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Hydrotreating of Jatropha-derived Bio-oil over Mesoporous Sulfide Catalysts to Produce Drop-in Transportation Fuels

Shih-Yuan Chen,[a,*] Takehisa Mochizuki,[a] Masayasu Nishi,[a] Hideyuki Takagi,[a] Yuji Yoshimura,[b] Makoto Toba[a]

[a] *Research Institute of Energy Frontier (RIEF), Department of Energy and Environment, National Institute of Advanced Industrial Science and Technology (AIST), 16-1 Onogawa, Tsukuba, Ibaraki 305-8569, Japan.*
[b] *Materials for Energy Research Unit, National Metal and Materials Technology Center (MTEC), Pahonyothin Rd. Klong 1, Klong Luang Pathumtani 12120, Thailand.*

To whom correspondence should be addressed:
Shih-Yuan Chen, Ph.D.
Senior researcher,
Energy Catalyst Technology Group, Research Institute of Energy Frontier (RIEF), National Institute of Advanced Industrial Science and Technology (AIST), 16-1 Onogawa, Tsukuba, Ibaraki 305-8569, Japan.
TEL: +81-29-861-2680
FAX: +81-29-861-4532
E-mail: sy-chen@aist.go.jp

Abstract

The bio-oil was largely produced by thermal pyrolysis of Jatropha-derived biomass wastes (denoted as Jatropha bio-oil) using a Pilot Plant with a capacity of 20 kg h^{-1} at Thailand Institute of Scientific and Technological Research (TISTR), Thailand. Jatropha bio-oil is an unconventional type of bio-oil, which is mostly composed of fatty acids, fatty acid methyl esters, fatty acid amides and derivatives, and consequently it contained large amounts of heteroatoms (oxygen ~ 20 wt.%, nitrogen ~ 5 wt.%, sulfur ~ 1000 ppm.). The heteroatoms, nitrogen especially, are highly poisonous to the metal or sulfide catalysts for upgrading of Jatropha bio-oil. To overcome this technical problem, we reported a stepwise strategy for hydrotreating of 100 wt% Jatropha bio-oil over mesoporous sulfide catalysts of CoMo/γ-Al_2O_3 and NiMo/γ-Al_2O_3 to produce drop-in transport fuels, such as gasoline- and diesel-like fuels. This study is very different from our recent work on co-processing of Jatropha bio-oil (ca. 10 wt%) with petroleum distillates to produce a hydrotreated oil as a diesel-like fuel (Chen *et al.*, Catalysts **2018**, 8, 59; http://dx.doi.org/10.3390/catal8020059). Jatropha bio-oil was pre-treated through a slurry-type high pressure reactor under severe condition, resulting in a pre-treated Jatropha bio-oil with relatively low amounts of heteroatoms (oxygen < 20 wt.%, nitrogen < 2 wt.%, sulfur < 500 ppm.). The light and middle distillates of pre-hydrotreated Jatropha

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bio oil was then separated by distillation at temperature below 240 ^oC, and the temperature of 240-360 ^oC. Deep hydrotreating of light distillates over sulfide CoMo/γ-Al_2O_3 catalyst was performed on a batch-type high pressure reactor at 350 ^oC and 7 MPa of H_2 gas for 5 h. The hydrotreated oil was a gasoline-like fuel, which contained 29.5 vol.% of *n*-paraffins, 14.4 vol.% of *iso*-paraffins, 4.5 vol.% of olefins, 21.4 vol. % of naphthene compounds and 29.6 wt.% of aromatic compounds, and little amounts of heteroatoms (nearly no oxygen and sulfur, and less than 50 ppm of nitrogen), corresponding to an octane number of 44, and it would be suitable for blending with petro-gasoline. The hydrotreating of middle distillates over sulfide NiMo/γ-Al_2O_3 catalyst using the same reaction condition produced a hydrotreating oil with diesel-like composition, low amounts of heteroatoms (no oxygen and less than 50 ppm of sulfur and nitrogen), and a cetane number of 60, which would be suitable for use in drop-in diesel fuel.

Keywords: Hydrotreating, mesoporous sulfide materials, waste Jatropha biomass, drop-in biofuels, upgrading technology

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1. Introduction

Biomass is one of the most abundant natural resource, which has supplied around 10% of annual primary energy consumption corresponding to a capacity of 50 EJ/yr globally in 2006-2007 [1-3]. It is generally agreed that the chemicals and fuel with low carbon footprint can be synthesized by conversion of biomass using various catalytic strategies, which contribute to the reduction of CO_2 emission and consequent avert global warming [4-10]. For example, the biodiesel fuel (BDF), which is so-called the first-generation biofuel, can be synthesized by base-catalyzed transesterification of refined vegetable oils with methanol, and it has been extensively used in the transport sector, particularly in America, European Union and ASEAN counties [6,11-16]. However, it has caused a new environmental problem in waste biomass treatment, such as discarded kernel shells and husks, which are massively produced as byproducts in the BDF industry. Recent studies have focused on post-treatment and utilization of those biomass wastes into valuable products, such as gasification to produce syngas, liquification to produce chemicals and fuels, and chip production for thermal power generation [7,17]. Similar to biomass gasification and liquification, bio-oil can be synthesized by thermal conversion of biomass, the wastes especially, through the catalytic pyrolysis or non-catalytic pyrolysis technology, and therefore it contains large amounts of heteroatom-containing

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hydrocarbons, oxygen and sulfur especially, water and unwanted impurities which were highly associated with the feedstocks and the processing parameters used in the pyrolysis and condensation steps [18-21]. The subsequent upgrading of bio-oil through hydrotreating technology using metal catalysts, such as Pd/C, or sulfide catalysts, such as Co- or Ni-promoted $MoS_2/\gamma\text{-}Al_2O_3$, is required to remove the heteroatoms, resulting in clean and drop-in biofuel with composition and fuel property closed to petro-fuels [22]. Unfortunately, the heteroatoms, water and unwanted impurities, which are originally presented in the bio-oil, poison the active sites of metal and sulfide catalysts, causing serious catalyst deactivation and consequently reducing the quality of hydrotreated bio-oil [23-30]. Yoshimura *et al.* reported that the sulfide NiMo catalysts were deactivated by the oxygen-containing compounds due to the oxidation of active sites [23]. Laurent and Delmon showed that the deoxygenation of model compounds of bio-oils over CoMo and NiMo catalysts was strongly inhibited in the presence of water and ammonia [24]. There is still room for development of innovative catalytic process using advanced catalysts with high resistance to heteroatoms, which can produce clean and drop-in fuel for directly formulating with petro-fuels.

Our recent study demonstrated that Jatropha bio-oil could be synthesized by thermal pyrolysis of waste Jatropha biomass (a mixture of kernel shell and husk) using a Pilot

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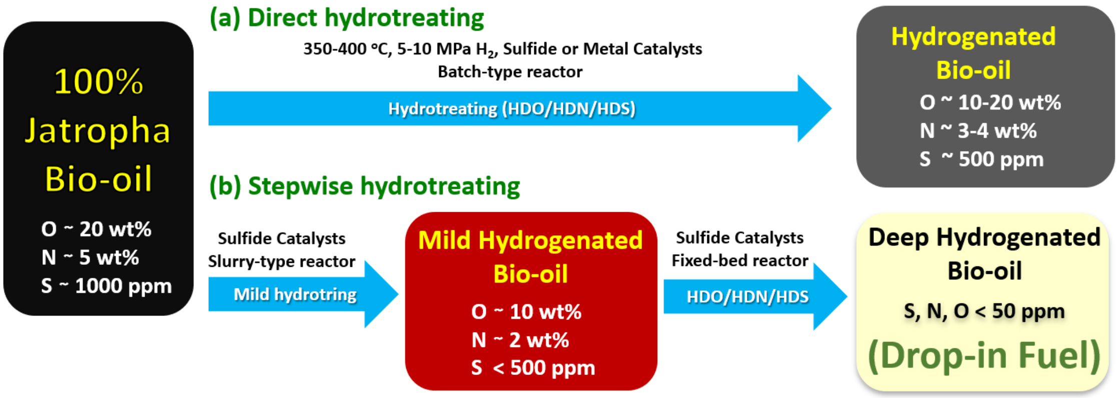
Plant with a capacity of ca. 20 kg/h at TISTR, Thailand [19]. The Jatropha bio-oil is an unconventional bio-oil with a high concentration of nitrogen (ca. 5 wt%) and relatively low concentrations of oxygen (ca. 20 wt%) and sulfur (<1000 ppm), which is mostly consisted of fatty acids, fatty acid methyl esters, fatty acid amides and their derivatives (> 50 wt%) in addition to other light organic compounds incorporated with heteroatoms. It is different from conventional bio-oils with high oxygen content (ca. 20-40 wt%) and low sulfur and nitrogen contents (<1 wt%), which were derived from cedar or pine biomass waste, and mostly consisted of carbohydrates and phenolic compounds. In the upgrading process, the upgraded catalysts as aforementioned were immediately deactivated by high concentration of nitrogen-containing compounds when Jatropha bio-oil was directly used as a feedstock (Scheme 1(a)). To prevent catalyst deactivation, our previous study demonstrated a co-processing method for upgrading of Jatropha bio-oil co-fed with petroleum distillates over sulfide CoMo and NiMo catalysts under severe conditions (330-350 ^{o}C and 5-7 MPa of H_2) [31]. The diesel-like fuel with nearly no heteroatoms (sulfur, oxygen and nitrogen < 10 ppm) could be obtained by hydrotreating of oil feedstock containing ca. 10 wt% of Jatropha bio-oil and ca. 90 wt% of light gas oil. In this study, a stepwise strategy was reported for hydrotreating of 100 wt% Jatropha bio-oil over sulfide catalysts to produce drop-in transport fuels including gasoline- and diesel-like fuels (Scheme 1(b)). The Jatropha bio-oil was pre-treated by a slurry bed reactor at 400 °C and 7 MPa of H_2 using waste NiMo/γ-Al_2O_3 catalyst, followed by distillation. The clean and drop-in transport fuels were then obtained by hydrotreating of pre-treated distillates over fresh CoMo/γ-Al_2O_3 or NiMo/γ-Al_2O_3 catalysts using a high-pressure stainless-steel batch-type reactor under severe conditions. Influence of catalysts and processing parameters on the composition and fuel property of upgraded Jatropha bio-oils was reported.



Scheme 1. (a) direct hydrotreating and (b) stepwise hydrotreating of the unconventional Jatropha bio-oil.

2. Results and discussion

The sulfide CoMo/γ-Al_2O_3 or NiMo/γ-Al_2O_3 catalysts were prepared by the same procedures as reported in our previous study [30], and their structural properties were

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completely studied by X-ray diffraction and absorption techniques, physisorption and chemisorption, and electron microscopes [30-33]. It has exhibited that the sulfide CoMo/γ-Al_2O_3 catalyst with relatively large amounts of acidic sites (NH_3 uptake = 0.92 mmol g^{-1}) and coordinatively unsaturated sites (NO uptake = 0.11 mmol g^{-1}) was associated with small Co-incorporated MoS_2-like slabs (4.5±1.2 nm in length and 2.0±0.53 nm in height) with relatively high stacking number (3.8±0.86) on the mesoporous alumina material. In contract, the sulfide NiMo/γ-Al_2O_3 catalyst with relatively small amounts of acidic sites (NH_3 uptake = 0.77 mmol g^{-1}) and coordinatively unsaturated sites (NO uptake = 0.093 mmol g^{-1}) was presumably due to large Ni-incorporated MoS_2-like slabs (5.9±1.2 nm in length and 1.5±0.53 nm in height) with relatively low stacking number (2.6±0.71) on the mesoporous alumina material. In this study, the structural property of sulfide CoMo/γ-Al_2O_3 or NiMo/γ-Al_2O_3 catalysts were examined again by the wide-angle XRD pattern (Fig. 1(A)), nitrogen physisorption (Fig. 1(B)) and high-resolution transmission electron microscope (HRTEM) images (Fig. 2), in comparison to those of γ-Al_2O_3 as a supporting material. The XRD study shows that two diffraction peaks of Co- or Ni-incorporated MoS_2-slabs are hardly observed at $2\theta \sim 33^o$ and 59^o, indicating that their sizes are smaller than 5 nm, and the diffraction peaks of mesoporous γ-Al_2O_3 framework are weakened by the impregnating. The N_2 physisorption

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study shows that the H_1 hysteresis loops of the type IV isotherms are reduced by the impregnation of Co- or Ni-incorporated MoS_2-slabs on the mesoporous γ-Al_2O_3 framework. The nitrogen physisorption study shows that the supporting material of γ-Al_2O_3 has surface area of 206 m^2 g^{-1}, pore volume of 0.68 cm^3 g^{-1} and pore size of 12 nm. The sulfide CoMo/γ-Al_2O_3 or NiMo/γ-Al_2O_3 catalysts have surface areas of 204-205 m^2 g^{-1} and pore sizes of 12 nm, which are close to those of γ-Al_2O_3 supporting material, whereas their pore volumes are decreased to 0.38-0.41 cm^3 g^{-1}. It indicates that the Co- and Ni-incorporated MoS_2-slabs were impregnated inside the pores of mesoporous γ-Al_2O_3 framework. The HRTEM images clearly show that the sulfide CoMo/γ-Al_2O_3 or NiMo/γ-Al_2O_3 catalysts are composed of the Co- or Ni-incorporated MoS_2-slabs and the mesostructured γ-Al_2O_3 particles. These results suggest that the sulfide CoMo/γ-Al_2O_3 or NiMo/γ-Al_2O_3 catalysts with well-dispersed Co- and Ni-incorporated MoS_2-slabs on the mesoporous γ-Al_2O_3 framework were successfully prepared.

Jatropha bio-oil was largely produced by fast pyrolysis of waste Jatropha biomass at 500 ^{o}C using a Pilot Plant equipped with an electrostatic precipitator [19]. The yields of Jatropha bio-oil, water-soluble phase and gases were 21.3, 28.6 and 50.1 wt%, respectively. Conventional bio-oil derived by fast pyrolysis of cedar or pine biomass is mostly composed of lignin-derived phenolic compounds, and it consequently contains

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high concentration of oxygen (> 30 wt%) and low concentrations of sulfur (ca. 50 ppm) and nitrogen (ca. 0.1 wt%) [19,20]. However, Jatropha bio-oil is mostly composed of fatty acids, fatty acid methyl esters, fatty acid amides and derivatives, presumably due to that Jatropha oil is partly remained in the waste Jatropha biomass after the oil extraction. As a result, Jatropha bio-oil contains high concentration of nitrogen (ca. 5 wt%), relatively high concentration of sulfur (ca. 1000 ppm) and relatively low concentration of oxygen (ca. 20 wt%). The heteroatoms, nitrogen especially, are extremely poisonous to metal and sulfide catalysts used in the upgrading process []. In scheme 1(a), the preliminary studies showed that direct hydrotreating of Jatropha bio-oil over sulfide and metal catalysts produced low-quality hydrotreated bio-oils with high heteroatoms, which was inapplicable for use in fuel oil blending, even if the severe conditions were used [unpublished results]. In other worlds, the sulfide and metal catalysts were immediately deactivated by strong adsorption of heteroatoms on the catalytically active sites, nitrogen especially, in the upgrading process. To solve this technical problem, we proposed a stepwise strategy for upgrading of Jatropha bio-oil over sulfide catalysts to produce drop-in biofuels (see Scheme 1(B) and Fig. 3). Jatropha bio-oil was pre-treated through a slurry-type high pressure reactor at 400 ºC and 7 MPa of H_2 for 2 h using 1 wt% of waste NiMo catalyst, resulting in a pre-treated Jatropha bio-oil with relatively low

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concentrations of heteroatoms (oxygen < 20 wt.%, nitrogen < 2 wt.%, sulfur < 500 ppm.). The yield of pre-treated Jatropha bio-oil was around 65%. The pre-treated bio-oil was then divided into three fractions through distillation: (a) light distillates (21.0%, distillation temperature (T_d) < 240 °C), (ii) middle distillates (59.3%, T_d = 240-360 °C) and (iii) heavy distillates (19.7%, T_d > 360 °C). We focused on deep hydrotreating of light distillates, which composition was closed to gasoline, over sulfide CoMo/γ-Al_2O_3 catalyst (Figure 3(a)) and deep hydrotreating of middle distillates, which composition was closed to diesel, over NiMo/γ-Al_2O_3 catalyst (Figure 3(b)). The results were discussed hereafter.

Deep hydrotreating of light distillates over the sulfide CoMo/γ-Al_2O_3 catalyst was performed on a stainless-steel batch-type reactor at 350 °C and 7 MPa of H_2 for 5 h (Figure 3(a)). The hydrotreating oil was characterized by GC-FID instrument and elemental analysis. Figure 4 shows that the hydrotreating oil is a gasoline-like fuel, except a small portion of paraffins with carbon number higher than 10. Table 1 shows that the hydrotreated oil contains 29.5 vol.% of *n*-paraffins, 14.4 vol.% of *iso*-paraffins, 4.5 vol.% of olefins, 21.4 vol. % of naphthene compounds, 29.6 wt.% of aromatic compounds and little amounts of heteroatoms (nearly no oxygen and sulfur, and ca. 50 ppm of nitrogen), corresponding to an octane number of 44. This result suggests that the hydrotreating oil would be suitable for blending with petro-gasoline. On the other hand, the paraffins with

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carbon number higher than 10 can be separated from the hydrotreating oil by further distillation, and it would be suitable for use in kerosene [34].

Deep hydrotreating of middle distillates over sulfide NiMo/γ-Al_2O_3 catalyst was performed by a large-scale batch-type high pressure reactor under the same reaction condition. (Figure 3(b)). In a typical synthesis, a 100 g of middle distillates was mixed with 40 g of sulfide NiMo/γ-Al_2O_3 catalyst under an atmosphere of H_2, followed by heating to 350 ^{o}C in 1 hr under pressured atmosphere of H_2 (7 MPa) and vigorously stirring. After 350 ^{o}C for 5 h, the hydrotreating oil was cooled to ambient condition and corrected by filtration. The yield of hydrotreating oil was 55.2%. The sulfur and nitrogen concentrations of hydrotreating oil were smaller than 10 and 50 ppm, respectively. In Figure 5, the GC analysis equipped with FID and mass detectors indicates that the composition of hydrotreating oil, produced by deep hydrotreating of middle distillates over sulfide NiMo/γ-Al_2O_3 catalyst, is similar to that of petro-diesel. The distillation curve of hydrotreating oil was analysed by the procedures of JIS K2254 method. The results show that the temperatures for initial distillation, 50 vol% fraction and 95 vol% fraction of hydrotreating oil are 116, 289 and 355 ^{o}C, respectively. According to the procedures of JIS K2249 and K2280-5 methods, the density and cetane number of hydrotreating oil are 0.8252 g cm^{-3} and 60.8, respectively. The fuel property of

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hydrotreating oil can meet with the international fuel standard. It indicates that the hydrotreating oil produced by deep hydrotreating of middle distillates over NiMo/γ-Al_2O_3 catalyst is a clean and drop-in diesel-like biofuel, which can be applicable for use in high blends.

3. Experimental

3.1. Preparation and characterization of sulfide catalysts

The sulfide catalysts were prepared by incipient impregnation method. The cobalt- and nickel-promoted molybdenum aqueous solutions (denoted at CoMo(cit) and NiMo(cit), respectively) were freshly prepared by the procedures as described in our previous study [30]. For the preparation of freshly prepared CoMo(cit) and NiMo(cit) aqueous solution, the molybdenum oxide (Wako) was dispersed in hot deionized water (ca. 90 ^{o}C) for 12 h under stirring. To this solution, the cobalt nitrate (or nickel nitrate) and citric acid were slowly added under heating and stirring conditions, resulting in freshly prepared CoMo(cit) or NiMo(cit) aqueous solution with molar composition of 1 MoO_3: 0.5 CoO (or NiO): 0.58 $C_6H_8O_7$: 1.67 H_2O. The extruded γ-Al_2O_3 particle as the supporting materials were dried at 120 ^{o}C for 6 h prior to the impregnation. For the preparation of sulfide catalysts, the CoMo(cit) and NiMo(cit) aqueous solutions were slowly dropped on the extruded γ-Al_2O_3 sample under low vacuum (ca. 0.1 torr). The as-made CoMo(cit) and NiMo(cit)-impregnated γ-Al_2O_3 samples were aged at the room temperature for 1 h under vacuum, followed by drying through microwave irradiation (1050W, 10Hz) for 10 min. The CoO (or NiO) and MoO_3 loadings were 6.1 wt% and 23.6 wt%, respectively. The sulfidation was carried out in a quartz tube reactor using a 5 vol%H_2S/H_2 standard gas at 360 ^{o}C for 6 h. As a result, the sulfide CoMo/Al_2O_3 and NiMo/Al_2O_3 catalysts could be prepared. Characterizations were performed by XRD using a Rigaku Miniflex diffractometer, N_2 physisorption using a Belsorp instrument and HRTEM determined by a TOPCON EM002B instrument [30].

3.2. *Stepwise hydrotreating of Jatropha bio-oil*

Jatropha bio-oil produced by thermal pyrolysis of waste Jatropha biomass was kindly supplied by TISTR, Thailand, using a Pilot Plant with a capacity of 20 Kg/h. The elemental and water analyses showed that Jatropha bio-oil contained 3.2 wt% of water and 96.8 wt% of heteroatom-containing hydrocarbon, which composition was 66.5 wt% of carbon, 8.80 wt% of hydrogen and 5.82 wt% of nitrogen and 18.9 wt% of oxygen. Scheme 1(b) shows a stepwise strategy for upgrading of Jatropha bio-oil over sulfide catalysts under severe conditions. To reduce viscosity and partly deoxygenation, the pre-

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treatment of Jatropha bio-oil was performed in a slurry bed reactor using waste sulfide NiMo/γ-Al_2O_3 catalyst (1 wt%) at 400 °C and 7 MPa of H_2 for 2 h. The pre-treated Jatropha bio-oil was distilled and separated into three fractions: (i) light distillates (< 240 °C), (ii) middle distillates (240-360 °C) and (iii) heavy distillates (> 360 °C). The yield of light distillates which composition was closed to gasoline was 21 wt% and that of middle distillates which composition was closed to diesel was around 59 wt%., In this study, we focused on the deep hydrotreating of light and middle distillates over sulfide CoMo/γ-Al_2O_3 or NiMo/γ-Al_2O_3 catalysts into clean and drop-in biofuels (Figure 3). The deep hydrotreating was performed on a high-pressure stainless-steel batch-type reactor at 350 °C and 7 MPa of H_2 for 5 h using a catalyst/oil weight ratio of 0.4. The hydrotreated oils were analysed by Agilent 6890 GC-FID instrument equipped with mass detector, elemental analysis of carbon, nitrogen, hydrogen, sulfur, and the fuel property.

4. Conclusions

Jatropha bio-oil was mostly composed of fatty acids, fatty acid methyl esters, fatty acid amides and derivatives, corresponding to high concentrations of heteroatoms, nitrogen especially. To overcome the catalyst deactivation by those heteroatoms, we had developed a stepwise strategy for hydrotreating of 100 wt% Jatropha bio-oil over sulfide

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catalysts to produce clean and drop-in transport biofuels, such as gasoline- and diesel-like biofuels. This stepwise strategy included (i) pre-treatment of Jatropha bio-oil over waste NiMo/γ-Al_2O_3 catalyst (1 wt%) using a slurry-type reactor under severe condition (400 ^oC, 7 MPa of H_2, 2 h), (ii) distillation of pre-treated Jatropha bio-oil into light distillates (T_d < 240 ^oC) and middle distillates (T_d = 240-360 ^oC), (iii) deep hydrotreating of light and middle distillates over sulfide CoMo/γ-Al_2O_3 and NiMo/γ-Al_2O_3 catalysts (40 wt%) using a batch-type reactor under severe condition (350 ^oC, 7 MPa of H_2, 5 h) to produce clean and drop-in biofuels. Among the step (iii), we found that the hydrotreating oil with gasoline-like composition and an octane number of 44 could be synthesized by deep hydrotreating of light distillates over sulfide CoMo/γ-Al_2O_3 catalyst, and it would be suitable for partly blending with petro-gasoline. On the other hand, the hydrotreating oil with diesel-like composition and a cetane number of 60.8 could be produced by deep hydrotreating of middle distillates over sulfide NiMo/γ-Al_2O_3 catalyst, and it would be suitable for use in diesel engine directly. Moreover, the waste NiMo/γ-Al_2O_3 catalyst could be recycled and used again in the step (i), which reduced the environmental pollution and production cost.

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Table 1. The elemental analysis, composition and octane number of gasoline-like fuel.[a]

Sulfur (ppm)	Nitrogen (ppm)	Octane number	H/C	Density (g/cm^3)	*n*-Paraffin (vol%)	*iso*-Paraffin (vol%)	Olefin (vol%)	Naphthene (vol%)	Aromatic (vol%)
0	49	44.5	1.77	0.7	29.5	14.4	4.99	21.4	29.6

a. Synthesized by stepwise hydrogenation of Jatropha bio-oil over sulfide CoMo/γ-Al_2O_3 catalysts. The reaction condition for deep hydrogenation (Scheme 1(b) and Figure 3(a)): 350 ºC, 5 h, 2 g of sulfided CoMo/γ-Al_2O_3 catalyst, 5 g of light distillate obtained by distillation of pre-treated Jatropha bio-oil at the temperature lower than 240 ºC.

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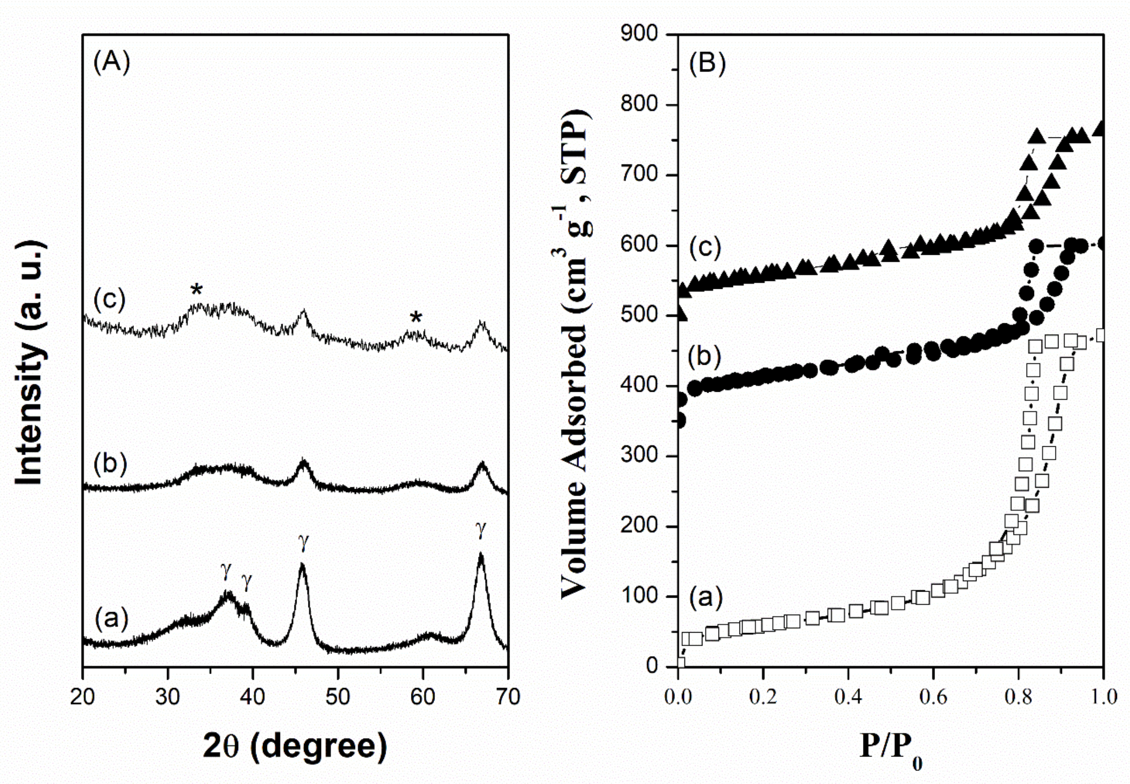

Figure 1. (A) powered XRD patterns and (B) N_2 adsorption-desorption isotherms of mesoporous sulfide catalysts: (b) CoMo/γ-Al_2O_3 and (c) NiMo/γ-Al_2O_3 catalysts, in comparison to those of a supporting material: (a) γ-Al_2O_3. The asterisk and gamma (γ) represent the characteristic peaks of Co-incorporated MoS_2-like slabs (or Ni-incorporated counterpart) and gamma-alumina framework, respectively.

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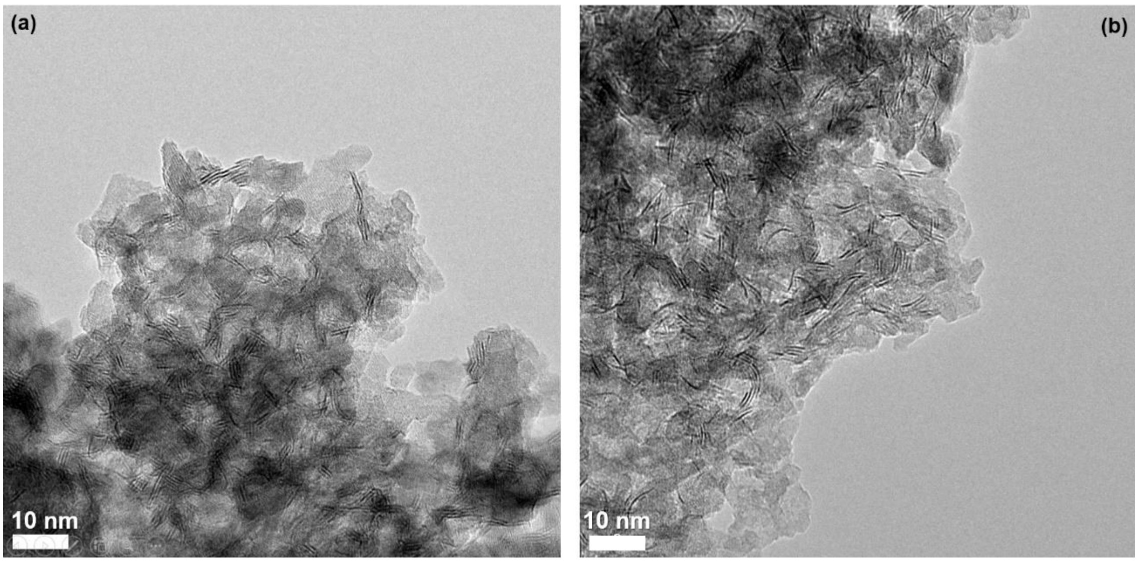

Figure 2. HRTEM images of mesoporous sulfide catalysts: (a) CoMo/γ-Al_2O_3 and (b) NiMo/γ-Al_2O_3.

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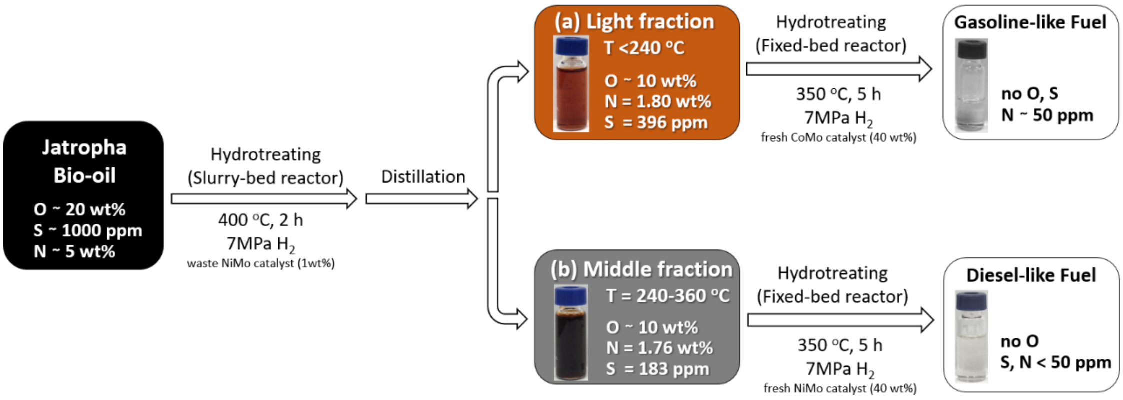

Figure 3. Stepwise hydrotreating of Jatropha bio-oil over sulfide catalysts to produce gasoline-like and diesel-like fuels.

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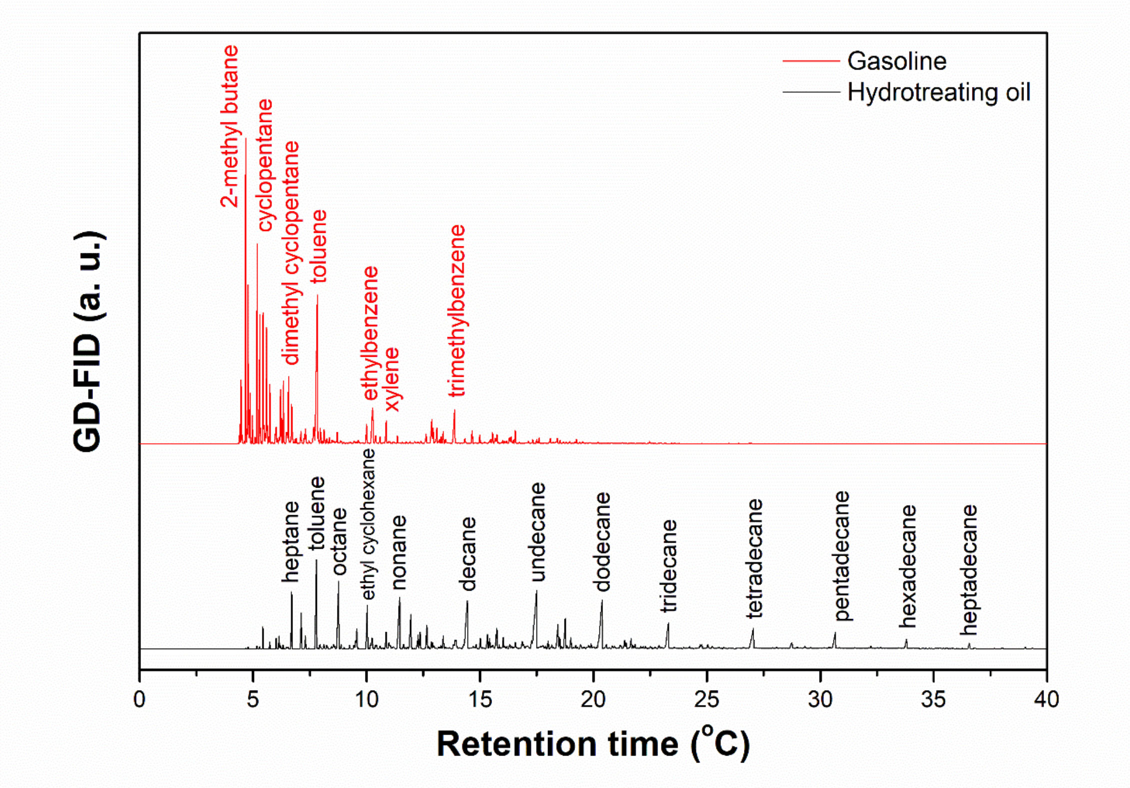

Figure. 4. GC-FID profiles of gasoline and hydrotreating oil, which is produced by deep hydrotreating of light distillates over sulfide CoMo/γ-Al_2O_3 catalyst at 350 °C and 7 MPa of H_2 for 5 h.

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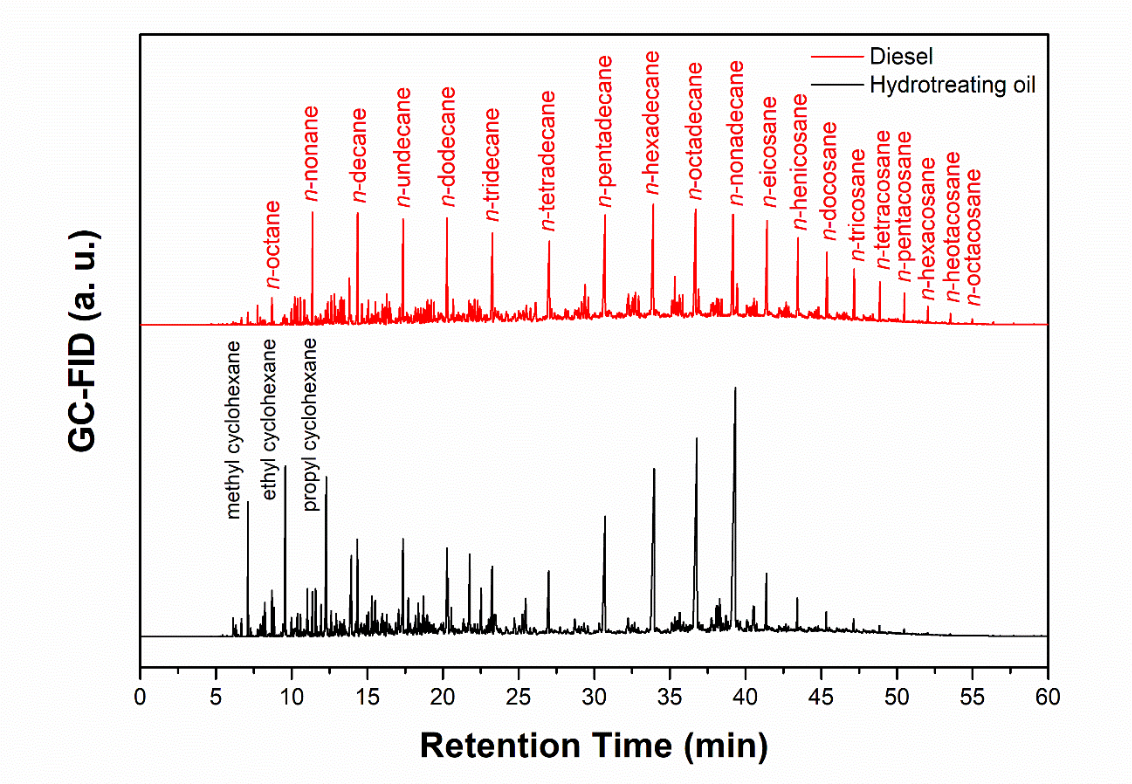

Figure 5. GC profiles of diesel and hydrotreating oil, which is produced by deep hydrotreating of middle distillates over sulfide NiMo/γ-Al_2O_3 catalyst at 350 °C and 7 MPa of H_2 for 5 h.

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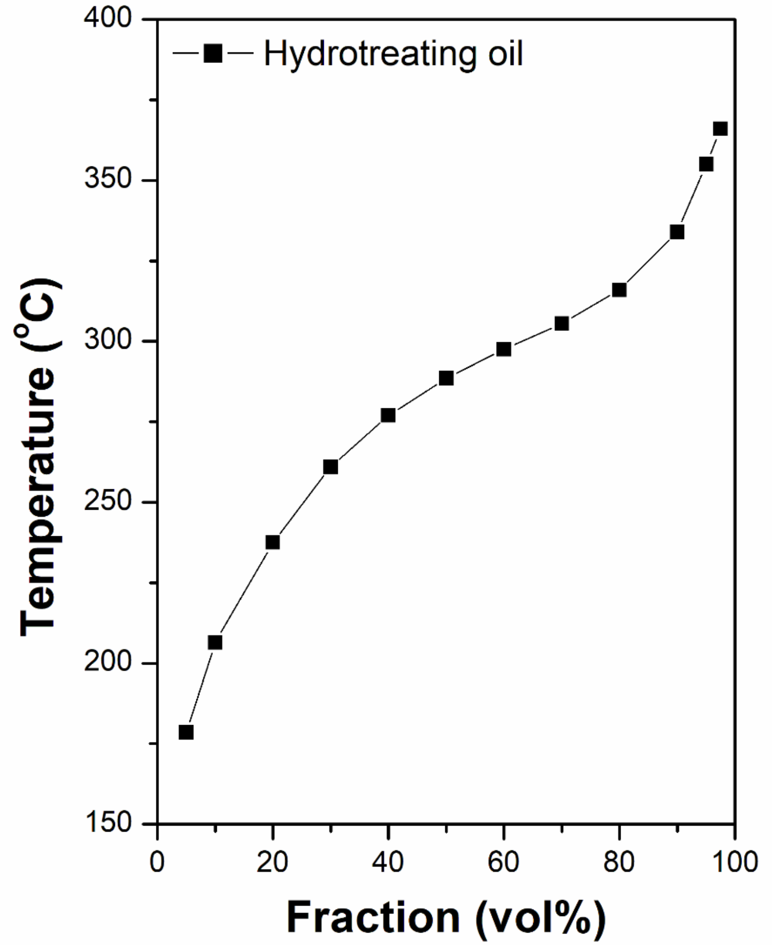

Figure 6. Distillation curve of hydrotreating oil, which is produced by deep hydrotreating of middle distillates over sulfide NiMo/γ-Al_2O_3 catalyst at 350 °C and 7 MPa of H_2 for 5 h.