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Effect of Re on the Catalytic Behavior of Sulfided Ni-Mo Catalyst Supported on γ-Al_2O_3 in Deoxygenation of Refined Palm Olein to Bio-hydrogenated Diesel

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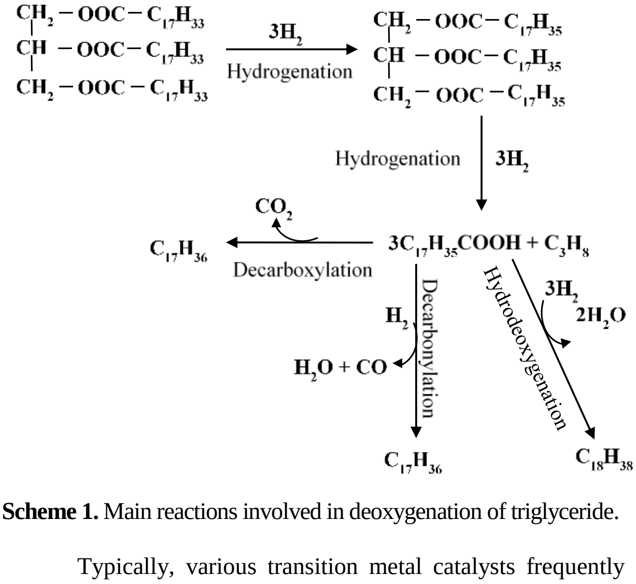
Abstract: This paper demonstrates the catalytic activities of trimetallic sulfided ReNiMo supported on γ-Al_2O_3 toward the deoxygenation of refined palm olein (RPO). The bimetallic sulfided NiMo was also tested for comparison. From the results revealed that ReNiMo sulfide catalyst exhibited significantly higher yields of diesel-like hydrocarbons than NiMo sulfide catalysts. The different product distributions depended on reaction temperature and reaction time. At 350-370°C for 1-1.5 h under a H_2 pressure of 40 bar, sulfided ReNiMo catalyst provided the diesel yield (C_{13}-C_{18}) of 75-78%. Based on BET surface area, SEM-EDS and H_2-chemisorption techniques, we found that the additional of Re promoter can increase surface area, reduce metal particle size and improve metal dispersion. Moreover, the catalyst reusability was also tested in this work. We found that the sulfided ReNiMo/γ-Al_2O_3 showed good reusability and maintained the diesel yield higher than 73% for at least six consecutive runs. In contrast with ReNiMo, NiMo sulfide catalyst was significantly deactivated due to high rate of carbon deposition according to TPO result. In addition, adding glycerol to use as a hydrogen donor in deoxygenation reaction was successful.

Keywords: Deoxygenation, Refined palm olein, Diesel-like hydrocarbon, Trimetallic sulfided ReNiMo.

1. Introduction

Nowadays, the increase in the world's energy demand and global climate change is more concerned. To alleviate these problems, the renewable fuels are a primary candidate for replacement fossil fuels and global warming concern. From statistic of energy consumption in the transportation sector, it has been reported that transportation fuel demand has been increasing from 1.1% per day in order to meet motorization industries demand and 63% share in global transportation consumption from 2010-2040 [1]. Therefore, worldwide researchers are focused on development of biofuel production from various renewable feedstocks and technologies in the recent years [1–5]. Among various raw materials in tropical countries (e.g. Thailand, Indonesia, and Malaysia), palm derivatives (e.g. palm fatty acids) are promising renewable feedstock for synthesizing diesel-like hydrocarbons via deoxygenation reaction [3–6]. Typically, diesel-like hydrocarbons are a mixture of straight chain hydrocarbons between 8 and 21 carbon atoms depending on types of fatty acid in feedstock [3,7]. However, the species of plant oil, climate, and geographical location are influenced on the difference of fatty acid compositions [8]. The principal compositions of fatty acid components from palm oil feedstock are triglycerides composed palmitic acid (hexadecanoic acid, $C_{16:0}$), stearic acid (octadecanoic acid, $C_{18:0}$), oleic acid (octadecenoic acid, $C_{18:1}$) and linoleic acid (octadecadienoic acid, $C_{18:2}$) [3,9]. Currently, the deoxygenation of fatty acid and/or triglyceride from renewable sources has attracted much attention for the production of diesel-like hydrocarbons or green diesel in the presence of a metal catalyst by removing oxygen atom from its component to form of H_2O or oxides of carbon (CO_x) as shown in Scheme 1. The process can be carried out in the presence of H_2 or H_2-free atmosphere environment via 3 main pathways including decarboxylation (DCO_2), decarbonylation (DCO) or hydrodeoxygenation (HDO) [3,4,9,10]. Additionally, unsaturated triglyceride of vegetable oil was hydrogenated and cleaved into saturated triglycerides, diglycerides and/or carboxylic acids, and propane. In detail, the co-product from DCO_2 and DCO are CO_2 or water and CO respectively; furthermore, itself is an endothermic reaction. Therefore, the consequent hydrocarbon product from DCO_2 and DCO has one carbon atom shorter than the original fatty acid feedstock. Meanwhile, HDO is exothermic reaction removing oxygen in form of water and yields the hydrocarbon product with the same number as the original fatty acid chain. Due to by-product in gaseous phases from DCO_2 and DCO are CO and CO_2, thus water gas shift and methanation should be considered. From the practical perspective, tuning of the hydrocarbon composition product is very important, which can be achieved via operating condition and catalyst [3,4,6,7].



Scheme 1. Main reactions involved in deoxygenation of triglyceride.

Typically, various transition metal catalysts frequently used in deoxygenation of triglycerides and/or fatty acids are following: (1) transition metal sulfide catalysts e.g. $NiMoS_2$, $CoMoS_2$, and $NiWS_2$ [9,11–15] (2) transition metal phosphide, carbide and nitride catalysts e.g. Ni_2P, Mo_2N and Mo_2C [16-17]. Many researchers have reported using transition metal sulfide catalysts in deoxygenation process demonstrated high activity and stability but their basic drawback is sulfur leaching caused of catalyst deactivation [9,15,18,19]. Metal phosphide and carbide catalysts show high performance in the removal of oxygen atoms from oxygenated biomass feedstocks and selectivity for diesel-range alkanes. However, the preparation procedures of metal phosphide or carbide catalysts are complicated and most of them are easily transformed during deoxygenation leading to low reusability [5,7,19,20]. Therefore, transition metal sulfides are mostly selected for large-scale production due to their performance in the production of green diesel and cost-effective application [9,10,21]. The effects of operating parameter and catalyst were explored in previous works. Based on some earlier works, E. Santillan-Jimenez et al. [22] investigated the catalytic deoxygenation of triglycerides and fatty acid via DCO_2 and DCO in a semi-batch mode over Ni/C and Pd/C catalysts. They found that using Pd/C in a semi-batch reactor under N_2 atmosphere shows better results compared with previous result which using a batch reactor. From this result, they believed that removing the evolved gas especially CO will alleviate poisoning of catalyst. Furthermore, most of alkane products are correlated to the major component of the feedstock and the catalyst employed. Brimont et al. [23] studied the deoxygenation of ethyl heptanoate catalyzed by unsupported MoS_2, Ni_3S_2 and Ni-promoted MoS_2 (with various Ni/Mo ratios) in a fixed-bed reactor. They found that there are competitions between HDO and DCO/DCO_2 in this experiment. The presence of MoS_2 is highly selective for HDO, while Ni_3S_2 favored DCO/DCO_2 pathways. When bimetallic NiMo sulfide catalyst used, it was found that Ni/Mo ratio influenced on the HDO/(DCO/DCO_2) selectivity. Additionally, the sulfided Ni, Mo and NiMo catalysts were prepared by commercial Al_2O_3 support and tested at 260-280°C, 3.5 MPa and 0.25-4 h^{-1} in a fixed-bed reactor. The bimetallic sulfided NiMo catalysts had a higher activity than a monometallic sulfided Mo and Ni catalysts [24]. Recently, hydrogen donors have been widely used for hydroconverion such as glycerol, formic acid and alcohol [25–27]. They donate hydrogen from itself to unsaturated organic compounds. For example, Vardon et al. [27] studied the catalytic hydrogenation and deoxygenation of oleic acid by using glycerol for in situ hydrogen production over Pt-Re/C. Furthermore, they examined the additional of Re promoter to enhance saturated fatty acid deoxygenation. They found that the conversion of oleic acid to heptadecane was achieved within 2 h with a net zero H_2 consumption using a 1:3 glycerol-to-fatty acid ratio. Moreover, the addition of Re on Pt/C can improve deoxygenation performance at low temperature due to improved CO turnover for decarbonylation, transformation to active site morphology or changes to active site electronic properties.

In the present work, the catalytic activity of sulfided ReNiMo supported on γ-Al_2O_3 through catalytic deoxygenation of refined palm olein (RPO) for diesel-like hydrocarbon production was studied and compared to bimetallic NiMo sulfide catalyst. The effects of operating parameters (i.e. reaction temperature, time and hydrogen donor) were examined in order to determine suitable operating condition. Next, catalyst reusability test was also performed. The characterizations of sulfide catalysts were evaluated using BET analysis, SEM-EDS, H_2-chemisorption and TPO to study the relation between their catalytic activity and physical-chemical properties.

2. Experimental

2.1 Materials

Glycerol (AR grade, ≥ 99.5), nickel (II) nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$, 99.999%) and ammonium perrhenate (NH_4ReO_4, 99.999%) were purchased from Sigma-Aldrich Chemical Co. LLC., Germany. Ammonium heptamolybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, 99.999%) was purchased from Carlo Erba Reagent, Italy. The γ-Al_2O_3 with 1.8 mm diameter was purchased from Sasol Company, Germany. The ASTM D2887-12 calibration standard of C_5-C_{44} linear hydrocarbon compounds was supplied by Restek Corporation, U.S. N-hexane (AR grade, 99.99) was obtained from Fisher Sceintific Co, U.S.

Refined palm olein (RPO) was purchased from a local market in Thailand. Main component of RPO composed triglyceride higher than 99 wt.%. Table 1 presents fatty acid composition of RPO.

Table 1. Composition of RPO from palm oil industry for biodiesel production.

Fatty acid	RPO (wt.%)
C16:0 (Palmitic acid)	39.8
C18:0 (Steric acid)	4.4
C18:1 (Oleic acid)	42.5
C18:2 (Linoleic acid)	11.2
Others	2.1

2.2 Catalyst preparation

Bimetallic (3%Ni-10%Mo) and trimetallic (1%Re-3%Ni-10%Mo) sulfide catalysts supported on γ-Al_2O_3 were calculated by weight and synthesized with impregnation technique. The commercial γ-Al_2O_3 as support was crushed and sieved to obtain 0.425 mm particle size. The metal precursors were calculated and dissolved in deionized water following the amount of requirement as shown in Table 2. Then, the metal aqueous solutions were impregnated on γ-Al_2O_3. The impregnated catalysts were dried overnight in an oven at 105°C and calcined at 500°C in air for 5 h to obtain metallic catalysts in oxide phase. Before testing reaction, the prepared catalysts were sulfided at 400°C for 4 h under a flow of 4Lh^{-1} of H_2S/H_2 (10/90) mixture.

2.3 Catalyst characterization

The specific surface area and porosity of catalysts were characterized by Brunauer-Emmett-Teller (BET) by using nitrogen adsorption/desorption analyzer at -196°C of in a Belsorp-max Bel Japan equipment. The fresh samples were pre-treated by removing gas at 150°C for 3 h. A scanning electron microscope were taken using a JEOL JSM-6610 LV connected with an Energy Dispersive X-Ray Spectrometer (EDS) analyzer determined the catalyst morphology, elemental mapping of catalyst, and elemental composition of these particles. H_2-TPD experiment was analyzed the dispersion of sulfide catalyst samples. The crystalline structures of the sulfide catalysts were analyzed by an X-ray diffraction (D8 ADVANCE, Bruker, Ltd., Germany) by using a Cu K $_\alpha$ radiation at 40 kV and 40 mA with a scanning rate of 0.02º/sec over the 2θ ranges from 10º to 80º. Temperature programmed oxidation (TPO) experiments were performed to identify the carbon species deposited on the surface of the spent catalysts after post-reaction.

2.4 Reaction procedure

The reactions were performed with loaded 25 cm^3 of RPO and 0.5 g sulfide catalyst into reactor with a volume of 150 cm^3. After the loading, the reactor was purged thoroughly with N_2 three times to remove air and then with 4 MPa pressurized H_2. Next, the reactor was heated to desired temperature (350-410ºC) and reaction time (1-2 h) which was counted after the inside temperature of reactor reached the desired temperature. After reaching the desired reaction time, the reactor was immersed in an ice-cool water bath to stop reactions. The liquid and gas samples collected from the reactor were quantitatively analyzed by various techniques. The spent catalyst was collected and rinsed with hexane for reusability test.

Table 2. Physicochemical properties of the catalysts.

Catalyst	BET surface area [a] (m^2g^{-1})	Elemental composition [b] (wt.%)			Metal dispersion [c] (%)
		Re	Ni	Mo	
γ-Al_2O_3	167.76	-	-	-	-
3%Ni-10%Mo/γ-Al_2O_3	117.00	-	3.05	10.75	6.87
1%Re-3%Ni-10%Mo/γ-Al_2O_3	140.83	0.86	3.60	9.25	7.21

[a] Measured from BET
[b] Measured from EDS
[c] Measure from H_2-TPD

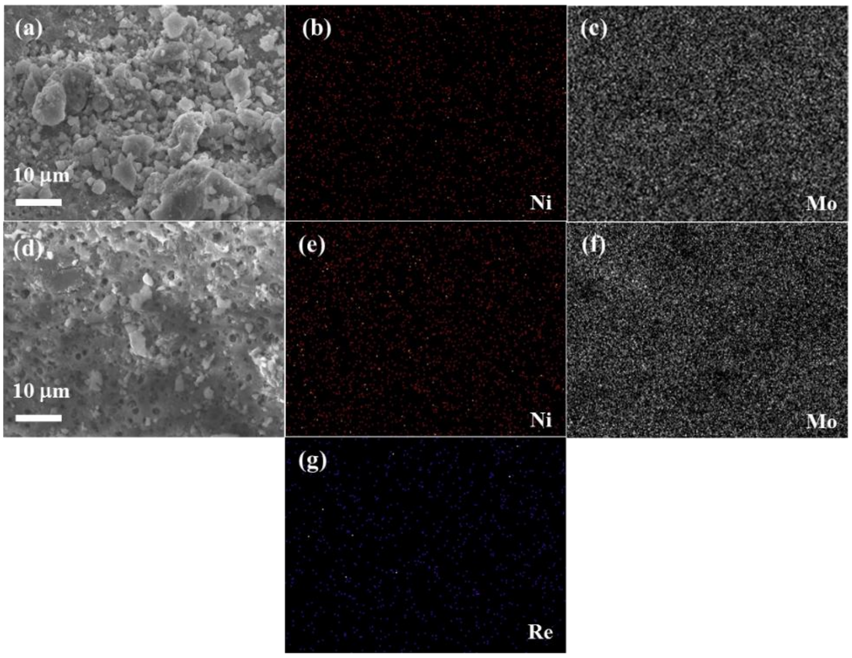


Figure 1. SEM images and elemental mapping images of (a-c) 3%Ni-10%Mo and (d-g) 1%Re-3%Ni-10%Mo sulfide catalysts supported on γ-Al_2O_3.

The liquid products were diluted with n-hexane (GC-grade) prior to analyze with GC-FID (Shimadzu GC-2014, Japan) equipped with Agilent DB-1HT column. The calibration curve of standards was used to determine the amount of each of n-alkane compounds (n-C_8 to n-C_{18}) in the liquid.

Product yield and conversion of RPO were calculated following Eqs. 1-2, respectively. The conversion of RPO was calculated from the different amount of total acid number (TAN) of carboxylic acid between feedstock and product. The TAN values determined from standard test method (ASTM D664) by using a titrator (Mettler Toledo T50, USA) equipment with an electrode DGi116-solvant. It was found that TAN of oleic acid was 208.18 mg_{KOH}/g_{oil}. The liquid hydrocarbon products are classified into 2 fractions: C_8-C_{12} is defined as gasoline range and C_{13}-C_{18} is defined as diesel range.

Conversion of oleic acid (%) =

$$\left(\frac{\text{total acid number of RPO} - \text{total acid number of the product}}{\text{total acid number of RPO}}\right) \text{X } 100 \qquad (1)$$

Product yield (%) =

$$\left(\frac{\text{total weight of desired hydrocarbons, } C_8 - C_{12} \text{ or } C_{13} - C_{18}}{\text{weight of feedstock}}\right) \text{X } 100 \qquad (2)$$

3.2 Effects of temperature and time over bimetallic NiMo and trimetallic ReNiMo sulfide catalysts

Firstly, the effect of reaction temperature on catalytic deoxygenation of RPO over NiMo and ReNiMo sulfide catalysts was studied by varying the reaction temperature from 350, 370, 390 and 410ºC. The effect of reaction time from 0.5 to 2 h was studied over ReNiMo sulfide catalyst. Both reaction temperature and time were tested by fixing H_2 pressure of 4 MPa and stirring rate of 200 rpm. Their performances in term of RPO conversion and product yield were evaluated and discussed. From all studied reaction temperature (350-410ºC) result, it was found that the RPO conversion over NiMo sulfide catalysts were within the range of 82.79-92.69%, as shown in Figure 3. Moreover, there were some intermediate chemicals (e.g. free fatty acids) from the reaction over NiMo sulfide catalysts. On the other hand, complete conversion was obtained over ReNiMo sulfide catalyst from 370-410ºC.

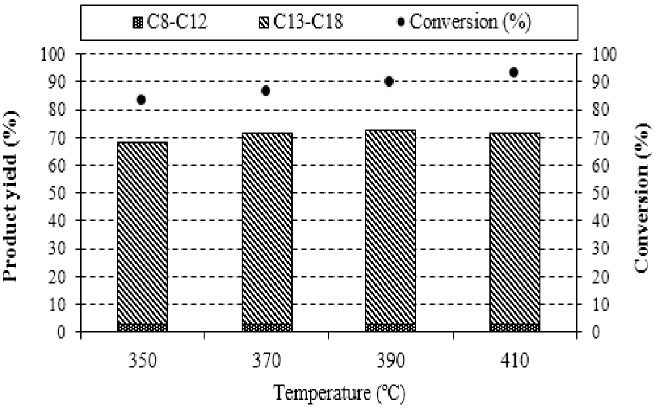


Figure 3. Effect of reaction temperature on conversion and product yield at (a) 350ºC (b) 370°C (c) 390ºC and (d) 410ºC for 1 h over bimetallic NiMo sulfide catalysts supported on γ-Al_2O_3.

From the study, it is clear that temperature provides dramatic impact on the deoxygenation of RPO (Figures 3 and 4). It could be seen that higher temperature could increase conversion of RPO deoxygenation. In part of total product yield, the results confirmed that 370-390ºC was successful to produce diesel-like hydrocarbon from triglycerides. On the other hand, the decrease in total product yield over NiMo and ReNiMo was observed at 410ºC. Furthermore, diesel yield over ReNiMo sulfide catalyst was significant decreased compared with NiMo sulfide catalyst. The gaseous phase product was increased due to cracking favored at high temperature and also accelerated with the increase of temperature. Among all synthesized catalysts, additional Re over sulfided NiMo catalyst at 390ºC for 1-1.5 h provided the highest total liquid fuel product in range of 83.98-84.59%.

For the effect of reaction time as presented in Figure 5, it was observed that the reaction time did not significantly affect on the conversion of RPO which 100% conversion was obtained at 0.5-2 h. It is clear that total product yield increased at longer reaction time (0.5-1.5 h) and turned into decreasing when the reaction reached to 2 h. These results suggest that increase of reaction time would promote cracking reaction since some light hydrocarbons (C_1-C_4) were also observed in the gaseous product under this reaction condition. Next, the additional of Re to NiMo sulfide catalyst was further studied and compared with NiMo sulfide catalyst in reusability test to confirm its performance as presented in the next session.

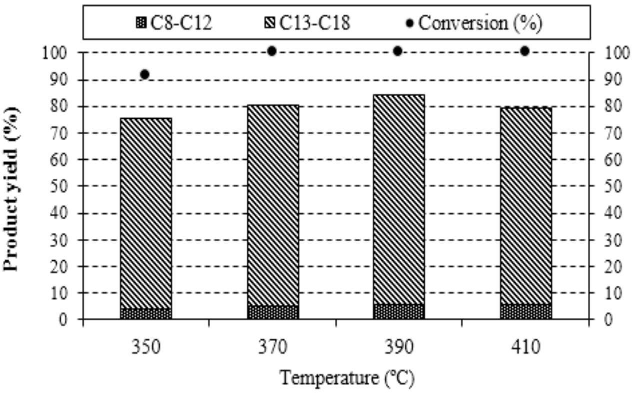


Figure 4. Effect of reaction temperature on conversion and product yield at (a) 350ºC (b) 370ºC (c) 390ºC and (d) 410ºC for 1 h over trimetallic ReNiMo sulfide catalysts supported on γ-Al_2O_3.

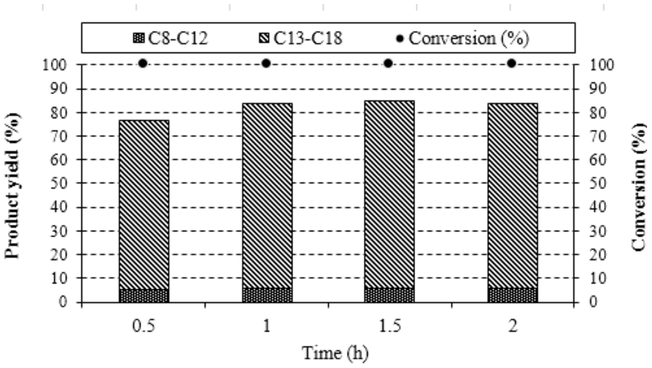


Figure 5. Effect of reaction time on conversion and product yield at (a) 0.5 h (b) 1 h (c) 1.5 h and (d) 2h at 390ºC over trimetallic ReNiMo sulfide catalysts supported on γ-Al_2O_3.

3.3 Catalyst reusability

The reusability of ReNiMo sulfide and NiMo sulfide catalysts were compared in six successive runs without any regeneration under optimal reaction condition and the results are shown in Figure 6. The catalytic activity of ReNiMo sulfide catalyst in term of conversion and total product yield remained constant in the first three runs and slightly decreased after the fourth run. After finished the sixth runs of ReNiMo sulfide catalyst, diesel yield was still higher than 73%. Conversely, when NiMo sulfide catalyst was tested, the conversion and the total product yield were significantly decreased following the number of running which the difference of product yield in the first run (71.26%) and the sixth run (56.38%) was 14.88%. After consecutive reactions, ReNiMo sulfide catalyst was characterized its textural properties. A slight change in the surface area of ReNiMo sulfide catalyst was decreased from 140.8 to 132.0 m^2g^{-1}. This result means that the strong adsorption of reactants, products or polymerized intermediates cover on surface or pore of catalysts during the reaction, which could partially block the active sites. Moreover, the amount of carbon formed on catalyst surface after six consecutive runs were determined by TPO technique. From TPO result, it was found that addition of Re into NiMo sulfide catalyst enhance better resistance toward carbon deposition (2.35 mmol g_{cat}^{-1} of carbon deposition for ReNiMo sulfide compared to 3.76 mmol g_{cat}^{-1} for NiMo sulfide). Thus, it implied that the addition of Re as a promoter could reduce particle agglomeration and enhance the growth of metal crystalline caused of increase dispersion of Ni and Mo particles which is related to with TPD measurement.

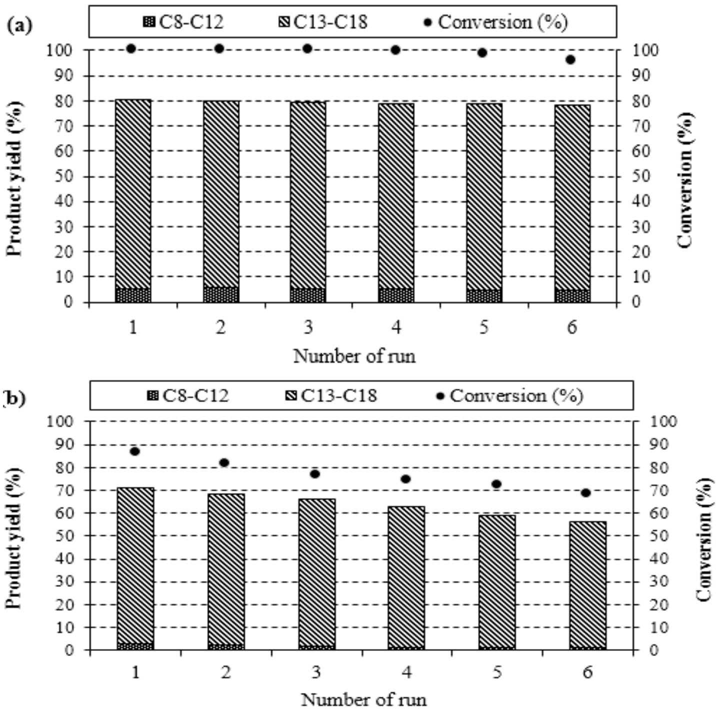


Figure 6. Reusability of the (a) ReNiMo and (b) NiMo sulfide catalysts supported on γ-Al_2O_3 at 370ºC for 1h.

3.4 Effect of glycerol as in situ H_2 donor

Nowadays several organic compounds have been investigated as hydrogen donors to alleviate the use of hydrogen gas consumption for hydroconversion reaction [25-27]. In this work, glycerol was selected and used as *in situ* H_2-donor for catalytic deoxygenation of RPO due to inexpensiveness and availability. The influences of glycerol as H-donors compared with external H_2 gas on the conversion and hydrocarbon yield over trimetallic ReNiMo sulfide supported on γ-Al_2O_3 as presented in Table 3. It can be seen that the presence of glycerol could be a good H_2 donor in producing diesel-like hydrocarbon, but the conversion (78.4%) and total product yield (66.53%) was low when compared with conversion (100%) and total product yield (83.98%) from external H_2 gas. Additionally, D.I. King and co-workers [28] studied plausible pathway of production H_2 gas from aqueous phase reforming (APR) of glycerol over Pt-Re supported on carbon. They found that there are competitive between hydrogen production (C-C cleavage) and consumption (C-Ox cleavage) pathway in APR of glycerol. This suggest that the other parameters such as the glycerol to triglyceride ratio, catalyst loading, and the effect of sulfide catalyst type on catalytic converted glycerol to H_2 selectivity may influence *in situ* H_2 production and reaction activity which should be further studied.

Table 3. Effect of glycerol as H_2 donor and external H_2 on conversion and product yield over trimetallic ReNiMo sulfide supported on γ-Al_2O_3 at 390ºC for 1h.

Hydrogen donor	**Conversion (%)**	**Product yield (%)**	
		C_8-C_{12}	**C_{13}-C_{18}**
-	100	5.69	78.29
Glycerol	78.4	4.09	62.44

4. Conclusions

The presence of Re into sulfided NiMo catalyst can greatly improve the catalytic activity toward the deoxygenation of refined palm olein (RPO). Experiments revealed that the reaction exhibited different product distributions and strongly depended on reaction temperature and time. Interestingly, complete conversion was achieved in short reaction time (0.5 h). The optimal condition for this experiment was 370-390ºC and 1-1.5 h under 4 MPa H_2 pressure over sulfided ReNiMo catalyst and provided high diesel yield (C_{13}-C_{18}) of 75-78% from RPO as a feedstock. From characterization analysis, additional of Re over NiMo sulfide catalyst could increase the specific surface are of NiMo about 20.4%. Moreover, the metal dispersion of NiMo sulfide catalyst was also increased when Re promoter was introduced into NiMo catalyst. From reusability test, it was observed that sulfided ReNiMo/γ-Al_2O_3 catalyst showed good reusability. The diesel yield can be maintained to be higher than 73% after six consecutive runs. In addition, it could be confirmed that adding glycerol could represent a good H_2 donor for deoxygenation over ReNiMo sulfide catalyst. For further implementation, the study on H_2 selectivity from glycerol as H_2 donor is recommended

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References

[1] Mahmudul HM, Hagos FY, Mamat R, Adam AA, Ishak WFW, Alenezi R, Production, characterization and performance of biodiesel as an alternative fuel in diesel engines – A review, *Renewable and Sustainable Energy Reviews* 72 (2017) 497-509.

[2] Huber GW, Iborra S, Corma A, Synthesis of transportation fuels from biomass: Chemistry, catalysts, and engineering, *Chemical Reviews* 106/9 (2006) 4044–4098.

[3] Pattanaik BP, Misra RD, Effect of reaction pathway and operating parameters on the deoxygenation of vegetable oils to produce diesel range hydrocarbon fuels: A review, *Renewable and Sustainable Energy Reviews* 73 (2015) 545-557.

[4] Hermida L, Abdullah AZ, Mohamed AR, Deoxygenation of fatty acid to produce diesel-like hydrocarbons: A review of process conditions, reaction kinetics and mechanism, *Renewable and Sustainable Energy Reviews* 42 (2015) 1223–1233.

[5] Furimsky E, Hydroprocessing challenges in biofuels production, *Catalysis Today* 217 (2013) 13–56.

[6] Kiatikittipong W, Phimsen S, Kiatkittipong K, Wongsakulphasatch S, Laosiripojana N, Assabumrungrat S, Diesel-like hydrocarbon production from hydroprocessing of relevant refining palm oil, *Fuel Processing Technology* 116 (2013) 16-26.

[7] Arun N, Sharma RV, Dalai AK, Green diesel synthesis by hydrodeoxygenation of bio-based feedstocks: Strategies for catalyst design and development, *Renewable and Sustainable Energy Reviews* 48 (2015) 240–255.

[8] Mahmudul HM, Hagos FY, Mamat R, Adam AA, Ishak WFW, Alenezi R, Production, characterization and performance of biodiesel as an alternative fuel in diesel engines – A review, *Renewable and Sustainable Energy Reviews* 72 (2017) 497-509.

[9] Srifa A, Faungnawakij K, Itthibenchapong V, Viriya-empikul N, Charinpanitkul T, Assabumrungrat S, Production of bio-hydrogenated diesel by catalytic hydrotreating of palm oil over $NiMoS_2$/γ-Al_2O_3, *Bioresource Technology* 158 (2014) 81-90.

[10] Itthibenchapong V, Srifa A, Kaewmeesri R, Kidkhunthod P, Faungnawakij K, Deoxygenation of palm kernel oil to jet fuel-like hydrocarbons using Ni-MoS_2/γ-Al_2O_3 catalysts, *Energy Conversion and Management* 134 (2017) 188-196.

[11] Kiatkittipong W, Phimsen S, Kiatkittipong K, Wongsakulphasatch S, Diesel-like hydrocarbon production from hydroprocessing of relevant re fi ning palm oil, *Fuel Processing Technology* 116 (2013) 16–26.

[12] Yang Y, Wang Q, Zhang X, Wang L, Li G, Hydrotreating of C18 fatty acids to hydrocarbons on sulphided NiW/SiO2-Al2O3, *Fuel Processing Technology* (2013) 116 165–74.

[13] Wang C, Wang D, Wu Z, Wang Z, Tang C, Zhou P, Effect of W addition on the hydrodeoxygenation of 4-methylphenol over unsupported NiMo sulfide catalysts, *Applied Catalysis A: General* (2014) 476 61–7.

[14] Hancsók J, Kasza T, Kovács S, Solymosi P, Holló A, Production of bioparaffins by the catalytic hydrogenation of natural triglycerides, *Journal of Cleaner Production* (2012) 34 76–81.

[15] Kordulis C, Bourikas K, Gousi M, Kordouli E, Lycourghiotis A, Development of nickel based catalysts for the transformation of natural triglycerides and related compounds into green diesel: A critical review, *Applied Catalysis B: Environmental* 181 (2016) 156-196.

[16] Boullosa-Eiras S, Lødeng R, Bergem H, Stöcker M, Hannevold L, Blekkan EA, Catalytic hydrodeoxygenation (HDO) of phenol over supported molybdenum carbide, nitride, phosphide and oxide catalysts, *Catalysis Today* (2014) 223 44-53.

[17] Pan Z, Wang R, Li M, Chu Y, Chen J, Deoxygenation of methyl laurate to hydrocarbons on silica-supported Ni-Mo phosphides: Effect of calcination temperatures of precursor, *Journal of Energy Chemistry* 24/1 (2015) 77-86.

[18] Vogelaar BM, Eijsbouts S, Bergwerff JA, Heiszwolf JJ, Hydroprocessing catalyst deactivation in commercial practice, *Catalysis Today* 154/3-4 (2010) 256-263.

[19] Liu Q, Bie Y, Qiu S, Zhang Q, Sainio J, Wang T, Ma L, Lehtonen J, Hydrogenolysis of methyl heptanoate over Co based catalysts: Mediation of support property on activity and product distribution, *Applied Catalysis B: Environmental* 147 (2014) 236-245.

[20] Srifa A, Faungnawakij K, Itthibenchapong V, Assabumrungrat S, Roles of monometallic catalysts in hydrodeoxygenation of palm oil to green diesel, *Chemical Engineering Journal* 278 (2015) 249-258.

[21] Hollak SAW, Gosselink RW, Van Es DS, Bitter JH, Comparison of tungsten and molybdenum carbide catalysts for the hydrodeoxygenation of oleic acid, *ACS Catalysis* 3/12 (2013) 2837-2844.

[22] Santillan-Jimenez E, Morgan T, Shoup J, Harman-Ware AE, Crocker M, Catalytic deoxygenation of triglycerides and fatty acids to hydrocarbons over Ni-Al layered double hydroxide, *Catalysis Today* 237 (2014) 136-144.

[23] Ruinart De Brimont M, Dupont C, Daudin A, Geantet C, Raybaud P, Deoxygenation mechanisms on Ni-promoted MoS_2 bulk catalysts: A combined experimental and theoretical study, *Journal of Catalysis* 286 (2012) 153-164.

[24] Kubička D, Kaluža L, Deoxygenation of vegetable oils over sulfided Ni, Mo and NiMo catalysts, *Applied Catalysis A: General* 372/2 (2010) 199-208.

[25] Wolfson A, Dlugy C, Shotland Y, Tavor D, Glycerol as solvent and hydrogen donor in transfer hydrogenation-dehydrogenation reactions, *Tetrahedron Letters* 50/43 (2009) 5951-5953.

[26] Panagiotopoulou P, Martin N, Vlachos DG, Effect of hydrogen donor on liquid phase catalytic transfer hydrogenation of furfural over a $Ru/RuO_2/C$ catalyst, *Journal of Molecular Catalysis A: Chemical* 392 (2014) 223-228.

[27] Vardon DR, Sharma BK, Jaramillo H, Kim D, Choe JK, Ciesielski PN, Strathmann TJ, Hydrothermal catalytic processing of saturated and unsaturated fatty acids to hydrocarbons with glycerol for in situ hydrogen production, *Green Chemistry* 16/3 (2014) 1507.

[28] King DL, Zhang L, Xia G, Karim AM, Heldebrant DJ, Wang X, Peterson T, Wang Y, Aqueous phase reforming of glycerol for hydrogen production over Pt-Re supported on carbon, *Applied Catalysis B: Environmental* 99/1-2 (2010) 206-213.