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Synthesis of Biodiesel from Refined Waste Cooking Oil with Active Natural Zeolite as Catalyst

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Abstract

This research evaluates refining waste cooking oil with active natural zeolite, utilizes it for biodiesel synthesis, and characterizes the synthesized methyl ester. This experimental laboratory research was carried out: (1) activation of natural zeolite, (2) refining waste cooking oil with active natural zeolite, (3) determination of free fatty acid (FFA) content of the oil, (4) transesterification with KOH catalyst, (5) characterization of the synthesized methyl esters according to the SNI 7182:2015, and (6) identification of the methyl ester component by GC-MS. The results showed that the FFA content of the refined waste cooking oil using active natural zeolite with concentrations of 10%, 20%, and 30% per mass of oil were 2.97, 2.0, and 1.56%, respectively. The yield of methyl ester transesterified with various concentrations of KOH (0.8, 1.0, and 2% per mass of oil), respectively, were 80.13, 85.34, and 74.98%. The synthesized methyl ester resulted in the characteristics: 0.867 g/mL of density; 5.72 cSt of viscosity; 1.449 of refractive index; 1.46 g KOH/g of acid number; and 0.023% of water content. Identification of GC-MS obtained the synthesized methyl esters, which include: 46.10% of methyl hexadecanoic, 41.68% of methyl 9-octadecanoic, 6.42% of methyl octadecanoic, and 5.80% of methyl eicosanoic.

Keywords: *Waste cooking oil**,** Activation, Natural Zeolite, Refinement, Transesterification*

INTRODUCTION

Highly fossil fuel-based transportation causes an increasing need for energy resources. Energy is a basic human need that increases the level of life. Energy resources include air, water, nuclear, solar, petroleum, and other energy which are used to support daily life (Zou, Zhao, Zhang, & Xiong, 2016). One of the most widely used energy sources is petroleum (Telussa, Fransina, Singerin, & Taipabu, 2023). Petroleum is a non-renewable fossil fuel in nature, and its formation takes thousands of years (Perea-Moreno, Samerón-Manzano, & Perea-Moreno, 2019). The use of petroleum has polluted the global environment. So for a sustainable future, renewable energy started to be explored. So, biodiesel is one of the new renewable energies that are potential to be developed (Santoso et al., 2021).

Biodiesel is a renewable fuel synthesized from vegetable/animal oils through a transesterification reaction (Musta, Haetami, & Salmawati, 2017). Biodiesel has advantages, i.e., better emissions and biodegradability, and does not contribute to global warming (Zulqarnain et al., 2021). Then, more than 90% of biodiesel can be biologically degraded for 21 days (Gebremariam & Marchetti, 2017).

Methyl ester (biodiesel) is a slow process of synthesis via transesterification reaction (Athar, Zaidi, & Hassan, 2020). To speed up the process, a catalyst is needed. Catalysts consist of several types, including acid, base, and enzyme. In this study, the catalyst used was an alkaline catalyst, namely KOH. The basic catalyst was chosen because the base catalyst has advantages compared to the acid catalyst in reactivity, completeness of the reaction, and mild reaction. (Santoso, Sumari, & Asrori, 2022).

Waste cooking oil is a potential raw material for biodiesel synthesis (Rachim, Raya, & Zakir, 2017). Waste cooking oil has a high free fatty acid content of up to 5-30% w/w (Thoai, Le Hang, & Lan, 2019). Highly free fatty acid cause saponification reactions. To solve the problem, pre-treatment is executed to reduce the free fatty acids in waste cooking oil.

Biodiesel can be synthesized from waste cooking oil without pretreatment assisted by microwave

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(Hong, Jeon, Kim, & Lee, 2016). This study's weakness is that the oil's highly free fatty acid content will increase the use of microwave energy and the amount of catalyst. Biodiesel processing technology of waste cooking oil showed that using microfiltration techniques can improve the quality of the raw materials by reducing the free fatty acid content by 13% - 72% (Setiawati & Edwar, 2012). However, the weakness of the microfiltration technique is its long-time operation, so it is less effective for large-scale production.

The reduction of free fatty acid (FFA) can be carried out through an esterification reaction. The treatment causes the remaining reactants to remain in the esterification product. If it is not properly washed, it will affect the next result (Sumari, Santoso, & Asrori, 2021). One technique to reduce free fatty acid content is adsorption using natural zeolite. Zeolites are a group of compounds consisted of hydrated aluminosilicate minerals with alkaline earth metal cations in a three-dimensional framework (Fattahi, Triantafyllidis, Luque, & Ramazani, 2019). Zeolite used as an adsorbent because it has a porous structure interacted with water and cations. Refinement of waste cooking oil with natural zeolite resulted that natural zeolite can reduce the acid number in waste cooking oil (Hartono & Suhendi, 2020).

Based on the above studies, it is necessary to research waste cooking oil to reduce free fatty acid levels using natural zeolite and the synthesis of methyl ester (biodiesel) from refined waste cooking oil. Therefore, this study aims to study: (1) the free fatty acid content of the refined waste cooking oil using natural zeolite, (2) the yield of methyl ester synthesized using KOH catalyst, (3) the character of methyl ester resulting from the transesterification of waste cooking oil, (4) component analysis resulting from the synthesized methyl ester.

METHODOLOGY

Materials and Instrumentals

The glassware in this study included a reflux apparatus, 100 ℃ thermometer, burette, separating funnel, Beaker, measuring cup, watch glass, three-neck flask, Erlenmeyer, glass bottle, dropper pipette, volume pipette, and test tube. The non-glass tools in this study were hoses, aluminum foil, label paper, filter paper, pycnometer, stopwatch, universal indicator paper, pestles, mortar, clamps, filler, magnetic stirrer spray bottles, hot plates, 100 mesh filters, furnaces, and ovens. The instruments used in this study included the GC-MS spectroscopy (Shimadzu, Type: GCMS QP2010 Plus), the Abbe refractometer, and the Oswald viscometer.

The materials used in this study included distilled water, KOH (p.a), phenolphthalein indicator, 96% ethanol, natural zeolite taken from Malang region, oxalic acid dihydrate (p.a), methanol (p.a), and household waste cooking oil.

Activation of Natural Zeolite

Natural zeolite was crushed by a 100 mesh sieve. Furthermore, the zeolite was activated at 300 ℃ for 2 hours. Then, the zeolite washed by distilled water. Furthermore, the zeolite was put in an oven for 2 hours at 150 ℃.

Refinement of waste cooking oil

Initially the waste cooking oil was tested for FFA levels as a comparison. Refinement of waste cooking oil is carried out by adding 10, 20, and 30% active zeolite respectively to 20 grams of oil in a glass beaker. Furthermore, the heating process was operated for 1 hour. After 1 hour, the oil was cooled for a while and continued filtering. The color of the refined oil was observed, and its FFA was calculated.

Determination of Free Fatty Acid (FFA)

Amount ±1 gram of oil put into the Erlenmeyer, then, 10 mL of methanol (p.a) was added to the oil and heated to boiling. After cooling, the mixture was titrated with 0.01 N KOH solution and 3 drops of phenolphthalein indicator. The volume of KOH used for the titration was recorded. The determination was carried out in duplicate. FFA content was calculated using Equation 1.

$$\text{FFA} = \frac{\text{N KOH x V KOH x MW}}{\text{M Sample x 1000}} \text{x } 100\% \qquad (1)$$

Notes: N KOH = Normality of KOH (N), V KOH = Volume of KOH (mL), M Sample = weigh of the oil (g), MW = molecular weight of fatty acid of the oil (g/mol).

Transesterification

Amount 20 g of refined waste cooking oil samples were put into a three-neck flask. The oil was then heated at ±65 ℃. Then, 9.02 g of methanol was added to the three-neck flask for each addition of KOH catalyst with KOH concentrations are 0.8%, 1%, 2% w/w oil (mole ratio of oil to methanol was 1:12).

Data Analysis

The methyl ester characterization steps included refractive index, density, viscosity, and acid number.

The refractive index was characterized by an Abbe refractometer. The reading of the refractive index value was observed by adjusting the light and dark lines to the exact cross position of the observation lens. The refractive index was calculated using Equation 2.

$$n = n' + k(T' - T) \qquad (2)$$

n is value of refractive index at 25 ℃, n is value of refractive index at temperature of observation, k is correction factor (0.00045), T' is temperature of observation, and T is temperature of 25 ℃. This test was carried out twice repetition.

The density test was carried out by weighing the empty pycnometer and recording the weight. The sample was then put in the pycnometer until full. It was then weighed. This test was carried out twice repetition. Density values can be determined by Equation 3.

$$\rho\left(\frac{\text{g}}{\text{mL}}\right) = \frac{\text{Mass picnometre + methyl ester – Mass picnometre}}{\text{Volume methyl ester}} \qquad (3)$$

Viscosity test was conducted using Ostwald viscometer, distilled water was used as a comparison. This test was carried out twice repetition. The value of viscosity can be determined by Equation 4.

$$\frac{\eta 1}{\eta 2} = \frac{\rho 1 \text{ x } t1}{\rho 2 \text{ x } t2} \qquad (4)$$

η1 is viscosity of methyl ester (cSt), η2 is viscosity of distilled water (cSt), ρ1 is density of methyl ester (g/mL), ρ2 is density of distilled water (g/mL), t1 is flow time of methyl ester (s), t2 is distilled water flow time (s)

The acid number test was carried out by weighing ±1 g of methyl ester sample from waste cooking oil into a 250 mL Erlenmeyer. Then added 10 methanol p.a. and heated on a hot plate until boiling. After cooling, this solution was titrated with 0.01 N KOH and 3 drops of phenolphthalein indicator. This test was carried out twice repetition. The value of the acid number can be determined by Equation 5.

$$\text{Acid number} = \frac{\text{V x N x Molar Mass KOH}}{\text{Sample mass}} \qquad (5)$$

V is volume of KOH (mL), N is normality of KOH (N), Molar mass of KOH is 56.1, and sample mass is sample weight (g). The water content test was carried out by weighing 3 grams of the methyl ester sample and placing it into a cup that was known mass. The sample and cup were then dried in an oven at 105 ^{o}C for 3 hours. Furthermore, the mixture was cooled, weighed, and dried again until a constant mass was obtained. The water content was calculated using Equation 6.

$$\text{Water content} = \frac{a-(b-c)}{a} \qquad (6)$$

Value (a) is initial sample mass, b is final sample mass + cup, and c is cup mass. The characterization was then compared with SNI (Standar Nasional Indonesia) biodiesel (SNI 7182:2015). The main component of methyl ester from waste cooking oil was determined by chromatogram analysis from gas chromatography-mass spectrometer (GC-MS) instrument analysis.

RESULTS AND DISCUSSION

Activation of Natural Zeolite

In this process, the size of the zeolite is reduced. This process is carried out to obtain a larger zeolite size. The water trapped in the cavities of the natural zeolite was removed by heating process at high temperatures (calcination) (Oktaviani, Hindryawati, & Panggabean, 2019). The refining waste cooking oil shown in Figure 1.

Figure 1. Natural Zeolite Size Reduction

Refinement of Waste Cooking Oil

Before refining waste cooking oil, the levels of free fatty acids (FFA) were first measured as a compared to the decrease in FFA content after refining. Photograph view of oil before and after refining can be seen in Figure 2. Waste cooking oil before refining have colur cloudy brownish yellow. There was a color change in waste cooking oil purified using the active natural zeolite. Waste cooking oil refined with 10% zeolite resulted in brownish yellow color, but it was clearer than the initial oil. In 20% of the zeolite, the color of the oil was the brown color. In 30% of the zeolite, the oil color was clear yellow.

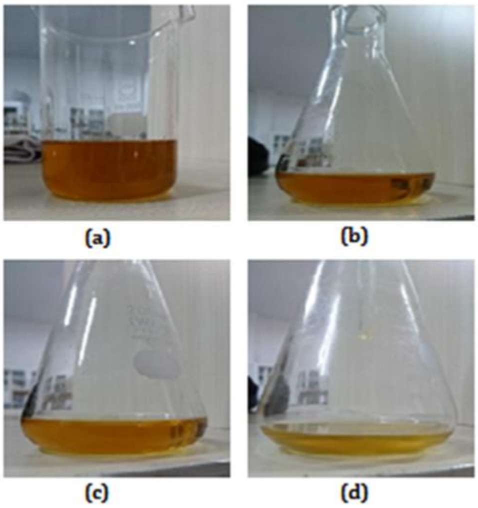

Figure 2. (a) Waste cooking oil before refining, and waste cooking oil after refining (b) using 10% of the zeolite, (c) using 20% of the zeolite, (d) using 30% of the zeolite

The oil's color change can be used as the first indicator of successful refining of waste cooking oil. Another indicator that shows the success of refining is the decrease in free fatty acids in the oil after refining (FFA < 2%), as listed in Table 1.

Table 1. Free Fatty Acid of Waste Cooking Oil

	Non-refined cooking oil	Waste Cooking Oil After Refinement		
		10% zeolite	20% zeolite	30% zeolite
Acid content	5.795	2.980	2.000	1.575

Based on Table 1, there was a decrease in free fatty acid levels in refine process with 10, 20 and 30% of the zeolite respectively to 2.980, 2.000, and 1.575%. The free fatty acid content meets the requirements (FFA<2%) to proceed to the transesterification reaction.

Transesterification Reaction

Synthesis of methyl esters of the refined waste cooking oil through the transesterification reaction was carried out under the conditions (the reaction temperature of 65 ℃, the mole ratio of methanol to KOH moles of 12:1, and the reaction time of 2 hours). KOH concentrations were 0.8, 1, and 2% of the oil mass. The final result of transesterification process can be seen in Figure 3. When the KOH catalyst was dissolved into methanol will form methoxide ions. This reaction takes place in equilibrium (Vakros, 2018). Figure 3 shows that the transesterification produces two layers. The top layer, clear yellow, was thought to be methyl ester. The bottom layer, brownish yellow was thought to be glycerol, catalyst residue, methanol residue, and unreacted oil residue (Zarli, 2020).

Figure 3. Results of transesterification: top layer (methyl ester) and down layer (glycerol and residues)

The separation results of the transesterification reaction after washing and heating can be seen in Figure 4. The yield of methyl ester from each variation in KOH concentration was then calculated. The yield of methyl ester can be seen in Table 2.

Table 2. Yield of Transesterified Methyl Esters

Molar ratio of oil : methanol	Oil	KOH (%)	Yield (%)
1 : 12	Waste cooking oil	0.8	81.12
		1	85.13
		2	74.64

Figure 4. Results of the transesterification reaction after washing and heating (left to right respectively: 0.8; 1.0; and 2% of KOH)

Based on Table 2, the highest yield of methyl ester was 85.34%. The more catalyst added after 1% KOH, the more likely it is to form soap (Zahan & Kano, 2018). Then, it will be continued by GCMS analysis.

Characterization of The Synthesized Methyl Esters

The methyl ester was further characterized by testing the acid number, viscosity, density, refractive index, and water content. Furthermore, the resulting methyl ester is compared with the SNI, as listed in Table 3.

Table 3. Characteristics of The Synthesized Methyl Ester

Parameter	Methyl ester	Biodiesel (INS, 2015)
Acid number (mg/g)	1.46	Max 0.50
Density (g/ml)	0.8663	0.850-0.890
Viscosity (cSt)	5.715	2.30-6.00
Refractive index	1.4495	Max 1.45
Water content	0.023	Max 0.02%

Based on Table 3, the acid number indicates biodiesel quality. A high acid number value indicates damage or a decrease in biodiesel quality. Biodiesel (methyl ester) with low acid numbers will not easily corrode the metals in the engine (Rocha et al., 2019). A high acid number value will cause a higher chance of engine damage. The acid value of biodiesel in this study was 1.46 mg KOH/g biodiesel which is more than the standard quality.

Based on Table 3, the density value exceeding the quality standard, it can accelerate the occurrence of damage to the engine. The density value has met the biodiesel quality standards, so it has the potential to be used as diesel fuel. The average density of the synthesized methyl ester is 0.8665 g/mL, which is different from the density of waste cooking oil, which is 0.9125 g/mL. The decrease in the density value is due to the triglyceride structure in the oil after the transesterification process. It showed that the synthesis had produced a new compound (methyl ester) as a product of the synthesis. Based on Table 3, viscosity is a measure of the thickness of a liquid. Viscosity has a significant influence on the effectiveness of methyl ester as fuel. The viscosity in the study was 5.715 cSt which is still suitable within the SNI standard.

The refraction index is the ratio between the speed of light in air and light in a particular medium. One factor affecting the value of the refractive index is the temperature factor. If the temperature is too high, the methyl ester will undergo oxidation, breaking the double bond in the molecule. The loss of the double bond results in the saturated oil and will lower the refractive index value of the methyl ester (Fitriana & Fitri, 2019). The refractive index of the synthesized methyl ester in this study differs from the refractive index of waste cooking oil, which is 1.465. This indicates that a methyl ester compound has been formed as a product of the synthesis. The refractive index of methyl ester is lower than that of common oils. The intermolecular forces of the synthesized methyl ester are weaker than the intermolecular forces of waste cooking oil. The weak intermolecular forces will cause the density between the molecules to be more tenuous (Effendy, 2017).

Water content is one of the biodiesel quality standards. The maximum water content based on SNI is a maximum of 0.05%. High water content in biodiesel causes a decrease in heat during combustion and provides a pollutant for biodiesel. The water content of the synthesized methyl ester meets the SNI requirement, namely 0.023%.

Identification of Compounds

Identification compound using GC-MS aims to determine the compounds of the synthesized methyl ester. The resulting GC-MS spectrum is then presented in the GC-MS chromatogram results of the synthesized methyl ester, as shown in Figure 5. Based on Figure 5, the methyl ester of waste cooking oil consists of four main constituent compounds, which can be seen in Table 4, and their mass spectrum (MS) can be observed in Figure 6.

The Mass Spectrum peaks of the synthesized methyl ester were then matched with the mass spectrum in the library of Library: NIST17.lib. Then, the peaks with similar or almost the same position are determined. At a retention time of 29.133 minutes, observations obtained peaks with positions similar or almost identical to those found in Library: NIST17.lib entry number: 144285. The compound was analyzed as methyl hexadecanoate or methyl palmitate. At a retention time of 35.599 minutes, observations obtained peaks with similar or almost identical positions in the library: NIST17.lib entry number: 172449. The compound was analyzed as methyl 9-octadecanoic or methyl oleate. At 36.336 minutes, the observations obtained peaks with similar or almost identical positions in the library: NIST17.lib entry number: 174885; the compound was analyzed as methyl octadecanoic or methyl stearate. At a retention time of 48,187 minutes, observations obtained peaks with positions similar or almost the same as those in the library: NIST17.lib entry number 185517, the compound was analyzed as methyl eicosanoid or methyl arachidonate.

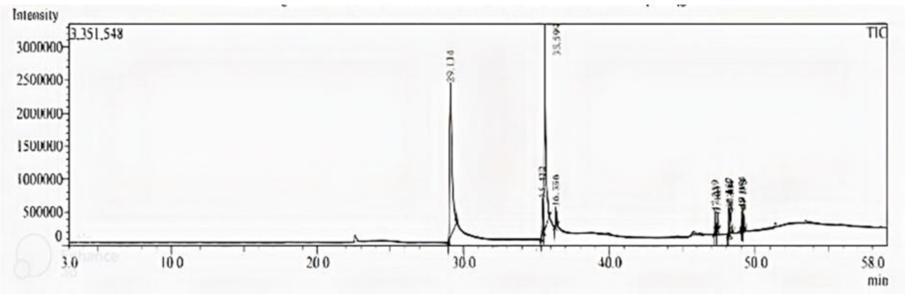

Figure 5. GC-MS Chromatogram of Methyl Ester

Table 4. Components of Methyl Ester

Peak	Retention time	Area	Area% (content)
1	29.133	26550447	46.10
3	35.599	24001909	41.68
4	47.239	1566616	6.42
7	48.187	3344382	5.80
Total		57591351	100.00

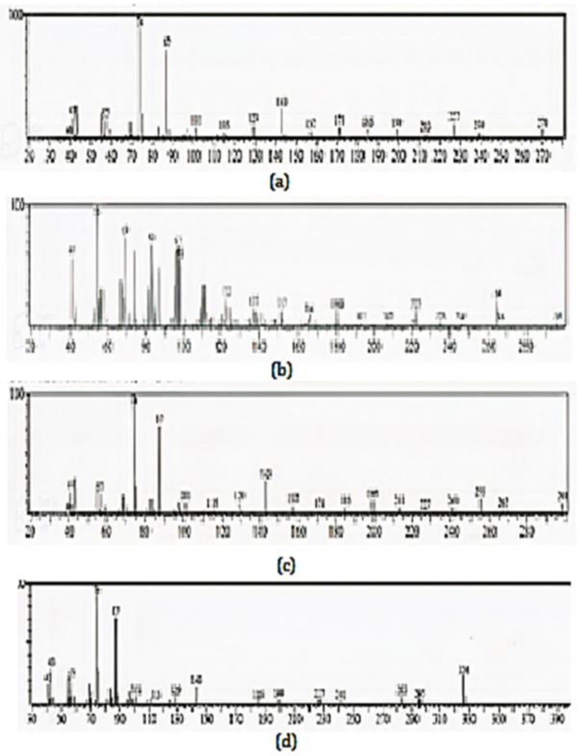

Figure 6. Methyl Ester Mass Spectrum with Retention Time (RT) (a) 29.133 Minutes (b) 35.599 Minutes, (c) 36.336 Minutes, and (d) 48.187 Minutes

Based on the GC-MS results, it is known that these four compounds are the main constituents of the methyl ester mixture. These compounds are methyl hexadecanoic or methyl palmitate (46.10%), methyl 9-octanoate or methyl oleate (41.68%), methyl octadecanoic or methyl stearate (6.42%), and methyl eicosanoid or methyl arachidonate (5.80%).

CONCLUSION

Based on the results, the following conclusions can be stated: (1) There was a decrease in the free fatty acids (FFA) content of waste cooking oil from 5.795% to 2.97%; 2.0%; and 1.56% after refinement using active natural zeolite at concentrations of 10, 20, and 30% per mass of oil, (2) Yields of the synthesized methyl ester with variations in KOH concentration of 0.8; 1.0; and 2% per mass of oil respectively were 80.125; 85.34; and 74.98%, (3) Characterization of the synthesized methyl ester has met SNI 7182:2015 with values namely, the density of 0.867 g/mL; viscosity 5.72 cSt; refractive index 1.449; and water content of 0.023%. However, the acid number of 1.46 mg KOH/mg methyl ester did not meet the SNI, (4) For GC-MS results, the synthesized methyl ester compounds were methyl hexadecanoic or methyl palmitate (46, 10%); methyl 9-octanoate or methyl oleate (41.68%); methyl octadecanoic or methyl stearate (6.42%); and methyl eicosanoid or methyl arachidonate (5.80%).

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