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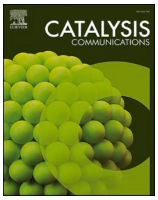

Catalytic bio-oil upgrading using Fe-Co/Al_2O_3 and co-processing with vacuum gas oil

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ABSTRACT

The current study explores the hydrodeoxygenation (HDO) of pine sawdust derived pyrolysis bio-oil and co-processing of raw bio-oil with Vacuum Gas Oil (VGO) in a micro-activity testing (MAT) unit. The catalytic performance of mono- and bi-metallic catalysts were tested for bio-oil upgrading. Notably, Fe—Co (2:1)/Al_2O_3 catalysts exhibited superior HDO activity compared to their mono-metallic counterparts. Co-processing of raw bio-oil (2–10 wt%) with VGO led to a notable increase in gasoline yield of ~48% with a 6 wt% blend. Maximum conversion was achieved with 8 wt% blend, further increasing the proportion, conversion decreased significantly affecting the product distribution.

1. Introduction

Rapid economic development has led to a significant surge in energy demand, particularly in the realm of transportation fuels. However, this escalating demand, coupled with environmental concerns and the uneven distribution of fossil fuels, has spurred interest in biomass that can be converted into liquid products *via* pyrolysis [1]. Bio-oil is the mixture of 50–65 wt% organic compounds, involving acids, aldehydes, phenols, ketones, furans, guaiacols and sugars; 15–30% moisture; and 20 wt% of colloidal fraction [2]. These oxygen containing compounds are responsible for undesirable properties such as low heating value, high acidity, instability, high viscosity, and immiscibility with petroleum fuel. Therefore, removing unnecessary oxygen atoms is required for bio-oil upgradation which includes methods such as catalytic pyrolysis, HDO, catalytic cracking, molecular distillation, supercritical fluids, emulsification, and esterification.

Several catalytic species have been used including noble metals, transition metals, metal sulfides, metal phosphides and metal nitrides with various supports like Al_2O_3, SiO_2, TiO_2 and ZrO_2 in HDO reactions [3]. The application of noble metal catalyst like Pt, Pd and Ru is limited by their low abundance and higher cost. Recently transition metal catalysts are considered to be more attractive due to their low cost for upgradation of bio-oil [4]. The major issues in the upgrading process are rapid catalyst deactivation and high hydrogen consumption along with low product yield [5]. Therefore, future research must be aimed towards reducing capital costs with the development of new catalysts and the number of unit operations [6].

Conventional hydrotreating catalysts in petroleum refineries mainly utilize NiMo and CoMo supported on alumina catalysts. CoMo catalyst that is mainly used for hydrodesulphurization was shown to have high activity when used for bio-oil model compounds such as guaiacol and phenol [7]. Recent reports have shown that NiFe/Al_2O_3 can also be used as a catalyst for HDO that improved the heating value from 37.8 MJ/kg to 43.9 MJ/kg of bio-oil produced from straw [8]. Although several studies were reported with various catalysts for the deoxygenation studies, most of these were limited to model compounds only. To the best of our knowledge, no study was conducted using both Co and Fe on Al_2O_3 for upgrading of bio-oil. Hence, the aim of this study was to investigate the effects of mono- and bi-metallic (Fe-Co/Al_2O_3) catalysts for HDO of pine sawdust bio-oil. The performance of Fe-Co/Al_2O_3 catalysts using different Fe/Co mole loading ratios for upgraded bio-oil was also evaluated in this study.

Co-processing of bio-oils derived from pyrolysis of biomass with petroleum feedstocks using existing processes, refinery catalysts and technologies provides advantages from both economic as well as technological perspectives [9].Bio-oils could be added to conventional Fluid Catalytic Cracking (FCC) feedstock, for converting the heavy petroleum feeds into lighter products such as liquefied petroleum gas (LPG),

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gasoline, and light cycle oil (LCO) [10]. Since bio-oil is cheaper than VGO, cracking a blend of bio-oil and VGO in FCC would be economically favorable assuming product distribution remains unchanged. The second aim of this study is to investigate the viability of incorporating raw bio-oil into Vacuum Gas Oil (VGO) and assess its impact on FCC product distribution. Bio-oil, ranging from 2 to 10 wt%, was co-processed with VGO and subjected to cracking in an FCC MAT unit. The resulting product distribution was compared to the base case, representing VGO without any bio-oil.

2. Experimental section

2.1. Materials and methods

In this study, we utilized locally sourced pine sawdust as the feedstock for pyrolysis. The sawdust was subjected to sun-drying for two days to remove the moisture content. Following sieving, particles with a diameter <1 mm were used for the bio-oil production.

For the co-processing of bio-oil with VGO, a commercial FCC equilibrium catalyst (*E*-Cat) was employed. Commercial alumina extrudates were impregnated with iron and cobalt with their respective precursors (Cobalt (II) nitrate hexahydrate (~98 wt%) and Iron (III) nitrate nonhydrate (~98 wt%).

2.1.1. Feed and bio-oil characterization

Proximate analysis of the feed was carried out to determine the moisture content, volatile content, ash, and fixed carbon by ASTM standard protocols. The moisture content was determined by the ASTM standard E-871-82, where the known mass of the sample was heated at 105 °C in a hot air oven till constant mass was achieved. The weight difference between a dry sample and a fresh sample provided the moisture content in sample. To determine volatile content, 1 g moisture free sample was heated in a covered crucible at 950 °C for 7 min and the weight loss recorded as volatile matter. For ash content, the dried sample was heated in a crucible at 550 °C for 4 h. After cooling, the sample was weighed, and this heating-cooling cycle was repeated until a constant mass was achieved. Fixed carbon was determined by the difference. The elemental compositions (carbon, hydrogen, nitrogen and sulfur) of the feed and of bio-oil were determined using an elemental analyzer.

Density and kinematic viscosity of oil was measured by Viscometer (SVM 3000). Flash point of bio-oil was determined by using Pensky-Martens closed-cup apparatus. Pour point of bio- oil was measured by automatic pour point apparatus as per standard procedure. The heating value of bio-oil was calculated using the modified Dulong's formula as mentioned below:

$$\text{Heating Value (MJ/Kg)} = (33.5^{*}\text{wt.\%C} + 142.3^{*}\text{wt.\%H}–15.4^{*}\text{wt.\%O})/100 \tag{1}$$

2.1.2. Catalyst preparation and characterization

Monometallic catalysts of 10 wt.% Co/Al_2O_3, 10 wt% Fe/Al_2O_3 and bimetallic catalysts of Fe-Co/ Al_2O_3 with different Fe/Co mole ratios (1:1, 2:1, 3:1), were synthesized using wet impregnation method. Monometallic catalysts were referred to as Co/Al_2O_3, Fe/Al_2O_3 and bimetallic catalysts with different Fe/Co mole ratios (1:1, 2:1, and 3:1) were referred as Fe-Co(1:1)/Al_2O_3, Fe-Co(2:1)/Al_2O_3 and Fe-Co(3:1)/Al_2O_3 respectively. A schematic representation of the catalyst preparation steps is enclosed in Fig. S1 (supplementary section).

Metal loading on alumina support was carried out by impregnating Al_2O_3 with aqueous solution of cobalt (II) nitrate hexahydrate and/or Iron (III) nitrate nonahydrate, stirred at room temperature for 24 h. The catalyst was then dried in hot air oven at 150 °C for 2 h and calcined in static air at 500 °C for 4 h in a muffle furnace.

The BET-surface area measurements for catalyst samples were done using nitrogen adsorption/ desorption measurements with an Autosorb-IQ (Quanta chrome, USA) unit. Fourier transform infrared (FTIR) analysis was conducted using a Bruker ALPHA instrument. X-ray powder diffraction (XRD) analysis of the catalysts was carried out using a Rigaku X-ray diffractometer (model: SMARTLAB). Thermogravimetric analysis (TGA) of the catalysts were carried out using a Shimadzu DTH-60H under inert conditions. The morphology of the catalysts was examined using scanning electron microscopy (SEM), and elemental dispersive X-ray spectroscopy (EDX) analysis was conducted using a JEOL JSM-7610FPlus field-emission scanning electron microscope.

2.2. Experimental procedure

2.2.1. Pyrolysis

The pyrolysis of pine sawdust was conducted in a laboratory-scale batch pyrolysis reactor made of stainless steel, measuring 18 cm in height and 5 cm in diameter. The reactor was externally heated using an electric furnace. An external PID controller was employed to regulate the temperature inside the reactor. The reactor featured two nozzles in the upper section: one for the continuous supply of N_2 to maintain an inert atmosphere within the reactor and another for the outlet of hot vapors. A glass condenser was attached at the reactor's outlet to condense the vapors, with cooling water circulating through it. The condensed liquid products were collected in a measuring cylinder and weighed to determine their yield. After the pyrolysis process, the reactor was cooled down to room temperature, and the remaining solid biochar was collected and weighed. The yield of gaseous products was calculated using a mass balance approach, which involved subtracting the sum of the bio-oil and biochar yields from the total biomass fed.

In a typical experimental procedure 30 g of the sample was loaded in reactor and purged with nitrogen to create an inert atmosphere at a stream rate of 50 cm^3/min. Biomass was heated at 500 °C continuously for 30 min and condensable volatile matters (bio-oil) were collected in a measuring cylinder. After 30 min reactor was cooled at room temperature and residue left as bio-char was collected from the reactor. This study utilized the pyrolysis oils obtained from approximately 40 tests conducted under identical conditions.

The yields of bio-oil, gas and bio-char were determined using the following formulas.

$$\text{Bio}-\text{oil (wt\%)} = (g_{\text{bio}-\text{oil}}/g_{\text{biomass}})\ \text{x}\ 100 \tag{2}$$

$$\text{Bio}-char\ \text{(wt\%)} = (g_{\text{bio}-char}/g_{\text{biomass}})\ \text{x}\ 100 \tag{3}$$

Where weight is in grams and the yield of gaseous fraction was determined from the difference.

$$\text{Gases (wt\%)} = 100-\text{Bio}-\text{oil (wt\%)}–\text{Bio}-char\ \text{(wt\%)} \tag{4}$$

2.2.2. Hydrodeoxygenation

The bio-oil HDO tests were conducted using a 300 ml autoclave batch reactor (Model 4848, Parr Instrument, USA). The reactor was externally heated by an electric furnace, with a maximum allowable operating pressure and temperature of approximately 345 bars and 350 °C, respectively. Precise control of the reactor temperature and impeller mixing speed was maintained through a control panel. In a typical experiment, 30 g of bio-oil, 30 g of methanol, and 3 g of catalyst (with a catalyst-to-oil ratio of 1:10) were loaded into the reactor. The reactor was purged with hydrogen followed by increasing the pressure up to 34.5 bars with hydrogen, and then reaction was carried at 300 °C for 3 h. After 3 h, the furnace was turned off, and the reactor was allowed to cool to room temperature. The liquid product was collected from the reactor, methanol was separated through distillation, and water was removed by adding anhydrous sodium sulfate to the resulting liquid product, followed by filtration. The resulting oil was subsequently analyzed for CHNSO content, viscosity, and density.

2.2.3. Co-processing studies

The FCC studies were conducted in a MAT unit, essentially a fixed bed reactor designed according to ASTM D-3907 as shown in Fig. 1. A syringe pump with a multiport, high-pressure valve enabled the entry of nitrogen and feed into the reactor *via* a common feed line. A three-zone furnace heated the reactor to maintain a steady temperature of 510 ± 1 °C across the catalyst bed's entire length. The reactor had a 15.6 mm internal diameter, with quartz wool placed both below and above the catalyst bed. Liquid products were collected in a glass receiver and analyzed using simulated distillation to determine boiling range distribution. The gasoline boiling range spanned 0 to 221 °C, light cycle oil (LCO) ranged from 221 to 343 °C, heavy cycle oil (HCO) from 343 to 370 °C and Clarified Oils (CLO) at 370 °C and above. Gaseous products were analyzed with a refinery gas analyzer to determine hydrogen and C1 to C5 hydrocarbon composition.

In the MAT unit, co-processing studies were conducted by blending VGO with varying proportions of bio-oil (2, 4, 6, 8, and 10 wt%). In a standard experiment, 4 g of *E*-Cat was packed into the reactor, which was then placed in a vertical furnace and purged with nitrogen until the reactor temperature reaches 510 °C. Controlled delivery of the feed was accomplished using a syringe pump, maintaining a steady feed flow rate of 0.64 g/min. The reactor outlet was connected to a liquid product receiver submerged in a water bath, with its outlet linked to a gas holder, displacing water. Upon injecting the feed, the reactor underwent a 15-min nitrogen purge to eliminate vapors and transfer non-condensed materials to the gas holder. The resulting reaction products were collected at three distinct locations: coke and a small liquid residue within the reactor, the majority of liquids were obtained in the receiver, and gaseous products in the gas holder.

3. Results and discussion

3.1. Catalyst Characterization

3.1.1. Proximate and Ultimate analysis

Table 1 represents the proximate and ultimate analysis of pine saw dust and the results indicate high volatile content with low ash and moisture content of the biomass making it favorable for the bio-oil production through pyrolysis process. The estimated calorific value based on the elemental composition was determined to be 23 MJ/kg.

3.1.2. Surface area analysis

The textural properties of fresh Fe-Co/Al_2O_3 catalysts are listed in Table 2. The BET specific surface area and total pore volumes of Fe and/or Co loaded Al_2O_3 catalysts decreased in comparison with Al_2O_3. This indicates that some of the pores of the parent Al_2O_3 support were filled with Co_3O_4 and/or Fe_2O_3 particles after impregnation.

Fig. 1. Experimental set-up of MAT unit (ASTM – D3907).

Table 1
Proximate and ultimate analysis of biomass feed.

Analysis	Weight %
Moisture	8.0
Volatile	79.0
Ash	3.3
Fixed Carbon	9.8
C	50.1
H	10.6
N	4.5
S	–
O	34.9

Table 2
Textural properties of different mono- and bi-metallic catalysts.

Catalyst	Total surface area (m^2/g)	Micro pore area (m^2/g)	External surface area (m^2/g)	Total pore volume (cc/g)	Micro pore volume (cc/g)
Al_2O_3	216.2	20.0	196.0	0.60	0.008
Co/Al_2O_3	180.5	11.1	169.4	0.58	0.004
Fe/Al_2O_3	186.5	8.4	178.1	0.60	0.004
Fe-Co (1:1)/Al_2O_3	158.6	9.8	148.7	0.51	0.004
Fe-Co (2:1)/Al_2O_3	181.8	11.6	170.2	0.58	0.005
Fe-Co (3:1)/Al_2O_3	180.0	10.4	169.6	0.58	0.004

3.1.3. FTIR analysis

The FTIR spectra of the fresh catalysts is shown in Fig. 2, in which the transmittance peaks at 3850–3671 cm^{-1} corresponds to the stretching vibrations of -OH groups due to the presence of moisture. The peaks between 1640 and 1690 correspond to Al-OH bond stretching vibrations. Peaks noticed between at 870–530 are assigned to bending vibration of Al—O and Al-O-Al bond in the gamma phase of alumina. The distinctive absorption bands in the fingerprint region of 500–550 cm^{-1} are usually assigned to metal oxide (Fe-O/Co-O) stretching vibrations.

3.1.4. XRD analysis

The XRD spectra of bare alumina consisted of two peaks at 45.8° and 66.8° (Fig. 3). Similar peaks identified in the other catalysts indicate that alumina support maintained its crystallinity after metal impregnation. Fe/Al_2O_3 catalyst has distinct peaks at 33.4, 36, 40.8 and 54.1° confirms the presence of α-Fe_2O_3 phase. Co/Al_2O_3 catalyst consisted of peaks at 31.5, 37.0, 65.4° which confirms the presence of Co_3O_4 phase [11]. Fe—Co (1:1)/Al_2O_3, Fe—Co (2:1)/Al_2O_3, Fe—Co (3:1)/Al_2O_3 catalysts showed the peaks of both α-Fe_2O_3 and Co_3O_4 phases indicating their deposition on the Al_2O_3 surface. Additionally, the metal deposition on the catalyst surface also led to slight decrease in the intensity of alumina peaks as evident from the figure.

3.1.5. TGA analysis

The TGA weight loss profiles of the catalysts are depicted in Fig. 4, which reveals a noteworthy weight loss ~14.5% for the γ-Al_2O_3 catalyst after 900 °C. In contrast, the metal-doped γ-Al_2O_3 catalysts exhibited comparatively minimal weight loss, around ~9.5%. The substantial weight loss observed in γ-Al_2O_3 can be ascribed to thermal transformations such as phase transitions and structural changes at higher temperatures. The presence of metal oxides, characterized by higher thermal stability than alumina, is believed to contribute to the observed lower weight loss by suppressing or modifying the thermal stability of the matrix.

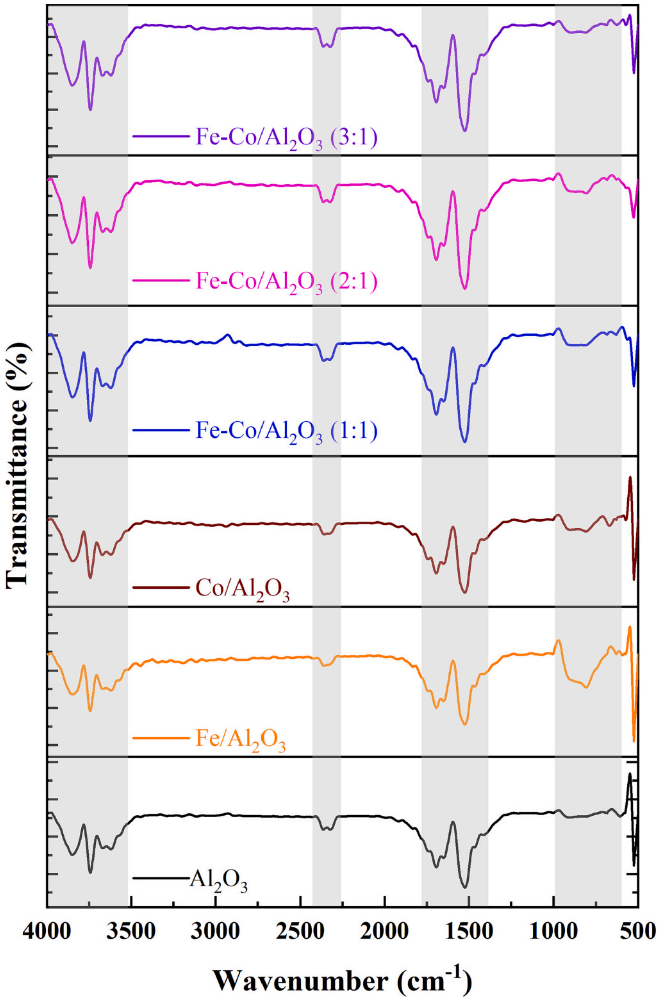

Fig. 2. FTIR spectra of the catalysts.

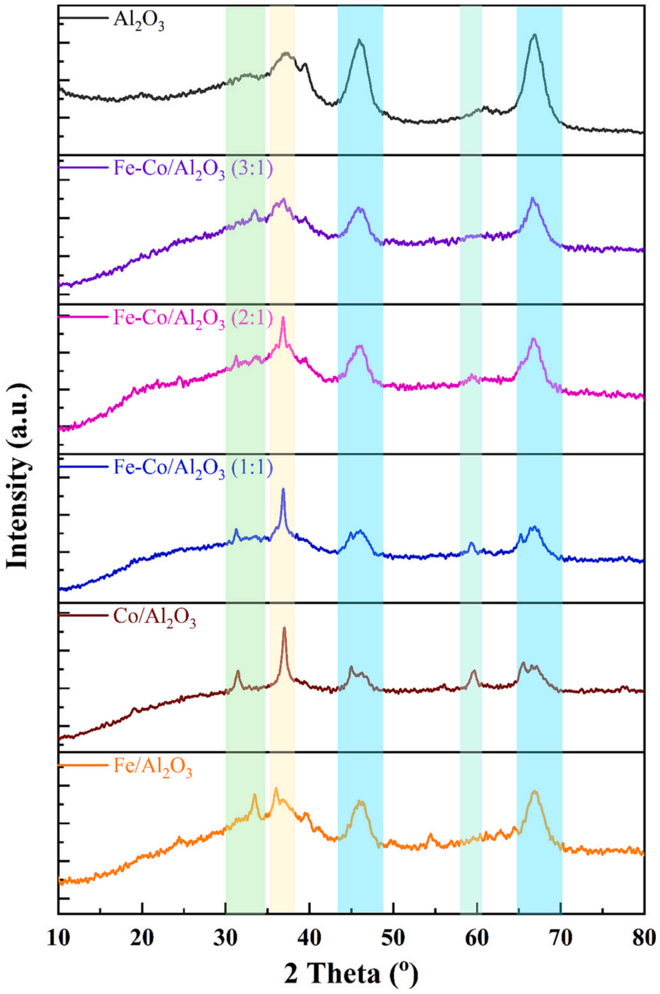

Fig. 3. XRD spectra of the catalysts.

3.1.6. FESEM and EDX analysis

Figure 5 illustrates the surface morphology of the catalysts, in which structural changes were noticed with the impregnation of the metal oxides on the alumina surface. The metal impregnation also showed an extent of pore blocking and resulting in the agglomeration of the particles when compared to bare alumina. The elemental composition of the metals deposited on the catalyst surface were analyzed with EDX analysis which confirms the metal loadings to be in line with the calculated amounts used in the synthesis process. A representative of the elemental mapping of the bi-metallic Fe—Co (2:1)/Al_2O_3 catalyst along with elements overlay is presented in Fig. S2 (supplementary section).

3.2. Pyrolysis product yields and properties

A total of 40 experiments were carried out in a batch pyrolysis unit, with each test involving the pyrolysis of 30 g of biomass. In total, 1.2 kg of biomass was processed, resulting in the production of 505 g of bio-oil, 341 g of char, and 354 g of gas. It is noteworthy that the yields of pyrolysis products were consistently reproducible across all these tests. Specifically, the obtained oil yield was determined to be 42.1 ± 2.8%, the char yield was 28.4 ± 2.4%, and the gas yield was 29.5 ± 2.2%.

The produced bio-oil exhibited a heating value of 17.8 MJ/kg and a density of approximately 1183 Kg/m^3, surpassing that of diesel fuel (832 Kg/m^3) due to its high amounts of water and oxygen content. Viscosity significantly influences the performance of fuel injection systems. The produced bio-oil was found to have a kinematic viscosity of 2.60 cSt at 40 °C, comparable to diesel fuel (1.9–4.0 cSt). The pour point of bio-oil, at −27 °C, falls within the acceptable range for various climatic conditions and aligns closely with that of diesel (−40 °C to - 1 °C). The flash point, a crucial indicator of liquid fuel volatility and ignition propensity, was determined to be 50.8 °C for the resulting bio-oil. This higher flash point enhances safety during handling and reduces the risk of accidents arising from vapor ignition. Considering the properties of bio-oil it is imperative to pretreat to meet the physical and chemical properties such that it can be blended and co-processed in any standard refinery infrastructure. Herein, further sections we attempt to upgrade the bio-oil with different catalyst compositions as well as test its performance characteristics in co-processing with VGO.

3.3. Hydrodeoxygenation results

The HDO of the bio-oil was carried out in the presence of different Fe, Co supported on γ-Al_2O_3 based mono- and bi-metallic catalysts as shown in Table 3. Reducing the viscosity of upgraded bio-oil is very much essential and beneficial as highly viscous liquid fuels pose numerous challenges when injected into an engine. The viscosity of upgraded bio-oil has substantially decreased by approximately 1.14 to 1.43 times compared to raw bio-oil. Specifically, the viscosity of upgraded bio-oil ranges from 1.82 to 2.28 cSt, while raw bio-oil has a viscosity of 2.60 cSt. The density of the bio-oil also dropped from 1183 to 990 kg/m^3 after the HDO with Fe—Co catalyst. Compared to mono-metallic catalysts, bi-metallics have shown to have remarkable effect in the reduction of viscosity and density. A noticeable increase from 17.83 to 27.63 MJ/kg in the heating value of the bio-oil is also observed with the HDO using

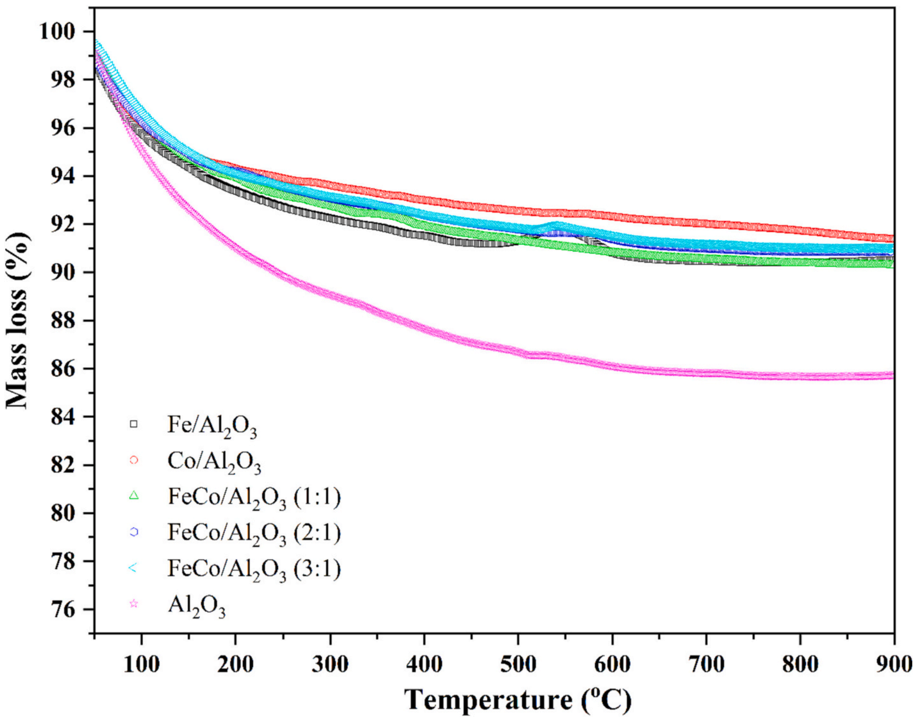

Fig. 4. TGA weight loss profiles of the catalysts.

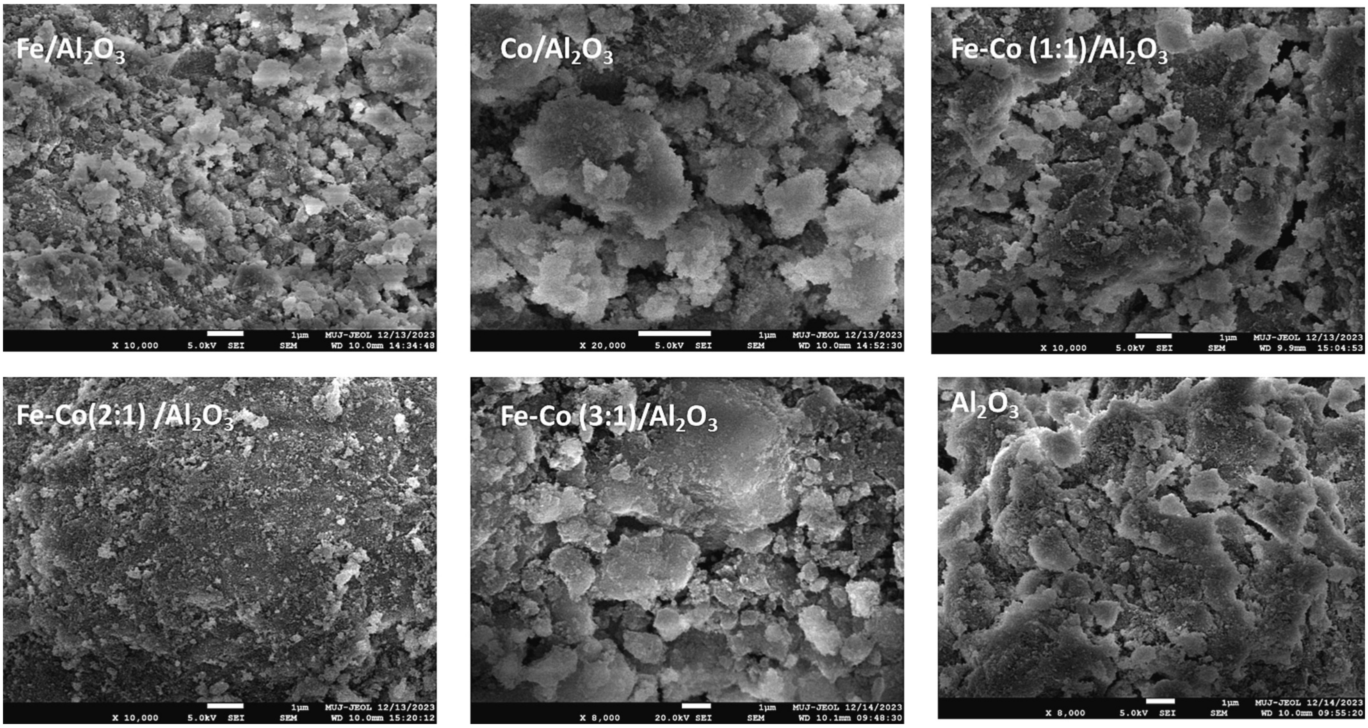

Fig. 5. Surface morphology of the catalysts.

Fe—Co bi-metallic catalysts. This improvement can be attributed to the significant reduction in the oxygen content from 44.1% to 25.7% as seen in the Table 3. The carbon and hydrogen content (55.6–64.68% and 6.46–6.97%) of the upgraded bio-oil exhibited an increase when compared to the raw bio-oil which had carbon and hydrogen contents of 48.6% and 5.86% respectively. The oxygen content (36.1–25.68%) of the upgraded bio-oil showed a significant decrease as compared to that of raw bio-oil (44.08%). This reduction can be attributed to series of reactions including HDO, deoxygenation, decarbonylation and decarboxylation which collectively contributed to the substantial decrease in oxygen content in the upgraded bio-oil.

Metallic Fe exhibits selective promotion of hydrocarbon formation through hydrodeoxygenation reactions, without concurrently promoting the hydrogenation of aromatic rings. Conversely, metallic Co serves as a catalyst for both hydrogenation and hydrogenolysis reactions in the bio-oil upgrading process [11]. In the presence of metallic Co, direct

Table 3
Physicochemical properties of bio-oil before and after HDO upgrading with different catalysts.

Property	Raw bio-oil	Fe/ Al_2O_3	Co/ Al_2O_3	Fe-Co (1:1)/ Al_2O_3	Fe-Co (2:1)/ Al_2O_3	Fe-Co (3:1)/ Al_2O_3
Viscosity (cSt) @ 40 °C	2.6	2.3	2.1	1.9	1.8	1.9
Density (Kg/ m^3) @ 40 °C	1183	1040	1080	993	990	995
C (wt%)	48.60	55.60	61.98	64.20	64.68	64.38
H (wt.%)	5.86	6.46	6.65	6.73	6.97	6.80
N (wt.%)	1.46	1.86	2.07	2.25	2.67	2.34
O (wt.%)	44.08	36.10	29.30	26.82	25.68	26.48
S (wt.%)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Heating Value (MJ/ Kg)	17.8	22.3	25.7	27.0	27.6	27.2

cleavage of C—O bonds occurs, resulting in the removal of more oxygenates compared to the Fe/Al_2O_3 catalyst. Bimetallic Fe-Co/Al_2O_3 catalysts demonstrated high activity relative to monometallic Fe/Al_2O_3 and Co/Al_2O_3 catalysts, attributable to the synergistic effects of Fe and Co. Both Fe and Co, when supported on alumina, provide active sites for the hydrodeoxygenation reaction in bio-oil upgrading. The addition of Fe to the Fe-Co/Al_2O_3 catalyst promotes hydrogenation and hydrogenolysis, and the loading of the second metal prevents coke deposition on the catalyst's active sites [11]. The catalyst's performance during bio-oil upgrading reactions is also contingent on the availability of active sites, with bimetallic Fe-Co/Al_2O_3 catalysts offering a greater abundance of active sites compared to their monometallic counterparts, Fe/Al_2O_3 and Co/Al_2O_3. Among various bi-metallic catalysts Fe—Co (2:1)/ Al_2O_3 resulted in a upgraded bio-oil with low viscosity, density and high heating values. The results highlight the efficacy of Fe-Co/Al_2O_3 catalysts in the deoxygenation of bio-oils. Following the HDO process, substantial changes were observed in the bio-oil properties, bringing it closer to potential co-processing within existing refinery infrastructure.

Figure 6 illustrates the van Krevelen plot consisting of biomass feed, raw bio-oil and different HDO treated bio-oils obtained with different catalysts. The H/C ratio of biomass was significantly reduced by 43% in the bio-oil obtained after pyrolysis due to thermal decomposition of biomass resulting in the formation of biochar and gases. The formation of volatile gases such as methane and hydrogen, result in lowering the H/C ratio. While the volatile gases lost in the form of carbon dioxide and carbon monoxide and the formation of oxygenated compounds increases the O/C ratio of raw bio-oil. Among the two mono-metallic catalysts Co/ Al_2O_3 led to significant reduction in the O/C ratio compared to Fe/ Al_2O_3. All the three bi-metallic Fe—Co combinations have comparable O/C ratios with 2:1 ratio of Fe:Co found to be the optimal metal combination in this study. Fig. S2 depicts the van Krevelen plot for the HDO of bio-oil using various catalysts, including those reported in previous studies and our current study.

HDO of bio-oil derived from actual cork oak was carried with Pt/HY zeolites was shown to enhance the C content of bio-oil with enhanced heating value (from 18.9 to 24.4 MJ/kg) and reduced oxygenates from 49% to 28%, whereas the moisture content decreased only slightly [12]. HDO of bio-oil using Ru/C and Pt/C was reported to improve various properties of bio-oil such as heating value (27.8 MJ/kg as compared to 17.3 of raw bio-oil), viscosity, acidity and de-moisturization [13]. HDO of bio-oil from palm empty fruit bunch using NiMo/Al_2O_3 and CoMo/ Al_2O_3 exhibited higher H/O, C/O and H/C ratios as compared to their monometallic counterparts. The O/C ratio of upgraded bio-oils were reported to be 0.69–0.78 which is higher to the conventional diesel fuel value of 0.5–0.7 due to oxygen reduction and hydrogenation [14]. NbMo/C catalyst was studied for upgradation of *prosopis juliflora* biomass derived bio-oil which improved the fuel properties in terms of viscosity (3.2 mm^2/s at 40 °C), density (0.98 g/cc at 15 °C) and HHV (30 MJ/kg) [15]. Bimetallic Fe-Co/SiO_2 was studied for HDO upgradation of bio-oil wherein the synergistic effect of Fe and Co on SiO_2 support outperformed monometallic counterparts [11]. Apparently, in this study, the physicochemical properties of bio-oil were enhanced significantly with the HDO process using bimetallic Fe-Co/Al_2O_3 catalysts with an optimum loading of Fe—Co (2:1) on Al_2O_3.

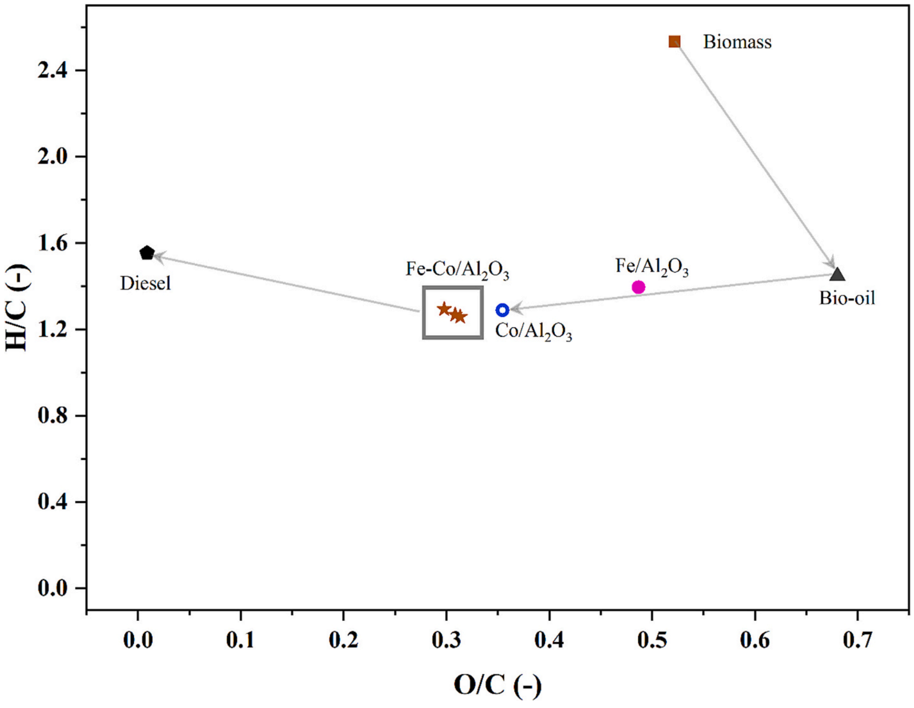

Fig. 6. van Krevelen plot of HDO treated bio-oils.

3.4. Co-processing of bio-oil with VGO

The co-processing of raw bio-oil with VGO was performed with VGO and different amounts of raw bio-oil in the range of 2, 4, 6, 8 and 10 wt% in a fixed bed reactor at 510 °C. The product yields of catalytic cracking results are presented in Fig. 7, where it is clearly seen that the liquid yields decreased, and coke yields increased proportionately with negligible changes in the gas yields were noticed with increasing amounts of bio-oil blending with VGO. These results are in agreement with the literature studies [16–18].

The individual product variation from FCC with different blends of bio-oil and VGO is shown in Table 4 and Fig. 8. The dry gas is a mixture of hydrogen, methane and ethylene and the LPG mainly comprised of C_3 and C_4 olefins. From the table it is observed that the hydrogen yield, dry gas and LPG yields decreased with increasing blend ratios of bio-oil with VGO. The conversion also increased from 71% to 77% with bio-oil blends of 8% but with further increasing the bio-oil blend by 10 wt% the conversion dropped and affected the product composition that can be attributed to possible catalyst deactivation. Additionally, the coke content also increased drastically from 4.5 wt% to 9.8 wt% with increasing the bio-oil blend with VGO. The obtained coke yields in such small scale fixed bed reactors can also be overestimated when compared to large scale operations due to the absence of vaporization as well as due to the heat and mass transfer limitations [19,20]. Moreover, bio-oils inherently contain various hetero atoms such as oxygen and nitrogen that acts as catalyst poisons, which accumulates on the catalyst surface, slowing down the cracking reactions tending to more coke formation [11]. Therefore, it is imperative to pretreat the bio-oils such that co-processing of bio-oils with refinery feeds is possible without compromising on the desired yields and possessing the high catalyst activity and stability over longer periods.

The gasoline yield increases with increase in bio-oil concentration in the feed and maximizes at 6 wt% of bio-oil in VGO. A 3.7 unit improvement (47.98 wt% in 6 wt% bio-oil as compared to 44.2 wt% in case of pure VGO) in gasoline was also achieved with 6 wt% of bio-oil in VGO. However, higher concentrations of bio-oil (8 and 10 wt%) resulted in decrease in gasoline yield presumably due to the dilution effect caused by the high water content in bio-oil. Except for the coke and gasoline yields, increasing conversions led to decreased LPG, LCO, HCO and residue yields. Overall, to obtain the desired product yields and maintaining the catalyst lifetime it is essential to have a deep HDO of bio-oils with low oxygenates that can be blended in higher proportions or to have a moderate HDO of bio-oils with low blend ratios with the refinery feeds.

Table S1 presents a comparative overview of co-processing studies involving bio-oil with refinery feeds from the literature. Studies reported in literature for co-processing of deoxygenated bio-oil derived from pyrolysis of forest biomass with VGO in a hydrocracking pilot plant did not have a major impact on hydrocracking selectivity, yielding similar amounts of naphtha and diesel without any enhancement in catalyst aging [21]. Similar co-processing studies carried out with dry bio-oil, catalytic pyrolysis oil and hydrotreated bio-oil in a MAT set up has shown that lower bio-oil blends (<20%) are required to avoid high coke formation. Furthermore, HDO oil yielded lower amounts of coke and higher liquid yields as compared to catalytic pyrolysis oil [22]. Few model compounds such as hydroxyacetone and glycolaldehyde dimer of pyrolysis oil was co-processed with VGO in an FCC ACE-R unit in which FCC conversion was reported to increase with the hydroxyacetone blending ratio from 5 to 20 wt% accompanied by increased LPG yields and reduced liquid yields (gasoline and cycle oils). Further, co-processing of glycolaldehyde with VGO to be limited to 5% to avoid over-cracking of liquid products and to restrict the polyaromatics formation [23]. Studies carried out in this direction have reported that co-processing bio- oils in lower proportions (typically 3 to 5 wt%) with VGO in an FCC unit did not have much impact on product yields. However, with catalytic pyrolysis oil co-processing, the aromatic composition of gasoline is increased as compared to HDO bio-oil co-processing. Higher proportions of bio-oils blending increased the coke deposition on the catalyst, with successful demonstration of blends up to 20 wt% were reported till date [16]. Wheat straw derived catalytic pyrolysis oil was co-processed with atmospheric residue in a MAT unit enhanced the dry gas yields and coke at the expense of naphtha that is related to the basic nitrogen content, degree of saturation of bio-oils [18]. Co-processing of treated and untreated pyrolysis liquids with VGO in a FCC riser set up resulted in reduced gas yields, and slightly enhanced gasoline yields with treated pyrolysis oils [17].

4. Conclusions

In this study, the pyrolysis of pine sawdust was conducted in a batch reactor to produce bio-oil in several batches for subsequent investigations into its quality enhancement (HDO) and its direct co-

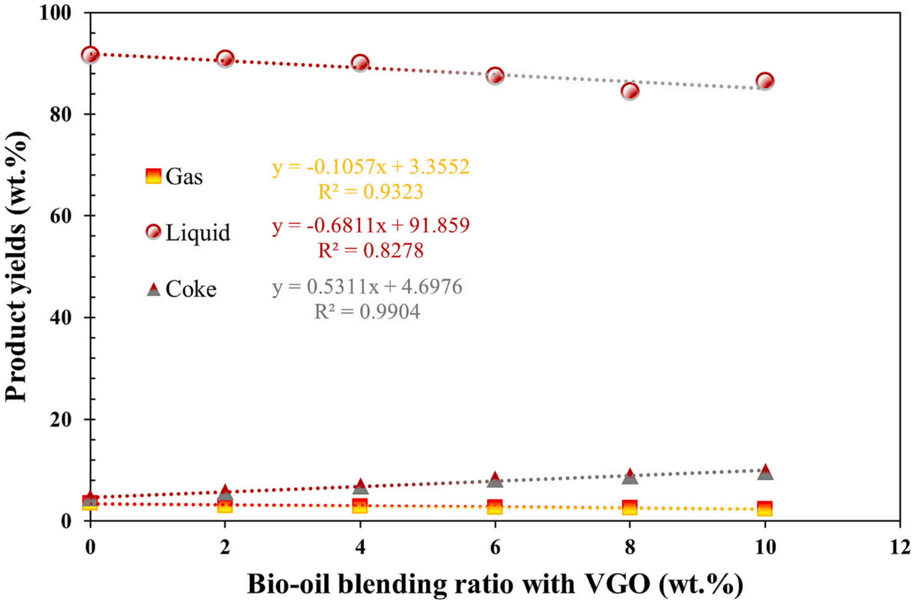

Fig. 7. Product yields with different bio-oil blending ratios from MAT tests.

Table 4
Product yields (wt%) with increasing blend ratio of bio-oil with VGO in MAT reactor.

Products	VGO	2 wt.% bio-oil + 98 wt% VGO	4 wt% bio-oil + 96 wt% VGO	6 wt% bio-oil + 94 wt% VGO	8 wt% bio-oil + 92 wt% VGO	10 wt% bio-oil + 90 wt% VGO
H_2	0.13	0.12	0.11	0.08	0.07	0.05
Dry Gas	3.5	3.0	2.9	2.6	2.6	2.3
LPG	18.8	17.0	16.9	15.1	14.9	14.8
Gasoline (IBP-221 °C)	44.2	45.6	46.6	48.0	46.9	43.6
LCO (221–343 °C)	14.5	14.4	14.2	13.7	13.3	16.8
HCO (343–370 °C)	5.4	5.2	5.2	3.6	4.0	3.2
Residue (370 °C+)	8.6	8.6	7.2	7.1	5.4	8.0
Coke	4.6	5.7	6.9	8.2	8.9	9.8
Conversion	71.4	71.8	73.5	75.7	77.4	72.0

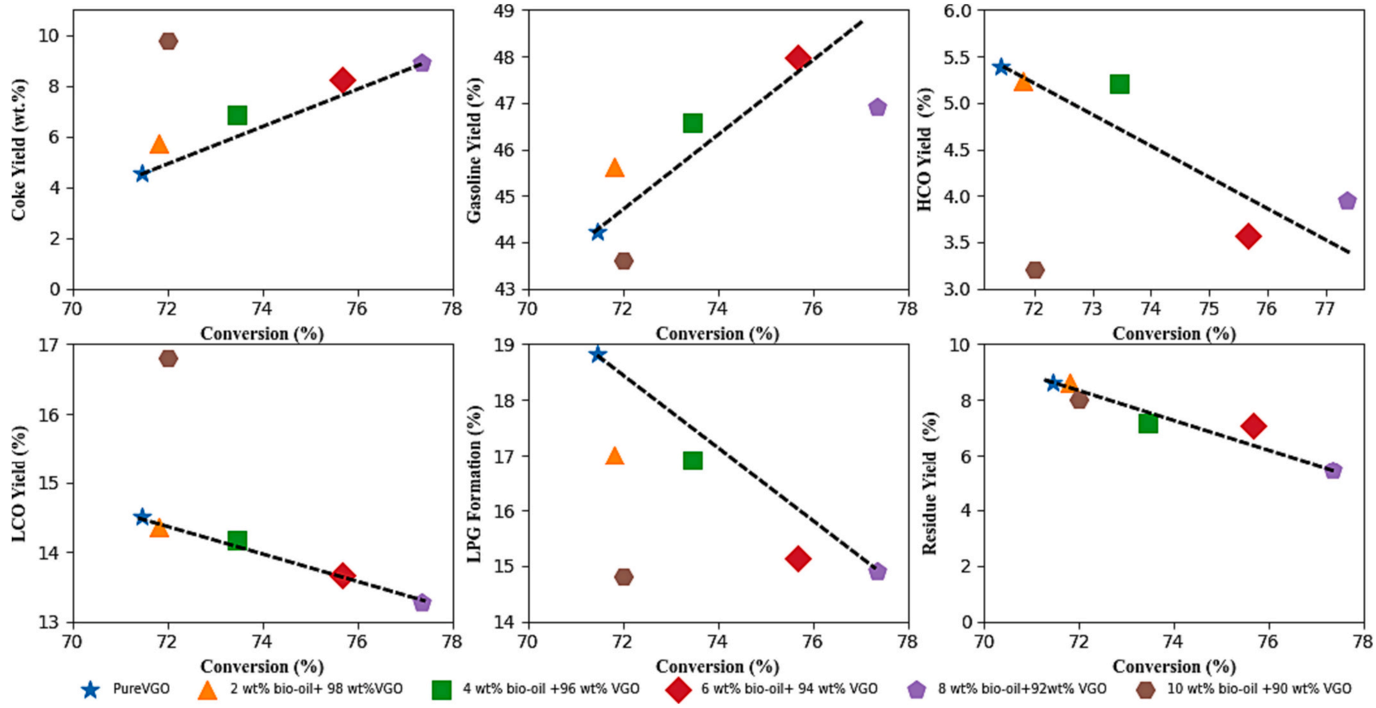

Fig. 8. Yields of different distilled products with increasing amounts of pyrolysis oil in VGO from MAT runs.

processing potential. Firstly, the HDO of the obtained bio-oil was carried out using mono- (Fe and Co) and bi-metallic (Fe—Co) supported on alumina catalysts. Bimetallic Fe-Co/Al_2O_3 catalyst showed higher HDO activity in comparison to monometallic Fe/Al_2O_3 and Co/Al_2O_3 catalyst in terms of reducing the O/C ratio. The physicochemical properties of the upgraded bio-oil including heating value and carbon content improved significantly compared to raw bio-oil with bi-metallic catalysts. Among the several bi-metallic combinations Fe—Co (2:1)/ Al_2O_3 resulted in better bio-oil properties due to the combined active sites and synergistic effects of Fe and Co. The direct co-processing of raw bio-oil with VGO in different blends ranging from 2 to 10 wt% was tested in a MAT reactor. Increased bio-oil blend ratio led to increased coke formation, and it significantly affected the product distribution of gasoline, LCO, HCO, dry gas, residue content. An optimal conversion and product distribution were achieved with a 6 wt% blend of bio-oil and VGO. Future studies should address increasing bio-oil blending proportions, minimizing coking tendencies, and developing advanced catalyst formulations for efficient deoxygenation. This study contributes to the innovative utilization of bio-oil derived from lignocellulosic feedstocks in refinery processes.

CRediT authorship contribution statement

Nand Kishore Saini: Formal analysis, Investigation. **Nandana Chakinala:** Formal analysis, Writing – original draft, Writing – review & editing. **Supriyo Majumder:** Conceptualization, Resources, Supervision, Methodology. **Pintu Maity:** Data curation, Supervision, Writing – review & editing, Methodology. **Chiranjeevi Thota:** Project administration, Resources, Supervision, Writing – review & editing. **Anand G. Chakinala:** Data curation, Formal analysis, Validation, Visualization, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.catcom.2023.106840.

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