

PRODUCTION OF GREEN DIESEL BASED ON PALM FATTY ACID DISTILLATE USING CATALYTIC HYDROGENATION METHOD

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ABSTRACT

Green diesel is an alkane compound that is equivalent to petroleum based diesel oil. One of the ingredients that can be converted into green diesel is Palm Fatty Acid Distillate (PFAD). PFAD is a by-product of the refinery process in the production of cooking oil from Crude Palm Oil (CPO) which has not been widely used. Green diesel is produced using a catalytic hydrogenation process at a temperature of 300°C with a hydrogen pressure of 25 psia for 1.0 hour. 300 ml of PFAD is reacted with gas (hydrogen) H₂ using NiMo / Al₂O₃ catalyst to accelerate the reaction. The variable that is used in this study is the number of catalysts of 0 gr; 0.1114 gr; 0.1507 gr; 0.2009 gr; 0.2541 gr; and 0.3075 gr. The use of a catalyst of 0.2009 grams per 300 ml of sample is the optimum condition in this study and yields a yield percentage of 36.5331%. The physical properties of green diesel obtained from this study include density at 400C (751.5056 – 816.9221 kg/m3), kinematic viscosity at 400C (3.6107 – 4.6831 mm2/s), moisture content (11.593 – 17.717 ppm), flash point (65.4 – 91.9°C), and heating value (43.2274 – 44.8834 MJ / kg).

Keywords: catalyst, catalytic hydrogenation, green diesel, hydrogen, PFAD

Received 4 April 2022 Accepted 13 June 2022

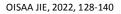
INTRODUCTION

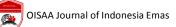
Fossil energy is the energy with the largest use in every aspect of human life, such as electricity, transportation and consumption purposes. The Minister of Industry stated that currently industry is still very dependent on fossil fuels, even the share of industry in national energy consumption reaches 49.4 percent (Kemenperin, 2019). The need for fossil energy is increasing every year, but fossil energy reserves are dwindling. Fossil energy in the world is projected to run out by 2050 (Gapki, 2016).

Therefore, the problem of the energy crisis, especially the decline in fossil fuel reserves, can be solved by producing alternative energy to replace renewable fossil energy in order to build sustainable energy security. Alternative energy produced should have several advantages, including being renewable, low in emissions, based on domestic resources to save foreign exchange, and not depending on other countries (Gapki, 2016). Indonesia, which is rich in biomass, can utilize available resources to produce efficient and environmentally friendly fossil fuels.

One of the plantations that has the potential to produce biomass in Indonesia is oil palm. Subdiktorat Statistik Tanaman Perkebunan (2018) states that the area of oil palm plantations tends to increase from 2013 to 2017 from 10.47 million hectares to 12.30 million hectares. The Director General of Plantations at the Ministry of Agriculture said that Indonesia is the largest producer of palm oil in the world (Kemenperin, 2019).

In general, palm oil is produced into palm oil or Crude Palm Oil (CPO) which is derived from the skin of palm oil. CPO can be re-produced into cooking oil which is generally used





in daily life for consumption purposes. Before becoming cooking oil, CPO is first processed through 2 stages, namely refining and fractionation. In the purification process, CPO containing about 5% free fatty acids is removed through a deodorization process. This deodorization process produces a by-product in the form of Palm Fatty Acid Distillate (PFAD). Therefore, the greater the production of cooking oil made from CPO, the more PFAD will be produced from the refining process.

Palm Fatty Acid Distillate (PFAD) is a by-product of palm oil processing which contains 80% free fatty acids. The abundance of CPO produced into cooking oil causes an abundance of PFAD produced from the refinery process. However, until now, the use of PFAD is still very limited, namely it is used as a raw material for low-quality soap.

Green diesel is a renewable alternative energy to replace diesel fuel. Green diesel is produced using vegetable oil as raw material, such as palm oil, seed oil, castor oil, and others. The resulting product generally has characteristics that are equivalent to products from fossil fuels.

Green diesel or second generation biodiesel (G2) has better quality than the first generation biodiesel (G1) transesterified (Kalnes et.al, 2007). The advantage of green diesel or G2 biodiesel is that it is able to reach a cetane number of 55-90 which is much higher than that of G1 biodiesel which is only 40-45, so the oil produced can be directly used as fuel for diesel engines without having to be added with diesel or engine modifications (Homgren et al. al, 2007).

Making green diesel as an alternative energy based on PFAD not only solves the energy crisis, but also prevents environmental pollution because PFAD itself is palm oil waste. The abundance of PFAD in palm oil mills throughout Indonesia, the more the amount of green diesel produced. Besides being abundant, PFAD is a resource that can be renewed every day.

RESEARCH METHODS

A. Tools and Material

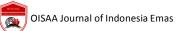
Palm Fatty Acid Distillate (PFAD) 1,8 liters, Hidrogen (H₂), Ammonium Heptamolybdate Tetrahydrate ((NH₄)₆Mo₇O₂₄.4H₂O) 27 grams, Nickel (II) Nitrate Hexahydrate (NiNO₃.6H₂O)15 grams, Alumina (Al₂O₃) 30 grams, Aquadest 2 liters, Condenser Water 60 liters, Solar 5 liters, Hydrogenation Reactor, Condenser. Spatula, Measuring Pipette, Rubber Ball, Stirring Rod, Watch Glass, Flash Point Tester, Boom Calorimeter, Desiccator, Compressor, Thermometer, Measuring Cup, Hot Plate, Magnetic Stirrer, Porcelain Cup, Mortar, Crusible, Oven, Furnace, Hoppler Viscometer, Beakers, Sample Containers, Regulators, Pycnometers, and Analytical Balances.

B. Catalyst Manufacturing Prosess

Alumina (Al_2O_3) was heated in an oven at 120°C for 2 hours. After being heated, the support is removed and then cooled in a desiccator. 10 ml of 0.87 M Ammonium Heptamolybdate Tetrahydrate $(NH_4)_6Mo_7O_{24}.4H_2O$ and 2.02 M Nickel (II) Nitrate $(Ni(NO_3)_2.6H_2O)$ were impregnated with 11.9047 grams of activated Al_2O_3 . The mixture was stirred and heated at 80°C until dry. The impregnated mixture was dried in an oven at 120°C for ±4 hours. After drying, the mixture was cooled in a desiccator. The cooled mixture was calcined in a furnace at 600°C for 5 hours. After calcination, the mixture was cooled in a desiccator. After that, the mixture can be used in hydroprocessing as a NiMo/Al₂O₃ catalyst.

C. Catalytic Hidrogenation Process

A total of 300 ml of raw material in the liquid phase was fed into the reactor along with the catalyst with a variation of 0; 0.10 grams; 0.15 grams; 0.20 grams; 0.25 grams; and 0.3 grams when the reactor temperature is ± 100 oC. Then, the reactor temperature was lowered to room temperature. After the reactor is at room temperature, hydrogen gas (H₂) enters the reactor with a pressure of 25 psia. Then, the reactor is connected to a condenser. Set a fixed variable in the form of a reaction temperature of 300°C and wait until the heater temperature reaches 300°C. The reactor process starts for 1 hour when the heater temperature reaches 300°C and open the



product valve when the reactor pressure reaches 500-700 psi. After 1 hour, the hydrogenation reactor was turned off. The green diesel product from the condenser water is separated using a separating funnel. Furthermore, the measurement of the volume of the green diesel product produced is carried out.

FINDINGS AND DISCUSSION

A. Manufacturing and Characterisation Catalyst NiMo/Al₂O₃

In this study, the catalyst acts as a substance that accelerates the rate of chemical reactions between the fatty acids contained in PFAD and hydrogen gas by lowering the activation energy.



Figure 1. Catalyst NiMO/Al₂O₃

NiMO/Al₂O₃ catalyst is a type of heterogeneous catalyst. The use of heterogeneous catalysts is because the catalyst has a different phase from the reactants. NiMO/Al₂O₃ catalyst is in solid phase and in powder form, while the reactants are PFAD in liquid phase and hydrogen in gas phase.

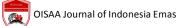
The process of making catalysts in this study is based on two previous studies, namely the research of Sangnikul et.al (2019) entitled "Role of Copper or Cerium Promoters on NiMo/Al₂O₃ Catalyst in Hydrodeoxygenation of Guaiacol and Bio-Oil" and Tsani's research (2011) entitled "Preparation and Characterization of NiMo/Al₂O₃ Catalysts for Synthesis of Biofuels from Castor Oil Through Catalyst Pyrolysis".

NiMo/Al₂O₃ catalyst consists of three components, including Nickel as the core/active component of the catalyst, Molybdenum as a promoter, and Alumina as a buffer.

Nickel which is an active component plays a role in accelerating and directing reactions in converting reactants into products. Molybdenum as a promoter plays a role in increasing the activity and performance of the catalyst, as well as protecting the buffer from all unwanted disturbances and obstacles, such as the formation of coke deposits on the catalyst surface. Alumina (Al₂O₃) which acts as a buffer serves as a place to spread nickel as an active component to expand the contact between the active component and the reactants.

The method used in the manufacture of NiMo/Al₂O₃ catalyst is the wet impregnation method. Impregnation aims to fill the impregnant solution in the form of active components Nickel and Molybdenum promoter into the Al₂O₃ pores with stirring and heating at 80°C until dry. However, prior to the impregnation process, the Al₂O₃ buffer was activated in an oven at 120°C for 2 hours. This activation process aims to remove the water content that is still trapped in the buffer component so that the diffusion process of the impregnant solution into the pores of the buffer is more effective.

After the impregnation process, a drying process was carried out to remove the water content in the catalyst before the calcination process was carried out. The catalyst calcination process took place at a temperature of 600°C for 6 hours. Calcination is a process of converting metal salts into its oxide phase by evaporating the free and bound water content, releasing gases such as CO_2 . Composition of Catalyst NiMo/Al₂O₃ can be seen in Figure 2.



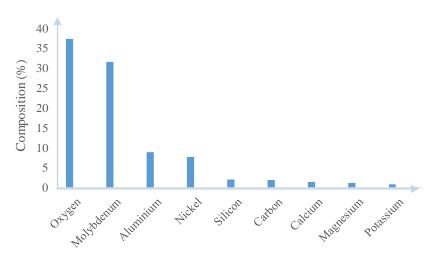


Figure 2. Composition of NiMo/Al₂O₃ Catalyst

The catalyst obtained contained 37.43% oxygen and 9.02% aluminum. Elements of oxygen and aluminum are elements that form alumina compounds (Al₂O3) as catalyst supports. Oxygen is the most dominant element in the catalyst, this is because the support used contains oxygen and oxidation or binding of oxygen from the air occurs during the wet impregnation process. The NiMo/Al₂O₃ catalyst in this study consisted of 31.68% molybdenum as the promoter and 7.80% nickel as the active core. The amount of molybdenum is more dominant. This is because the use of molybdenum during impregnation is twice that of nickel. Then other chemical elements contained in the catalyst in the form of silicon, carbon, calcium, magnesium, and potassium are obtained as a by-product of the reaction between nickel, molybdenum, and alumina support. NiMo/Al₂O₃ catalyst is easy to regenerate because it is difficult to dissolve in oil.

B. Catalytic Hydrogenation Process

In the catalytic hydrogenation process, the observed variable is the amount of catalyst fed with 6 variations, including 0 grams; 0.10 grams; 0.15 grams; 0.20 grams; 0.25 grams; and 0.3 grams. This hydrogenation catalytic process is based on several previous studies, including:

- Ameen et.al (2018) which produces rubber seed oil into green diesel with a diesel range (C15-C18) using a NiMo/Al₂O₃ catalyst with a reaction temperature of 350oC, 35 bar, and H2/Oil 1000 N produces a product with a %yield of 80, 87%.
- 2) Salamah and Setyawan (2013) who designed a hydrogenation reactor with an operating temperature of 250°C and a heating power of 1000 watts.
- 3) Orozco et.al (2017) which produces green diesel using a fixed-bed continuous reactor with two reaction stages, namely temperatures of 270°C and 350°C. The catalyst used is NiMo/Al₂O₃. % yield green diesel produced is 98% with a purity of 95.3%.

For process safety, the temperature used in this study was 300°C with a hydrogen pressure of 25 psia. This is because the hydrogenation reactor is a batch reactor with a small capacity of ± 600 ml.

Before feeding the raw materials, the catalyst is first introduced into the reactor with certain variations. This is because the catalyst tends to be insoluble in the feed. The raw material is fed into the reactor when the reactor conditions are ± 100 °C because PFAD has a solid phase at room temperature. If the reactor temperature is hot, the PFAD will be in a liquid phase and will not clog the feed and hydrogen inlet and product outlets in the reactor. After the addition of feed and catalyst, the feed inlet in the reactor is closed to prevent the oxidation process between PFAD oil and oxygen in the air.

Hydrogen is injected into the reactor when the reactor conditions are at room temperature. This is because hydrogen is flammable when exposed to heat. So after the addition of the feed, the reactor temperature is lowered first. OISAA Journal of Indonesia Emas

The time required to raise the reactor temperature from room temperature to 300° C is ± 30 minutes. However, when the heater temperature is more than 200° C, the reactor pressure shows an increase. This is because the hydrogen injected into the reactor is hydrogen with a pressure of 25 psia, then according to the laws of thermodynamics, the greater the temperature, the greater the pressure. In addition, the increasing reactor pressure is also caused by the large number of gases formed from the reaction. These gases move in all directions and fill the reactor chamber so that the reactor pressure increases with increasing temperature.

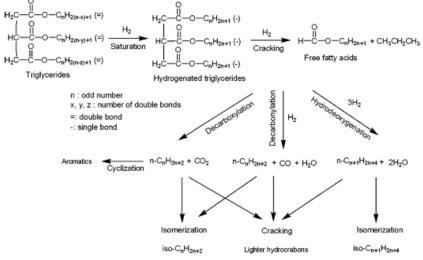


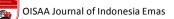
Figure 3. Hydroprocessing Step (Veriansyah et.al, 2012)

The catalytic hydrogenation process uses a hydroprocessing step to crack PFAD into hydrocarbons. PFAD contains $\pm 80\%$ free fatty acids with palmitic acid as the largest fatty acid component in PFAD. Palmitic acid (C₁₆H₃₂O₂) is a saturated fatty acid, so PFAD tends to be solid phase at room temperature. In addition to free fatty acids, $\pm 20\%$ in PFAD contains triglycerides and secondary oxidation resulting from the CPO deodorization process, such as aldehydes and ketones.

From Figure 3, it can be observed that the hydroprocessing steps in the catalytic hydrogenation of PFAD to green diesel are:

- 1) There is saturation of the chain (C-O) in a small part of the triglycerides in the PFAD by hydrogen to become hydrogenated triglycerides.
- 2) Hydrogenated triglycerides are cracked using hydrogen into intermediate products, such as monoglycerides, diglycerides, and free fatty acids.
- 3) The intermediate products of saturation and cracking are converted into hydrocarbon products along with ±80% of free fatty acids (FFA) contained in PFAD through three reaction pathways, including:
- Decarboxylation: Converts carboxylic acids from FFA to straight chain alkanes, then releases CO₂.
- Decarbonylation: Produces alkanes through the reaction of carboxylic acids in FFA with hydrogen, then forms CO and H2O as by-products.
- Hydrodeoxygenation: Producing alkanes using hydrogen through the reaction of carboxylic acids in FFA and forming by-products in the form of H2O.

This reaction mechanism is in line with the research of Veriansyah *et.al* (2012) which produces green diesel using several stages, including triglyceride saturation, triglyceride cracking, and conversion of free fatty acids resulting from cracking through decarboxylation, decarbonylation, and hydrodeoxygenation processes. Then Mijan *et.al* (2017) produced green diesel from castor oil using several stages without the presence of hydrogen, including hydrolysis of triglycerides into glycerol and free fatty acids, then converting glycerol and free fatty acids into long chain hydrocarbons through decarboxylation and decarbonylation processes, then the results conversion is cracked back to produce short chain hydrocarbons.



For safety reasons, the feed valve is opened slightly every time the reactor pressure shows 500-700 psia. The feed back valve is closed when the pressure is 300-400 psia. This is because if the feed valve is opened until the pressure is too low, the substances that have not reacted completely and raw materials that have not reacted will come out through the product exit.

The catalytic hydrogenation process in this experiment lasted for 1.0 hours because the hydrogen pressure showed a not very significant increase at approaching one hour. After one hour, the pressure did not tend to increase, even the reactor pressure decreased to 0 psia. This indicates that the hydroprocessing reaction in the reactor only lasts for ± 1.0 hours.

The resulting product is a gas phase product. Therefore, the gas is condensed into a liquid phase in the condenser water. The gas is in direct contact with the water so that the temperature of the gas decreases and then changes to a liquid phase. The product is separated from the condenser using a separating funnel with the principle of difference in density. Oil with a lower density is on the top, while water with a higher density is at the bottom.

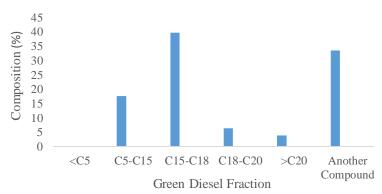


Figure 4. Green Diesel Product in This Research

Green diesel products produced tend to be brownish yellow, clear brown, to dark brown. The green diesel has a distinctive smell like diesel. However, some samples such as sample 2 and sample 6 tend to have a rancid smell. This allows the presence of unwanted residues and impurities, so that the color of sample 2 and sample 6 is the most concentrated color among other samples.

C. Chemical Compound and Green Diesel Content Analysis

In this study, analysis of the chemical compounds and composition of green diesel was carried out using Gas Chromatography-Mass Spectrometry (GC-MS) on samples with the use of a catalyst of 0.1507 grams. From testing using GC-MS, it is assumed that the results of the analysis of chemical compounds and composition of green diesel represent the entire sample.





From Figure 5, it can be seen that the green diesel produced contains the diesel fraction $(C_{15}-C_{18})$ as the dominant fraction of 39.63%. The other compound fractions also showed the dominant yield after diesel, which was 33.44%. This is presumably because the fatty acids contained in PFAD have not reacted completely, and secondary oxidation in PFAD also triggers the formation of compounds other than hydrocarbons in green diesel. In addition, the catalytic

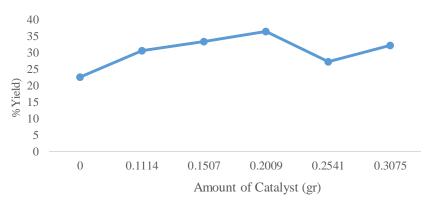
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hydrogenation process produces side reactions such as isomerization, alkylation, and cracking, so that the catalytic hydrogenation process can produce by-products in the form of iso-alkanes, aromatics, and light hydrocarbons.

The content of gasoline, naphtha, and kerosine (C_5 - C_{15}) of 17.55% is due to the continuous cracking process so that more light hydrocarbon chains are produced. In addition, the content of C_{18} - C_{20} and $>C_{20}$ is due to the fact that PFAD has not fully cracked into the desired product, namely diesel in the C_{15} - C_{18} range. The green diesel produced does not contain substances that have a fraction $<C_5$ because the hydrocarbons below C_5 are gas-phase hydrocarbons and cannot be condensed, so they evaporate into the air.

D. Effect of Catalyst Amount to Yield Persentage

Yield percentage is a percentage that states the amount of product produced from the amount of raw materials fed. In this study, the calculated percent yield is the amount of green diesel to the amount of PFAD that is fed.



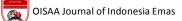


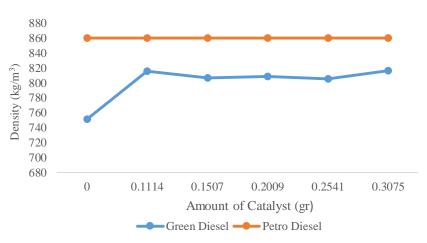
From Figure 6, it can be observed that the percent yield tends to increase to the optimum at point 4 with a catalyst amount of 0.2009 grams. This is because the more the number of catalysts, the more substances that can lower the activation energy and speed up the reaction, so that the cracking process is more effective and the resulting product is more and more. However, at point 5 with a catalyst amount of 0.2541 grams, the percent yield decreased drastically from 36.5331% to 27.2832%. This is because the cracking process produces light fractions that form a gas so that it cannot be condensed. However, at the 6th point with a catalyst amount of 0.3075 grams, the percent yield again increased to 32.2858%. This is due to the formation of residues and impurities so that the volume of the product increases, but the color of the oil becomes more concentrated and smells slightly rancid.

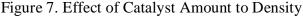
The yield percentage obtained in this study is only around 22-33%. This is because the condensation process occurs in the open and the condenser water used is not too cold, so that a lot of product gases are released into the air.

E. Effect of Catalyst Amount to Density

Density or specific gravity is the amount of mass per total volume of a liquid. Density is one of the physical properties that can be used as an indication in knowing the type of product or certain compound.







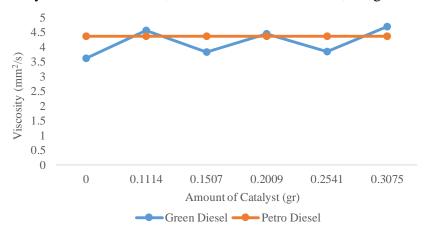
Petroleum diesel has a density of 860.4 kg/m³ (Orozco et.al, 2017), while in this study, the product density obtained ranged from 751-817 kg/m³. The density of the green diesel product in this study is lower than the density of petroleum diesel. This is because the product still contains a lot of light fractions below C₁₅, heavy fractions <C₁₈, as well as compounds in the form of byproducts of the hydrogenation catalytic process contained in green diesel up to 33.44%.

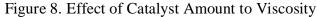
The lowest density value is at point 1, which is 751.5056 kg/m³. This is because point 1 is a green diesel product without the use of a catalyst, so that the cracking that occurs is thought to be incomplete. In addition, uncatalyzed cracking generally requires very high temperatures. So that with the same conditions as the use of a catalyst, green diesel without the use of a catalyst is thought to not react perfectly at a temperature of 300°C because there is no substance that is able to accelerate the reaction and lower the activation energy.

F. Effect of Catalyst Amount to Viscosity

Viscosity is the viscosity of a fluid. Viscosity is related to the friction between layers of fluid when one layer moves to another layer. In this study, the viscosity of green diesel was measured based on the time taken by the nickel iron alloy ball across the hoppler viscometer with a distance of 10 cm.

Measurement of a viscosity aims to determine the viscosity of the oil at a certain temperature so that the oil can flow at that temperature. The lighter the petroleum fraction, the smaller the viscosity. On the other hand, the heavier the oil fraction, the greater the viscosity.





The viscosity of petroleum diesel is $4.36 \text{ mm}^2/\text{s}$ (Orozco et.al, 2017). The observed viscosity is the kinematic viscosity, which is the ratio between the dynamic viscosity and the density of a product. From Figure 8, it can be observed that the 4th point with a catalyst amount of 0.2009 grams is the point closest to the viscosity of petroleum diesel, which is $4.452 \text{ mm}^2/\text{s}$. While the 1^{st} point has the farthest viscosity value with the viscosity of petroleum diesel compared to other

samples. This is because the first sample did not use a catalyst, so the cracking that occurred was thought to be incomplete.

The 3^{rd} point shows a lower viscosity than petroleum diesel, which is 3.8297 mm²/s. This is presumably because some of the products are converted into gasoline, naphtha, and kerosene which have lighter fractions than diesel.

At points 2, 3, and 4, the resulting viscosity tends to be higher than the viscosity of petroleum diesel. It is suspected that there are heavy fractions above the diesel range (> C_{18}) so that the resulting viscosity is higher.

G. Effect of Catalyst Amount to Water Content

Moisture content is the amount of water content in green diesel. The reaction in the hydroprocessing stage produces H_2O as a by-product. But the less water, the better the quality of green diesel.

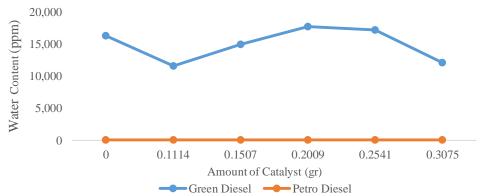


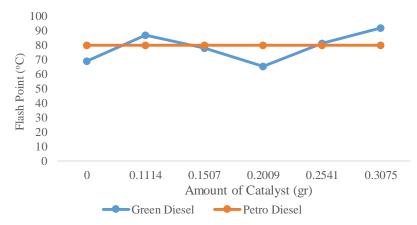
Figure 9. Effect of Catalyst Amount to Water Content

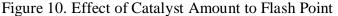
From Figure 9, it can be observed that the content of green diesel tends to be very high compared to petroleum diesel which is only <100 ppm (Orozco et.al, 2017). This high water content is due to the condensation process of product gases directly in contact with water so that the resulting oil mixes with condenser water. In addition, the process of separating water and oil using a separating funnel is not optimal. However, the presence of this water content can also be caused by a by-product of the reaction itself.

Another factor that can cause high water content is the evaporation of volatile substances in non-alkane compounds contained in green diesel. These volatile substances have a boiling point below 100oC so that these substances also evaporate when in the oven.

H. Effect of Catalyst Amount to Flash Point

The flash point is the lowest temperature at which the oil will ignite when exposed to a spark. The flash point measurement is done using a flash point tester. The higher the flash point, the easier the process of storing fuel.





From Figure 10, it can be observed that the 4th point has the lowest flash point of 65.4°C. While the 3rd point with a catalyst amount of 0.1507 grams is the optimal flash point because it

is close to the flash point of petroleum diesel of 80°C. However, at the 6th point, the flash point tends to be high at 91.9°C.

The lower the flash point, the more light fraction products contained in green diesel, because the gasoline fraction has a low flash point of -10 to -15° C. At point 6, the product is thought to contain many fractions of other compounds, especially ester compounds so that the flash point tends to be high up to 91.9°C.

CONCLUSION

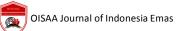
The optimum condition for making green diesel using catalytic hydrogenation is the use of a NiMO/Al₂O₃ catalyst of 0.2009 grams in 300 ml of PFAD with a maximum yield percentage of 36.5331%. The minimum yield percentage is obtained from green diesel products without the addition of a catalyst, which is 22.6289%. Green diesel produced in this study has physical properties, including density at 40°C 751.5056 – 816.9221 kg/m³, kinematic viscosity at 40°C 3.6107 – 4.6831 mm²/s, Moisture Content 11.593 – 17.717 ppm, Flash Point 65.4 – 91.9°C. The content of green diesel in this study was dominated by the diesel fraction (C₁₅-C₁₈) of 39.63%.

ACKNOWLEDGEMENTS

This research received funding from Ristekdikti through Program Kreativitas Mahasiswa (PKM) in research field.

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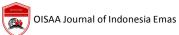


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