Hydrotreating of Sunan Candlenut (*Reutealis trisperma* Airy Shaw) Oil by Using NiMo-γAl_2O_3 as Renewable Energy

Daliya Indra Setiawan[1,2,*], Tun Tedja Irawadi[2], and Zainal Alim Mas'ud[2]

[1]*Research and Development Center Oil and Gas Technology "PPPTMGB LEMIGAS", Ministry of Energy and Mineral Resources, Jl. Ciledug Raya Kav 109, Cipulir, Kebayoran Lama, Jakarta Selatan 12230, Indonesia*

[2]*Department of Chemistry, Bogor Agricultural University, Jl. Tanjung Kampus IPB Darmaga, Bogor 16680, West Java, Indonesia*

*** Corresponding author:**

tel: +62-81386661750
email: dindra@lemigas.esdm.go.id

Received: August 4, 2017
Accepted: June 7, 2018

DOI: 10.22146/ijc.27274

Abstract: *Hydrotreating process of Sunan candlenut oil by using NiMo-γAl_2O_3 catalyst has been successfully investigated. Preparation of NiMo-γAl_2O_3 catalyst by using dipping impregnation method generated catalyst used for hydrotreating process. This method consists of three stages: support activation, impregnation, and calcination. This factors influencing the process including temperature, pressure, and the ratio of Sunan candlenut oil to the H_2 gas factor were examined. The hydrotreating product of fuel similar to oil was obtained at a minimum temperature of 380 °C, a pressure of 30–60 bar, and the ratio of the sample to H_2 gas of 0.5–1. The diesel fuel from physical properties range for the density of 0.82–0.86 g/cm^3, and kinematic viscosity of 2–6 cSt have been fulfilled by hydrotreating result. Gasoline, naphtha, diesel oil, and gas oil products of Sunan candlenut oil were obtained by distillation from hydrotreating process. Sunan candlenut oil fuel qualified fuel requirement.*

Keywords: *hydrotreating; NiMo-γAl_2O_3 catalyst; renewable diesel; Sunan candlenut oil; distillation*

INTRODUCTION

Recently, Indonesia still encounters problem to reach energy development target. Fossil energy dependency especially oil supply for domestic energy consumption, is still high as much as 96% (oil 48%, gas 18%, and coal 30%) of the total national energy consumption, while any effort to increase the use of renewable energy maximally cannot work as planned yet [1]. Fuel consumption of diesel oil commodity in Indonesia increases significantly. This increase is due to the growth in industry and transportation sectors as the most widely consumed fuel. Availability of national refined oil production available cannot supply domestic diesel oil need. Thus, the import of fuel is carried out to answer it.

Oil produced by both national refinery and import contains sulfur which is affecting air quality when being combusted. Therefore, alternative energy technologies with low sulfur level are needed to decrease or to substitute oil, especially diesel oil commodity.

One of the renewable energies developed nowadays is biodiesel. Even though FAME (Fatty Acid Methyl Ester) has shown potency to decrease carbon dioxide emission, biodiesel still has many weaknesses, such as high viscosity, low melting point, low heat value and stability due to high oxygen level. An interesting route is to convert renewable oil to a hydrocarbon having much higher cetane number than that of conventional diesel fuel by using hydrodeoxygenation, decarbonylation, decarboxylation, isomerization, and hydrocracking or combination of those processes [2].

Indonesia as a tropical country is rich with vegetable oil sources which can be transformed to HVO (Hydrotreated Vegetable Oil) through hydrotreating process [3]. Hydrotreating process adopts available technology in a refinery. Furthermore, purification between product and catalyst is not difficult. Vegetable oil sources to feed hydrotreating process are palm oil by using NiMo-γAl_2O_3 [4], coconut, *Jatropha curcas* by using NiMoCe/γAl_2O_3 [5] and NiMoP/γAl_2O_3 [6], sunflower by using NiMo-γAl_2O_3 [7-8], and Canola by using NiMo-γAl_2O_3 [9].

Sunan candlenut is a plant producing vegetable oil as non-food material. It comes from Philippine, spreads into Indonesia, especially West Java. It can produce 300–500 kg of dry seeds per tree per year with an oil concentration of 50–56%. Thus, it has an excellent potency. In 1 hectare can be planted 100 trees and produces 50 tons of dry seeds that equal to 15–25 tons oil that higher than palm oil [10]. Furthermore, Sunan candlenut age can reach 75 years that longer than a palm tree. Sunan candlenut is conservation plant avoiding erosion and fixing soil fertility [20]. On the other hand, 1 ha of a palm tree can produce 2.50–4.82 tons of CPO and 0.33–0.90 ton of PKO, palm tree age can only reach 25 years, it needs many nutrients, and water consumption which can reach 12 L/day.

Sunan candlenut oil is relatively new raw material that can be used for renewable fuel resources by using hydrotreating process. Sunan candlenut choice as a raw material does not affect food stock as Sunan candlenut is poisonous to a human. This poisonous property is due to the high concentration of α-elaeostearic acid reaching 50%. Sunan candlenut (*Reutealis trisperma* Airy Shaw) is one of vegetable oil producers having potency as non-food raw material or oil that cannot be consumed by a human to produce hydrotreated vegetable oil (HVO) or green diesel [3]. Hydrotreating process of Sunan candlenut oil using NiMo-γAl_2O_3 [4-9] can be performed in the suitable operating condition.

The main contents of Sunan candlenut oil are palmitic, stearic, oleic, linoleic, and α-elaeostearic acids through hydrotreating process. Triglyceride can be transformed into *n*-alkane similar to diesel oil. Hydrotreating reaction of vegetable oil into alkane is shown in Fig. 1 [11].

The first step is unsaturated (reductive hydrogenation) triglyceride hydrogenation (C=C double bond) to form a saturated triglyceride. The next step is triglyceride hydrogenolysis forming three molecules of fatty acid. Finally, fatty acid is reacted by three kinds of reactions: (1) hydrodeoxygenation (HDO), exothermic reaction, losing oxygen as water and generates *n*-alkane with the same number of fatty acid carbons, (2) decarbonylation (DCO), endothermic reaction, losing oxygen as CO and water, and (3) decarboxylation (DCO_2), endothermic reaction, losing oxygen as CO_2. In the DCO and DCO_2 mechanisms, n-alkane differs one carbon atom than initial fatty acid [6,10-14,18-19].

This study was performed to obtain suitable operating condition to convert Sunan candlenut oil by using NiMo-γAl_2O_3 catalyst into renewable diesel oil by

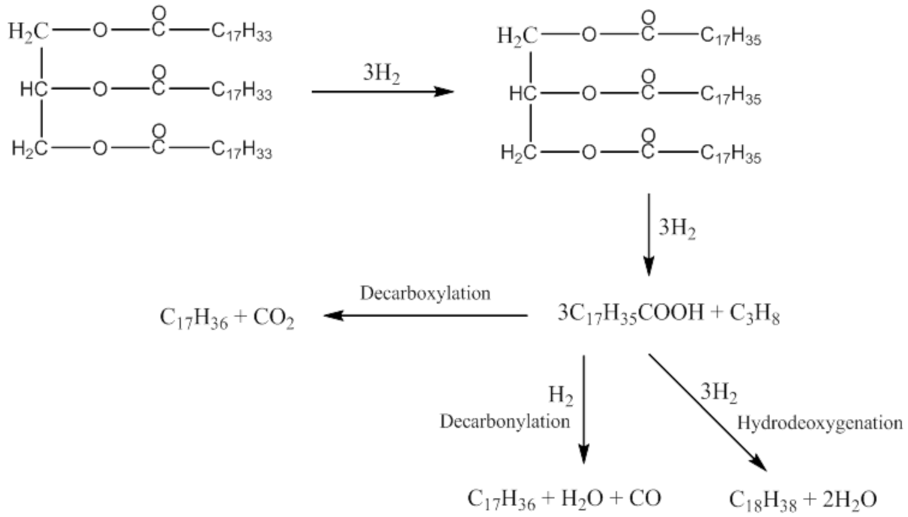

Fig 1. Hydrotreating reaction stages of vegetable oils. [11]

using a hydrotreating process. NiMo-γAl_2O_3 with PDO 120–1.3 T promotor and NiMoCe-γAl_2O_3 in hydroprocessing of jatropha oil have been used in order to convert refined bleaching deodorized palm oil (RBDPO) into green diesel [5], and NiMo-γAl_2O_3 commercial catalyst in a tubular reactor has been applied for hydrotreating process in order to convert sunflower oil to be fuel [7].

■ EXPERIMENTAL SECTION

Materials

The required materials were γ-Al_2O_3 support, ammonium heptamolybdate tetrahydrate (Merck), $Ni(NO_3)_2 \cdot 6H_2O$ (Merck), distilled water, Sunan candlenut oil (Masyarakat Energy Bandung), toluene, hydrogen gas, silicone grease, nitrogen gas 99.99%, liquid nitrogen, dry ice, and acetone.

Instrumentation

Instruments used were density meter digital Anton Paar DMA 4500 M, distillation true boiling point manual, distillation D 86 ORBIS BV Holland PAMv2, pour point and cloud point phase Technology, flash point PMCC, LAUDA Visco temp 24, RVP Eravap eralytics, Carl Zeiss–Bruker type EVO MA 10 (SEM), Trace elemental-Total nitrogen analyzer, ED XRF sulfur analyzer- ASE-2, Bourevesnik, INC, Karl Fischer coulometer, Mettler Toledo, TAN – Mettler Toledo, Aquamax coulometric (water content), Flash 2000 (CHO), GC Agilent 7890A (column: DB5-HT).

Procedure

Preparation and characterization of Sunan candlenut oil material

The harvested fruit was ripe for one week. It was then peeled, and the shell was removed to get the seed. The seed was dried in the sun until its moisture content reaches 7–9% which takes 5–7 days. The dried seed was pressed using a pressing tool to get the oil which still presents in the seed pulp. Then it was filtered to get the clean oil and the water content, gum content and free fatty acid in the clean oil was analyzed.

Sunan candlenut oil was performed proximate analysis to determine the content and analyses of free fatty acid by using a titrimetric method, acid value using ASTM D.974 method, a density at 40 °C using ASTM D.4052-11 method, and iodine value using AOCS Cd 1-25 method. Those are needed to determine the effectiveness of hydrotreating process of Sunan candlenut oil to be fuel similar with oil.

Catalyst synthesis

The catalyst used was Ni-Mo with γAl_2O_3 support. Impregnation of Ni and Mo metals into the support was carried out by using dipping impregnation method. This method consists of three stages: support activation, impregnation, and calcination.

Catalyst support activation was done by heating 200 g of γAl_2O_3 in an oven (120 °C, 2 h), then cooled at room temperature. The next process was impregnation that is to dilute 37 g of ammonium heptamolybdate tetrahydrate in 250 mL of distilled water and stirred until evenly mixed (Solution 1). Then, 40 g $Ni(NO_3)_2$ was added to Solution 1. NiMo salt solution was added into γAl_2O_3 support catalyst dropwise until whole catalyst surface was submerged in NiMo salt solution. It was then heated in a water bath at 70 °C while stirred slowly for 240 min to let the NiMo solution was absorbed into the catalyst. The catalyst was dried in the oven (120 °C, 12 h), and followed by calcination (600 °C, 6 h) under a nitrogen gas stream. The catalyst was put in a desiccator prior to use in the hydrotreating process.

Hydrotreating process of Sunan candlenut oil

Hydrotreating process of Sunan candlenut oil was performed in autoclave reactor (capacity of 1 L, a maximum pressure of 100 bar and a maximum temperature of 500 °C) as shown in Fig. 2. Before hydrotreating, presulfiding process was conducted on the NiMo-γAl_2O_3 catalyst using dimethyl sulfide (DMDS) and hydrogen. After presulfiding, the metal was converted to metal sulfide having a function as the active metalcore. The amount of catalyst used for the reaction was 50 g and the reaction time was 3 h [7,9,14]. Variables of operating condition of hydrotreating process were pressure of 30–60 bar [3,7,9-10,12,16-17] temperature 350–400 °C [2,4,6-10,15-17], and ratio between H_2 gas and sample (ranges 0.5–1.0) [15-16].

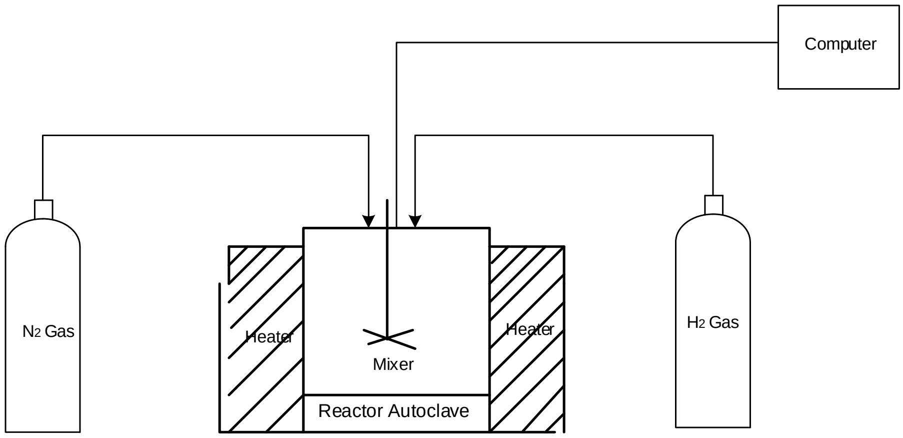

Fig 2. Schematic illustration of experimental hydrotreating reactor

Table 1. Proximate analysis of Sunan candlenut oil

Parameter	Value	Unit	Method
Ash content	0	%	SNI. 01-2891-1992, point 6.1
Protein content	0	%	SNI. 01-2891-1992, point 7.1
Fat content	99.9	%	AOAC. 938.06/33.6.04.2005
Carbohydrate content	0.07	%	Reduction
Energy	899	cal/100 g	Calculation

Table 2. Characteristics of Sunan candlenut oil

Parameter	Unit	Value	Biodiesel req. (SNI 7182.2012)	Method
FFA	%	7.70	-	Titrimetric
Acid number	mg KOH/g	15.32	≤ 0.6	ASTM D.974
Density at 40 °C	kg/m^3	919.70	850-890	ASTM D.4052-11
Kinematic viscosity at 40 °C	cSt	89.05	2.3	ASTM D.445-11a
Water content	wt.%	0.10	≤ 0.05	ASTM D.4377
Iodine number	wt.%	131.06	≤ 115	AOCS Cd. 1-25
Phosporus content	mg/kg	33.18	≤ 10	ASTM D6481

Physical properties of the product obtained from the hydrotreating process analyzed were the density at 15 °C and the kinematic viscosity at 40 °C. Both test results were used to select initial product qualifying the fuel requirement.

Data processing by using Response Surface Method

Data processing was done by using Minitab software. Response Surface Methodology or RSM is a method used to determine relation among 3 or more variables in a reaction directly. This method can simplify the study by minimizing samples number that will be tested.

■ RESULTS AND DISCUSSION

Characterization of Sunan Candlenut Oil

The proximate analysis of the clean oil result is shown in Table 1. The ash content was 0% showing that Sunan candlenut oil didn't have inorganic components as residue left after burning. Carbohydrate content was 0.07%. Carbohydrate in sample composition could cause oil to become dirty and dark. The protein content was 0 %, as it could be seen as the oil color was clear.

The analysis result is shown in Table 2. Those data show the parameters were out of specification for biodiesel. Density, kinematic viscosity, iodine value, acid value, and water content need to be lowered for qualifying the fuel requirement. A high kinematic viscosity of Sunan candlenut oil showed triglyceride property as long-chain carbon. High iodine value will affect machine performance. Thus, hydrotreating process was performed as an effort to adjust parameter values that did not qualify for fuel in Sunan candlenut oil.

Characterization of NiMo-γAl_2O_3

Characterization result of NiMo-γAl_2O_3 by using Brunaeur-Emmett-Teller (BET) is shown in Table 3. According to the analysis using BET, the catalyst was categorized as a stable mesoporous at the reaction temperature ranges and has relatively strong mechanical property, so that it can be used at high pressure. The initial pore volume was 0.9848 mL/g and decrease to 0.5480 mL/g after impregnation. It showed that the impregnation process of Ni and Mo metal into the buffer catalyst, γAl_2O_3 was running successfully. This pore volume reduction showed that about 0.4368 mL/g were filled with Ni and Mo metals.

Analysis using XRF showed that catalyst consists of 4.49% of Ni, 11.09% of Mo, and 40.82% of Al. This shows that the amount of nickel and molybdenum metals impregnated at catalyst synthesis was successfully performed. Morphology analysis using SEM is shown in Fig. 3. Show the shape of that NiMo-γAl_2O_3 has catalyst crystal. BET analysis of impregnated catalyst (Table 3) showed the surface area of 199.4 m^2/g, average pore diameter of 54.98Å, and pore volume of 0.5480 cc/g. This pore volume was significantly decreased from pre-impregnated alumina which was 0.9848 cc/g. The pore volume decreased as much as 0.4368 cc/g indicating that the pore surfaces were occupied by the Ni and Mo metals. It is suspected that the impregnation of metal dispersed in the alumina support as well as calcination and reduction has led to the formation of new pores. Based on these results, it can be said that NiMo-γAl_2O_3 material has good characteristics to be used as a catalyst.

The catalyst used was heterogeneous catalysts which has several advantages, including: its selectivity properties of the form to get the desired product, its solid structure that modified the intrinsic activity of the active nucleus, the surface composition that can minimize or increase the adsorption of certain compounds, its ease to separate properties from the product by filtration and reused it without/by regeneration, and its impact on reducing waste (usually salt) produced from Bronsted or Lewis acid homogenized catalyst neutralization [21].

Sunan candlenut (*Reutealis trisperma* Airy Shaw) is one of vegetable oil producers having potency as non-food raw material or oil that cannot be consumed by a human to produce hydrotreated vegetable oil (HVO) or

Table 3. Specific surface area, total pore volume, and pore diameter of NiMo-γAl_2O_3 catalyst

	Unit	Result	Method
Surface Area	m^2/g	199.4	
Total pore volume	cc/g	0.548	BET
Pore diamater	Å	54.98	

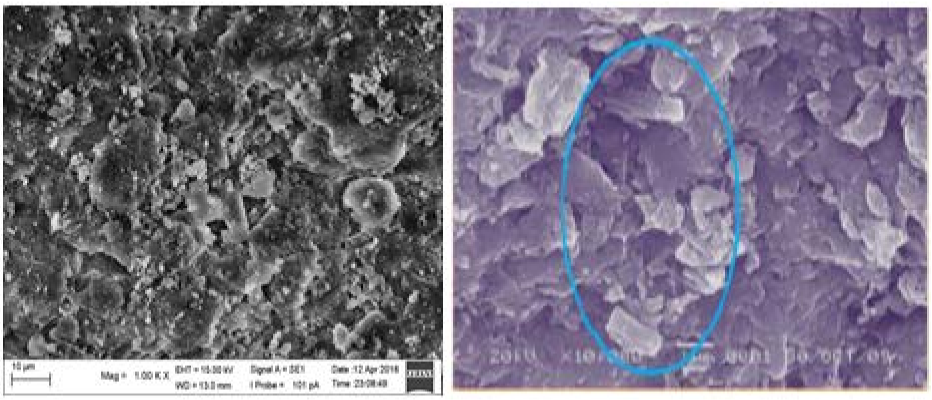

Fig 3. The appearance of the external morphology of NiMo-γAl_2O_3 catalyst

Table 4. Density at 15 °C and a kinematic viscosity at 40 °C of hydrotreated products

No	Variable-variable			Result	
	Temperature (°C)	Pressure (bar)	Ratio (Oil/H_2)	Density at 15 °C (g/cm^3)	Viscosity at 40 °C (cSt)
1	350	45	1.00	0.9037	45.39
2	400	60	0.75	0.8480	2.832
3	375	60	1.00	0.8814	13.19
4	375	60	0.50	0.8469	5.983
5	350	45	0.50	0.8943	33.74
6	350	30	0.75	0.9170	31.63
7	375	45	0.75	0.8608	9.490
8	375	30	0.50	0.8586	8.065
9	400	30	0.75	0.8366	2.556
10	350	45	0.75	0.8970	59.03
11	400	45	0.50	0.8314	2.509
12	350	60	0.75	0.8846	25.47
13	375	30	1.00	0.8823	15.67
14	375	45	0.75	0.8608	9.490
15	400	45	1.00	0.8533	2.900

Fig 4. Hydrotreating products of Sunan candlenut oil

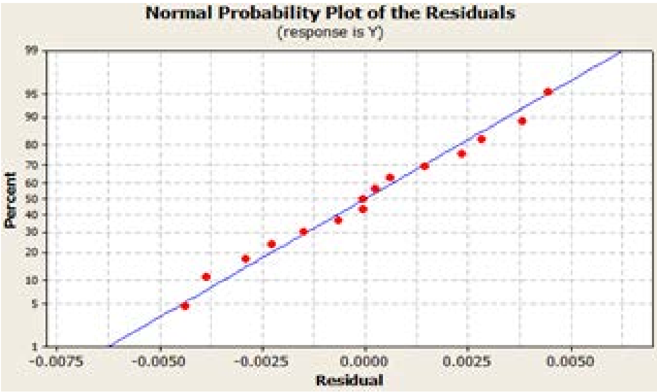

Fig 5. Normal probability plot of the residuals

green diesel [3]. Hydrotreating process of Sunan candlenut oil by using NiMo-γAl_2O_3 [4-9] can be performed in the suitable operating condition.

Hydrotreating Process of Sunan Candlenut Oil and Data Processing

Parameters varied in hydrotreating process were temperature, pressure, and ratio of H_2 gas and Sunan candlenut oil. Hydrotreating product is shown in Fig. 4. As shown in Fig. 4, the hydrotreating process made the oil clearer. Table 4 shows density analysis result and kinematic viscosity of hydrotreating products at several variations of the process. From those results, only sample 2, 4, 9, 11, and 15 were physically qualified. Those qualified samples have a density ranges of 0.82–0.86 g/cm^3 and a kinematic viscosity of 2–5 cSt which are acceptable for the Directorate General of Oil and Gas, Ministry of Energy and Mineral Resources requirements (Number: 3674 K/24/DJM/2006).

Data obtained was processed by using Surface Response Method of Minitab software. The empirical relation between the density of 15 °C and variables could be stated as:

$$Y1 = 3.58001 - 0.01133X_1 - 0.01323X_2 - 0.24155X_3 + 0.00001X_1^2 + 0.0002X_2^2 + 0.04427X_3^2 + 0.0003X_1X_2 + 0.0005X_1X_3 + 0.00072X_2X_3$$

where: X_1 = Temperature; X_2 = Pressure; X_3 = Ratio of H_2 gas and Sunan candlenut oil.

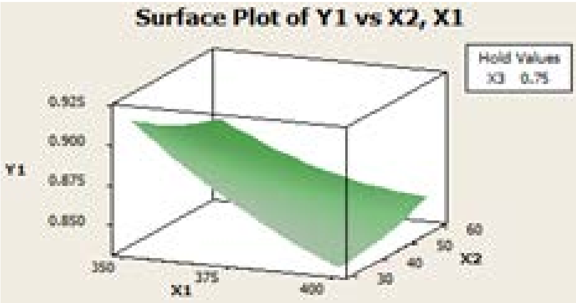

Fig 6. Surface Plot: Effect of temperature and pressure on the density of hydrotreated products

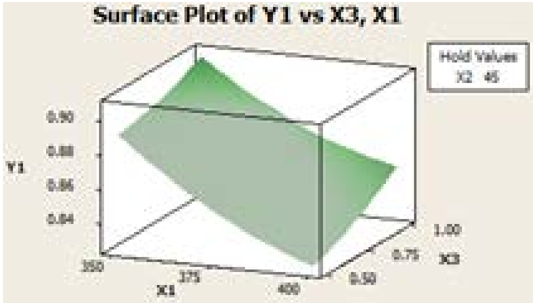

Fig 7. Surface Plot: Effect of temperature and H_2/feed ratio on the density of hydrotreated products

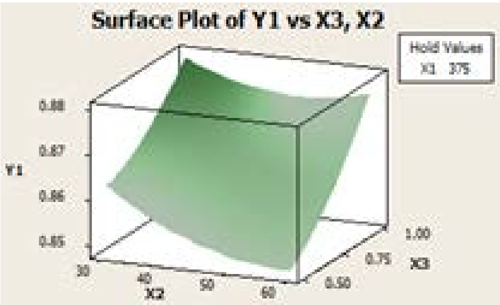

Fig 8. Surface Plot: Effect of pressure and H_2/feed ratio on the density of hydrotreated products

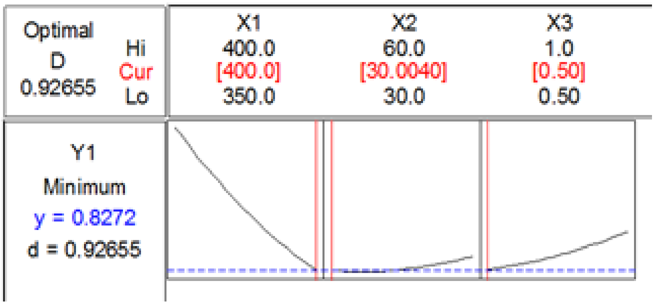

Fig 9. Response optimization of temperature(X1), pressure(X2), and the H_2/feed ratio(X3) on the density

Fig. 5 shows that the model created could describe the system well (observed in the experiment). Thus, the model was good due to the approach to a linear model. Residue cumulative approached the linear model showing that it had a relatively small error and data were spread normally. Operation target of hydrotreating process was a density of 0.82–0.86 kg/m^2 at 15 °C and a kinematic viscosity of 2–6 mm^2/sec that were suitable for diesel fuel requirements.

Fig. 6 of density surface plot on temperature and pressure of the experiments did not find any minima indicating that the hydrotreating process has not reached optimum condition yet. Minimal operation temperature should be 380 °C to obtain a density target of 15 °C (the higher the temperature, the lower the density obtained). Meanwhile, pressure performed in this study which has a range of 30–60 bar did not affect targeted density significantly.

Fig. 7 of surface plot between temperature and ratio of Sunan candlenut oil and H_2 gas also shows that the hydrotreating process has not reached optimum condition yet indicated by the absence of minima in the graph. In order to obtain the target, minimal operation temperature should be 375 °C (the higher the temperature, the lower the density obtained). Meanwhile, a ratio of Sunan candlenut oil and H_2 gas needed to reach target was 0.5–0.98 approximately.

Fig. 8 of surface plot between pressure and ratio of Sunan candlenut oil and H_2 gas shows that hydrotreating process has not reached the optimum condition yet because of the graph did not get an optimum point for the operating conditions. To achieve the target, the pressure should be 30 bar, and the maximum ratio should be 0.575. At the pressure condition of 35–60 bar, the maximum ratio needed was 0.70.

Response optimization of density at 15 °C is analysis result of temperature, pressure, and the ratio of H_2 and Sunan candlenut oil entirely in hydrotreating product. The analysis result of response optimization toward density shown in Fig. 9 was reached at a temperature of 400 °C, a pressure of 30 bar, and 0.5 ratios.

Among those three variables, factors affecting density 15 °C at hydrotreating process were temperature

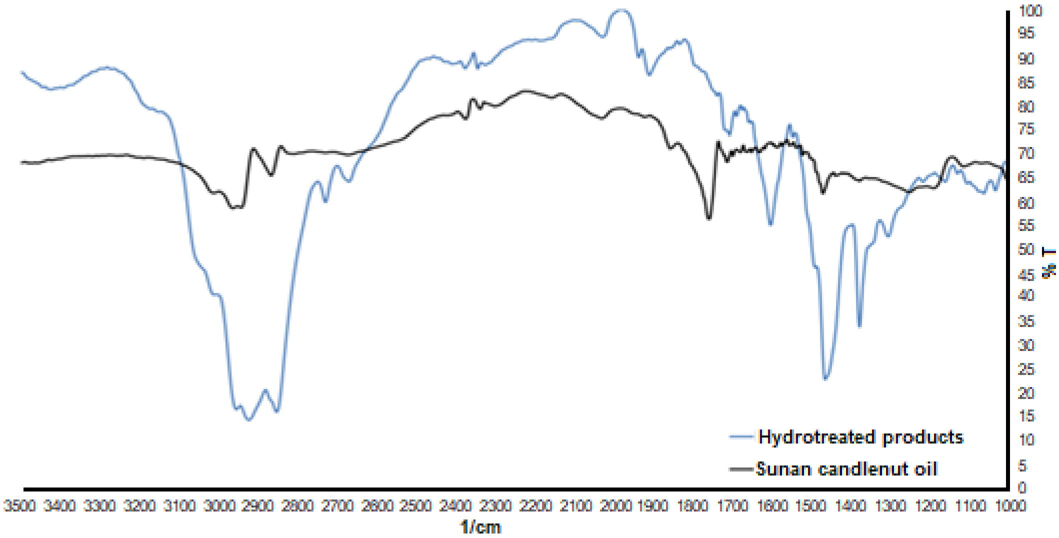

Fig 10. FTIR spectrum of Sunan candlenut oil and the hydrotreated products

Table 5. Physical and chemical properties of hydrotreated products

No	Characteristics	Unit	Product Hydrotreating (No.)					Range*		Method
			2	4	9	11	15	Min	Max	
1	Density at 15°C	g/m^3	0.8480	0.8469	0.8366	0.8314	0.8533	0.82	0.86	D 613-95
2	Viscosity at 40 °C	mm^2/sec	2.832	5.983	2.556	2.509	2.900	2.00	6.00	D 445-97
3	Sulfur content	wt.%	0.0061	0.0371	0.0036	0.0148	0.0031	-	0.05	D 2622-98
4	Pour point	°C	-21	-9	-9	-15	-24	-	18	D 97
5	Cloud point	°C	-22.2	14	-10.9	-11.1	-23.4			
6	Water content	wt.%	0.0487	0.1376	0.0204	0.0725	0.0236	-	0.5	D 4377
7	Acid numbers	mg KOH/g	0.030	0.0500	0.0100	0.0100	0.0400	-	0.3	D 664
8	Iodine numbers	wt.%	66.06	80.99	71.47	61.65	79.27	-	115	AOCS Cd-1-25

*Source Directorate General of Oil and Gas, Ministry of Energy and Mineral Resources requirement (Number: 3674 K/24/DJM/2006)

and ratio of Sunan candlenut oil and H_2 meanwhile pressure performed did not affect the result significantly. Yields obtained of some variable above were 68–76% approximately.

FTIR analysis results in Fig. 10 shows that carbonyl group disappeared at hydrotreating product showed by disappearing of a peak at 1690–1760 cm^{-1}, while *n*-alkane peak appeared at 1350–1470 (C-H) cm^{-1} and 2850–3000 (C-H strong) cm^{-1} and triple bond of carbons disappeared at 2100–2260 (-C≡C-) cm^{-1}. The good activity of NiMo-γAl_2O_3 catalyst caused oxygen disappearance, water formation, and breaking of the triple bond [6].

Product Purification and Separation Processes

Distillation vacuum process of the liquid sample (petroleum and Syncrude) to some fractions avoiding cracking or breaking of molecules. Thus, distillation can be done by decreasing distillation pressure so that heavy fraction boils at a lower temperature.

Product fractionation of Sunan candlenut by oil hydrotreating process was performed to omit black color in syncrude at fractionation by using distillation instrument of True Boiling Point (TBP).

Then, the best experiment result was chosen to be distilled further. The chosen sample distilled based on analysis data in Table 5 was number 15 as it had qualifying kinematic viscosity and density. Furthermore, it had the least sulfur content (0.0031%), the least pour point (–24), low cloud point, and the highest yield (76%). The water content (0.0236 wt.%) and acid value (0.04 mg KOH/g) were relatively fair.

Separation process by True Boiling Point (TBP)

Table 6. Characteristics of diesel product and solar-48 specification

No	Characteristics	Unit	Solar	Range*		Method
				Min	Max	
1	Density at 15 °C	g/cm³	0.8398	0.815	0.860	D 613-95
2	Viscosity at 40 °C	mm²/sec	2.213	2.00	6.00	D 445-97
3	Sulfur content	% m/m	0.0036	-	0.05	D 2622-98
4	Flash point "PMCC"	°C	77	55	-	D 93-99C
5	Pour point	°C	-30	-	18	D 97
6	Cloud point	°C	-19	-	-	D 2500
7	Water content	wt.%	0.155	-	0.5	D 6304
8	Color	No ASTM	3	-	3.0	D 1500
9	Index cetane	-	46.3	45	-	D 6890
10	Iodine numbers	wt.%	61.44	-	115	AOCS Cd 1-25
11	Distillation: 90% evaporation	°C	281	-	370	D 86
12	Carbon residue	% m/m	0.1732	-	0.3	D 4530
13	Visual appearance	-	clear	clear		
14	Acid number	Mg KOH/g	0.197	-	0.6	ASTM D 664

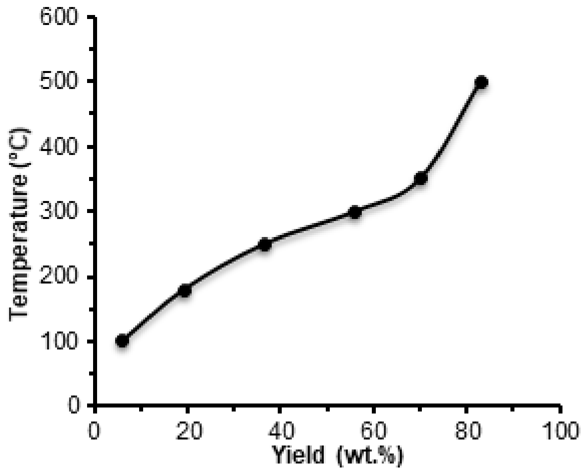

Fig 11. True Boiling Point (TBP) distillation curve


Fig 12. TBP distillation product of the renewable fuels: gasoline, naphtha, and diesel

distillation was performed toward hydrotreating product of number 15. As much 839.4 g was obtained. Distillation fraction result under 100 °C was 5.81%, fraction of 100–180 °C was 13.28%, fraction of 180–250 °C was 17.31%, fraction of 250–300 °C was 19.69%, fraction of 300–350 °C was 13.94%, and fraction of 350 °C–EP was 12.91% of weight. Curve and distillation product is shown in Fig. 11 and 12, respectively. As represented in those pictures, the diesel oil fraction was the largest.

From the distillation result, equivalent fuel grade diesel fuel product was obtained that analysis result is shown in Table 6. A product similar with diesel fuel obtained had relatively low acid value as much 0.197 mg KOH/g, suitable density and kinematic viscosity were 0.8398 g/cm³ and 2.231 mm²/sec, respectively, and cetane index was 46.3 qualifying with minimal value required of 45.

■ CONCLUSION

Hydrotreating process of Sunan candlenut oil by using NiMo-γAl_2O_3 catalyst in a batch produced fuel qualifying the requirement with Directorate General of Oil and Gas, Ministry of Energy and Mineral Resources requirement (Number: 3674 K/24/DJM/2006). Variables that affect the hydrotreating process of Sunan candlenut oil were temperature, pressure, and the ratio of Sunan candlenut oil and H_2 gas. Catalyst synthesis by using the impregnation method produced a good catalyst. To obtain diesel product with a density of 0.82–0.86 g/cm³ and a kinematic viscosity of 2–6 mm^2/sec, the minimum temperature of operation condition was 380 °C, the ratio of Sunan candlenut oil and H_2 gas of 0.5–1, while the pressure did not affect the hydrotreating process significantly. The hydrotreating product obtained was separated by true boiling point distillation. According to the distillation process, a fuel similar to gasoline, naphtha, diesel oil, and gas oil were obtained.

ACKNOWLEDGMENTS

The author thank to the Ministry of Energy and Mineral Resources and Research and Development Center Oil and Gas Technology "PPPTMGB LEMIGAS" providing scholarship, tools, and infrastructures for this study.

REFERENCES

[1] Dewan Energi Nasional, 2014, *Outlook Energy Indonesia 2014: Energy Development in Supporting Fuel Substitution Program*, Pusat Teknologi Pengembangan Sumberdaya Energi (PTPSE), Jakarta, pp.2

[2] Yang, Y., Wang, Q., Zhang, X., Wang, L., and Li, G., 2013, Hydrotreating of C18 fatty acids to hydrocarbons on sulphided NiW/SiO_2-Al_2O_3, *Fuel Process. Technol.*, 116, 165–174.

[3] Aatola, H., Larmi, M., Sarjovaara, T., and Mikkonen, S., 2008, Hydrotreated vegetable oil (HVO) as a renewable diesel fuel: Trade-off between NO_x particulate emission, and fuel consumption of a heavy duty engine, *SAE Int. J. Engines*, 1 (1), 1251–1262.

[4] Kiatkittipong, W., Phimsen, S., Kiatkittipong, K., Wongsakulphasatch, S., Laosiripojana, N., and Assabumrungrat, S., 2013, Diesel-like hydrocarbon production from hydroprocessing of relevant refining palm oil, *Fuel Process. Technol.*, 116, 16–26.

[5] Liu, J., Fan, K., Tian, W., Liu, C., and Rong, L., 2012, Hydroprocessing of jatropha oil over NiMoCe/Al_2O_3 catalyst, *Int. J. Hydrogen Energy*, 37 (23), 17731–17737.

[6] Gong, S., Shinozaki, A., Shi, M., and Qian, E.W., 2012, Hydrotreating of jatropha oil over alumina based catalysts, *Energy Fuels*, 26 (4), 2394–2399.

[7] Krár, M., Kovács, S., Boda, L., Leveles, L., Thernesz, A., Wáhlné, I.H., and Hancsók, J., 2009, Fuel purpose hydrotreating of vegetable oil on NiMo–γAl_2O_3 catalyst, *Hung. J. Ind. Chem.*, 37 (2), 107–111.

[8] Kovács, S., Kasza, T., Thernesz, A., Horváth I.W., and Hanscók, J., 2011, Fuel production by hydrotreating of triglycerides on NiMo/Al_2O_3/F catalyst, *Chem. Eng. J.*, 176-177, 237–243.

[9] Kwon, K.C., Mayfield, H., Marolla, T., Nichols, B., and Mashburn, M., 2011, Catalytic deoxygenation of liquid biomass for hydrocarbon fuels, *Renewable Energy*, 36(3), 907-915.

[10] Pranowo, D., Syakir, M., Prastowo, B., Herman, M., Aunilah, A., and Sumanto, 2014. *Pembuatan Biodiesel dari Kemiri Sunan (*Reutealis trisperma *Airy Shaw) dan Pemanfaatan Hasil Samping*, IAARD Press, Jakarta.

[11] Sotelo-Boyás, R., Trejo-Zarrage, F., and Hernandez-Loyo, F.J., 2012, *Hydroconversion of Triglycerides into Green Liquid Fuels*, IntechOpen.

[12] Susanto, B.H., Nasikin, M., Sukirno, and Wijo, A., 2014, Synthesis of renewable diesel through hydrodeoxygenation using Pd/zeolite catalysts, *Procedia Chem.*, 9, 139–150.

[13] Attanatho, L., 2012, Performance and Kinetic Studies of Hydrotreating of Bio-Oils in Microreactor, *Dissertation*, Oregon States University, Eugene (US).

[14] Hermida, L., Abdullah, A.Z., and Mohamed, A.R., 2015, Deoxygenation of fatty acid to produce diesel–like hydrocarbon: A review of process conditions, reaction kinetics and mechanism, *Renewable Sustainable Energy Rev.*, 42, 1223–1333.

[15] Sankaranarayanan, T.M., Banu, M., Pandurangan, A., and Sivasanker, S., 2011, Hydroprocessing of sunflowers oil-gas oil blends over sulfide Ni-Mo-Al-zeolite beta composites, *Bioresour. Technol.*, 102 (22), 10717–10723.

[16] Choudhary, T.V., and Phillips, C.B., 2011, Renewable fuels via catalytic hydrodeoxygenation, *Appl. Catal., A*, 397 (1-2), 1–12.
[17] Egeberg, R., Michaelsen, N., Skyum, L., and Zeuthen, P., 2010, *Hydrotreating in the production of green diesel: A novel scheme enables co–processing of light gas oil and tall diesel to produce a renewable diesel meeting EN 590 specifications*, http:/www.digitalrefining.com/article/1000156.
[18] Srifa, A., Faungnawakij, K., Itthibenchapong, V., Viriya-empikul, N., Charinpanitkul, T., and Assabumrungrat, S., 2014, Production of bio-hydrogenated diesel by catalytic hydrotreating of palm oil over $NiMoS_2/\gamma$-Al_2O_3 catalyst, *Bioresour. Technol.*, 158, 81–90.
[19] Wang, H., Yan, S., Salley, O.S., and Simon, K.Y., 2013, Support effects on hydrotreating of soybean oil over NiMo carbide catalyst, *Fuel*, 111, 81–87.
[20] Srifa, A., Faungnawakij, K., Itthibenchapong, V., and Assabumrungrat, S., 2015, Roles of monometallic catalysts in hydrodeoxigenation of palm oil to green diesel, *Chem. Eng. J.*, 278, 249–258.
[21] Nasikin, M., and Susanto, B.H., 2010, *Katalis Heterogen*, UI Press, 18–19.