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Research Article

Effect of Process Conditions on Single-Stage Hydroprocessing of Bio-oil in a Continuous Packed-bed Reactor for the Production of Fuel

Divya R. Parapati[1] and Philip H. Steele[2,*]

Department of Sustainable Bioproducts, Mississippi State University
*Corresponding author E mail: sstillman@cfr.msstate.edu
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Abstract-Single-stage hydroprocessing of raw bio-oil was performed in a continuous packed-bed reactor utilizing sulfided CoMo/γ-Al_2O_3 catalyst at different process conditions to determine the most effective temperature, hydrogen pressure, hydrogen flow rate and liquid hourly space velocity. The most effective process conditions for the sulfided CoMo/γ-Al_2O_3 catalyst were for a temperature of 375-400 °C, pressure of 1500 psig, liquid hourly space velocity of 0.3 h^{-1} and hydrogen flow rate of 1000 ml/min. These conditions produced both higher yields and satisfactory properties. The product properties of the hydroprocessed raw bio-oil for the best combination of treatment conditions were an acid value of 0.7 mg KOH/g, higher heating value of 44.01 MJ/kg, and percentage water content of 0.1%. The elemental carbon, hydrogen, nitrogen and oxygen properties were 87.0, 13.0, 0.3 and 0.1%, respectively. The total liquid yields, organic fraction and aqueous fraction were 85.1, 24.6 and 60.6%, respectively. The organic fraction was also analyzed by detailed hydrocarbon analysis.

Index terms: Hydroprocessing, Bio-oil, Continuous packed-bed reactor, Fuel.

I. INTRODUCTION

Bio-oil derived from fast pyrolysis of biomass has the potential to serve as substitute for petroleum in the transportation fuel sector. However, bio-oil has deleterious properties such as high viscosity, water content, corrosiveness, low heating value and low stability [1]. Therefore, bio-oil must be upgraded before its utilization in gasoline and diesel engines. Pyrolysis bio-oil is a complex mixture of oxygenates with a single bio-oil type containing up to more than 300 different compounds [1]. Typical bio-oils contain water (20-30 wt%), lignin fragments (15-30 wt%), aldehydes (10-20 wt%), carboxylic acids (10-15 wt%), carbohydrates (5-10 wt%), phenols (2-5 wt%), furfurals (1-4 wt%), alcohols (2-5 wt%) and ketones (1-5 wt%) [2].

The undesirable properties of bio-oil are largely due to its high oxygen content. Current upgrading techniques are focused on removal of bio-oil oxygen content. These include catalytic hydroprocessing [3], esterification [4-6], olefination [7-9], catalytic pyrolysis [10, 11], HDO [3, 12-14], steam reforming [15, 16], and decarbonylation and decarboxylation [17]. Hydrodeoxygenation (HDO) has been studied extensively for conversion of bio-oil to liquid hydrocarbons. A variety of catalysts, have been applied for the HDO of bio-oil including conventional catalysts for petroleum hydroprocessing and noble metal catalysts such as CoMo, NiMo, NiW, Ni, Co, Pd and CuCrO [3], Rh, Pt, and Pd/ZrO_2 [18] and Ru/Al_2O_3, Ru/C, Ru/TiO_2, Pd/C and Pt/C [12, 19, 20].

Elliot et al. [21] developed a two-stage HDO process for upgrading at a temperature of 270 °C and 13.6 MPa pressure to avoid polymerization of oxygen-containing compounds, catalyst coking and reactor plugging. This hydrotreating step was then followed by a higher temperature hydrocracking performed at 400 °C and 13.6 MPa pressure to remove oxygen in presence of the sulfided CoMo/γ-Al_2O_3 and NiMo/γ-Al_2O_3 catalysts. This process of low temperature hydrotreating followed by higher-temperature hydrocracking is now widely applied by many HDO practitioners [3, 22-27]. The Elliot et al. [21] experiment with this two-stage method was performed in a continuous flow reactor, the experiment resulted in a decreased oxygen content from 21 wt% to 10 wt% when decreasing the LHSV from 0.7 to 0.25 h^{-1} over Pd/C at 340 ^oC and 140 bar pressure [21]. In general LHSV should be in the range of the 0.1 to 1.5 h^{-1} for both stages of the HDO method [28].

Sulfided catalysts are commonly utilized in petroleum refineries for hydrotreatment in the presence of hydrogen to remove heteroatoms, such as sulfur, nitrogen, oxygen and metals, from crude oil [29, 30]. The conventional CoMo/γ-Al_2O_3 and NiMo/γ-Al_2O_3 catalysts have been the most commonly applied catalysts in HDO studies. In these catalysts Mo serves as an active element while Co or Ni act as promoters supported on γ-Al_2O_3 or without support [13, 14, 30-33]. The concentration of the active metals on the support usually varies from 8 to 25 wt% and the promoter percentage varies from 1 to 4 wt%.

The CoMo and NiMo catalysts are more active in the sulfided form than in the non-sulfided form. Therefore, the catalysts are either presulfided with a sulfiding agent or sulfided on stream by the addition of a sulfiding agent to the feed. The sulfiding agent can be either hydrogen sulfide or a carbon containing sulfur compound [32, 33]. The relatively higher activity of sulfided CoMo or NiMo/γ-Al_2O_3 can be attributed to the formation of the active Co(Ni)MoS phase, consisting of

highly dispersed MoS_2 crystallites coated with Co or Ni atoms that act as promoters when the oxide form is subjected to the sulfidation process [32-34]. Then, the sulfur anion vacancies can play a role in the scission of carbon-heteroatom bonds [26].

With regard to other HDO operating conditions, a pressure ranging from 75 to 300 bars has been reported by researchers [35-37, 21]. The presence of high operating pressure ensures higher solubility of hydrogen in the bio-oil and thereby increases the availability of hydrogen in the vicinity of the catalyst; this also increases the reaction rate and further decreases reactor coking [35, 36, 38].

Little research has been focused on single-stage hydroprocessing conversion of bio-oil since Elliot et al. [21] developed the 2-stage hydroprocessing method. Earlier single-stage HDO conversion experiments were unsuccessful due to rapid coking of the catalyst and polymerization of bio-oil from the high temperatures applied for hydrocracking [3, 31]. The objective of this study was to determine the potential for application of a single-stage hydroprocessing process for effective conversion of bio-oil. Single-stage hydroprocessing conversion of bio-oil in a packed-bed reactor was tested and when found successful the best process conditions were identified by testing the levels of various process variables (temperature of 325-350, 375-400, 400-425°C, hydrogen pressure of 1000, 1500 psig, hydrogen flow rate of 500, 1000ml/min and liquid hourly space velocity of 0.1, 0.3, 0.7, 1 h^{-1}).

II. MATERIAL AND METHODS

$CoMo/\gamma\text{-}Al_2O_3$ (3.4-4.5% Co and 11.5-14.5% Mo on gamma-alumina support) was purchased from Alfa Aesar. Cyclohexane and carbondisulfide were purchased from Fisher Scientific. The oxide forms of catalysts was activated by subjecting them to a sulfidation process prior to hydroprocessing experiments. $CoMo/\gamma\text{-}Al_2O_3$ was sulfided with a solvent mixture of 2 vol % carbondisulfide and cyclohexane. To 800 ml of cyclohexane solvent, 16 ml (2 vol %) of carbondisulfide was added and the solvent mixture was pumped through a high-pressure dual-pump system. Sulfiding of the catalyst was performed at 300 ^oC, a pressure of 750 psi and LHSV of 1 h^{-1} for a period of 4 h. Bio-oil was produced by the fast pyrolysis process at a temperature of 400-450 ^oC under nitrogen gas atmosphere using a 7 kg/h auger-fed pyrolysis reactor located in the Department of Sustainable Bioproducts, Mississippi State University. Mean yield for the pyrolysis required to produce the study bio-oil was 62.4%. The bio-oil produced was a single phase product containing a mean water content value of 28.9%.

Continuous packed-bed reactor

The study continuous packed-bed reactor **(Figure 1)** consisted of a 1” I.D tubular reactor enclosed in a three-zone electric furnace (three 6” zones each independently controlled by its own temperature controller) followed by a condensation system. The temperatures inside the reactor were monitored with a point profile thermocouple equipped with ten sensing points (Omega Instruments). Three temperature sensing points were located in each of the 3 reactor heater zones for a total of 9. The tenth temperature sensing point was located at the condenser orifice. The catalyst bed temperature zones were maintained as closely as possible to the desired temperature set point through the course of the experiment. The hydroprocessing catalytic reaction is exothermic such that temperatures were difficult to control due to the adiabatic nature of the reaction. Temperature control was only possible within a 25 ^oC temperature range (for example 375-400 °C). The bio-oil was pumped into the catalyst tube with a high-pressure dual-pump system (Teledyne Isco 500D). The hydrogen flow rate was controlled with a mass flow controller (MFC; Brooks Instruments), and the reactor pressure was controlled with a back-pressure regulator. Only two pressures were tested, due to reactor's design limitation. **Figure 1** shows a diagram of the schematic of the continuous packed-bed reactor. Figure 2a and b show the method of catalyst loading in the continuous packed-bed reactor.

For all experiments the reactor was loaded with catalyst at a temperature initially set to 150 °C. Once this initial temperature set point was attained, the reactor temperature was raised by another 100 °C; upon reaching the resultant temperature of 250 ^oC, the reactor temperature was raised by another 100 ^oC to 350 °C. A final 25 to 50 ^oC increase was often applied to raise the actual reaction temperature as close to the target temperature range as possible (for example 375-400 ^oC). Following heating the reactor was pressurized to the desired 1500 psi hydrogen reaction pressure. Hydroprocessing of raw bio-oil was performed in the continuous packed-bed reactor utilizing sulfided $CoMo/\gamma\text{-}Al_2O_3$ catalyst. Process conditions were varied to determine the most effective temperature (325-350, 375-400, 400-425°C) , pressure (1000, 1500 psig), hydrogen flow rate (500, 1000ml/min) and liquid hourly space velocity (0.1, 0.3, 0.7, 1 h^{-1}).

The exit gas flow rate in milliliters per minute (ml/min) was monitored by an Agilent gas flow meter. Products exiting the packed-bed reactor were cooled in the condenser and the liquid products were collected in a sampling bottle at 2 h intervals. Periodic gas sampling was also performed 10 min prior to the liquid sampling at the 2 h intervals using Tedlar sampling bags. The collected liquid products were centrifuged for 1 h to separate the aqueous fraction (AF) and the converted organic fraction (OF). The packed-bed reactor bio-oil was catalyzed in the packed-bed reactor for a period of 8 h for all experiments.

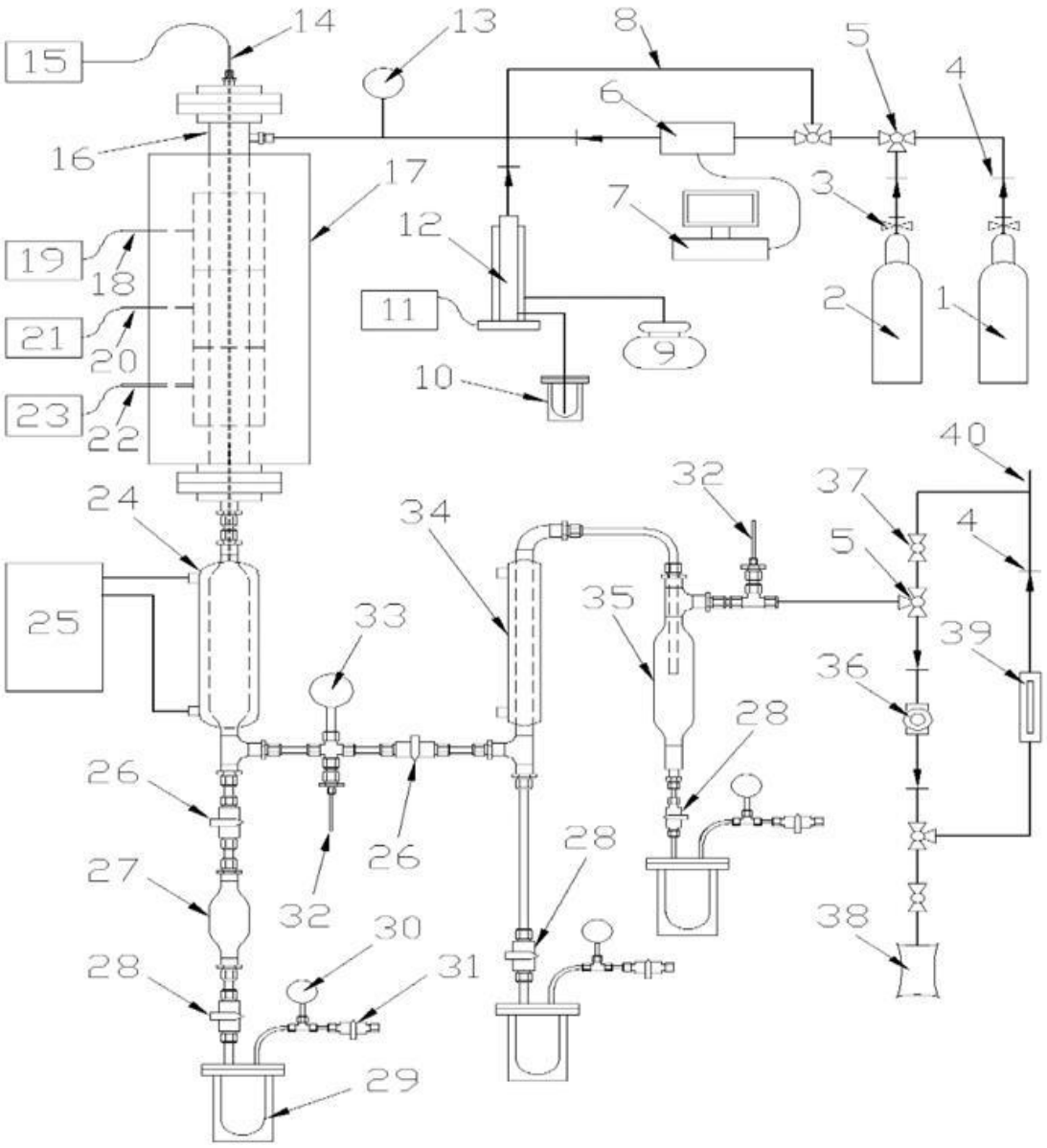

Figure1. Schematic of the continuous packed-bed reactor.

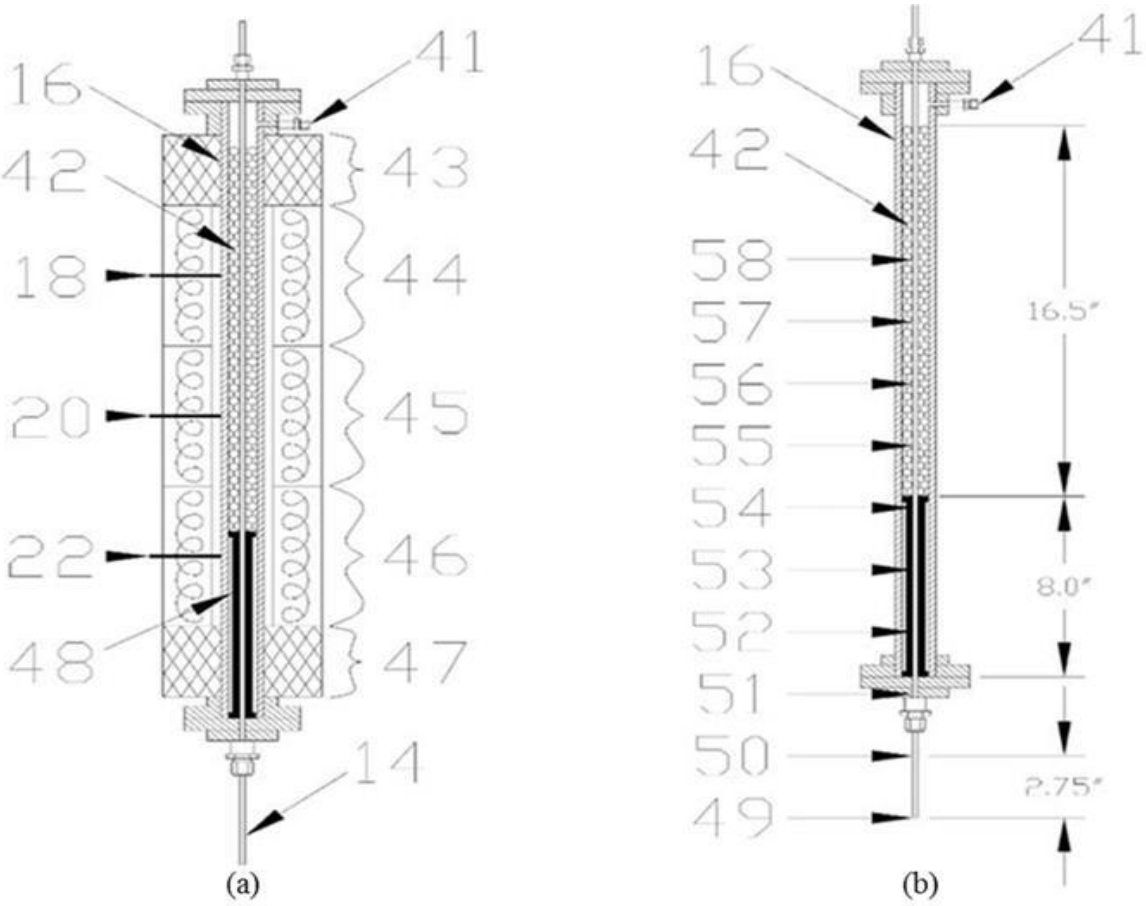

Figure 2. Method of catalyst loading in the continuous packed-bed reactor. a. Method of catalyst loading inside the reactor showing the loaded catalyst tube, enclosed in the furnace; b. Reactor loaded catalyst tube.

Table 1. The numbered components of the continuous packed-bed reactor corresponding to Figure 1 numerical labels.

1	Hydrogen cylinder	30	Sampling vessel pressure gauge
2	Air cylinder	31	Sampling vessel ball valve
3	Cylinder regulator	32	Thermocouple
4	Check valve	33	Reactor exit pressure gauge
5	Three-way valve	34	Condenser 2
6	Mass flow controller (MFC)	35	Condenser 3
7	Computer-MFC program	36	Back pressure regulator
8	MFC bypass line	37	Needle valve
9	Air compressor	38	Gas sample bag
10	Bio-oil	39	Exit gas flow meter

11	High pressure pump controller	40	Gas exit line
12	High pressure pump	41	Bio-oil inlet
13	Reactor inlet pressure gauge	42	Catalyst
14	Ten zone reactor thermocouple	43	Heater top insulation, 3” long
15	Ten zone thermocouple monitor	44	Heater zone 1, 6” long
16	Reactor tube	45	Heater zone 2, 6” long
17	Reactor tube heater	46	Heater zone 3, 6” long
18	Heater zone 1 thermocouple	47	Heater bottom insulation, 3” long
19	Heater zone 1 controller	48	Catalyst support
20	Heater zone 2 thermocouple	49	Reactor thermocouple zone 1
21	Heater zone 2 controller	50	Reactor thermocouple zone 2
22	Heater zone 3 thermocouple	51	Reactor thermocouple zone 3
23	Heater zone 3 controller	52	Reactor thermocouple zone 4
24	Condenser 1	53	Reactor thermocouple zone 5
25	Chiller	54	Reactor thermocouple zone 6
26	Ball valve	55	Reactor thermocouple zone 7
27	Hydrocarbons storage vessel	56	Reactor thermocouple zone 8
28	Needle valve	57	Reactor thermocouple zone 9
29	Sampling vessel	58	Reactor thermocouple zone 10

Raw bio-oil (RBO) was catalyzed in the packed-bed reactor by sulfided CoMo/γ-Al_2O_3 catalyst. This catalyst was tested as the hydroprocessing catalyst at various process conditions: temperature, pressure, hydrogen flow rate (HFR) and liquid hourly space velocity (LHSV). Three temperature ranges of 325-350 °C, 375-400 °C, 400-425 °C, two pressures of 1000 and 1500 psig, two HFRs of 500 ml/min and 1 ltr/min and four LHSV’s of 0.1, 0.3, 0.7 and 1 h^{-1} were tested in several combinations for a total of 11 treatments as shown in Table 2. The combinations were arrived at by testing all three temperatures at a pressure of 1500 psig, an HFR of 1000 ml/min and LHSV of 0.3 h^{-1} for three replicated temperature treatments. These initial test values for pressure (1500 psig), HFR (1000 ml/min) and LHSV (0.3 h^{-1}) were selected from values found best in previous single-stage HDO studies [3, 21, 28, 35, 36, 37]. Of the three different temperature treatments tested the temperature that provided the best OF yield and its properties was selected as that applied for testing the pressure, HFR and LHSV conditions. All remaining treatments were also compared and the best-performing treatment was also selected by choosing the treatment with the best OF yield and it properties. For the best-performing temperature the hydrogen pressure variable was tested at 1000 psig and 1500 psig which provided two more treatments. For the best-performing temperature and pressure two HFR treatments (500 and 1000 ml/min) were tested giving another two treatments. The HFR with the best performance was selected and treated with four levels of LHSV for the total of 11 treatments. Liquid and gas samples were collected at defined time intervals and were subjected to analysis.

Table 2. The temperature, pressure, hydrogen flow rate (HFR) and liquid hourly space velocity (LHSV) treatment combinations applied.

Treatment number (T.No)	Temperature (^oC)	Pressure (psig)	HFR (ml/min)	LHSV (h^{-1})
0 (RBO)	NA	NA	NA	NA
1	325-350	1500	1000	0.3
2	375-400	1500	1000	0.3
3	400-425	1500	1000	0.3
4	375-400	1000	1000	0.3
5	375-400	1500	1000	0.3
6	375-400	1500	500	0.3
7	375-400	1500	1000	0.3
8	375-400	1500	1000	0.1
9	375-400	1500	1000	0.3
10	375-400	1500	1000	0.7
11	375-400	1500	1000	1

Physical and chemical analysis

Raw bio-oil (RBO) and the OF produced from the hydroprocessing treatments were characterized following ASTM methods. For the acid value (AV) test, 1 g of sample was dissolved in isopropanol/water (v/v =35:65) solution and then titrated with 0.1 N NaOH to a pH of 8.5. The AV was then calculated as the required milligrams (mg) amount of NaOH equivalent to 1 g of sample, according to ASTM D664. The HHV was determined with a Parr 6400 automatic isoperibol calorimeter according to ASTM D240. The Karl Fischer method was employed to determine water content by ASTM E203 with a Cole-Parmer Model C-25800-10 titration apparatus. Elemental analysis (CHNO) for determination of percent carbon (C), percent hydrogen (H), percent nitrogen (N) and percent oxygen (O) were determined by EAI CE-440 elemental analyzer, with oxygen content determined by difference by the ASTM D5291 method. Based on significantly superior product properties and yields, the organic fraction (OF) of the best process conditions was chosen for more detailed analysis by detailed hydrocarbon analysis (DHA). DHA was performed by a PerkinElmer Clarus 680 GC equipped with a built-in model Arnel 4060 DHA analyzer, performed by ASTM D6730-01 method.

Experimental design

Each experiment was performed in triplicate. A factorial arrangement of treatments in a completely randomized design was employed with the single factorial representing the levels of process variables applied. The analysis of variance (ANOVA) model as shown in Eq's. 1, 2, 3 and 4 were comprised of a completely randomized design with a factorial arrangement having a single variable type (temperature, pressure, HFR and LHSV) to determine the influence on the physical properties of AV, HHV, oxygen content and WC produced by hydroprocessing of raw bio-oil (RBO). ANOVA Eq's. 1, 2, 3 and 4 were also applied to yield analysis.

All statistical tests were performed at the 0.05 level of significance. The ANOVA treatment significance satisfied the requirement of Fisher's protected LSD (Steel et al. 1980). The least significant difference (LSD) comparison of means test was performed to separate the physical property means, run times and yields (total yields (TY), organic fraction (OF) and aqueous fraction (AF)) as influenced by the process variable type treatments.

The ANOVA model was performed for each of the physical properties and liquid yields.

$$Y_i = \beta_0 + \beta_1 A_i + e_i$$

Where:

Y_i represents dependent variable physical or chemical testing values: acid value,

HHV, oxygen percent, WC and yields,

β_0 represents the intercept term,

β_1 A_i represents the influence of temperature (325-350, 375-400 and 400-425 ^oC) for raw bio-oil by maintaining other variables constant (Pressure 1500 psi, HFR 1000 ml/min and LHSV of 0.3 h^{-1})

e_i represents the random error term.

The ANOVA model was performed for each of the physical properties and liquid yields.

$$Y_i = \beta_0 + \beta_1 A_i + e_i \quad \text{Eq. 2}$$

Where:

Y_i represents dependent variable physical or chemical testing values: acid value,

HHV, oxygen percent, WC and yields,

β_0 represents the intercept term,

β_1 A_i represents the influence of pressure(1000 and 1500 psi) for raw bio-oil by maintaining other variables constant (temperature 375-400 ^oC, hydrogen flow rate 1000 ml/min and LHSV of 0.3 h^{-1})

e_i represents random error term.

The ANOVA model was performed for each of the physical properties and liquid yields.

$$Y_i = \beta_0 + \beta_1 A_i + e_i \quad \text{Eq. 3}$$

Where:

Y_i represents dependent variable physical or chemical testing values: acid value,

HHV, oxygen percent, WC and yields,

β_0 represents the intercept term,

β_1 A_i represents the influence of HFR (500 and 1000 ml/min) for raw bio-oil by maintaining other variables constant (temperature 375-400 ^oC ,pressure 1500 psi, and LHSV of 0.3 h^{-1})

e_i represents random error term.

The ANOVA model was performed for each of the physical properties and liquid yields.

$$Y_i = \beta_0 + \beta_1 A_i + e_i \quad \text{Eq. 4}$$

Where:

Y_i represents dependent variable physical or chemical testing values: acid value,

HHV, oxygen percent, WC, and yields,

β_0 represents the intercept term,

β_1 A_i represents the influence of LHSV (0.1, 0.3, 0.7 and 1.0 h^{-1}) for raw bio-oil by maintaining other variables constant (temperature 375-400 ^oC, pressure 1500 psi and hydrogen flow rate 1000)

e_i represents random error term.

III. RESULTS AND DISCUSSION

Testing of different process conditions

Tables 3, 4 and 5 describe the properties of OF obtained by the HDO treatments of the RBO to determine the effect of temperature (325-350, 375-400 and 425-450 ^oC) by maintaining other variables, of pressure (1500 psi), HFR (1000 ml/min) and LHSV (0.3 h^{-1}) constant. The properties of RBO (treatment 0) are given in Table 3, as the control to allow comparison of the RBO properties to the upgraded properties from the treatments. The AV values of the treated bio-oils were only a small fraction, 4.1, 0.7 and 4.1%, of the AV value (96.4 mg KOH/g) of the RBO. The significantly lowest AV of the three variable temperature treatments was 0.67 (0.7% of the RBO AV) for the temperature treatment of 375-400 ^oC, pressure of 1500 psig, HFR of 1000 ml/min and LHSV of 0.3. The highest HHV was a significant 44.0 MJ/kg for the temperature treatment of 375-400 ^oC.

The CHNO properties of the OF's at the three tested temperatures differed little with one exception for the O value of treatment 1 (temperature of 325-350 ^oC). The O value of this treatment was significantly high at 4.0% as compared to the values for treatments 2 and 3 (0.1 and 0.0%) for the respective temperature values of 375-400 and 400 to 425 ^oC.

Table 3. OF property values (AV, HHV, CHNO, %WC, TY, OF and AF) of sulfided CoMo/γ-Al_2O_3 catalysis of RBO for three temperature's (325-350, 375-400, 400-425 ^oC), pressure of 1500 psig, LHSV of 0.3 h-1 and HFR of 1000 ml/min.

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T.No	Temp (^oC)	AV (mg of KOH/g)	HHV (MJ/Kg)	C %	H %	N %	O %	WC %
0	RBO	96.5 (a)	16.5 (d)	37.3 (d)	7.7 (d)	0.6 (a)	54.5 (a)	28.9 (a)
1	325-350	4.1 (b)	41.6 (c)	83.7 (c)	12.0 (c)	0.3 (c)	4.0 (b)	0.5 (b)
2	375-400	0.7 (c)	44.0 (a)	87.1 (a)	13.0 (a)	0.3 (c)	0.1(c)	0.1 (c)
3	400-425	4.1 (b)	42.9 (b)	86.9 (b)	12.8 (b)	0.4 (b)	0 (d)	0.1 (c)

The percentage WC properties for temperature treatments 2 and 3 (375-400 and 400 to 425 ^oC) were both 0.1%. However, the percentage value for treatment 1 (325-350 ^oC) was 5 times higher at 0.5%. Table 4 shows TY, OF and AF yields

for the three temperatures (325-350, 375-400, 400-425 ^{o}C). For temperatures of 325-350, 375-400, 400-425 ^{o}C the TY yields differed significantly (75.1, 85.2 and 77.4 wt%, respectively). AF yields for these three temperatures also differed significantly at 54.9, 60.5 and 53.0 wt%, respectively; the OF yields also differed significantly at 20.3, 24.6 and 24.4 wt%, respectively.

Hydrogen consumption was similar for the three temperature treatments as shown in Table 5. The OF yield of 24.6% was higher for temperature treatment 2 (375-400 ^{o}C), as compared to respective yields of 20.3% for treatment 1 (325-350 ^{o}C) and 24.4% for treatments 3 (400-425 ^{o}C). From Tables 3, 4 and 5, based on OF properties and yields, treatment 2 (375-400 ^{o}C) was considered as the best temperature treatment. While the oxygen value was slightly higher for treatment 1, the remaining OF properties and yield were significantly better for treatment 2. This temperature was chosen for further treatment variable type (pressure, HFR and LHSV) experiments.

Table 4. Yields of OF at three temprature's (325-350, 375-400, 400-425 ^{o}C) at pressure of 1500 psig, LHSV of 0.3 h^{-1} and HFR of 1000 ml/min.

T.No	Yields wt%	TL wt%	OF wt%	AF wt%
1	325-350	75.1 (c)	20.3 (c)	54.9 (b)
2	375-400	85.2 (a)	24.6 (a)	60.5 (a)
3	400-425	77.4 (b)	24.4 (b)	53.0 (c)

Table 5. Gas analysis of three temperature's (325-350, 375-400, 400-425 ^{o}C) at pressure of 1500 psig, LHSV of 0.3 h^{-1} and HFR of 1000 ml/min.

T.No	Temp (^{o}C)	H_2 %	O_2 %	N_2%	CH_4 %	CO %	CO_2 %	C_2H_6 %
1	325-350	75.1	0.8	2.5	0.3	0	0.3	0.3
2	375-400	76.1	0.4	1.3	0.1	0.1	1.6	1
3	400-425	73.2	0.5	1.5	2	0.1	1.5	1.3

Tables 6, 7 and 8 describe the properties of OF obtained by hydroprocessing treatments of RBO to determine the effect of pressure (1000 and 1500 psi) by maintaining other variables, of temperature (375-400 ^{o}C), HFR (1000 ml/min) and LHSV (0.3 h^{-1}) constant. Again, as for the pressure value of treatments 4 and 5 (1000 and 1500 psi), the respective AV values of the treated RBO's are only a small fraction, 2.9 and 0.7%, of the AV value (96.4 mg KOH/g) of the RBO. For treatment 4 the HHV was 41.6 MJ/kg. No difference in % WC (0.1 and 0.1%) was observed between treatments 4 and 5. For pressures 1000 and 1500 psi the TY yields significantly differed at 73.8 and 85.2 wt%, respectively. AF yields for two pressures were 53.0 and 60.5 wt%, respectively and the OF yields also differed significantly at 20.8 and 24.6 wt% respectively. From the tested pressure treatment variables 4 and 5 (1000 and 1500 psig pressure), treatment 5 (1500 psig) was considered as the best treatment for pressure based on OF yields and properties. Therefore, pressure of 1500 psi was chosen for further treatment variable type (HFR and LHSV) studies. The hydrogen consumption for treatments 4 and 5 was 53.9 and 76.1% respectively (Table 7). Though treatment 5 (1500 psig pressure) contained higher hydrogen percentage than treatment 4, showed higher deoxygenation activity.

Table 6. Results of OF (AV, HHV, CHNO, %WC, TL, HCF and AF) at two pressures (1000 and 1500 psi) for a temperature of 375-400 °C, LHSV of 0.3 h-1 and HFR of 1000 ml/min in presence of sulfided CoMo/γ-Al_2O_3 catalyst).

T.No	Pressure (psig)	AV (mg KOH/g)	HHV (MJ/Kg)	C %	H %	N %	O %	WC %
0	RBO	96.5 (a)	16.5 (c)	37.3 (a)	7.7 (c)	0.6 (a)	54.5 (a)	28.9 (a)
4	1000	2.9 (b)	41.6 (b)	86.6 (b)	12.7 (b)	0.4 (b)	0.3 (b)	0.1 (b)
5	1500	0.7 (c)	44.0 (a)	87.1 (a)	13.0 (a)	0.3 (c)	0.1 (c)	0.1 (b)

Table 7. Yields of OF for two pressures (1000 and 1500 psi) at temperature of 375-400 °C, LHSV of 0.3 h^{-1} and HFR of 1000 ml/min).

T.No	Pressure (psig)	TL wt%	HCF wt%	AF wt%
4	1000	73.8 (a)	20.8 (b)	53.0 (b)
5	1500	85.2 (a)	24.6 (a)	60.5 (a)

Table 8. Gas analysis for a T of 375-400 °C, two pressures, LHSV of 0.3 h^{-1} and HFR of 1000 ml/min.

T.No	Pressure (Psig)	H_2 %	O_2 %	N_2%	CH_4 %	CO %	CO_2 %	C_2H_6 %
4	1000	53.9	0.6	8.2	2.2	0.2	3.9	1.8
5	1500	76.1	0.4	1.3	0.1	0.1	1.6	1.0

Tables 9, 10 and 11 describe the OF properties obtained by hydroprocessing of the bio-oil to determine the effect of HFR (500 and 1000 ml/min), by maintaining other variables, of temperature (375-400 ^oC), pressure (1500 psi) and LHSV (0.3 h^{-1}), constant. These experiments were performed utilizing the previously determined best temperature (375-400 ^oC) and pressure (1500 psi). The respective AV values for treatments 6 and 7 were much lower at 4.3 and 0.67 mg/g KOH than the RBO AV value (96.4 mg KOH/g). The treatment 6 AV value of 4.3 mg KOH/g was more than 6 times higher than the treatment 7 value of 0.67 mg KOH/g. The HHV for treatment 6 was 43.0 MJ/kg and for treatment 7 slightly higher at 44.0 MJ/kg. The CHNO properties differed little between treatments 6 and 7 (500 and 1000 ml/min HFR). The oxygen value of treatment 6 was 1.8% which was 18 times higher than the 0.1% value for treatment 7. The percentage WC values were 2.1 and 0.1% for treatments 6 and 7, respectively. The OF yield was somewhat higher for treatment 6 (26.1%) compared to treatment 7 (24.6%). For the HFR's of 500 and 1000 ml/min the TY yields were 84.9 and 85.2 wt%, respectively. Whereas, AF yields for these two HFR's were 58.8 and 60.5 wt%, respectively and the OF yields were 26.1 and 24.6 wt%, respectively. The best treatment based on most of the property comparisons was treatment 7. Therefore, the HFR of 1000 ml/min for treatment 7 was selected as the best HFR compared to the 500 ml/min for treatment 6.

Table 9. Results of OF (AV, HHV, CHNO and %WC) for two HFR's (500, 1000 ml/min) at temperature of 375-400 °C, pressure of 1500 psig and LHSV of 0.3 h^{-1}.

T.No	HFR (ml/min)	AV (mg KOH/g)	HHV (MJ/Kg)	C %	H %	N %	O %	WC %
0	RBO	96.5 (a)	16.5 (c)	37.3 (c)	7.7 (c)	0.6 (a)	54.5 (a)	28.9 (a)
6	500	4.3 (b)	43.0 (b)	85.3 (b)	12.5 (b)	0.6 (a)	1.8 (b)	2.1 (b)
7	1000	0.7 (c)	44.0 (a)	87.1 (a)	13.0 (a)	0.3 (b)	0.1 (c)	0.1(c)

Table 10. Yields for HFR's, of 500 and 1000 ml/min temperature of 375-400 °C, pressure of 1500 psig and LHSV of 0.3 h^{-1}.

T.No	HFR (ml/min)	TL wt %	OF wt%	AF wt%
6	500	84.9 (b)	26.1 (a)	58.8 (b)
7	1000	85.2 (a)	24.6 (b)	60.5 (a)

Table 11. Gas analysis for HFR's, of 500 and 1000 ml/min, temperature of 375-400 °C, pressure of 1500 psig and LHSV of 0.3 h^{-1}.

T.No	HFR (ml/min)	H_2 %	O_2 %	N_2%	CH_4 %	CO %	CO_2 %	C_2H_6 %
6	500	80.7	0.5	1.5	0.3	0	0.24	0.1
7	1000	76.1	0.4	1.3	0.1	0.1	1.6	1

Tables 12, 13 and 14 describe the properties of OF obtained by the hydroprocessing of the RBO to determine the effect of applied LHSV values of 0.1, 0.3, 0.7 and 1.0 h^{-1} by maintaining other variables (temperature (375-400 ^{o}C), pressure (1500 psi) and HFR (1000 ml/min)) constant. The results of treatments 8, 9, 10 and 11 are shown in Tables 12, 13 and 14. The AV values of treatments 8, 9, 10 and 11 were much lower than the 96.4 mg KOH/g value for RBO at 0.7, 17.8 and 32.1 mg KOH/g, respectively. The HHV's for treatments 8, 9, 10 and 11 were 43.7, 44.0, 38.7 and 35.4 MJ/kg, respectively. The properties of OF obtained from treatments 8, 9, 10 and 11 differed little in terms of CHNO and % WC. For the LHSV's of 0.1, 0.3, 0.7 and 1.0 h^{-1}, the TY yields were 71.6, 85. 2, 87.1 and 87.2 wt%, respectively. AF yields for the four LHSV's were 57.5, 60.5, 59.5 and 54.9 wt%, respectively, and the OF yields were 14.1, 24.6, 27.6 and 32.2 wt%, respectively. These OF yields increased significantly for each increase in LHSV level. The LHSV treatments did not differ much in gas consumption. The respective product qualities for the LHSV treatments were satisfactory in terms of properties: AV of 17.8 and 32.1 mg KOH/g, HHV of 38.7 and 35.4 MJ/kg, oxygen content of 13.0 and 16.8% and WC percentage of 3.7 and 4.4%. The best treatment based on most of the property comparisons was treatment 9. Therefore, the LHSV of 0.3 h^{-1} for treatment 9 was selected as the best compared to the 0.1, 0.7 and 1.0 h^{-1} for treatment 8, 10 and 11, respectively

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Table 12. Results of OF (AV, HHV, CHNO, %WC, TL, HCF and AF) for four LHSV's (0.1, 0.3, 0.7, 1.0 h^{-1}) at temperature of 375-400 °C, pressure of 1500 psig and HFR of 1000 ml/min.

T.No	LHSV (h^{-1})	AV (mg of KOH/g)	HHV (MJ/Kg)	C %	H %	N %	O %	WC %
0	RBO	96.5 (a)	16.5 (e)	37.3 (e)	7.7 (e)	0.6 (a)	54.5 (a)	28.9 (a)
8	0.1	0.7 (d)	43.7 (b)	85.4 (b)	14.3 (a)	0.4 (b)	0 (e)	0.1 (d)
9	0.3	0.7 (d)	44.0 (a)	87.1 (a)	13.0 (b)	0.3 (c)	0.1 (d)	0.1 (d)
10	0.7	17.8 (c)	38.7 (c)	78.7 (c)	10.3 (c)	0.3 (c)	13.0 (c)	3.7 (c)
11	1	32.1 (b)	35.4 (d)	78.1 (d)	10.0 (d)	0.2 (d)	16.8 (b)	4.4 (b)

Table 13. Yields for four LHSV's, temperature of 375-400 °C, pressure of 1500 psig and HFR of 1000 ml/min.

T.No	LHSV (h-1)	TL (wt%)	OF (wt%)	AF (wt %)
8	0.1	71.6 (d)	14.1 (d)	57.5 (c)
9	0.3	85.2 (c)	24.6 (c)	60.5 (a)
10	0.7	87.1 (b)	27.6 (b)	59.5 (b)
11	1	87.2 (a)	32.2 (a)	54.9 (d)

Table 14. Gas analysis for four LHSV's, temperature of 375-400 °C, pressure of 1500 psig and HFR of 1000 ml/min.

T.No	LHSV (h^{-1})	H_2 %	O_2 %	N_2%	CH_4 %	CO %	CO_2 %	C_2H_6 %
8	0.1	78.8	0.6	2	1.2	0	0.4	0.87
9	0.3	76.1	0.4	1.3	0.1	0.1	1.6	1
10	0.7	76.4	0.9	3.1	0.3	0	0.5	0.3
11	1	70.5	1.0	9.0	0.2	0	0.2	0.2

For this best combination of process conditions (temperature of 375-400 °C, pressure of 1500 psig, LHSV of 0.3 h^{-1} and HFR of 1000 ml/min), a DHA of the OF was performed with results shown in Figure 3. The OF contained iso-paraffins, naphthenes, compounds greater than C14 and olefins. The other compounds that were identified in minor amounts in comparison to iso-paraffins, olefins, naphthenes and compounds greater than C14 were aromatics and paraffins. The OF octane value for the best-performing conditions was determined by DHA to be 50.3.

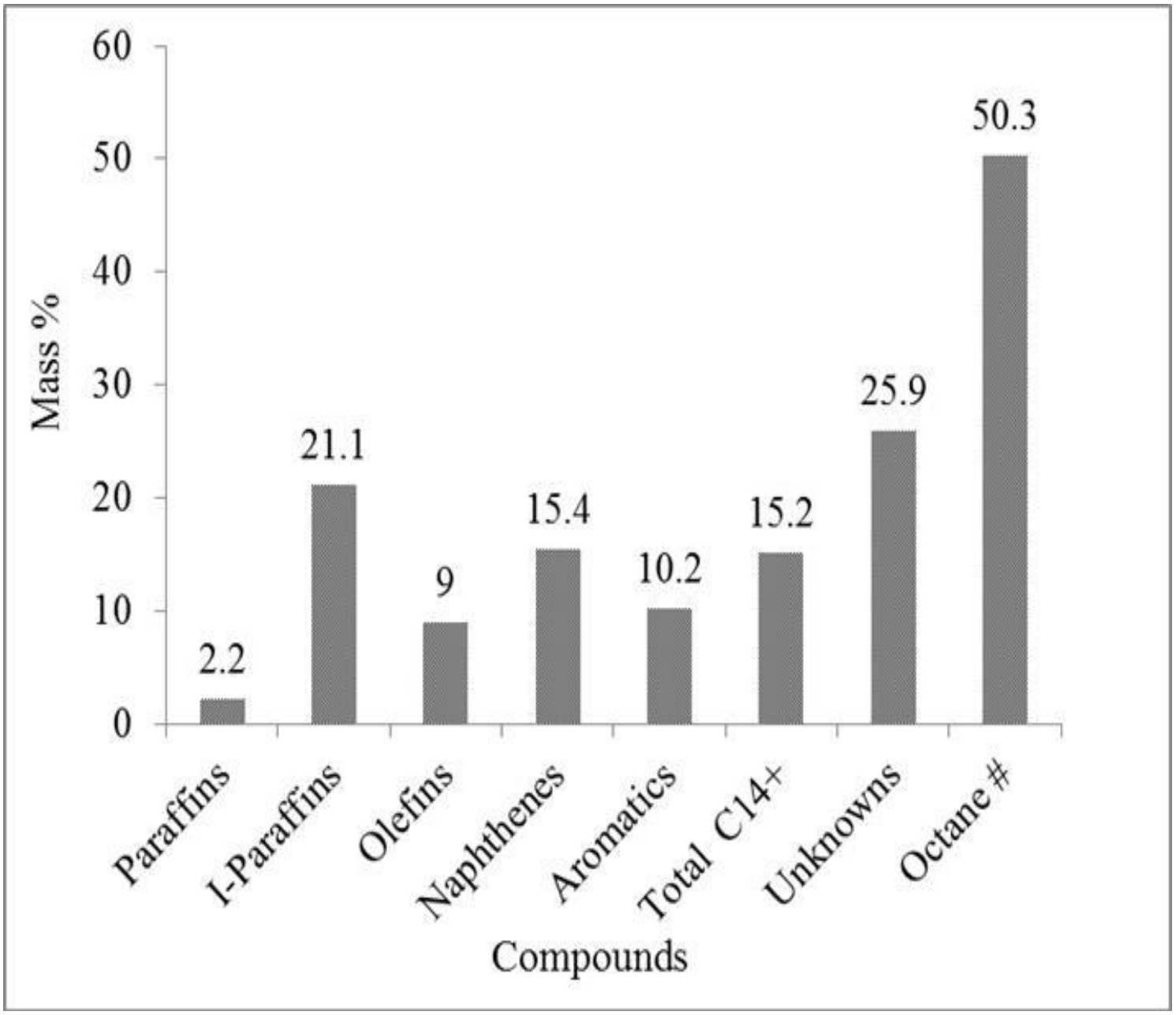

Figure 3. DHA of mass percentage (%) of OF obtained hydroprocessed product from sulfided CoMo/γ-Al_2O_3 catalyst from most effective process conditions (temperature of 375-400 °C, pressure of 1500 psig, LHSV of 0.3 h^{-1} and HFR of 1000 ml/min).

IV. CONCLUSION

Sulfided CoMo/γ-Al_2O_3 catalyst was applied in a single-stage HDO treatment in a continuous packed-bed reactor. Process conditions were varied to determine the most effective temperature (325-350, 375-400, 400-425°C), hydrogen pressure (1000, 1500 psig), HFR (500, 1000ml/min) and LHSV (0.1, 0.3, 0.7, 1 h^{-1}) by single-stage hydroprocessing. The most effective process conditions for the sulfided CoMo/γ-Al_2O_3 catalyst were for a temperature of 375-400 °C, pressure of 1500 psig, LHSV of 0.3 h^{-1} and HFR of 1000 ml/min. The product properties of the hydroprocessing RBO for the best combination of treatment conditions were an AV of 0.7 mg KOH/g, HHV of 44.01 MJ/kg, and percentage WC of 0.1%. The elemental CHNO values were 87.0, 13.0, 0.3 and 0.1%, respectively. The TY, OF and AF yields were 85.1, 24.6 and 60.6%, respectively. The DHA of the upgraded product predominately contained iso-paraffins, naphthenes, compounds greater than C14 and olefins. Other compounds that were identified in minor amounts were aromatics and paraffins. DHA of the OF measured an octane value of 50.3. The yields and properties of single-stage treatment with sulfided CoMo/γ-Al_2O_3 catalyst appear to have potential lifetime that the catalyst may perform with good results. Further research is required to test the deactivation of the CoMo/γ-Al_2O_3 catalyst.

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DISCLAIMER

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