive silicon-drift X-ray (EDX)
101 spectrometer [25].

102 BET specific surface area and pore texture of catalysts were analyzed by an automatic Micromeritics
103 ASAP 2020 apparatus with nitrogen adsorption measurements operated at 77.2 K. Specific surface area
104 was determined by Brunauer–Emmett–Teller method.

105 Acidity of fresh catalysts was determined by a Micromeritics Autochem II Chemisorption Analyzer
106 with a thermal conductivity detector (TCD). The fresh catalyst sample (300 mg) was firstly added to
107 ammonium hydroxide (37.1 wt.%, 4.5 g), and the mixture was kept at room temperature (20 °C) for 3 h.
108 Then, the mixture was dried at 60 °C for 12 h. The dried sample was used for NH₃-TPD analysis. The
109 helium flow in the chemisorption analyzer was 60 mLmin⁻¹. The catalyst sample was heated and
110 maintained at 100 °C for 30 min to remove the physically absorbed ammonia. Then the sample
111 temperature was increased from 100 °C to 700 °C at a rate of 10 °Cmin⁻¹. The final temperature of 700
112 °C was held for 30 min. During the period of heating from 100 °C to 700 °C, abundant dilute HCl
113 solution (1.0 mol/L) was used to collect the chemisorbed ammonia from the catalyst sample. Then,
114 NaOH solution (0.1 mol/L) was employed to titrate the HCl solution to determine the total acid sites of
115 the catalyst sample [26].

116 2.4. Bio-oil HDO test

117 The batch bio-oil HDO tests were performed in an autoclave reactor (500 mL, Parr 4575). The
118 maximum allowable operating pressure and temperature of the reactor were 5000 psig and 400 °C,
119 respectively. The reactor temperature and impeller mixing speed were continuously controlled by
120 an electronic controller panel. The controller panel also monitored the reactor pressure. The impeller
121 mixing speed used in the experiment was 1000 rpm.

122 Water was the solvent used during pyrolysis bio-oil upgrading to lower the activation barrier and
123 increase the proton diffusion coefficient [27]. The autoclave reactor was loaded with 6 g of fresh catalyst,
124 60 g of raw pine sawdust bio-oil and 100 g of deionized water. In control 1 test, 6 g Al_2O_3 , 60 g raw
125 pine sawdust bio-oil and 100 g deionized water were loaded in the reactor. In control 2 test, 6 g
126 15%Ni-5%Zn/ Al_2O_3 catalyst, 60 g raw pine sawdust bio-oil and 100 g deionized water were loaded in
127 the reactor. In catalyst recycle test, 6 g used 15%Ni-5%Zn/ Al_2O_3 catalyst (washed by ethanol and dried
128 at 120 °C for 12h), 60 g raw pine sawdust bio-oil and 100 g deionized water were loaded in the reactor.
129 The reactor with reactants was installed and flushed three times with hydrogen at 50 psig (50 psig
130 nitrogen for control 2 test) to remove the inside air. The reactor was then pressurized with hydrogen at
131 500 psig (or 20 psig nitrogen for control 2 test), and heated to the reaction temperature of 250 °C at a rate
132 of 5 °C min⁻¹. This reaction temperature was maintained for 5 h. These reaction conditions, the
133 catalyst/bio-oil ratio of 1:10, and mixing rate of 1000 rpm were determined by our preliminary tests and
134 literature review [28, 29]. At the end of 5 hours, the furnace turned off and the reactor vessel was
135 allowed to cool to room temperature (20 °C). The liquid bio-oil product separated into the oil phase
136 (upgraded bio-oil) and aqueous phase using a separator funnel. The gas product was collected in gas
137 sample bags. The oil and aqueous phases were filtered (0.2 μm PTFE filter) to remove the catalysts and
138 coke. The separated catalysts were washed with ethanol and dried at 110 °C for 3h in a drying oven. The
139 mass of coke was determined by the mass difference between used and fresh catalyst. The coke yield (Y
140 coke) was calculated by the ratio of coke mass (M coke) to bio-oil mass (M bio-oil) according to

equation (1). Oil phase and aqueous phase yields (Y product) were determined by determining the ratio of product mass (M product) to bio-oil mass (M bio-oil) using equations (2) [6]. The gas yield was calculated via mass balance following equation (3).

$$Y_{\text{coke}} = M_{\text{coke}} / M_{\text{bio-oil}} \times 100\% \quad (1)$$

$$Y_{\text{product}} = M_{\text{product}} / M_{\text{bio-oil}} \times 100\% \quad (2)$$

$$Y_{\text{gas}} = 100 - (Y_{\text{oil phase}} + Y_{\text{aqueous phase}} + Y_{\text{coke}}) \quad (3)$$

where Y_{gas} is the yield of gas product.

2.5. Physicochemical properties determination

Physicochemical properties of bio-oils including water content, pH, higher heating value (HHV) and chemical compositions were determined. Water content was determined using a Karl Fischer Titrator V20 (Mettler Toledo Company) based on ASTM E1064. Bio-oil pH was determined using a pH meter (Accumet Company). HHV was determined in accordance with ASTM D4809 using a bomb Calorimeter System (C2000, IKA-Works) [30].

Chemical compositions of upgraded bio-oils and raw bio-oil were determined by gas chromatography–mass spectrometry (GC–MS) using an Agilent GC-7890A (DB-5 column: 30 m × 0.25 μm × 0.25 mm) and MSD-5977B (electron ionization of 70 eV, mass range at 50–500 m/z) [21]. The injection temperature and injection volume were 300 °C and 1 μL respectively. The column temperature was initially set at 60 °C and held at this temperature for 1 min. The column temperature was then ramped up at a rate of 3 °C min⁻¹ to 140 °C, then at 10 °C min⁻¹ to 180 °C, then at 3 °C min⁻¹ to 260 °C and finally at 10 °C min⁻¹ to 300 °C. The set temperature was maintained for an additional 2 min after each ramp was completed. Helium was the carrier gas at a flow rate of 1 mL min⁻¹. The chemical composition of samples was determined using the NIST mass spectral library and related references

163 [31-33].The relative content of compounds in the samples was calculated using the ratio of its peak area
164 to the total peak area of GC–MS spectrogram.

165 Gas compositions were determined using an Agilent 7890A GC system (19095P-S25 column:
166 50m×15μm×0.53mm). H₂, CO₂ and CO were identified using a thermal conductivity detector. Light
167 hydrocarbons (C₁–C₅) were determined using a flame ionization detector. Argon was the carrier gas.
168 GC calibration was conducted using standardized gas mixtures.

169 **3. Results and discussion**

170 *3.1.XRD characterization*

171 The x-ray diffraction (XRD) spectra of the Al₂O₃ based catalysts are shown in Fig.1. In the XRD
172 patterns of all Al₂O₃ based catalysts, diffraction peak positions of Al₂O₃ structure at 25.58°, 35.15°,
173 37.78°, 43.36°, 52.55°, 57.50°, 61.30°, 66.52°, 68.21° and 77.23° were determined using JCPDS No.
174 00-046-1212[21]. The peak characteristics of Al₂O₃ structure were consistent with the study of Yang et
175 al [34]. The results indicate that the crystalline structure of the Al₂O₃ support was maintained after Ni
176 and/or Zn loading. Ni/Al₂O₃ catalysts showed peaks of NiO phase at 37.32°, 63.00°, 75.56° and
177 79.57° according to PDF Card No.1010381. Similar peak positions of NiO were identified by Thyssen et
178 al[35]. Zn/Al₂O₃ catalysts showed ZnO with peaks of 32.07°, 36.53° and 81.65° that are consistent with
179 PDF Card No.1011258. Liewhiran et al. also identified similar peak positions of
180 ZnO[36]. Ni-Zn/Al₂O₃ catalysts showed peaks of both NiO and ZnO phases. These results indicate that
181 NiO and ZnO particles formed on Ni-Zn/Al₂O₃ catalysts.

182 *3.2.TEM and EDS characterizations*

The TEM images of Al_2O_3 catalysts are shown in Fig.2. There were no obvious dark spots in Al_2O_3 image (Figure 2a), indicating no NiO and/or ZnO loading take place. Dark spots were found in the TEM image of 20%Ni/ Al_2O_3 catalyst (Figure 2b), and these were attributed to NiO particles. Dark spots were found on 20%Zn/ Al_2O_3 catalyst (Figure 2f), which was attributed to the loading of ZnO particles. Kasatkin et al. showed similar dark spots on TEM images of Cu-Zn/ Al_2O_3 . These were attributed to copper oxide and/or zinc oxide [37]. Dark spots were identified in the TEM images of 15%Ni-5%Zn/ Al_2O_3 catalyst (Figure 2c), 10%Ni-10%Zn/ Al_2O_3 catalyst (Figure 2d) and 5%Ni-15%Zn/ Al_2O_3 catalyst (Figure 2e), indicating these might be attributed to the metal oxides particles of NiO and/or ZnO. TEM results of Al_2O_3 based catalysts are in accordance with the XRD results which showed the existence of metal oxides such as NiO and/or ZnO. The metal contents of Ni-Zn/ Al_2O_3 catalysts are shown in Table 1. The Ni and/or Zn elements were detected in Ni and/or Zn loaded Al_2O_3 catalysts. The Ni and/or Zn metal contents of Ni-Zn/ Al_2O_3 catalysts were a bit lower than calculated metal contents, which might be due to a nonquantitative immobilization and non-uniform distribution of the metals on the Al_2O_3 support [38]. Similar results were found by Thangalazhy-Gopakumar et al [39].

3.3. BET and NH_3 -TPD characterizations

The textural properties and total acidity of the Ni-Zn/ Al_2O_3 catalysts are listed in Table 2. The BET specific surface area and total pore volume of Ni and/or Zn loaded Al_2O_3 catalysts decreased significantly compared to Al_2O_3 support. The average pore diameter of Ni-Zn/ Al_2O_3 catalysts was lower than that of Al_2O_3 support. Some micropores and mesopores of the Al_2O_3 support were filled with metal oxides after the metal-loading, which might result in the decrease of these textural properties [21]. Similar decrease of textural properties of metal loaded Al_2O_3 catalysts were confirmed by Cheng et al [40]. The total acidity of 20%Ni/ Al_2O_3 was lower than Al_2O_3 support, and this is consistent with the study of Lu et al [41]. The total acidity of higher Zn loading Al_2O_3 catalysts was higher than Al_2O_3

support [21], and total acidity of Zn loaded Al_2O_3 catalysts increased with the Zn loading ratio. Similar results were found by Karnjanakom et al [42].

3.4. Products yields

The bio-oil obtained from the HDO process can be separated into two phases: oil phase (targeted upgraded bio-oil, mainly composed of organic compounds) and aqueous phase (contained mainly water and a few organic compounds). The yields of bio-oil HDO products (upgraded bio-oil (BP), aqueous phase (AP), coke and gas) are shown in Fig. 3. Bimetallic catalysts such as 15%Ni-5%Zn/ Al_2O_3 and 10%Ni-10%Zn/ Al_2O_3 increased upgraded bio-oil yields compared to monometallic catalysts (Ni/ Al_2O_3 and Zn/ Al_2O_3). This change might be due to the hydrodeoxygenation and hydrogenation promoted reactions due to the bimetallic Ni-Zn/ Al_2O_3 catalysts increasing the content of hydrophobic hydrocarbon compounds in upgraded bio-oils [43]. The bimetallic Ni-Zn/ Al_2O_3 catalysts decreased coke yield when compared to monometallic Ni/ Al_2O_3 and Zn/ Al_2O_3 catalysts. These results indicate that bimetallic catalysts might inhibit polymerization and poly-condensation reactions that are responsible for coke formation during bio-oil HDO process [44]. Similar results were confirmed by Ardiyanti et al [16]. 15%Ni-5%Zn/ Al_2O_3 catalyst generated the highest upgraded bio-oil yield at 44.64 wt.% and the lowest coke yield at 4.67 wt.%. The statistical analysis of 15%Ni-5%Zn/ Al_2O_3 and 10%Ni-10%Zn/ Al_2O_3 catalysts on bio-oil yields was conducted by SPSS statistics software. At 0.05 significant level, the P-value (0.005) < 0.05. Therefore, the effect of 15%Ni-5%Zn/ Al_2O_3 and 10%Ni-10%Zn/ Al_2O_3 catalysts on bio-oil yields are significantly different. Besides, the mean value of these two catalysts were higher than other Ni-Zn/ Al_2O_3 catalyst, and thus bimetallic catalysts such as 15%Ni-5%Zn/ Al_2O_3 and 10%Ni-10%Zn/ Al_2O_3 increased upgraded bio-oil yields. The yields of upgraded bio-oil of control 1 and control 2 tests were lower than Ni-Zn/ Al_2O_3 catalysts due to the lack of metal active centers and enough hydrogen supply, respectively. The upgraded bio-oil yield of reused

15%Ni-5%Zn/Al₂O₃ catalyst was lower than fresh 15%Ni-5%Zn/Al₂O₃ catalyst, and this might be due to the higher coke deposition that deactivated catalyst quickly.

3.5. Physicochemical properties of upgraded bio-oil

Physicochemical properties including pH, water content and higher heating value of upgraded bio-oils and raw bio-oil are shown in Table 3. Water content has a negative effect on the combustion performance of upgraded bio-oils in engines [22]. The water content of upgraded bio-oil ranged from 11.48 wt.% to 20.43 wt.%, and it was reduced significantly from the water content of 26.91 wt.% present in raw bio-oil. The reduced water content was due to the increased hydrocarbon hydrophobic products in the oil phase [45]. There is an obvious increase in the higher heating values of upgraded bio-oil (17.13-30.47 MJ kg⁻¹) compared to raw bio-oil (15.54 MJ kg⁻¹). This is attributed to the lower contents of water and oxygenated compounds present in the upgraded bio-oils. The HDO process effectively improved the energy content of upgraded bio-oil products. HHV of upgraded bio-oil produced by Ni-Zn/Al₂O₃ was higher than control 1 and control 2 tests. This indicated that hydrogen was necessary for bio-oil HDO reactions. The loading of Ni and/or Zn on Al₂O₃ improved bio-oil HDO activity. Low pH values of bio-oil have a strong corrosive effect on combustion engines. The pH of upgraded bio-oil (3.27-3.43) increased slightly in comparison with raw bio-oil (3.24). This might be due to the conversion of some acids compounds into other compounds including hydrocarbons in upgraded bio-oils. However, the upgraded bio-oil was still very acidic with pH comparable to that of bio-oil due to the high content of acidic compounds.

The carbon contents of upgraded bio-oil was higher than raw bio-oil due to the removal of oxygen in bio-oil HDO reactions. The carbon content of upgraded bio-oil produced by Ni-Zn/Al₂O₃ catalysts was higher than control 1 and control 2 tests. The carbon balance of bio-oil HDO processes (Table 3) over Ni-Zn/Al₂O₃ catalysts was ranging from 74.34 wt.% to 94.58 wt.%.

3.6. Chemical compositions of upgraded bio-oil

In order to determine catalytic effects of Ni-Zn/Al₂O₃ catalysts on upgraded bio-oil products, GC-MS was used to analyze the chemical compositions of both upgraded bio-oil and raw bio-oil. The major chemical components of the upgraded bio-oils and raw bio-oil are displayed in Table 4. Chemical groups identified consisted of phenols, ethers, aldehydes, ketones, esters, alcohols, acids, furans and hydrocarbons.

The raw bio-oil main compositions were organic oxygenated compounds that included phenols (21.10%), acids (17.62%), ketones (9.77%), esters (6.86%), alcohols (5.64%) and aldehydes (5.40%). The total amount of detected oxygenated compounds was 70.70%. These compounds are responsible for the low quality of the raw bio-oil. The amount of valuable hydrocarbons in the raw bio-oil was 16.94% (as shown in Table S1 in supplemental materials). Similar hydrocarbons content in raw pine sawdust bio-oil was found by Huang et al [23].

The chemical compositions of upgraded bio-oils changed significantly after the raw bio-oil HDO over different Ni-Zn/Al₂O₃ catalysts. The contents of undesirable acids in upgraded bio-oil were decreased. This decrease may be due to the conversion of acids into hydrocarbons caused by decarbonylation, hydrogenation and cracking reactions [46]. Transfer of some carboxylic acids from the oil phase to aqueous phase might also contribute to the decrease of acids content in upgraded bio-oils [6]. This decrease in acid compounds reduces the requirements of special vessels and pipelines that would be used for upgraded bio-oil storage, transportation and processing.

The contents of ketones in upgraded bio-oils decreased during catalytic upgrading treatments. Ketones might be transformed into hydrocarbons and CO₂ through decarboxylation reactions [47]. Alcohols were most probably converted to hydrocarbons and phenols during bio-oil HDO process [6], resulting in decreased alcohols levels in upgraded bio-oil products. Some esters were transformed into hydrocarbons

275 through hydrogenation, decarboxylation and decarbonylation reactions [46]. This led to the decreased
276 content of esters present in upgraded bio-oil samples. During bio-oil HDO processes, the content of
277 aldehydes and phenols decreased in the upgraded bio-oil products. Aldehydes and phenols might be
278 transformed into coke-like polymers in the presence of acidic catalyst[48].

279 Hydrocarbons are the mainvaluable components in upgraded bio-oil product. The content of
280 hydrocarbons in upgraded bio-oil increased significantly in comparison with raw bio-oil. This was
281 probably due to the bio-oil HDO reactions including cracking, decarbonylation, decarboxylation,
282 hydrocracking, hydrodeoxygenation and hydrogenation that converted oxygenated organic compounds
283 to hydrocarbons on Ni-Zn/Al₂O₃ catalysts[44]. Compared to monometallic catalysts, the bimetallic
284 15%Ni-5%Zn/Al₂O₃ produced the upgraded bio-oil with the highest hydrocarbons content at 50.12%.
285 This was probably due to the synergistic effect of Ni and Zn on Al₂O₃ support[49]. The hydrocarbons
286 content of upgraded bio-oil produced by control 1 and control 2 test was lower than
287 Ni-Zn/Al₂O₃ catalysts, which indicated the important role of metal active centers and
288 hydrogenconsumption for bio-oil HDO reactions [50]. The hydrocarbons content of upgraded bio-oil
289 produced by reused 15%Ni-5%Zn/Al₂O₃ was lower than fresh 15%Ni-5%Zn/Al₂O₃, and this indicated the
290 reduced catalyst activity for bio-oil HDO reactions in this reused catalyst.

291 3.7. Conversion and selectivity of compounds in bio-oil

292 The conversion rates of main oxygenated compounds present in bio-oil are shown in Fig.4. The high
293 conversion rates of ketones and aldehydes indicate that a large proportion of them were converted into
294 hydrocarbons and coke-like polymers on Ni-Zn/Al₂O₃ catalysts [47-48]. The massive transformation of
295 alcohols into other compounds such as hydrocarbons resulted in the high conversion rate of alcohols in
296 bio-oil over Ni-Zn/Al₂O₃ catalysts [6]. Similarly, the large amount of acids and esters were transformed
297 into hydrocarbons, and this led to high conversion rates of acids and esters compounds [46]. The
298 selectivities of compounds present in bio-oil are shown in Fig.5. The high conversion rate of

oxygenated compounds including ketones, alcohols, acids and esters into hydrocarbons compounds on Ni-Zn/Al₂O₃ catalysts led to the high selectivity of hydrocarbons in upgraded bio-oil products [44].

3.8. Synergistic effect of Ni and Zn on Al₂O₃ support

Metallic Ni and Zn reduced from NiO and ZnO are the catalytic active centers for catalytic hydrogenation reactions on Ni-Zn/Al₂O₃ catalysts. There are three factors which resulted in the improved catalytic activity of binary Ni-Zn/Al₂O₃ (synergistic effect of Ni and Zn) than singular Ni/Al₂O₃, Zn/Al₂O₃ or Al₂O₃ catalyst. Firstly, the incorporation of Zn enhanced the interaction between NiO and alumina and improved the nickel dispersion [49]. Secondly, binary catalysts had higher stability and activity than singular catalyst [15]. Finally, the loading of second metal prevented excessive carbon deposition on metal active sites of singular catalysts, and this led to lower coke formation of binary catalyst than singular catalyst [16].

3.9. Gas distributions

The compositions of gases produced in the HDO processes were determined by GC. The compositions of gas are shown in Table 5. The main component of the produced gas was unreacted hydrogen. This indicates abundant hydrogen present for the bio-oil HDO reactions. However, the efficiency of Ni-Zn/Al₂O₃ catalysts still needs to be improved to further reduce the contents of oxygenated compounds in upgraded bio-oil. More research will be conducted to improve the catalyst activity in the future research. The other main gas product was CO₂, which indicates decarboxylation reactions of organic acids on Ni-Zn/Al₂O₃ catalysts during the bio-oil HDO processes [51]. Light hydrocarbons such as CH₄ and C₂-C₅ were detected. These were probably due to the cracking of organic compounds [6].

In the gas compositions, the hydrogen content of 15%Ni-5%Zn/Al₂O₃catalyst (90.26 %) was a bit higher than other Ni-Zn/Al₂O₃catalysts (89.50-89.77%). CO₂ content of this catalyst (9.27%) was lower than other Ni-Zn/Al₂O₃catalysts(9.73-10.02%). However, based on the actual H₂ consumption results (calculated from the initial H₂ and final H₂ in the autoclave reactor in Table 6), the relatively higher amount of H₂ (0.18 g) was consumed for 15%Ni-5% Zn/Al₂O₃catalyst when compared to other Ni-Zn/Al₂O₃catalysts (0.09-0.19 g). Decarboxylation level of 15%Ni-5%Zn/Al₂O₃was lower than other catalyst due to the lower CO₂formation. The rest of consumed hydrogen might be used in other HDO reactions such as hydrocracking, hydrodeoxygenation and hydrogenation [43]. This indicated that the hydrogenation level of 15%Ni-5%Zn/Al₂O₃might not be lower than other Ni-Zn/Al₂O₃catalyst due to the higher hydrogen consumption.

3.10. Reactor pressures

The reactor pressuresmonitored during the HDO reactions are shown in Table 6. The initial, maximum and final pressures of the HDO reactor wererecorded. The initial pressure was the hydrogen pressure measured at 20 °Cat the beginning of the test. The maximum pressure was the reactor pressure during the bio-oil HDO process at reaction temperature of 250°C. The final pressure was the reactor pressure when the HDO reactor was cooled to 20°C after reaction. The amount of hydrogenconsumed in bio-oil HDO processes over Ni-Zn/Al₂O₃ catalysts was calculated and shown in Table 6. Higher amount of hydrogen consumption was found for 15%Ni-5%Zn/Al₂O₃, 10%Ni-10%Zn/Al₂O₃and 20%Zn/Al₂O₃ catalysts. This indicatethe higher hydrogen consumption for bio-oil HDO reactions on these catalysts. This is beneficial for improving catalytic performance ofthe Ni-Zn/Al₂O₃ catalysts thatconverted oxygenated compounds into hydrocarbons. The result is higherhydrocarbonscontents in upgraded bio-oils produced using these Ni-Zn/Al₂O₃catalysts.

4. Conclusions

Pine sawdust raw bio-oil was upgraded using HDO processes over a series of Ni-Zn/Al₂O₃ catalysts. The HDO processes were carried out in a batch autoclave reactor at 250°C and 500 psig. The effects of Ni-Zn/Al₂O₃ catalysts are evaluated by determining the products (bio-oil and gas) yield and quality. Bimetallic Ni-Zn/Al₂O₃ was more effective in improving bio-oil yield and quality compared to monometallic Ni/Al₂O₃ or Zn/Al₂O₃ catalyst. The highest upgraded bio-oil yield at 44.64 wt.% and the highest hydrocarbon content at 50.12% were produced using 15% Ni-5% Zn/Al₂O₃ catalyst. Physicochemical properties of upgraded bio-oils including pH, water content and higher heating value were improved compared to the raw bio-oil. The hydrocarbon contents of upgraded bio-oils produced over Ni-Zn/Al₂O₃ catalysts improved when compared to the raw bio-oil. Undesirable acids, aldehydes and ketones contents of upgraded bio-oils produced by catalysts reduced when compared to raw bio-oil.

Acknowledgements

This work was supported by U.S. Department of Energy (Award No. SA0900160) and Department of Transportation (Award No. SA0700149) through the North Central Sun Grant Initiative. This study was also partially supported by the South Dakota Innovation Partner (Grant No. SA1600799).

References

- [1] E. Reyhanitash, M. Tymchyshyn, Z. Yuan, K. Albion, G. van Rossum, C.C. Xu, Hydrotreatment of fast pyrolysis oil: Effects of esterification pre-treatment of the oil using alcohol at a small loading, Fuel 179 (2016) 45-51.
- [2] J. Wildschut, I. Melian-Cabrera, H. Heeres, Catalyst studies on the hydrotreatment of fast pyrolysis oil, Appl. Catal., B 99 (2010) 298-306.

- 363 [3] S. Cheng, L. Wei, X. Zhao, Y. Huang, D. Raynie, C. Qiu, J. Kiratu, Y. Yu, Directly catalytic
364 upgrading bio-oil vapor produced by prairie cordgrass pyrolysis over Ni/HZSM-5 using a two stage
365 reactor, *AIMS Energy* 3 (2015) 227-240.
- 366 [4] C.A. Fisk, T. Morgan, Y. Ji, M. Crocker, C. Crofcheck, S.A. Lewis, Bio-oil upgrading over
367 platinum catalysts using in situ generated hydrogen, *Appl. Catal., A* 358 (2009) 150-156.
- 368 [5] Z. Tang, Q. Lu, Y. Zhang, X. Zhu, Q. Guo, One step bio-oil upgrading through hydrotreatment,
369 esterification, and cracking, *Ind. Eng. Chem. Res.* 48 (2009) 6923-6929.
- 370 [6] S. Cheng, L. Wei, X. Zhao, E. Kadis, Y. Cao, J. Julson, Z. Gu, Hydrodeoxygenation of prairie
371 cordgrass bio-oil over Ni based activated carbon synergistic catalysts combined with different metals,
372 *New Biotechnol.* 33 (2016) 440-448.
- 373 [7] J. Wildschut, F.H. Mahfud, R.H. Venderbosch, H.J. Heeres, Hydrotreatment of fast pyrolysis oil
374 using heterogeneous noble-metal catalysts, *Ind. Eng. Chem. Res.* 48 (2009) 10324-10334.
- 375 [8] C. Zhao, J. He, A.A. Lemonidou, X. Li, J.A. Lercher, Aqueous-phase hydrodeoxygenation of
376 bio-derived phenols to cycloalkanes, *J. Catal.* 280 (2011) 8-16.
- 377 [9] F. de Miguel Mercader, M.J. Groeneveld, S.R. Kersten, C. Geantet, G. Toussaint, N.W. Way, C.J.
378 Schaverien, K.J. Hogendoorn, Hydrodeoxygenation of pyrolysis oil fractions: process understanding
379 and quality assessment through co-processing in refinery units, *Energy Environ. Sci.* 4 (2011)
380 985-997.
- 381 [10] R. Gunawan, X. Li, C. Lievens, M. Gholizadeh, W. Chaiwat, X. Hu, D. Maurant, J. Bromly, C.-Z.
382 Li, Upgrading of bio-oil into advanced biofuels and chemicals. Part I. Transformation of
383 GC-detectable light species during the hydrotreatment of bio-oil using Pd/C catalyst, *Fuel* 111 (2013)
384 709-717.

- 385 [11] S. Cheng, L. Wei, X. Zhao, J. Julson, Application, Deactivation, and Regeneration of
386 Heterogeneous Catalysts in Bio-Oil Upgrading, *Catalysts* 6 (2016) 195.
- 387 [12] A. Popov, E. Kondratieva, L. Mariey, J.M. Goupil, J. El Fallah, J.-P. Gilson, A. Travert, F. Maugé,
388 Bio-oil hydrodeoxygenation: Adsorption of phenolic compounds on sulfided (Co) Mo catalysts, *J.*
389 *Catal.* 297 (2013) 176-186.
- 390 [13] N. Joshi, A. Lawal, Hydrodeoxygenation of pyrolysis oil in a microreactor, *Chem. Eng. Sci.* 74
391 (2012) 1-8.
- 392 [14] Z. He, X. Wang, Hydrodeoxygenation of model compounds and catalytic systems for pyrolysis
393 bio-oils upgrading, *Catal. Sustainable Energy* 1 (2012) 28-52.
- 394 [15] Y. Xu, T. Wang, L. Ma, Q. Zhang, W. Liang, Upgrading of the liquid fuel from fast pyrolysis of
395 biomass over MoNi/ γ -Al₂O₃ catalysts, *Appl. Energy* 87 (2010) 2886-2891.
- 396 [16] A. Ardiyanti, S. Khromova, R. Venderbosch, V. Yakovlev, H. Heeres, Catalytic hydrotreatment of
397 fast-pyrolysis oil using non-sulfided bimetallic Ni-Cu catalysts on a δ -Al₂O₃ support, *Appl. Catal.,*
398 *B* 117 (2012) 105-117.
- 399 [17] S. Leng, X. Wang, X. He, L. Liu, Y.e. Liu, X. Zhong, G. Zhuang, J.-g. Wang, NiFe/ γ -Al₂O₃: a
400 universal catalyst for the hydrodeoxygenation of bio-oil and its model compounds, *Catal. Commun.*
401 41 (2013) 34-37.
- 402 [18] X. Zhao, L. Wei, S. Cheng, Y. Cao, J. Julson, Z. Gu, Catalytic cracking of carinata oil for
403 hydrocarbon biofuel over fresh and regenerated Zn/Na-ZSM-5, *Appl. Catal., A* 507 (2015) 44-55.
- 404 [19] X. Zhao, L. Wei, S. Cheng, J. Julson, Optimization of catalytic cracking process for upgrading
405 camelina oil to hydrocarbon biofuel, *Ind. Crops Prod.* 77 (2015) 516-526.

- 406 [20] X. Zhao, L. Wei, S. Cheng, Y. Huang, Y. Yu, J. Julson, Catalytic cracking of camelina oil for
407 hydrocarbon biofuel over ZSM-5-Zn catalyst, *Fuel Process. Technol.* 139 (2015) 117-126.
- 408 [21] X. Zhao, L. Wei, S. Cheng, E. Kadis, Y. Cao, E. Boakye, Z. Gu, J. Julson, Hydroprocessing of
409 carinata oil for hydrocarbon biofuel over Mo-Zn/Al₂O₃, *Appl. Catal., B* 196 (2016) 41-49.
- 410 [22] Y. Huang, L. Wei, X. Zhao, S. Cheng, J. Julson, Y. Cao, Z. Gu, Upgrading pine sawdust pyrolysis
411 oil to green biofuels by HDO over zinc-assisted Pd/C catalyst, *Energy Convers. Manage.* 115 (2016)
412 8-16.
- 413 [23] Y.Huang, L.Wei, Z.Crandall, J.Julson, Z.Gu, Combining Mo-Cu/HZSM-5 with a two-stage
414 catalytic pyrolysis system for pine sawdust thermal conversion, *Fuel* 150 (2015) 656-663.
- 415 [24] S.M. Sajjadi, M. Haghighi, A.A. Eslami, F. Rahmani, Hydrogen production via CO₂-reforming of
416 methane over Cu and Co doped Ni/Al₂O₃ nanocatalyst: impregnation versus sol-gel method and
417 effect of process conditions and promoter, *J. Sol-Gel Sci. Technol.* 67 (2013) 601-617.
- 418 [25] S.Cheng, L.Wei, J.Julson, K.Muthukumarappan, P. R.Kharel, Y.Cao, E.Boakye, D.Raynie, Z. Gu,
419 Hydrodeoxygenation upgrading of pine sawdust bio-oil using zinc metal with zero valency, *J. Taiwan*
420 *Inst. Chem. Eng.*(2017)<http://dx.doi.org/10.1016/j.jtice.2017.02.011>.
- 421 [26] X.Zhao, L.Wei, J.Julson, Z.Gu, Y.Cao, Catalytic cracking of inedible camelina oils to hydrocarbon
422 fuels over bifunctional Zn/ZSM-5 catalysts, *Korean J. Chem. Eng.* 32 (2015)1528-1541.
- 423 [27] G. Feng, Z. Liu, P. Chen, H. Lou, Influence of solvent on upgrading of phenolic compounds in
424 pyrolysis bio-oil, *RSC Advances* 4 (2014) 49924-49929.
- 425 [28] P. Duan, P.E. Savage, Upgrading of crude algal bio-oil in supercritical water, *Bioresour. Technol.*
426 102 (2011) 1899-1906.

- 427 [29] W. Chen, Z. Luo, C. Yu, G. Li, Y. Yang, H. Zhang, Upgrading of bio-oil in supercritical ethanol:
 428 Catalysts screening, solvent recovery and catalyst stability study, *J. Supercrit. Fluids* 95 (2014)
 429 387-393.
- 430 [30] L. Wei, Y. Gao, W. Qu, X. Zhao, S. Cheng, Torrefaction of Raw and Blended Corn Stover,
 431 Switchgrass, and Prairie Grass, *Trans. ASABE* 59 (2016) 717-726
- 432 [31] X. Zhao, L. Wei, S. Cheng, J. Julson, G. Anderson, K. Muthukumarappan, C. Qiu, Development of
 433 hydrocarbon biofuel from sunflower seed and sunflower meat oils over ZSM-5, *J. Renewable*
 434 *Sustainable Energy* 8 (2016) 013109.
- 435 [32] S. Cheng, L. Wei, X. Zhao, E. Kadis, J. Julson, Conversion of Prairie Cordgrass to Hydrocarbon
 436 Biofuel over Co -Mo/HZSM - 5
- 437 [33] S. Cheng, L. Wei, X. Zhao, Development of a bifunctional Ni/HZSM-5 catalyst for converting
 438 prairie cordgrass to hydrocarbon upgraded bio-oil, *Energy Sources, Part A* 38 (2016) 2433-2437.
- 439 [34] Z. Yang, J. Yu, C. Li, Y. Zhong, W. Xuan, Z. Ren, Q. Wang, Y. Dai, H. Wang, Preparation of
 440 textured porous Al₂O₃ ceramics by slip casting in a strong magnetic field and its mechanical
 441 properties, *Cryst. Res. Technol.* 50 (2015) 645-653.
- 442 [35] V.V. Thyssen, T.A. Maia, E.M. Assaf, Cu and Ni Catalysts Supported on γ -Al₂O₃ and SiO₂
 443 Assessed in Glycerol Steam Reforming Reaction, *Journal of the Brazilian Chemical Society* 26
 444 (2015) 22-31.
- 445 [36] C. Liewhiran, S. Phanichphant, Effects of palladium loading on the response of thick film
 446 flame-made ZnO gas sensor for detection of ethanol vapor, *Sensors* 7 (2007) 1159-1184.

447 [37] I. Kasatkin, P. Kurr, B. Kniep, A. Trunschke, R. Schlögl, Role of lattice strain and defects in
 448 copper particles on the activity of Cu/ZnO/Al₂O₃ catalysts for methanol synthesis, *Angew. Chem.*
 449 119 (2007) 7465-7468.

450 [38] Y. Önal, S. Schimpf, P. Claus, Structure sensitivity and kinetics of D-glucose oxidation to
 451 D-gluconic acid over carbon-supported gold catalysts, *J. Catal.* 223(2004)122-133.

452 [39] S. Thangalazhy-Gopakumar, S. Adhikari, R. B. Gupta, Catalytic pyrolysis of biomass over H⁺
 453 ZSM-5 under hydrogen pressure, *Energy fuels* 26(2012)5300-5306.

454 [40] C. K. Cheng, S. Y. Foo, A. A. Adesina, Glycerol steam reforming over bimetallic Co–Ni/Al₂O₃, *Ind.*
 455 *Eng. Chem. Res.* 49(2010)10804-10817.

456 [41] H. Lu, H. Yin, Y. Liu, T. Jiang, L. Yu, Influence of support on catalytic activity of Ni catalysts in
 457 p-nitrophenol hydrogenation to p-aminophenol, *Catal. Commun.* 10(2008)313-316.

458 [42] S. Karnjanakom, G. Guan, B. Asep, X. Du, X. Hao, J. Yang, C. Samart, A. Abudula, A green method to
 459 increase yield and quality of bio-oil: ultrasonic pretreatment of biomass and catalytic upgrading of
 460 bio-oil over metal (Cu, Fe and/or Zn)/ γ -Al₂O₃, *RSC Adv.* 5(2015)83494-83503.

461 [43] P. M. Mortensen, J.-D. Grunwaldt, P. A. Jensen, K. Knudsen, A. D. Jensen, A review of catalytic
 462 upgrading of bio-oil to engine fuels, *Appl. Catal., A* 407 (2011) 1-19.

463 [44] R. Nava, B. Pawelec, P. Castaño, M. Álvarez-Galván, C. Loricera, J. Fierro, Upgrading of
 464 bio-liquids on different mesoporous silica-supported CoMo catalysts, *Appl. Catal., B* 92 (2009)
 465 154-167.

466 [45] T. Yang, Y. Jie, B. Li, X. Kai, Z. Yan, R. Li, Catalytic hydrodeoxygenation of crude bio-oil over
 467 an unsupported bimetallic dispersed catalyst in supercritical ethanol, *Fuel Process. Technol.* 148
 468 (2016) 19-27.

- 469 [46] R.O. Idem, S.P. Katikaneni, N.N. Bakhshi, Thermal cracking of canola oil: reaction products in the
470 presence and absence of steam, *Energy Fuels* 10 (1996) 1150-1162.
- 471 [47] X. Xu, C. Zhang, Y. Liu, Y. Zhai, R. Zhang, Two-step catalytic hydrodeoxygenation of fast
472 pyrolysis oil to hydrocarbon liquid fuels, *Chemosphere* 93 (2013) 652-660.
- 473 [48] X. Zhang, T. Wang, L. Ma, Q. Zhang, T. Jiang, Hydrotreatment of bio-oil over Ni-based catalyst,
474 *Bioresour. Technol.* 127 (2013) 306-311.
- 475 [49] Y. Qian, S. Liang, T. Wang, Z. Wang, W. Xie, X. Xu, Enhancement of pyrolysis gasoline
476 hydrogenation over Zn-and Mo-promoted Ni/ γ -Al₂O₃ catalysts, *Catal. Commun.* 12 (2011)
477 851-853.
- 478 [50] W. M.Xiong, Y.Fu, F. X.Zeng, Q. X.Guo, An in situ reduction approach for bio-oil
479 hydroprocessing, *Fuel Process. Technol.* 92(2011)1599-1605.
- 480 [51] S. Wang, Z. Guo, Q. Cai, L. Guo, Catalytic conversion of carboxylic acids in bio-oil for liquid
481 hydrocarbons production, *Biomass Bioenergy* 45 (2012) 138-143.

Figures:

Fig. 1. XRD spectra of catalysts: (a) Al_2O_3 , (b) 20%Ni/ Al_2O_3 , (c) 15%Ni-5%Zn/ Al_2O_3 , (d) 10%Ni-10%Zn/ Al_2O_3 , (e) 5%Ni-15%Zn/ Al_2O_3 and (f) 20%Zn/ Al_2O_3 .

Fig. 2. TEM images of catalysts: (a) Al_2O_3 , (b) 20%Ni/ Al_2O_3 , (c) 15%Ni-5%Zn/ Al_2O_3 , (d) 10%Ni-10%Zn/ Al_2O_3 , (e) 5%Ni-15%Zn/ Al_2O_3 and (f) 20%Zn/ Al_2O_3 .

Fig. 3. Product yields of different treatments.

Fig. 4. Conversion rates of compounds present in upgraded bio-oil.

Fig. 5. Selectivities of compounds present in upgraded bio-oil.

Fig. 1. (a) Al₂O₃, (b) 20% Ni/Al₂O₃, (c) 15% Ni-5% Zn/Al₂O₃,
(d) 10% Ni-10% Zn/Al₂O₃, (e) 5% Ni-15% Zn/Al₂O₃ and (f) 20% Zn/Al₂O₃.

Fig. 2. TEM images of catalysts: (a) Al_2O_3 , (b) 20%Ni/ Al_2O_3 , (c) 15%Ni-5%Zn/ Al_2O_3 ,

(d) 10%Ni-10%Zn/Al₂O₃, (e) 5%Ni-15%Zn/Al₂O₃ and (f) 20%Zn/Al₂O₃.

Fig.3. Product yields of different treatments.

Fig.4. Conversion rates of different compounds present in upgraded bio-oil.

Fig.5. Selectivities of compounds present in upgraded bio-oil.

Tables:

Table 1. Metal contents of Ni-Zn/Al₂O₃ catalysts.

Table 2. Textural properties and acidity of different catalysts.

Table 3. Physicochemical properties of raw bio-oil and different upgraded bio-oils.

Table 4. Chemical compositions of different upgraded bio-oils and raw bio-oil.

Table 5. Gas compositions of different treatments.

Table 6. Reactor pressures of different treatments.

Table 1

Metal contents of Ni-Zn/Al₂O₃ catalysts.

Catalysts	20%Ni/Al ₂ O ₃	15%Ni-5%Zn/Al ₂ O ₃	10%Ni-10%Zn/Al ₂ O ₃	5%Ni-15%Zn/Al ₂ O ₃	20%Zn/Al ₂ O ₃
Ni content (wt.%)	16.35	12.83	9.51	4.32	0
Zn content (wt.%)	0	4.46	8.75	13.76	16.48

Table 2

Textural properties and acidity of different catalysts.

Catalyst	S_{BET} (m ² /g)	d_{average} (nm)	Total pore volume (cm ³ /g)	Total acidity (mmol NH ₃ /g _{cat})
Al ₂ O ₃	341.08	3.33	0.28	2.80
20% Ni/Al ₂ O ₃	187.47	3.12	0.16	2.49
15% Ni-5% Zn /Al ₂ O ₃	186.31	3.11	0.14	2.39
10% Ni-10% Zn/Al ₂ O ₃	186.12	3.10	0.13	3.95
5% Ni-15% Zn/Al ₂ O ₃	184.20	3.08	0.12	3.96
20% Zn/Al ₂ O ₃	189.69	3.13	0.17	3.98

Table 3

Physicochemical properties of raw bio-oil and different upgraded bio-oils.

Treatments	Raw	20%Ni	15%Ni-5%Zn	10%Ni-10%Zn	5%Ni-15%Zn	Used 15%Ni-5%Zn			
						20%Zn/Al ₂ O ₃	Control 1	Control 2	
	bio-oil	/Al ₂ O ₃	/Al ₂ O ₃	/Al ₂ O ₃	/Al ₂ O ₃				/Al ₂ O ₃
Water content (wt.%)	26.91±0.29	17.53±0.22	14.00±0.14	12.98±0.14	15.33±0.21	11.48±0.22	13.02±0.12	20.43±0.14	14.45±0.03
pH	3.24±0.28	3.41±0.01	3.31±0.01	3.34±0.08	3.43±0.03	3.43±0.01	3.33±0.04	3.27±0.05	3.29±0.04
HHV(MJ kg ⁻¹)	15.54±0.04	28.47±1.34	30.47±0.42	30.39±0.22	29.37±0.79	27.85±1.25	26.67±0.20	17.13±0.17	29.59±0.21
Carbon (wt.%)	40.37±0.04	54.37±0.12	55.92±0.36	55.27±0.15	52.06±0.38	51.05±0.42	48.07±0.31	42.05±0.08	51.07 ±0.04
Carbon balance(wt.%)	N/A	91.92±0.11	92.75±0.13	94.58±0.16	78.73±0.18	87.46±0.38	74.34±0.23	74.05±0.14	92.53±0.24

Table 4

Chemical compositions of different upgraded bio-oils and raw bio-oil.

Relative content (%)	Raw bio-oil	20% Ni	15% Ni-5% Zn	10% Ni-10% Zn	5% Ni-15% Zn	20% Zn	Used		
							Control 1	Control 2	15% Ni-5% Zn
		/Al ₂ O ₃	/Al ₂ O ₃	/Al ₂ O ₃	/Al ₂ O ₃	/Al ₂ O ₃	/Al ₂ O ₃		/Al ₂ O ₃
Phenols	21.10	15.48	12.55	19.34	15.46	18.36	16.18	20.03	13.87
Ethers	3.59	1.62	6.21	0.36	0	0.70	0.89	3.23	5.74
Aldehydes	5.40	1.17	0	0.62	0.92	0.48	4.21	5.1	3.04
Ketones	9.77	3.92	0.23	0.28	3.11	4.79	7.61	8.76	6.52
Esters	6.86	3.90	0	3.53	3.72	3.19	5.73	6.02	2.34
Alcohols	5.64	2.18	0.21	1.30	2.23	0.91	4.38	4.98	2.32
Acids	17.62	9.80	6.65	6.39	9.73	6.99	12.34	16.73	10.12

Furans	0.72	0	0	0.35	0	0.23	0.56	0.34	0.63
Hydrocarbons	16.94	38.58	50.12	49.91	39.62	43.86	21.36	17.09	40.12
Others	12.36	23.35	24.03	17.92	25.21	20.49	26.74	17.72	15.3

Table 5

Gas compositions of different treatments.

								Used
	20%Ni/	15%Ni-5%	10%Ni-10%	5%Ni-15%	20%Zn			
Treatments						Control 1	Control 2	15%Ni-5%Zn
	Al ₂ O ₃	Zn/Al ₂ O ₃	Zn/Al ₂ O ₃	Zn/Al ₂ O ₃	/Al ₂ O ₃			
								/Al ₂ O ₃

	H ₂	89.77±0.04	90.26±0.05	89.50±0.01	89.71±0.03	89.56±0.02	89.80±0.11	0.74±0.26	94.16±0.15
	CO ₂	9.73±0.04	9.27±0.03	10.02±0.02	9.84±0.02	9.80±0.07	9.26±0.07	89.84±0.23	5.62±0.18
Gas									
composition	CO	0.36±0.00	0.29±0.00	0.31±0.00	0.30±0.00	0.31±0.00	0.30±0.01	3.05±0.01	0.12±0.00
(vol.%)									
	CH ₄	0.11±0.00	0.09±0.00	0.10±0.00	0.09±0.00	0.10±0.00	0.06±0.00	0.38±0.00	0.02±0.00
	C ₂ -C ₅	0.03±0.01	0.09±0.01	0.07±0.01	0.06±0.01	0.23±0.02	0.58±0.02	5.99±0.02	0.09±0.03

Table 6

Reactor pressures of different treatments.

		Treatments					Control		Used
		20%Ni/ Al ₂ O ₃	15%Ni-5%Zn /Al ₂ O ₃	10%Ni-10%Zn /Al ₂ O ₃	5%Ni-15%Zn /Al ₂ O ₃	20%Zn /Al ₂ O ₃	Control 1	Control 2	15%Ni-5%Zn /Al ₂ O ₃
Pressure (psig)	Initial	500±0.00	500±0.00	500±0.00	500±0.00	500±0.00	500±0.00	20±0.00	500±0.00
	Maxim um	1105±15	1135±35	1145±35	1115±45	1100±10	1010±10	560±10	1050±10
	Final	480±10	470±0	475±5	485±5	465±15	480±10	50±0	485±10
	Hydrogen consumption (g)	0.10±0.03	0.18±0.04	0.12±0.02	0.10±0.01	0.19±0.01	0.11±0.01	N/A	0.09±0.01