

Study of Reaction Conditions for the Synthesis of Methyl Oleic from Used Cooking Oil

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Abstract

Research on the study of the reaction conditions for the synthesis of methyl oleic from used cooking oil has been carried out. This study aims to: (1) reduce levels of free fatty acids (FFA) used cooking oil using activated charcoal adsorbent avocado seed; (2) determining the optimum conditions for the synthesis of methyl oleic from used cooking oil; (3) determining the quality of methyl oleic; (4) characterized methyl oleic by FTIR. Methyl oleic was obtained in two stages, namely the purification and synthesis stages. In the purification stage, 150 mL of used cooking oil was adsorbed with (2, 4, 6, 8, and 10) g of avocado seed activated charcoal for 2 hours at 70°C. The purification results showed that the avocado seed activated charcoal could reduce the FFA content of used cooking oil by 93.79% (w/w). In the synthesis stage, methyl oleic was synthesized using the mol ratio (triolein : methanol) (1 : 3), (1 : 6), and (1 : 9), as well as the concentration of NaOH (1, 8, and 16)% (w/w) by weight of oil. The results showed that the optimum condition for the synthesis of methyl oleic from used cooking oil with the highest yield (84.32% w/w) was the mol ratio (triolein : methanol) (1 : 9) with a concentration of NaOH 1% (w/w). The quality of the resulting methyl oleic meets the requirements as biodiesel according to INS 04-7182-2015 with an iodine number value of 4.44 g I₂/sample, saponification number of 114.44 mg KOH/g sample, cetane number of 82.96, water content of 0.03% (w/w), and the acid number of 0.71 mg KOH/g sample. The results of characterization of methyl oleic by FTIR showed that methyl oleic had a typical functional group absorption type of unsaturated fatty acid esters.

Keywords: used cooking oil, avocado seed activated charcoal, triolein, methyl oleic, biodiesel, transesterification.

Abstrak

Penelitian tentang studi kondisi reaksi sintesis metil oleat dari minyak jelantah telah dilakukan. Penelitian ini bertujuan untuk: (1) menurunkan kadar asam lemak bebas (ALB) minyak jelantah dengan menggunakan adsorben arang aktif biji alpukat; (2) menentukan kondisi optimum reaksi sintesis metil oleat dari minyak jelantah; (3) menentukan kualitas metil oleat; (4) mengkarakterisasi metil oleat dengan FTIR. Metil oleat diperoleh melalui dua tahap, yaitu tahap pemurnian dan sintesis. Pada tahap pemurnian, 150 mL minyak jelantah diadsorpsi dengan (2, 4, 6, 8, dan 10) g arang aktif biji alpukat selama 2 jam pada suhu 70°C. Hasil pemurnian menunjukkan bahwa arang aktif biji alpukat dapat menurunkan kadar ALB minyak jelantah sebesar 93,79% (b/b). Pada tahap sintesis, metil oleat disintesis dengan menggunakan perbandingan mol (triolein : metanol) (1 : 3), (1 : 6), dan (1 : 9), serta konsentrasi NaOH (1, 8, dan 16) % (b/b) dari berat minyak. Hasil penelitian menunjukkan bahwa kondisi optimum reaksi sintesis metil oleat dari minyak jelantah dengan rendemen tertinggi (84,32% b/b) adalah rasio mol (triolein : metanol) (1 : 9) dengan konsentrasi NaOH 1% (b/b). Kualitas metil oleat yang dihasilkan memenuhi syarat sebagai biodiesel menurut SNI 04-7182-2015 dengan nilai bilangan iodin 4,44 g I₂/sampel, angka penyabunan 114,44 mg KOH/g sampel, angka setana 82,96, kadar air 0,03% (b/b), dan bilangan asam 0,71 mg KOH/g sampel. Hasil karakterisasi metil oleat dengan FTIR menunjukkan bahwa metil oleat memiliki tipe serapan gugus fungsi yang khas dari senyawa ester asam lemak tak jenuh.

Kata Kunci: minyak jelantah, arang aktif biji alpukat, triolein, metil oleat, biodiesel, transesterifikasi.

1. Introduction

Domestic demand for fuel oil is estimated to increase from 327 million barrels in 2011 to 578 million barrels in 2030 [1]. If this increase in fuel demand is not matched by an increase in production, then the availability of fuel in the future is a serious problem for us. Therefore, we need to make efforts to develop alternative fuels from renewable sources such as vegetable oils and animal fats. One of the vegetable oils that is quite abundant and wasted is used cooking oil. Used cooking oil contains triglycerides, so that used cooking oil can be used as a raw material for making methyl oleic (biodiesel) [2].

Biodiesel is an environmentally friendly alternative fuel. The advantages of biodiesel are reducing exhaust gas emissions which include hydrocarbon (HC), carbon monoxide (CO), sulfur monoxide (SO), and other particles [3]. Biodiesel also has a fairly high cetane number (CN), excellent lubricity, a relatively high flash point at 154°C, and is biodegradable [4] [5]. Biodiesel can be synthesized from vegetable oil derived from renewable natural resources and Indonesia is rich in vegetable natural resources [6] [7]. Several studies have been carried out in search of raw materials that have the potential to make biodiesel, including

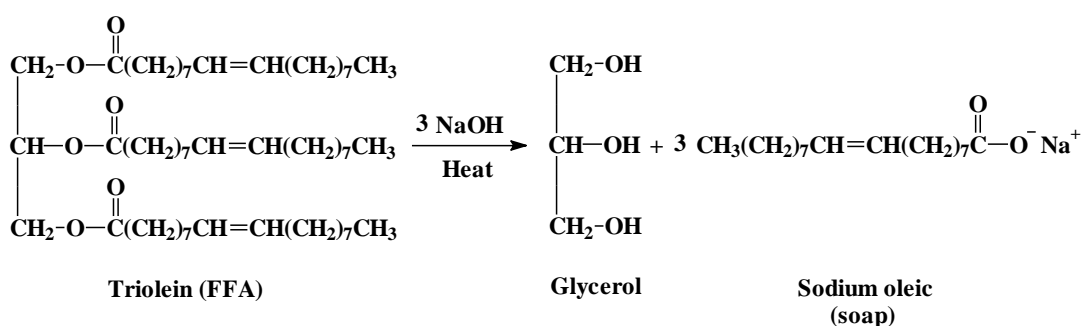


Figure 1. The saponification reaction of triolein (FFA) to form glycerol and soap

jatropha seeds [8] [9], avocado seeds [10] [11] [12], soybean [13], peanuts [14], sunflower [15] [16], moringa seeds [17], and used cooking oil [18] [19] [20].

Used cooking oil contains 84% (w/w) of oleic acid as FFA [20] [21]. If the FFA level of used cooking oil is > 2% (w/w) directly transesterified with an alkaline catalyst, the triolein or FFA will be hydrolyzed by the base (saponification) to form soap and glycerol (Figure 1). If a large enough amount of soap is formed, it can inhibit the separation of glycerol from methyl ester because emulsions can be formed during washing [2].

There are two ways that you can do to reduce the FFA level of used cooking oil. First, the method of purification using activated charcoal as an adsorbent. One of the

activated charcoal that can be used as adsorbent is avocado seeds. The use of avocado seeds as an adsorbent has been studied by Fitriani [22] and Kartika [23]. Second, the method of esterification by reacting FFA with methanol using a 98% (v/v) H₂SO₄ catalyst. The method of esterification can reduce the FFA level of used cooking oil by 78.34% (w/w), namely from 1.57 - 0.34% (w/w) [2].

The reaction used to synthesize methyl ester from used cooking oil is transesterification. The transesterification reaction is an interconversion reaction from an ester, triester or triglyceride to an ester by heating with an alcohol and an acid or base catalyst [24].

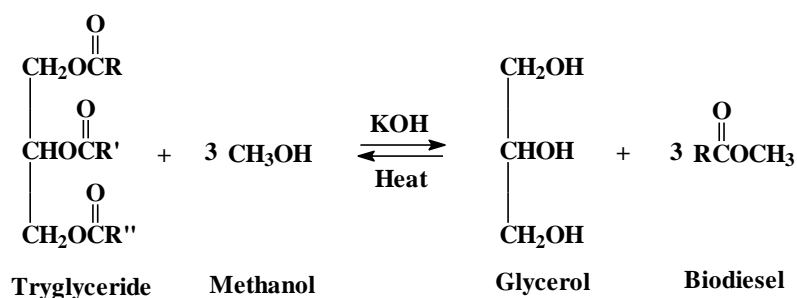


Figure 2. The transesterification reaction of triglyceride to form glycerol and biodiesel

The equilibrium of the above reactions can be pushed towards the formation of the product by using excess alcohol or triglycerides, or by removing glycerol as it is formed. Therefore, the method that can be used to produce biodiesel from used cooking oil with the highest yield is by adjusting the reaction conditions such as the mole ratio between the substrate and the reagent, temperature, reaction time, and the weight of the catalyst needed to activate the initial raw material.

2. Experiment

a. Tools and Materials

The tools used are a blender (Miyako), analytical balance (Ohaus), oven (Konka), bench furnace (BF-01), magnetic stirrer, spatula, filler, clamp, centrifuge tube (Merck), centrifuge (Kaida), 100 mesh sieve, statif and clamps, hot plate, three neck round bottom flask (Pyrex), desiccator. (Pyrex), dark bottle, stirring rod, measuring cup (Pyrex), beaker (Pyrex), Erlenmeyer (Pyrex), funnel (Pyrex),

separating funnel (Pyrex), porcelain mortar and pestle, and Buck M500 FTIR spectrometer (Scientific).

The materials used are used cooking oil, avocado seeds, methanol p.a, potassium hydroxide p.a, phenolphthalein (PP) indicator, chloroform p.a, concentrated hydrochloric acid p.a, concentrated sulfuric acid p.a, concentrated nitric acid p.a, starch indicator, potassium iodide p.a, sodium thiosulfate p.a, hexane p.a, Whatman filter paper No. 42, universal indicators, aluminum foil, tissue, and aquabidest (Onelab Waterone).

b. Production of Avocado Seed Active Charcoal

Avocado seeds are separated from the husk. Avocado seeds are dried in the sun for 3 days. Avocado seeds are carbonated in an aluminum tin container for 6 hours. Avocado seed charcoal crushed in a porcelain mortar. Avocado seed charcoal finely sifted to a size of 100 mesh. The avocado seed

charcoal was activated in 5% (v/v) HCl solution for 24 hours. Avocado seed activated charcoal is filtered and washed with aquabidest until the pH of the solution becomes neutral. Avocado seed activated charcoal dried in the oven at 110°C for 2 hours. Avocado seed activated charcoal characterized by FTIR.

c. Purification of Used Cooking Oil

Used cooking oil (150 mL) and avocado seed activated charcoal (2, 4, 6, 8, and 10) g are put into 5 different 500 mL beakers. The mixture was stirred with a magnetic stirrer for 2 hours at 70 °C. The mixture was allowed to stand for 12 hours then the mixture was filtered with Whatman No. 42 filter paper. Pure oil is collected in a beaker and the avocado seed activated charcoal residue is discarded [25].

d. Determination of FFA Content (ASTM D 664)

Pure oil (2 g), hexane (15 mL), and 95% (v/v) ethanol (20 mL) are put into the erlenmeyer flask. The mixture is stirred until homogeneous. To the mixture are added 3 drops of phenolphthalein indicator. The mixture was titrated with 0.1 M KOH until a pink color was formed. The FFA content of oil is calculated using equation (1).

$$\%FFA = \frac{V \text{ KOH}(\text{mL}) \times M \text{ KOH} \left(\frac{\text{mol}}{\text{mL}}\right) \times Mr \text{ FFA} \left(\frac{\text{g}}{\text{mol}}\right)}{\text{Sample Mass}(\text{g}) \times 1000} \times 100\% \quad (1)$$

If the FFA content of oil is < 2% (w/w), then biodiesel synthesis can be continued to the transesterification stage. Conversely, if the FFA content of oil is > 2% (w/w), then biodiesel synthesis starts from the esterification stage.

e. Synthesis of Methyl Oleic (Biodiesel)

Pure oil (triolein) (100 mL, 1 mol) (Mr triolein = 885.432 g/mol; d = 0.9078 g/mL) [26], methanol (121.394 mL, 3 mol) (Mr methanol = 32.04 g/mol; d = 0.7918 g/mL) [27], and (1, 8, and 16) % (w/w) NaOH by weight of oil put into the bottom flask round neck three which is equipped with a condenser and thermometer. The mixture was refluxed at 65 °C while stirring with a magnetic stirrer for 1 hour. The mixture was centrifuged for 60 minutes until two layers were formed. The top layer was methyl oleic as the main product and the bottom layer was glycerol as a side product. The layers were separated by a separating funnel. Methyl oleic was washed with aquabidest until the pH of the solution became neutral. Methyl oleic was dried with anhydrous magnesium sulfate until it became water free [32]. The same procedure was carried out for mol ratios (oil : methanol) (1 : 6) and (1 : 9),

as well as (1, 8, and 16) % (w/w) NaOH by weight of oil. The percentage of methyl oleic yield was calculated using equation (2).

$$\%Yield = \frac{\text{Mass of methyl oleic obtained}}{\text{Total mass of oil}} \times 100\% \quad (2)$$

f. Quality Test of Methyl Oleic [29]

Methyl oleic quality was tested based on Indonesian National Standard (INS) 04-7182-2015. Methyl oleic quality parameters tested were iodine number, saponification number, cetane number, water content, and acid number. The parameters of iodine number, saponification number, cetane number, water content, and acid number were determined using standard procedures of the International American Society for Testing and Materials [30].

3. Result and Discussion

a. Purification of Used Cooking Oil

The color change of used cooking oil before and after refining using avocado seed activated charcoal is shown in Figure 3. Figure 3 shows that the color of used cooking oil before and after purification has changed from reddish brown to yellow. This indicates that the particles causing turbidity and reddish brown color of used cooking oil have been absorbed by the activated charcoal adsorbent of avocado seed. This adsorption process occurs because the activated charcoal adsorbent of avocado seeds has a large surface area. The larger the adsorbent surface area, the greater the adsorbent capacity to adsorb an adsorbate.

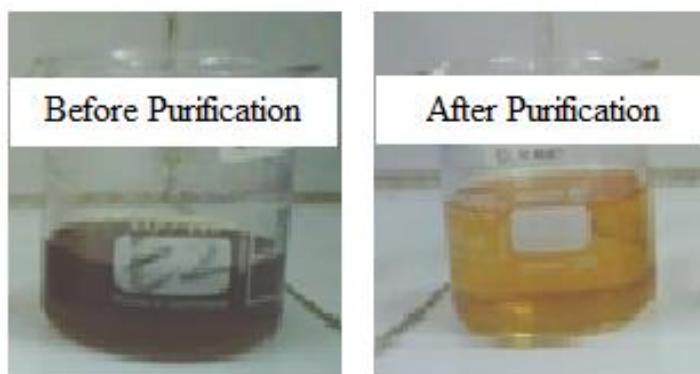


Figure 3. Changing color of used cooking oil before and after purification using avocado seed activated charcoal

No.	Frequency (cm ⁻¹) and Intensities	Frequency Ranges (cm ⁻¹)*	Group or Class	Type of Vibrations
			Alcohols, R-OH	

1	3414.00 (s)	3600 - 3200 (s)	Bonded -OH	OH stretch
2	1438.90 (s)	1440-1260 (s)		C-OH deformation
3	1042.20 (s)	1150 - 1040 (s)	Primary -CH ₂ OH	C-OH stretch
4	1101.60 (m)	1150 - 1050 (m)		C-O antisym stretch
5	809.00 (m) 800.46 (m)	970 - 800 (s)		C-C-O sym stretch
6	1375.25 (m)	1450 - 1350 (m)		C-OH in-plane bend
7	600.30 (m)	700 - 600 (m)		C-OH out-of-plane deformation
			Carboxylic acids, R-CO ₂ H	
8	3630.30 (m)	3650 - 3590 (s)	Free -OH	OH stretch
9	1695.43 (s)	1710 - 1680 (vs)		C=O stretch of dimer
10	1704.16 (m)	1705 - 1680 (m)		Aryl
11	1600.02 (s)	1610 - 1550 (s)		Antisymmetrical stretch
			Aliphatic, RH	
12	2922.10 (s)	2940 - 2920 (s)	Methylene, -CH ₂ -	C-H stretches in alkanes
13	2868.61 (s)	2970 - 2850 (s)	Methyl, -CH ₃	C-H stretch in C-CH ₃
14	1901.01 (m)	2000 - 1660 (w)	Aromatic, ArH	Overtone and combination bands
15	762.24 (m)	900 - 650 (s)		Out-of-plane CH deformations
16	2360.04 (s)	2400 - 2000 (s)	Nitriles, -C-C≡N	C≡N stretch
17	368.40 (s)	380 - 280 (s-vs)		C-C≡N bend
18	1234.44 (m)	1280 - 1220 (s)	Ethers, ROR'	C-O-C stretch in alkyl aryl ethers
19	570.03 (m)	675 - 570 (s)		O-C-O bend

Table 1. The results of the FTIR spectrum interpretation of avocado seed activated charcoal

The results of the FTIR spectrum interpretation of avocado seed activated charcoal are shown in Table 1. The FTIR spectrum of avocado seed activated charcoal (Table 1) shows that there is a wide absorption band at 3414.00 cm⁻¹ originating from the OH stretch vibration and strong and sharp absorption band at 1695.43 cm⁻¹ which comes from the C=O stretch vibration. This indicates that the activated charcoal of

avocado seeds has OH and C=O groups which function as active sites on the adsorbent surface. These active sites absorb impurities in used cooking oil, so that the used cooking oil becomes pure again. This is indicated by a reddish brown discoloration of used cooking oil which changes to a yellow color in pure oil.

b. Determination of FFA Content

The results of determining the FFA content of used cooking oil in various

variations of the active charcoal mass of avocado seeds can be seen in Figure 4. Figure 4 shows that avocado seed activated charcoal can reduce the FFA content of used cooking oil by 93.79% (w/w), namely from 7.08% (w/w) before purification (0 g of avocado

seed activated charcoal) to 0.44% (w/w) after purification (10 g of avocado seed activated charcoal). These results indicate that the higher the activated charcoal mass of the avocado seeds used, the lower the FFA content of used cooking oil.

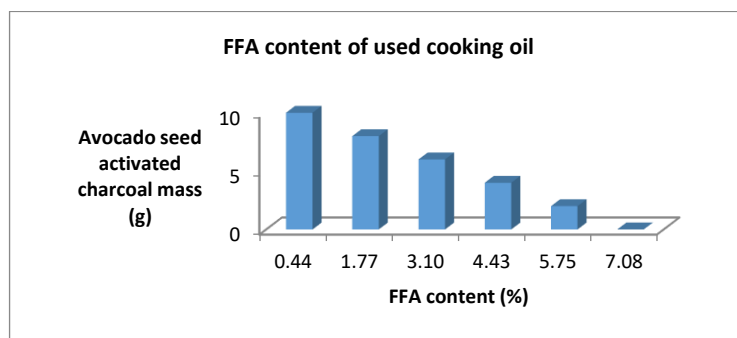


Figure 4. The results of determining the FFA content of used cooking oil in various variations of the avocado seed activated charcoal mass

The decrease in the FFA content of used cooking oil was due to the -OH sites on the surface of the avocado seed activated

charcoal reacting with FFA to form methyl oleic (ester) through an esterification reaction (Figure 5).

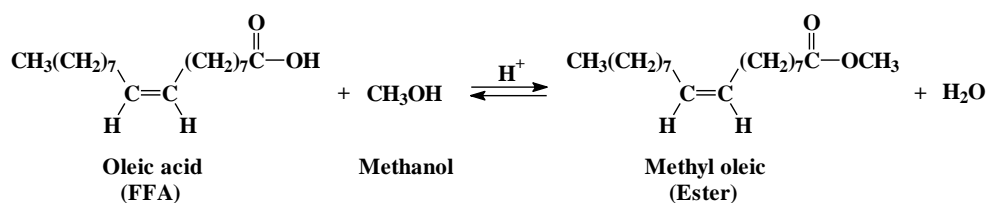


Figure 5. The esterification reaction of oleic acid (FFA) with methanol to form methyl oleic (ester)

According to Hashatan [34], if the FFA content of used cooking oil is < 2.00% (w/w), then the synthesis of methyl oleic (biodiesel) can only go through the transesterification stage. Conversely, if the FFA content of used cooking oil is > 2.00% (w/w), then the synthesis of methyl oleic (biodiesel) must go through two stages, namely esterification

and transesterification. The data in Figure 4 also shows that the FFA content of used cooking oil after purification using 10 g of avocado seed activated charcoal is 0.44% (w/w) < 2.00% (w/w). Therefore, the synthesis of methyl oleic in this study only went through the transesterification stage.

c. *Transesterification*

The result of transesterification of used cooking oil was a bifasa liquid (Figure 6). The lower phase is glycerol ($M_r = 92.09382$ g/mol; $\rho = 1.26$ g/cm³) [35] blackish brown.

Whereas the upper phase is biodiesel or methyl oleic ($M_r = 296.5$ g/mol; $\rho = 0.874$ g/cm³) [36] yellow, fragrant, and has a boiling point of 218°C.



Figure 6. Results of transesterification of used cooking oil

The yield of methyl oleic obtained from the transesterification reaction of

triolein and methanol using NaOH as a catalyst is shown in Table 2.

Mass of Triolein (g)	Mol Ratio (Triolein : Methanol) (mol)	Concentration of NaOH (% w/w)	Mass of Methyl Oleic (g)	Yield of Methyl Oleic (% w/w)
90.78	1 : 3	1	58.75	64.72
		8	54.18	59.68
		16	50.81	55.97
	1 : 6	1	62.54	68.89
		8	58.42	64.35
		16	54.58	60,12
	1 : 9	1	76.55	84.32
		8	71.97	79.28
		16	67.29	74,12

Table 2. The yield of methyl oleic obtained from various mol ratios of triolein and methanol and various NaOH concentrations as catalysts

The data in Table 2 shows that the transesterification reaction conditions that produce methyl oleic with the highest yield (84.32% w/w) was the mol ratio (triolein :

methanol) (1 : 9) with a concentration of 1% (w/w) NaOH. These results indicate that the higher the number of mol of methanol used, the higher the yield of methyl oleic. This is

because the addition of mol of methanol in the equilibrium system will increase the methanol concentration. To compensate for this pressure, part of the triolein reacts with the added methanol, and the equilibrium was shifted from left (reactants) to right

(products) (Figure 7). This is consistent with Le Chatelier's equilibrium principle, which states that when an external pressure is applied to an equilibrium system, the system adjusts in such a way that some of the pressure is balanced.

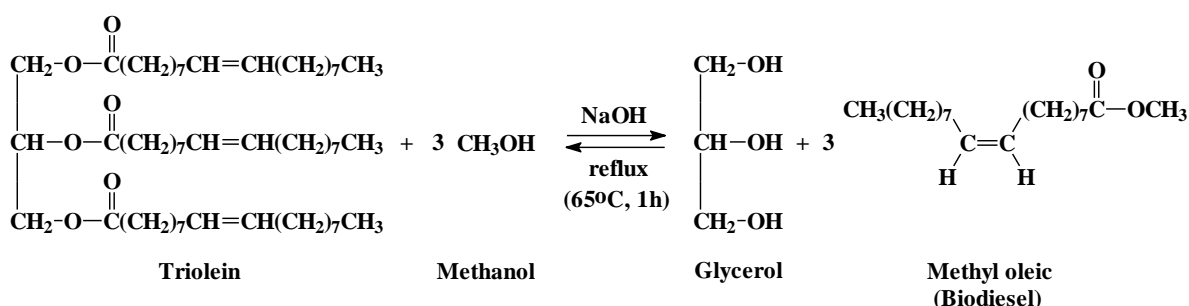


Figure 7. The transesterification reaction of triolein and methanol produces glycerol and methyl oleic (biodiesel)

The data in Table 2 also shows that the higher the concentration of NaOH catalyst, the lower the yield of methyl oleic obtained. We know that the catalyst increases the rate of reaction by decreasing the activation energy of the reaction. The catalyst lowers the activation energy of the forward and reverse reactions to the same level. Therefore, we can conclude that the presence of a catalyst does not change the equilibrium constant, nor does it shift the position of the equilibrium system. The

addition of the concentration of NaOH catalyst to 8% and 16% actually triggers the saponification reaction, in which triolein was hydrolyzed by alkalis (saponification) to form soap and glycerol. This is in accordance with the results of research by Ningtyas [37] and Ramdja [38] which concluded that the use of NaOH catalyst concentrations above 1.5% (w/w) will cause a saponification reaction.

No.	Frequency (cm ⁻¹) and Intensities		Frequency Ranges (cm ⁻¹)*	Group or Class	Type of Vibrations
	Triolein	Methyl oleic (biodiesel)			
1	2857.65 (s)	2854.65 (vs)	2970 - 2850 (s)	Aliphatic, RH Methyl, -CH ₃	C-H stretch in C-CH ₃
2	1441.89 (m)	1438.90 (s)	1470 - 1435 (m)		CH ₃ antisym deformation

3	1375.27 (m)	1367.53 (m)	1390 - 1360 (m)		CH ₃ sym deformation
4	2922.16 (s)	2924.09 (vs)	2940 - 2920 (s)	Methylene, -CH ₂ -	C-H stretches in alkanes
5	1457.25 (s)	1460.11 (s)	1470 - 1450 (m)		CH ₂ deformation
6	3007.02 (m)	3003.17 (m)	3040 - 3005 (m)	Vinylene or Ethenyl -CH=CH-	=CH ₂ stretch
7	1651.07 (m)	1649.14 (w)	1665 - 1635 (w)		C=C stretch (cis isomer)
8	730.15 (s)	721.38 (s)	730 - 665 (s)		CH out-of-plane def (trans isomer)
9	1741.72 (vs)	1743.65 (vs)	1765 - 1720 (vs)	Esters, RCOOR'	C=O stretch
10	1160.86 (vs)	1160.86 (vs)	1290 - 1110 (vs)		C-O-C antisym stretch
11	671.23 (s)	580.30 (s)	675 - 575 (s)		O-C-O bend

°Notes: vbr = very broad; vs = very strong; v = variable; s = strong; m = medium; w = weak.

*Sources: [31] [32] [33]

Table 3. The results of the interpretation of the FTIR spectrum of triolein and methyl oleic (biodiesel)

d. Analysis of FTIR Spectrum

The results of the interpretation of the FTIR spectrum of triolein and methyl oleic (biodiesel) are shown in Table 3.

The FTIR spectrum data in Table 3 shows that both triolein and methyl oleic (biodiesel) have a typical functional group absorption type of unsaturated fatty acid ester compounds. This can be seen by the presence of three absorption bands from the vinylene or ethenyl (-CH=CH-) groups, namely the medium absorption bands from the =CH₂ and C=C stretch appearing at 3003.17 and

1649.14 cm⁻¹, respectively, and the absorption bands strength of CH out-of-plane deformation at 721.38 cm⁻¹. The strong absorption bands of the C-H stretch of methylene (-CH₂-) and methyl (-CH₃) groups appeared at 2924.09 and 2854.65 cm⁻¹, respectively. Meanwhile, the very strong absorption band of the ester (RCOOR') groups, namely the C=O stretch, the C-O-C antisymmetric stretch, and the O-C-O bend appeared at 1743.65, 1160.86, and 580.30 cm⁻¹, respectively.

Parameter	Methyl Oleic (Biodiesel)	INS 04-7182-2015
Iodine number (g I ₂ /g sample)	4.44	Max. 115
Saponification number (mg KOH/g sample)	114.44	Min. 96.5

Cetane number	82.96	Min. 51
Water content (% b/b)	0,03	Max. 0.05
Acid number (mg KOH/g sample)	0.71	Max. 0.8

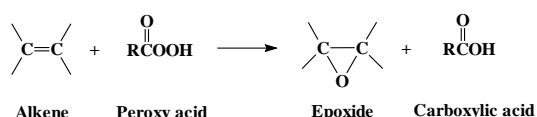
Table 4. The results of methyl oleic quality testing

e. Quality Test of Methyl Oleic

The results of the methyl oleic quality test are shown in Table 4. The data in Table 4 appears that the quality of the methyl oleic produced is in accordance with the quality requirements of biodiesel according to INS 04-7182-2015.

Iodine Number

The analysis results in Table 4 show that the iodine number of methyl oleic is 4.44. The higher the iodine number, the more double bonds $>C=C<$ there will be in the methyl oleic. Therefore, the high iodine number is an unfavorable property for methyl oleic. This is because methyl oleic which has a double bond $>C=C<$ in high amounts will be easily oxidized to form epoxide when the methyl oleic comes in contact with epoxy acid. This process is known as epoxidation.



The epoxidation reaction above appears that peroxy acid breaks down into carboxylic acids. This carboxylic acid will

cause corrosion in the combustion engine when methyl oleic is used as fuel.

Saponification Number

The saponification number is the amount of milligrams of KOH needed to lather one gram of biodiesel. The large saponification number indicates that biodiesel has a relatively small molecular weight. Conversely, a small saponification number shows that biodiesel has a relatively large molecular weight. So, the parameter of saponification number is a measure of the relative molecular mass of all the fatty acids present in biodiesel. The saponification number of methyl oleic obtained in this study was 114.44 mg KOH/g sample. Therefore, the saponification number of methyl oleic are in accordance with the quality requirements for biodiesel according to INS-04-7182-2015.

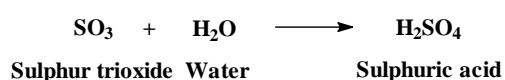
Cetane Number

Cetane number is a measure that shows the quality of diesel engine fuel. The cetane number shows how fast biodiesel can be injected into the fuel chamber so that it

can ignite spontaneously. The higher the cetane number, the easier it is for biodiesel to burn if it is compressed. Conversely, the lower the cetane number, the more difficult it is for biodiesel to burn if it is compressed. The implication, if the fuel is more easily compressed, the knock on the diesel engine will be reduced so that the engine noise can be smoother. The methyl oleic cetane number obtained in this study was 82.96. Therefore, this methyl oleic cetane number is in accordance with the quality requirements of biodiesel according to INS-04-7182-2015.

Water content

Based on the INS, the water content contained in biodiesel is a maximum of 0.05% (w/w). The data in Table 4 shows that the water content contained in methyl oleic is 0.03% (w/w). So, the water content contained in methyl oleic is lower when compared to INS. The high water content in biodiesel can cause combustion heat to decrease, foaming, and corrosive if it reacts with sulfur trioxide because it will form sulphuric acid.



Acid Number

The acid number is the number of milligrams of KOH needed to neutralize 1 gram of sample. The methyl oleic acid number as a result of the study was 0.71 mg KOH/g sample. This value meets biodiesel standards according to INS, which is a maximum of 0.8 mg KOH/g sample. This low acid number indicates that FFA can be removed through the adsorption process. Acid numbers that are too high are undesirable because at high temperatures FFA can react with metals such as iron, zinc, lead, manganese, cobalt, tin and other metals. This can accelerate the deterioration of diesel engine components.

4. Conclusion

Avocado seed activated charcoal can reduce the FFA content of used cooking oil by 93.79% (w/w), from 7.08% (w/w) before purification (0 g of avocado seed activated charcoal) to 0.44% (w/w) after purification (10 g of avocado seed activated charcoal). The optimum condition for the synthesis of methyl oleic from used cooking oil with the highest yield (84.32%) was the mol ratio (triolein : methanol) (1 : 9) with a concentration of 1% (w/w) NaOH. The quality of the resulting methyl oleic fulfills the requirements as biodiesel according to INS

04-7182-2015 with an iodine number value of 4.44 g I₂/sample, saponification number of 114.44 mg KOH/g sample, cetane number of 82.96, water content of 0.03% (w/w), and the acid number of 0.71 mg KOH/g sample.

The results of characterization of methyl oleic by FTIR showed that methyl oleic had a typical functional group absorption type of unsaturated fatty acid esters. This is indicated by the presence of a strong absorption band from the C-H stretch of methyl (-CH₃) and methylene (-CH₂-) groups appearing at 2854.65 and 2924.09 cm⁻¹, respectively. The medium absorption band of the vinylene or ethenyl (-CH=CH-) groups of =CH₂ and C=C stretch appeared at 3003.17 and 1649.14 cm⁻¹, and the strong absorption band from the CH out-of-plane deformation at 721.38 cm⁻¹. The very strong absorption band of the ester (RCOOR') groups, namely the C=O stretch, C-O-C antisymmetry stretch, and O-C-O bending appeared at 1743.65, 1160.86, and 580.30 cm⁻¹, respectively.

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References

- [1] Sugiono, A. 2014. Current Energy Problems and Policies. *Proceedings of the Launch Outlook Book of Indonesia Energy 2014 & Joint Seminar with BPPT and BKK-PII*. 9-16.
- [2] Dali, N., and Dali, A. 2019. Synthesis of Nitro Ethyl Oleic from Used Cooking Oil. *Al-Kimia*. Vol. 7(1): 46-55. doi: 10.24252/al-kimia.v7i1.7642
- [3] Zang, T. 2020. The Benefits of Biodiesel. *Green America*. (On line). (<https://www.greenamerica.org/green-living/benefits-biodiesel>, accessed September 17, 2020).
- [4] BPPT. 2018. Biodiesel Manufacturing and Testing Process. *Deepening of Material 3 Bioenergy 2 Technique (Bioethanol and Biodiesel)*. Jakarta.
- [5] Aziz, I., Nurbayti, S., and Ulum, B. 2011. Biodiesel Production from Used Cooking Oil by Esterification and Transesterification. *Valensi*. Vol. 2 (3): 443-448.
- [6] Dahlan, M. H., Siregar, H. P., and Yusra, M. 2013. The Use of Activated Carbon from Moringa Seeds Can Purify Cooking Oil. *J. Teknik Kimia*. Vol. 2, No. 19, 44-53.
- [7] Taufiq, M. 2007. *Purification of Used Cooking Oil Using Moringa Oleifera*

- Lamk Seeds.** Unpublished Thesis, Malang.
- [8] Niken, H., and Djajeng, S. 2011. Processing of *Jatropha curcas* L. Seeds Into a Source of Biofuels and Utilization of Side Products. **Buletin Teknologi Pascapanen Pertanian.** Vol. 7 (1): 37-43.
- [9] Kolo, S. M. D., Siburian, R. A. F., and Lulan, T. Y. K. 2016. Biodiesel Production from *Jatropha curcas* L. Seed Oil. **Bio-Edu: Jurnal Pendidikan Biologi.** Vol. 1 (1): 6-8.
- [10] Berghuisi, N. T., Tamako, P. D., and Supriadin, A. 2019. Utilization of Avocado Seeds (*Persea americana*) Waste as Biodiesel Raw Material. **al-Kimiya.** Vol. 6 (1): 36-45.
- [11] Rachmanita, R. E. and Safitri, A. 2020. Utilization of Avocado Seeds Oil (*Persea americana* Mill) as Raw Material for Making Biodiesel by Purifying Water Washing. **Jurnal Ilmiah Sains.** Vol. 20 (2): 88-99. doi: <https://doi.org/10.35799/jis.-20.2.2020.28266>
- [12] Risnoyatiningsih, S. 2010. Biodiesel from Avocado Seeds by Transesterification Process. **Jurnal Teknik Kimia.** Vol. 5(1): 345-351.
- [13] Buchori, L., Sasongko, S. B., Anggoro, D. D., and Aryanti, N. 2012. Soybean Oil Extraction from Tofu Dregs as Raw Material for Making Biodiesel. **Jurnal Ilmu Lingkungan.** Vol. 10 (2): 49-53.
- [14] Faputri, A. and Setiorini, I. 2020. Production of Biodiesel from Peanut Oil from Satay Traders Using 3 Process Stages and Differences in KOH Catalyst Concentrations. **Jurnal Teknik Patra Akademika.** Vol. 10 (02): 15-22.
- [15] Winarti, S. and Wicaksono, L. A. 2020. Utilization of Sunflower Seeds as Raw Material for Tempe Fermentation. **Agrointek.** Vol. 14(1): 112-121. doi: <https://doi.org/10.21107/agrointek.v14i1.6315>
- [16] Katja, D. W. 2012. Quality of Commercial Sunflower Oil and The Extraction Result Oil of Sunflower Seeds (*Helianthus annuus* L.). **Jurnal Ilmiah Sains.** Vol. 12 (1): 60-64.
- [17] Riskah, F., Ridhay, A., Mappiratu, and Rahim, E. A. 2019. Production of Methyl Oleat Through Methanolysis Reaction of *Moringa oleifera* Lam Seeds Oil. **KOVALEN: Jurnal Riset Kimia.** Vol. 5(1): 1-8.
- [18] Prasetyo, J. 2018. Study of Utilization of Used Cooking Oil as a Raw Material for Making Biodiesel. **Jurnal Ilmiah Teknik Kimia.** Vol. 2(2): 1-10. doi: [10.32493/jitk.v2i2.1679](https://doi.org/10.32493/jitk.v2i2.1679)
- [19] Yandri, V. R. 2012. Utilization of Used Cooking Oil as Biodiesel to Fuel Unand Campus Buses in Padang. **Jurnal Aplikasi Ipteks untuk Masyarakat.** Vol. 1(2): 119-125.
- [20] Rezeika, S. H., Ulfin, I., and Ni'mah, Y. L. 2018. Synthesis of Biodiesel from Used Cooking Oil Using NaOH Catalysts with

- Variations in Transesterification Reaction Time and Performance Test with a Diesel Engine. *Akta Kimindo*. Vol. 3(2): 175-189. doi: <http://dx.doi.org/10.12962/j25493736.v3i2.3098>
- [21] Ouellette, R. J. 2018. *Introduction to General, Organic, and Biological Chemistry*. Macmillan Publishing Company, New York.
- [22] Fitriani and Nurulhuda. 2018. Purification of Used Cooking Oil Using Activated Avocado Seeds Adsorbent. *Jurnal Pendidikan Matematika dan IPA*. Vol. 9(2): 65-75. doi: [10.26418/jpmpipa.v9i2.26770](https://doi.org/10.26418/jpmpipa.v9i2.26770)
- [23] Kartika, G. F., Itnawita, T., Hanifah, A., Anita, S., Dewi, N. O. M., and Absus, S. 2017. Effect of Activators on The Ability of Avocado Seeds Powder (*Persea americana* Mill) to Absorb Lead(II) Ions. *Chimica et Natura Acta*. Vol. 5(1): 9-12. doi: <https://doi.org/10.24198/cna.v5.n1.12814>
- [24] Solomons, T. W. G. 1988. *Organic Chemistry*. 4th Edition. John Wiley & Sons, New York.
- [25] Marlinda, M., Sangi, M. S., and Wuntu, A. D. 2012. Analysis of Secondary Metabolite Compounds and Toxicity Test for Ethanol Extract of Avocado Seeds (*Persea Americana* Mill). *J. MIPA Unsrat*. Vol. 1(1): 27-32.
- [26] Wikipedia. 2020. *Triolein*. (On line). (<https://en.wikipedia.org/wiki/Triolein>, accessed June 07, 2020).
- [27] Wikipedia. 2020. *Methanol*. (On line). (<https://id.wikipedia.org/wiki/Metanol>, accessed September 15, 2020).
- [28] Aufar, A., and Hendra, K. R. 2017. *Synthesis of Methyl Ester Nitrate as a Solar Fuel Additives to Increase Cetane Numbers (CN)*. Department of Chemical Engineering ITS, Surabaya.
- [29] SNI. 2015. Biodiesel, SNI 04-7182-2015. Indonesian National Standard Agency, Jakarta.
- [30] ASTM. 1998. Standard Test Methods of Petroleum Products. *Annual Book of ASTM Standards*. 05.01, 845-847.
- [31] Kemp, W. 1991. *Organic Spectroscopy*. 3rd Edition. Macmillan Education Ltd, London.
- [32] Lambert, J. B., Gronert, S., Shurvell, H. F., Lightner, D. A. 2011. *Organic Structural Spectroscopy*. 2nd Edition. Prentice Hall, Boston.
- [33] Sastrohamidjojo, H. 1992. *Infrared Spectroscopy*. 1st Edition. Liberty, Yogyakarta.
- [34] Hashatan, D., Sunaryo, J., and Komariah, L. N. 2012. Effect of H₂SO₄ Ratio and Reaction Time on the Quantity and Quality of Biodiesel from Jatropha Oil. *J. Teknik Kimia*. Vol. 2(18): 26-36.
- [35] Wikipedia. 2020. *Glycerol*. (On line). (<https://en.wikipedia.org/wiki/Glycerol>, accessed May 02, 2020).

- [36] Pubchem. 2020. **Methyl oleate**. (Online). (https://pubchem.ncbi.nlm.nih.gov/compound/methyl_oleate, accessed August 17, 2020).
- [37] Ningtyas, D. P. 2013. Effect of Base Catalyst (NaOH) in the Transesterification Reaction Stage on the Quality of Biofuel from Sardine Fish Meal Oil. **Jurnal Teknosains**. Vol. 2(2): 35-40.
- [38] Ramdja, A. F., Febriana, L., and Krisdianto, D. 2010. Purification of Used Cooking Oil Using Sugarcane Dregs as Adsorbent. **Jurnal Teknik Kimia**. Vol. 17(1): 23-33.