



Synthesis of Renewable Diesel from Pure Plant Oil of Kapuk (*Ceiba pentandra*) Seed Using NiMo/ γ -Al₂O₃ Catalysts

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Abstract

Ceiba pentandra (Kapok) is a tropical plant belonging to the Malvales that contain oil. Naturally, Pure Plant Oil (PPO) can be used as a renewable energy source that is a promising energy alternative instead of fossil. Somehow, one of the effects of the quality of PPO is the presence of unsaturated bonds and the presence of oxygen. The most appropriate method to overcome these problems is hydrodeoxygenation using a batch system autoclave reactor. In the present work, we synthesized of Green Diesel using hydrodeoxygenation and NiMo/ γ -Al₂O₃ catalyst to saturate double bonds and remove oxygen. The yield of PPO was 42.77-74.72% while the yield of green diesel at pressure conditions of 30 and 50 bar at temperatures of 300, 350 and 400°C produced was in the range of 76.73 – 94.06%. Then, the best condition for the hydrodeoxygenation reaction for the biggest yield was at the pressure of 50 bar at the temperature of 350°C. The results of the characterization of gas products using GC-TCD showed the composition of gases was H₂, O₂, CO, CH₄, and CO₂. Whereas for green diesel liquid products, pure plant oil, and kapok seed oil were analyzed using GC-MS obtained hydrocarbon compounds with interval of C₁₀-C₂₀. Quality analysis of kapok seed oil, pure plant oil, and green diesel has been following quality standards except for FFA and viscosity.

Keywords: Green diesel, hydrodeoxygenation, NiMo/ γ -Al₂O₃ catalyst, pure plant oil

1. Introduction

The large utilization of fossil fuels has caused serious issues in national energy security and the crisis of energy (Zhao et al., 2017). Somehow the decrease in available fossil fuels resources and harmful environmental impact induces an increasing interest in alternative and renewable energy such as the use of biomass (Regmi and Nitorisavut, 2020). Renewable energy resources are supposed to reduce energy dependence on fossil fuels. Indeed, biofuel is a potential alternative for fossil fuels substitution (Douvartzides et al., 2019). Indeed, biofuel is a potential alternative for fuel substitution. Some research efforts have been made from various plants that can produce oil as alternative energy, one of which is cotton plants. PPO as a biofuel derived from plants containing seeds possesses both process degumming and neutralization (Prihandana and Hendroko, 2008).

Kapok is a tropical plant belonging to the Malvales order and Malvaceae family, which is originally driven from Southeast Asia and

grown in the tropical region (Parahita et al., 2018). Kapok seed has great potential due to lack of utilization, somehow in Indonesia, it is used as animal feed. Albeit, the oil content in Kapok seeds ranges from 25% - 40% (Santoso et al., 2017), which has a dominant linoleic acid composition, around 68.452% and contains a mixture of glycerol and fatty acid triesters which are generally called triglycerides (Vedharaj et al., 2013). Moreover, kapok seed oil (KSO) has the capability of sustainable biodiesel feedstock due to simple cultivation and short harvest time by synthesis PPO and Hydrotreating process (Parahita et al., 2018).

Naturally, PPO is produced through two main stages called degumming and neutralization. Degumming is a process for removing gum containing hydrated phosphate compounds and non-hydrated phosphate compounds, while neutralization is the process of making soap to remove free fatty acid levels in oil (Santoso et al., 2017). The quality of PPO is determined by the presence of unsaturated bonds and the presence of oxygen, which causes oxidation stability and low thermal

conditions in the pure plant oil to be produced (Zhou and Lawal, 2015). Furthermore, to remove oxygen from these oxygen-containing compounds can be done through the hydrodeoxygenation (HDO) method (Deliy et al., 2011).

HDO is a promising upgrading technology to remove the oxygen from material oxygen-containing compounds by cutting the carbon-oxygen bonds using hydrogen gas (Sotelo-boy et al., 2011). The previous studies reported that the HDO reaction is influenced by temperature and pressure. At a temperature of 320-360°C, the yield was 54.69-71.43%, while the pressure factor is 20-60 bar, the yield was 44.50-54.69%. In addition, it was also found that at a pressure of 30 bar the yield was 98.72% which was higher than at a pressure of 60 bar with a yield of 97.74 (Heriyanto et al., 2018).

Hydroprocessing is a well-known technology in the petroleum refining industry, which can be carried out either by hydrocracking technology or by the less severe hydrotreating technology (Srihanun et al., 2020). Hydroprocessing of plant oil leads to the production of hydrocarbons in the boiling range of diesel, and therefore it is commonly known as green diesel. The basic idea is to change and transform by several effects such as high pressure, high temperature, and a bifunctional catalyst the triglycerides in the plant oil into high cetane hydrocarbons (Bezergianni et al., 2011). In the HDO reaction, high H₂ gas pressure aims to increase the solubility of H₂ gas in vegetable oils, as well as prevent the formation of carbon deposits on the catalyst surface. The higher the temperature used in the reaction, the degree of deoxygenation will be greater and shows that the oxygen in the reaction has been reduced. This is indicated by the formation of a lot of gas, somehow the type of catalyst used in the HDO reaction can affect the conversion/yield and selectivity of the product produced. The produced of biodiesel from Kapok seed oil with Methanol and sodium hydroxide as a catalyst. The maximum yield of 95% was obtained in the use of 21 percent methanol at 60% reaction temperature for 2h reaction period. In other studies that reported the production of biofuels by Catalytic hydrocracking using NiMo/HZSM-5 catalysts found that the optimum temperature at 350°C for 2 h of reaction (Santoso et al., 2017).

In this study, we used NiMo/ γ -Al₂O₃ catalyst due to it has high activity in the hydrogenolysis process. It is supposed to be supported by γ -Al₂O₃ used in the HDO

process because it has large pores (Deliy et al., 2011). This study aims to synthesize renewable energy based on biodiesel from Kapok Seed Palm Oil through a hydrotreating reaction with the Al₂O₃ catalyst. The results of the Renewable Biodiesel synthesis will be characterized by a Gas Chromatography Thermal Conductivity Detector (GC-TCD) and Mass Spectrometry (GC-MS) to see the profile of the biodiesel content. Besides that, biodiesel will be characterized by its physical-chemical properties to be compared with standard biodiesel FFA, flash point, density, pour point, and viscosity.

2. Methodology

2.1. Materials

The kapok seeds were collected from a village in Indonesia, which is the main material used in this research to obtain kapok seed oil by oil extraction (Vedharaj et al., 2013). The oil was given by the Center for Energy Resources Technology and Chemical Industry (PTSEIK) Agency for the Assessment and Application of Technology (BPPT) Indonesia, aquadest, NaOH 14°Be, KOH 0.12 N, H₂C₂O₄, ethanol 96%, phenolphthalein indicator and NiMo / γ -Al₂O₃ catalyst (Sigma-Aldrich). The equipment used is a set of glassware, a set of titration tools, a set of batch system autoclave reactors, drip pipettes, volumetric pipettes, hot plates, magnetic stirrers, thermometers, separating funnels, analytical balance sheets, pycnometers (Pyrex), Mini flash FLP Touch, Pour Point Proline Kyromat RP 4050 C LAUDA, Viscotemp 18 LAUDA, NOVA Touch Surface Area Analyzer, Gas Chromatography using Thermal Conductivity Detector (TCD) and Mass Spectrometry (MS) (Shimadzu).

2.2. Synthesis Pure Plant Oil (PPO)

200 grams of Kapok seeds were heated at a temperature of 70°C and added NaOH solution of 14o Be (11.7%) at a temperature of 70°C for 60 minutes, stirred at a speed of 300 rpm. The compound was separated into an oil layer and aquadest, then the oil layer was dissolved with 14oBe NaOH for 10 minutes then filtered, then washed with distilled water until the pH was neutral. Furthermore, to obtain PPO we continue by heating at 100°C

2.3. Catalyst Preparation

NiMo/ γ -Al₂O₃ catalyst prepared by crushed and sieved to 100 Mesh. The prepared NiMo/ γ -Al₂O₃ catalyst is then characterized

by the BET (Brunner-Emmet-Teller) method using the NOVA Touch Surface Area Analyzer to analyze the surface area of the catalyst, and used 5% wt of the weight of PPO (Deliy et al., 2011).

2.4. Hydrodeoxygenation of Pure Plant Oil

170 ml of PPO has added 5% NiMo/-Al₂O₃ catalyst and put into a batch system autoclave reactor tube with variations in reaction temperature conditions of 300, 350, and 400°C at a pressure of 30 bar with a stirring speed of 400 rpm for 1 hour and a gas flow rate of 20 mL/ minute. The gaseous products were taken and analyzed using GC-TCD while the liquid products were characterized using GC-MS. Pressure variations of 50 bar at temperatures of 300, 350, and 400°C were carried out (Zhou and Lawal, 2015).

2.5. Characterization of Green Diesel

The green diesel that has been produced then analyzed for its yield value and characterized by its physicochemical properties.

% Yield

The percent of yield determination is done to determine the amount of kapok seed oil that is converted to pure plant oil and the conversion of pure plant oil to green diesel (Sotelo-boy et al., 2011).

$$\% \text{ Yield} = \frac{\text{Product Mass (g)}}{\text{Sample Mass (g)}} \times 100\% \quad (1)$$

Free Fatty Acid Levels

The determination of the FFA was carried out to determine the levels of free fatty acids contained in the sample by reacting 1 gram of sample with 96% ethanol as much as 25 mL, pp indicator, and titrated (Heriyanto et al., 2018).

$$\% \text{ FFA} = \frac{\text{Volume (KOH)} \times \text{Molarity (KOH)} \times \text{MW FA}}{\text{Sample Weight} \times 1000} \times 100\% \quad (2)$$

MW Fatty Acid (Linoleate Acids) = 280,45 g/mol; Volume of KOH = Volume of KOH was used (mL) ; Molarity of KOH = Concentration of KOH (M)

Density

Determination of density is done using a pycnometer based on the ASTM D 1298/ASTM D 40052 test method by weighing the pycnometer in an empty and dry state

and recording its weight (W) (Handoyo et al., 2007).

$$\rho = \frac{Wt-W}{V} \quad (3)$$

ρ = density (g/mL); Wt = Pycnometer + Sample (g); W = Pycnometer (g); V = Pycnometer volume (mL)

Viscosity

Determination of viscosity was done using Viscotemp 18 LAUDA by ASTM D 445 standard protocol, then calculated by the formula (Heriyanto et al., 2018):

$$\text{Viscosity} = t \times \text{coefficient of viscosity} \quad (4)$$

t = Sample flow time (s); coefficient of viscosity = 0,041129

Flash point

The determination of the flash point was carried out by the FLP Touch Miniflash, the Hexadecan program with the ASTM D6450 test method. Whereas the pouring point is carried out using the RP 4050 C LAUDA Pour Point Proline Kyromat tool with the ASTM D97 test method with the LA 4040 C LAUDA series when poured. If when the temperature of 9°C has not shown the pour point value, the batch temperature is reduced to -18°C and when 0°C is reduced to -33°C. The pour point value is determined by adding 3°C to the results of the experiment (Heriyanto et al., 2018).

Flash Point = Values at Temperature + 3°C

The chemical compound

The gas product of hydrodeoxygenation reaction was analyzed using GC-TCD Shimadzu 8A TCD type, used argon gas with Shincarbon ST column type with column's temperature 50°C, injector's temperature 100°C and detector's 100°C, while liquid samples determined the quantity and quality of components compound in the sample using GC-MS-QP2010S Shimadzu with an Rtx 5 MS column, 30 meters long, Helium carrier gas and RI70 Ev ionization (Asokan and Vijayan, 2014).

3. Results and Discussion

3.1. The PPO hydrotreating reaction

The synthesized of PPO from Kapook seed was carried out through the degumming process, neutralization using 140H Be NaOH base (11.7%), saponification, and heating of PPO to remove the water content of oils. Furthermore, the hydrotreating process was

carried out by flowing hydrogen with variations of pressure conditions and reaction temperature. The initial hydrogen pressure was 30 and 50 bar, then the temperature was 300, 350, and 400°C with stirring 400 rpm for 60 minutes of the reaction. Changes in temperature and pressure affect the rate of the PPO hydrotreating reaction (Figure 1).

The temperature increases gradually, the reaction reached the optimal temperature and is influenced by the difference in reaction pressure (preheating). At optimal temperature conditions, the HDO reaction lasted for 60 minutes/was kept constant. The slow change in reaction temperature is also due to the influence of activation energy and catalyst activity. Generally, good performance of catalyst will obtain lower activation energy earlier and will achieve faster of the optimal temperature of the

reaction. Furthermore, changing the temperature conditions is directly proportional to changes in pressure that occur within 6 minutes with the graph results obtained (Figure 2).

The variations of temperature changes in the time interval pressure were observed periodically. It shows that at 0th minutes, there is an initial pressure variation of 30 and 50 bar. The results obtained at an initial pressure HDO of 30 and 50 bar per-reaction temperature of 300, 350, and 400°C occurs a significant increase until reaching the reaction conditions even exceeding the reaction conditions which then are in a constant state. The reaction condition before preheating temperature, a significant increase in pressure due to influenced by temperature (Heriyanto et al., 2018).

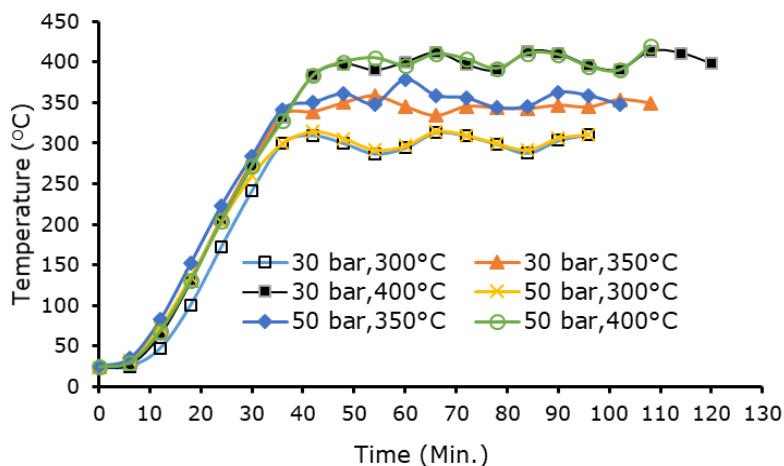


Figure 1. The effect of both temperature and pressure to reaction rate.

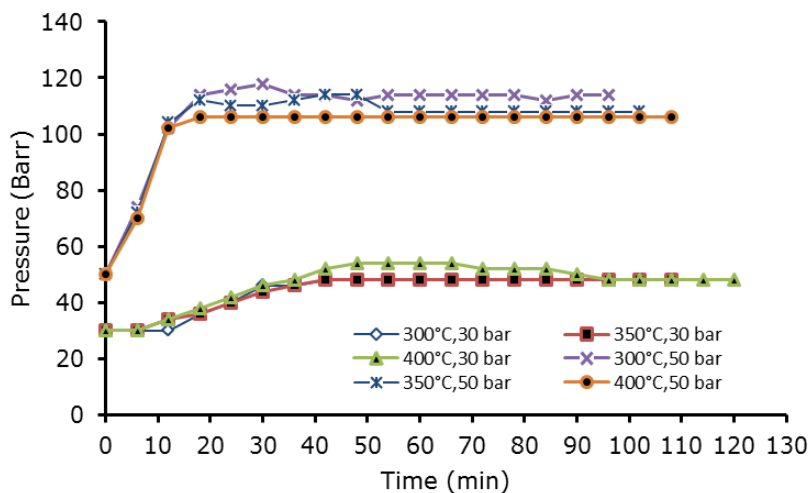


Figure 2. Graph of change in reaction pressure.

It is shown that there is a difference in the use of hydrogen, where the decrease in pressure indicates that the use of hydrogen is increasing which indicates the occurrence of the HDO process which is the fulfillment of the double bond and subsequently reaches the deoxygenation conditions for binding of oxygenate to pure plant oil (Eduardo et al., 2017). The decrease of hydrogen consumption indicated by pressure shows that the hydrotreating of HDO reaction is selectivity to the DCO and DCO₂ reactions. The DCO and DCO₂ reactions of H₂ consumption are not needed too much to break the -CO or -COO bond. The hydrotreating gas product then separated the liquid product with the rest of the catalyst by filtration techniques. The results was obtained that the pressure and temperature of the reaction affect the yield (yield) produced (Figure 3).

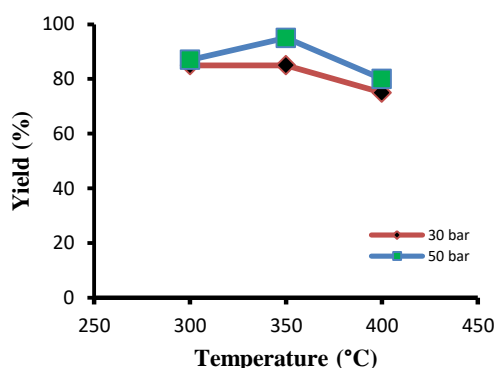


Figure 3. The percent yield process in differences of pressure and temperature.

Our data showed that the high temperature of the HDO reaction has a low percent yield produced, at any pressure variation at 400 °C obtained the lowest yield supposed due to the separation of the liquid product, the product purity. The percent yield at pressure 30 bar and 50 bar with temperatures 300 and 350°C is 86.27-94.06% respectively

instead of 76.73% and 82.80 % at 300 and 50 bar with 400°C temperatures.

The products then we analyzed, the gas products were analyzed using gas chromatography with thermal conductivity detectors (GC-TCD), while the liquid products were analyzed using gas chromatography with mass spectroscopic detectors (GC-MS). The product quality was analyzed by knowing FFA levels, densities, flashpoints pour point, and viscosity.

3.1. Catalyst Characterization

The catalyst characterization was carried out using the NOVA touch surface area and pore size analyzer to measure the surface area and pore size of the catalyst (Hebert and Stöwe, 2020). The catalyst surface area NiMo/ γ -Al₂O₃ is 172.329 m²/g. The greater the surface area of a catalyst, the more space for reactants to react so that the reaction can run faster and maximum. The catalyst surface area of the catalyst will give the number of active sites on the surface that can be occupied by the reactants. The gas products: Gas product was characterized using the GC-TCD instrument and the characterization results were compared with the standard based on retention time. The results showed several gas components namely hydrogen (H), oxygen (O), Nitrogen (N), Carbon monoxide (CO), Methane (CH₄), and Carbon dioxide (CO₂) (Table 1).

In the HDO reaction temperature variations, the highest oxygen reduction occurs at 300°C (optimal conditions) is shown at the highest oxygen concentration compared to the HDO reaction temperature. Furthermore, the reaction temperature of HDO at 400°C DCO and DCO₂ reactions occur. In the reaction at 300°C, there was none of the DCO or DCO₂ reactions occurred. While at 350°C, the DCO reaction occurs while DCO₂ does not. Unfortunately, the methane gas (CH₄) was obtained at 350 and 400°C.

Table 1. The resultant of GC-TCD gas product at difference temperature.

Gas Compound	Percentage of Compound					
	GC-TCD at 30 bar			GC-TCD at 50 bar		
	300°C	350°C	400°C	300°C	350°C	400°C
H ₂	14.189	79.000	82.306	82.870	83.306	83.939
O ₂	16.786	1.560	0.074	0.508	0.296	0.143
CO	-	0.111	0.753	-	0.132	0.130
CH ₄	-	0.020	0.376	-	0.042	0.037
CO ₂	-	-	0.672	-	-	-

That indicated the release of the alkyl group which occurs due to the cracking reaction of the carbon chain. Unfortunately, the methane gas (CH_4) was obtained at 350 and 400°C. That indicated the release of the alkyl group which occurs due to the cracking reaction of the carbon chain. The gas product at the initial HDO (50 bar) was obtained at the 300°C temperature variation the highest oxygen reduction occurred compared to the other HDO reaction temperatures, then at 350°C, the DCO occurred and did not occur decarboxylation DCO_2 . Then at 400°C, the DCO and decarboxylation DCO_2 reactions occur at a pressure of 50 bar, but there is no release of the alkyl group during the cracking of the carbon chain (Zhao et al., 2017). The deoxygenation processes of triglyceride could be carried out through several different routes such as hydrodeoxygenation, decarboxylation/ decarbonization, and even hydrocracking.

The reaction product of hydrodeoxygenation is the formation of hydrocarbons with the same amount of carbon chain as the byproducts in the form of water and propane. DCO and DCO_2 produce paraffin with one carbon, that is incompatible with fatty acids and releases CO_2 or CO.

The hydrocracking form alkanes with shorter chains. The route in the above scheme depends on the temperature, pressure, and catalyst used. Paraffin formed from the hydrodeoxygenation pathway. Nickel (Ni) catalysts belong to group VIII of transition metals, with outermost electrons in d orbitals (3d) orbitals that are not full yet, which might affect the Ni catalyst properties. Ni plays an important catalytic reaction role and makes Ni the active phase in which the reaction occurs (Parahita et al., 2018). The active phase of Ni catalyst has the active converting properties reactant and selective in product formation, while molybdenum (Mo) is one of the transition elements with half-full electron configurations in 4d orbitals (unfair electron). The Mo metal atom has an active property in the catalytic reaction acts as a promoter. The promoter induced the buffer and the active site of the catalyst to control the catalyst stability (Heriyanto et al., 2018).

The $\gamma\text{-Al}_2\text{O}_3$ buffer serves as a place to spread the active phase to expand the contact surface between the active phase and the reactant phase without reducing the activity of the phase itself. Besides that, the

buffer also functions as a stable surface. The chemical properties of $\gamma\text{-Al}_2\text{O}_3$ as a buffer identified by the acidic site where the acid- Al_2O_3 surface acid site strongly influences the activity and selectivity of the hydrotreating catalyst. Al_2O_3 buffer catalyst tends to have lewis acid site will cause excessive hydrogen transfer and cause coke formation while bronsted-lowry acid sites will better direct the reaction to be more conducive to cracking and can reduce the formation of coke (Srihanun et al., 2020; Zhou and Lawal, 2015).

The phases of Both Ni and Mo metal dispersed on the Al_2O_3 surface. It was preceded by hydrogen adsorbed on the metal surface, then broken off the H_2 sigma bond and form the H-metal bond. The unsaturated bonding molecules also adsorbed on the surface of the metal catalyst, the phi-bond interacting with the empty orbitals of the metal. The bonds that interact are more dominant to the Ni metal because the Ni metal has a higher hydrogenation power. It is more active in increasing catalytic activity in the reactions that occur. Ni metal also has a strong adsorption power towards the reactants. It can adsorb hydrogen gas on its surface and activate its hydrogen bonds so that hydrogen gas becomes easier to react, while the Mo metal is a promoter that can control the stability of the active phase of the catalyst. Unsaturated molecules move on the surface of the metal, hit the hydrogen atoms that are bound to the metal so that a reaction occurs, and release as a saturation product (He and Wang, 2013; Heriyanto et al., 2018).

The catalytic cracking process can take place at the Lewis acid site which is derived from the empty Ni orbitals. Then the interaction between the reactants and the bronsted acid site occurs in alumina. Cracking a long chain compound on the surface of the catalyst will go through the mechanism of carbonium ion formation (Bezergianni et al., 2011; Mirzayanti et al., 2017). After the process of fulfilling the double bond, an attack of carbonium ions and radicals is carried out on the reactant molecule. In this stage, there is an interaction between the reactant molecules and the surface of the catalyst so that the cracking reaction occurs with shorter hydrocarbon molecules. Besides, at this stage, new radicals and carbonium ions are formed. After the cracking reaction occurs, the reactants and catalyst will undergo a termination stage, with the incorporation of

stabilized radicals (at the Lewis acid site) and the formation of double bonds (at the bronsted acid site). Then the product of lewis acid is hydrogenated successively into aldehydes, alcohols, and aliphatic paraffin compounds. Products from bronsted acid are also hydrogenated successively to produce aliphatic/alkane paraffin compounds (Soteloboy et al., 2011).

3.2. Liquid product

After separating the liquid product from the rest of the catalyst using the filtration technique the following results are obtained (Figure 4). The hydrogenating of liquid products at a pressure 30 bar and temperature 300°C, seems more transparent than other products with variations of both pressure and temperature. At a pressure of 50 bar temperature 300°C also looks transparent compared to others. It supposed to reaction effect which is at the higher the pressure used related to higher the viscosity and simultaneously effect to the presence of more sediment resulting in affecting the

visual of the oil even though it has been filtered. Furthermore, to verify the chemical compounds of the green diesel liquid product, we were characterized using GC-MS. The interpretation of GC-MS analysis was presented in Table 2 and Table 3.

P	30 bar			50 bar		
	300°C	350°C	400°C	300°C	350°C	400°C



Figure 4. Hydrodeoxygenated liquid product.

Based on the GC-MS characterization results (Table 2 and Table 3), it can be seen that at 30 bar, 400°C contained alkyl esters with C₁₀-C₂₀ intervals and the largest areas are oleic acid, methyl ester/C₁₉H₃₆O₂ (29.98%), palmitic acid, methyl ester/C₁₇H₃₄O₂ (17.16%) and linoleic acid, methyl ester / C₁₉H₃₄O₂ (5.46%).

Table 2. The profile of Chemical Compound of Green diesel at 30 bar 400°C and 50 bar 300°C.

R.T (min)	Compound 30 bar, 400°C	Percentage (%)	R.T (min)	Compound 50 bar, 300°C	Percentage (%)
19.081	C ₁₇ H ₃₄ O ₂	17.16	19.046	C ₁₇ H ₃₄ O ₂	22.60
19.936	C ₁₇ H ₃₂ O ₂	0.36	19.855	C ₁₇ H ₃₂ O ₂	0.30
20.710	C ₁₉ H ₃₆ O ₂	1.09	20.912	C ₁₉ H ₃₄ O ₂	32.54
20.906	C ₁₈ H ₃₂ O ₂	5.46	21.541	C ₁₀ H ₁₈	0.91
21.097	C ₁₉ H ₃₆ O ₂	29.98	21.801	C ₁₈ H ₃₁ O ₂	1.49
21.235	C ₁₉ H ₃₈ O ₂	2.85	21.992	C ₂₀ H ₃₈ O ₂	0.39
21.819	C ₁₉ H ₃₄ O ₂	0.79	22.079	C ₁₃ H ₁₂ O	1.47
21.917	C ₁₆ H ₃₀ O ₂	0.15	22.521	C ₁₃ H ₂₆ O ₂	0.03
21.980	C ₂₀ H ₃₈ O ₂	0.21	22.746	C ₁₈ H ₁₀ O ₄	0.04
22.304	C ₁₀ H ₁₈ O	0.06			

Table 3. The profile of Chemical Compound of Green diesel at at 50 bar 350°C and 50 bar 400°C.

R.T (min)	Compound, 50 bar, 350°C	Percentage (%)	R.T (min)	Compound, 50 bar, 400°C	Percentage (%)
19.023	C ₁₇ H ₃₄ O ₂	22.41	19.052	C ₁₇ H ₃₄ O ₂	21.80
19.855	C ₁₇ H ₃₂ O ₂	0.40	19.930	C ₁₇ H ₃₂ O ₂	0.44
20.894	C ₁₉ H ₃₄ O ₂	27.24	20.889	C ₁₈ H ₃₂ O ₂	8.09
20.964	C ₁₉ H ₃₆ O ₂	17.89	20.987	C ₁₉ H ₃₄ O ₂	21.24
21.195	C ₁₉ H ₃₈ O ₂	2.16	21.056	C ₁₉ H ₃₆ O ₂	22.02
21.986	C ₂₀ H ₃₈ O ₂	0,38	21,385	C ₁₈ H ₃₁ O ₂	1.88

Table 4. Comparison Green Diesel and the ASTM D445 Standard.

Green Diesel Product	FFA (%)	Density (g/mL)	Flash Point (°C)	Pour Point (°C)	Viscosity (mm ² /s)
ASTM D445	0.8	0.86-0.90	130 min	-15 to 16	Max 24
<i>Biodiesel</i> 30 bar, 300 °C	2.54	0.8986	>200	0	50.70
<i>Green Diesel</i> 30 bar, 350 °C	3.67	0.896	>200	0	54.42
<i>Green Diesel</i> 30 bar, 400°C	20.03	0.902	>200	15	51.42
<i>Green Diesel</i> 50 Bar, 300°C	4,67	0.8996	>200	0	52,35
<i>Green Diesel</i> 50 bar, 350°C	10.68	0.8988	>200	6	53,15
<i>Green Diesel</i> 50 bar, 400°C	14.38	0.8986	>200	6	53,53

Moreover, at 50 bar and 300°C, containing alkyl esters with C₁₀-C₂₀ intervals and the largest areas are linoleic acid, methyl ester/C₁₉H₃₄O₂ (32.54%) and palmitic acid, methyl ester/C₁₇H₃₄O₂ (22.60%), while at 50 bar, 350°C produced the largest yield containing alkyl esters at C₁₇-C₂₀ intervals and the largest areas are linoleic acid, methyl ester/C₁₉H₃₄O₂ (27.24%), palmitic acid, methyl ester / C₁₇H₃₄O₂ (22,41%) and oleic acid, methyl ester / C₁₉H₃₆O₂ (17.89%). At a pressure variation of 50 bar temperature 400°C containing alkyl esters at C₁₇-C₁₉ intervals and the largest areas are oleic acid, methyl ester/C₁₉H₃₆O₂ (22.02%), palmitic acid, methyl ester/C₁₇H₃₄O₂ (21.80%) and methyl linoleate, methyl ester/C₁₉H₃₄O₂ (21.24%). At the condition, 50 bar and 350°C, it can be seen that the largest peak area is 27.24% with a retention time of 20.894 minutes. Based on these results seems that the major compound obtained was linoleic acid, methyl ester/C₁₉H₃₄O₂. However, at some peaks, it appears that there is cracking from the long-chain c atoms to the shorter chain of c atoms. Where C₁₀ hydrocarbons are obtained at variations in pressure of 30 bar 400°C and 50 bar 300°C.

Based on the results was presented on table 2 and 3 it shows that still not dominant that the pure alkane due to compound is influenced by several factors, namely because the flow of H₂ gas in the process of fulfilling the double bond and deoxygenation has not had a significant effect, the reaction time used is too short and the use of catalysts that contribute less to when the reaction occurs. The catalyst sulfidation leads to the nature of the bronsted acid site so that the reaction will run optimally (He and Wang, 2013). In this study, the sulfidation process was not carried out so that the cracking that occurred was less than optimal. However, the

results obtained several peaks have compounds that have saturated hydrocarbon chains such as Octadecanoic acid, methyl ester, and hexadecanoic acid, methyl ester.

3.2. Quality Analysis

The quality analysis was carried out included FFA levels, density, pour point, flash point, and viscosity aimed at kapok seed oil, pure plant oil, and HDO (green diesel) products where the results were compared with ASTM D445 standard (Asokan and Vijayan, 2014; Suriaini et al., 2019). The FFA level was carried out by titration method and repeated triplo. The results show that the value of FFA Green diesel below quality standards, it seems due to the Bronsted's acid site of the catalyst in the hydrocatalytic reaction which increases acidity by releasing protons so that the acidity value will increase (Table 4).

In addition, our biodiesel meets the standards, even after the HDO reaction there is almost unchanged. However, for the high-density value such in the HDO at 30 bar and 400°C, seems due to the maximum pure plant oil has not been converted into green diesel. Density will increase with increasing double bonds and decreasing chain length and higher molecular weights (Table 4) (Zhao et al., 2017).

In the treatment results obtained results that are by quality standards that are above 200°C. In the FLP Touch Miniflash tool can only measure flash points up to 200°C, so that the exact value of the flash point couldn't be known. From the results obtained it can be stated that Green diesel can be stored as a fuel safely at room temperature conditions. The higher the flash point of a fuel, the more non-flammable or safe in the storage process.

Based on the results obtained, that the pour point lies in the ASTM specification range. Nevertheless, green diesel at 30 bar pressure at 400°C still has a high pour point value, supposed there are still unsaturated chain contents in the constituent components of their compounds. The visual is that green diesel at a pressure of 30 bar temperature of 400°C is still quite thick or has a high enough viscosity compared to variations in pressure and other temperatures (Douvartzides et al., 2019). The pour point is related to the viscosity value, where the higher the pour point, the higher the viscosity will be. Viscosity is a measure of a fluid's resistance to flow. The higher fluid viscosity resists motion due to its high molecular cohesiveness gives a lot of internal friction. A fluid with low viscosity flows easily because its low molecular cohesiveness results in very small friction when it is in motion.

The viscosity value of green diesel within the ASTM specification range, somehow due to the results of the obtained green diesel is still too thick, so the viscosity value is high. Viscosity needs to be limited because too low viscosity can result in leakage at the fuel injection pump, while too high viscosity can affect the fast work of the fuel injection device and make it difficult to refuel the fuel oil (Asokan and Vijayan, 2014).

4. Conclusion

Our finding in this research is that the yield of pure plant oil is 42.77-74.72%, while Green diesel at pressure 30 bar and 50 bar with temperatures 300, 350, and 400°C produce 76.73-94.06 % respectively. The optimum conditions based on the yield of green diesel are obtained at a pressure variation of 50 bar temperature of 350°C with a percent yield of 94.06%. The composition of green diesel hydrocarbons from various variable effect obtained by hydrocarbon compounds at C₁₀-C₂₀ intervals. However, it has not yet been obtained the desired pure alkane compound due to several factors previously described. The composition of inorganic gases produced after hydrodeoxygenation is H₂, O₂, CO, CH₄, and CO₂. The quality of pure plant oil and green diesel are following quality standards except for the FFA content in green diesel.

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References

- Asokan, M.A., Vijayan, R., 2014. Effective conversion of kapok seed (Ceiba pentandra) oil into biodiesel and investigation of effects of catalyst concentrations and chromatographic characterization. *Int. J. ChemTech Res.* 6, 5709–5715.
- Bezergianni, S., Dimitriadis, A., Voutetakis, S., 2011. Catalytic hydrotreating of waste cooking oil for white diesel production. *Proc. First Int.* 1–6.
- Deliy, I. V, Vlasova, E.N., Nuzhdin, A.L., Bukhtiyarova, G.A., 2011. The comparison of sulfide CoMo / γ -Al₂O₃ and NiMo / γ -Al₂O₃ catalysts in methyl palmitate and methyl heptanoate hydrodeoxygenation. *Proc. 2nd Eur. Conf. Control. Proc. 2nd Eur. Conf. Mech. Eng. World Sci. Eng. Acad. Soc.* 24–29.
- Douvartzides, S.L., Charisiou, N.D., Papageridis, K.N., Goula, M.A., 2019. Green diesel: Biomass feedstocks, production technologies, catalytic research, fuel properties and performance in compression ignition internal combustion engines. *Energies* 12. <https://doi.org/10.3390/en12050809>
- Eduardo, E., Fernando, E., V, M.C., 2017. Biomass and Bioenergy Hydrotreatment of vegetable oils: A review of the technologies and its developments for jet biofuel production 105. <https://doi.org/10.1016/j.biombioe.2017.07.008>
- Handoyo, R., Anggraini, A.A., Anwar, S., 2007. Biodiesel dari Minyak Biji Kapok (Biodiesel from Kapok Seed Oil). *J. Enj. Pertan.* V, 57–64.
- He, Z., Wang, X., 2013. Hydrodeoxygenation of model compounds and catalytic systems for pyrolysis bio-oils upgrading. *Catal. Sustain. Energy* 1, 28–52. <https://doi.org/10.2478/cse-2012-0004>
- Hebert, S.C., Stöwe, K., 2020. Synthesis and characterization of bismuth-cerium oxides for the catalytic oxidation of diesel soot. *Materials (Basel)*. 13. <https://doi.org/10.3390/ma13061369>
- Heriyanto, H., Murti Sumbogo, S., Heriyanti,

- S.I., Sholehah, I., Rahmawati, A., 2018. Synthesis of Green Diesel from Waste Cooking Oil Through Hydrodeoxygenation Technology with NiMo/ γ -Al₂O₃ Catalysts. MATEC Web Conf. 156, 1–6. <https://doi.org/10.1051/mateconf/201815603032>
- Mirzayanti, Y.W., Prajitno, D.H., Roesyadi, A., 2017. Catalytic hydrocracking of Kapuk seed oil (*Ceiba pentandra*) to produce biofuel using Zn-Mo supported HZSM-5 catalyst. IOP Conf. Ser. Earth Environ. Sci. 67. <https://doi.org/10.1088/1755-1315/67/1/012023>
- Parahita, I.G.A.A., Mirzayanti, Y.W., Gunardi, I., Roesyadi, A., Prajitno, D.H., 2018. Production of Biofuel via Catalytic Hydrocracking of Kapuk (*Ceiba pentandra*) Seed Oil with NiMo/HZSM-5 Catalyst. MATEC Web Conf. 156, 1–5. <https://doi.org/10.1051/mateconf/201815606001>
- Prihandana, R., Hendroko, R., 2008. Energi Hijau. Penebar Swadaya, Jakarta.
- Regmi, R., Nitorisavut, R., 2020. Azolla Enhances Electricity Generation of Paddy Microbial Fuel Cell. ASEAN Eng. J. 10, 55–63.
- Santoso, F.A., Soe'eib, S., Suryandari, A., Asri, N., 2017. Utilization of Kapok Seed Oil (*Ceiba pentandra*) for Biodiesel Production using MgO/CaO Bimetallic Oxide Catalysts. Proc. Int. Conf. Green Technol. 8, 209–215.
- Sotelo-boy, R., Liu, Y., Minowa, T., 2011. Renewable Diesel Production from the Hydrotreating of Rapeseed Oil with Pt / Zeolite and NiMo /Al₂O₃ Catalysts. Ind. Eng. Chem. Res. 50, 2791–2799. <https://doi.org/10.1021/ie100824d>
- Srihanun, N., Dujjanutat, P., Muanruksa, P., Kaewkannetra, P., 2020. Biofuels of green diesel–kerosene–gasoline production from palm oil: Effect of palladium cooperated with second metal on hydrocracking reaction. Catalysts 10, 1–13. <https://doi.org/10.3390/catal10020241>
- Suriaini, N., Febriana, T.T., Yulanda, A., Adisalamun, A., Syamsuddin, Y., Supardan, M.D., 2019. Purification of Biodiesel from Waste Cooking Oil Using Bentonite as Dry Washing Agent. J. Rekayasa Kim. Lingkung. 14, 155–162. <https://doi.org/10.23955/rkl.v14i2.13165>
- Vedharaj, S., Vallinayagam, R., Yang, W.M., Chou, S.K., Chua, K.J.E., Lee, P.S., 2013. Experimental investigation of kapok (*Ceiba pentandra*) oil biodiesel as an alternate fuel for diesel engine. Energy Convers. Manag. 75, 773–779. <https://doi.org/10.1016/j.enconman.2013.08.042>
- Zhao, X., Wei, L., Cheng, S., Julson, J., 2017. Review of heterogeneous catalysts for catalytically upgrading vegetable oils into hydrocarbon biofuels. Catalysts 7. <https://doi.org/10.3390/catal7030083>
- Zhou, L., Lawal, A., 2015. Evaluation of Presulfided NiMo/ γ -Al₂O₃ for Hydrodeoxygenation of Microalgae Oil To Produce Green Diesel. Am. Chem. Soc. 29, 262–272. <https://doi.org/10.1021/ef502258q>