
Research article

Synthesis of biodiesel from waste cooking oil using heterogeneous catalyst of $\text{Na}_2\text{O}/\gamma\text{-Al}_2\text{O}_3$ assisted by ultrasonic wave

Aman Santoso^{1,*}, Titania Nur Kusumah¹, Sumari Sumari¹, Anugrah Ricky Wijaya¹, Rini Retnosari^{1,2}, Ihsan Budi Rachman^{1,3}, Siti Marfuah¹ and Muhammad Roy Asrori¹

¹ Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Malang, Jalan Semarang No. 5, Malang, 65145, Indonesia

² Department of Chemistry, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600, UKM Bangi, Selangor, Malaysia

³ Graduate School of Engineering and Science, Shibaura Institute of Technology, Fukasaku 307, Saitama 337-8570, Japan

* **Correspondence:** Email: aman.santoso.fmipa@um.ac.id; Tel: +6281559959691.

Abstract: The synthesis of biodiesel *via* transesterification needs to be improved by the heterogeneous catalysts. So, the study aimed to determine the best conditions for the synthesis of biodiesel produced through a transesterification reaction using waste cooking oil with a $\text{Na}_2\text{O}/\gamma\text{-Al}_2\text{O}_3$ catalyst assisted by ultrasonic wave. The steps were: catalyst preparation, oil preparation, esterification, transesterification reactions using methanol and various $\text{Na}_2\text{O}/\gamma\text{-Al}_2\text{O}_3$ catalysts, and characterization. The results showed that the refined waste cooking oil using FTIR was known that there was still a carbonyl group indicating the presence of triglycerides. Free Fatty Acid content of waste cooking oil after esterification was 0.40%, so that the transesterification reaction could be carried out. The XRD results of the catalyst showed a conformity with the reference and it was determined by the Scherrer formula that the crystal size of the catalyst was 30.59 nm. The best condition for biodiesel synthesis was obtained at a catalyst ratio of 1:1 as much as concentration 3% w/w for 15 minutes of ultrasonication, 65 °C, and molar ratio of methanol: oil (12:1), for the yield of 83.51%. After identification through GC-MS, it was known that the main components in the transesterified biodiesel from waste cooking oil were methyl elaidate (38.54%), methyl palmitate (30.90%) and methyl linoleate (16.61%).

Keywords: heterogeneous catalyst; biodiesel; transesterification; ultrasonic wave; renewable energy

1. Introduction

Petroleum exploitation can affect environmental damage [1]. So, currently it is necessary to develop renewable and environmentally friendly fuels such as biodiesel. Biodiesel was an alternative fuel with a composition of fatty acid esters from vegetable oils [2]. One of the renewable natural resources was waste cooking oil because it contained triglycerides [3,4]. It is reusable raw materials and do not compete with food any more [5]. The waste cooking oil which was directly discharged into the environment without any prior processing can cause environmental pollution [6]. In addition, waste cooking oil can also affect the mineral content in clean water [7]. Therefore, the production of biodiesel from waste cooking oil is very profitable because it is cheap and can minimize environmental pollution.

Biodiesel can be produced by transesterification reaction between waste cooking oil and methanol assisted by a heterogeneous catalyst in recent years. For example, transesterification of oil with CuO-Al₂O₃ catalyst produced 78.5% biodiesel for 4 hours [8]. Study of biodiesel synthesis of waste cooking oil using CaO catalyst yielded biodiesel of 77,76% with 2 hours duration [9]. Study of Sodium Potassium Silicate as catalyst for transesterification of waste cooking oil showed 93.89% yield at 200 rpm, 2 hours, 2.5% concentration, 70 °C, and alcohol:oil (9:1) [10], and the use of Tangerine peel ashes for the same reaction showed 92% yield [11]. From the previous study, the biodiesel produced was still very little and required a long time. The reaction could be due to the low basicity of the catalyst. An alternative was to use a metal oxide which has a very strong base as the catalyst support [12]. The metal oxide which has a strong base source for the transesterification process was Na₂O [13]. The use of Na₂O catalyst needed to be supported or added to solids with large surfaces such as carriers or supports because Na₂O easily reacts with free fatty acid to form soap. [14]. Research on biodiesel synthesis using a Na₂O_{(20 wt%)/CNTs} catalyst with a 3% concentration resulted in the highest FAME yield at 65 °C, molar ratio of oil: methanol 1:20 for 3 hours, which was 97% yields [15].

A good buffer was γ -Al₂O₃ because it was stable at high temperatures and has a larger surface area [16]. Cr/Ca/ γ -Al₂O₃ catalyst in transesterification of cooking oil produced 92.79% yields at 18:1 ratio of methanol:oil, 65 °C, 6% wt, and 3 hours [17]. K₂O/ γ -Al₂O₃ catalyst in transesterification of rapessed oil produced 94% yields at 12:1 ratio of methanol:oil, 70 °C, 3% wt, and 3 hours [18]. NaOH/ γ -Al₂O₃ catalyst in transesterification of coconut oil produced 90% yields at 2:1 ratio of ethanol:oil, 60 °C, 3% wt, and 3 hours [19]. However, the reaction took a very long time, so that the other efforts were needed to increase the yield with a short reaction time [20]. The use of ultrasonic wave in the transesterification of waste cooking oil obtained the higher yield as compared to conventional [21]. Ultrasonic waves propagating in a liquid were able to make molecules compressed under pressure and increased the mass transfer rate of immiscible liquids [22,23].

Based on the description above, research on the synthesis of biodiesel from waste cooking oil using a heterogeneous catalyst Na₂O/ γ -Al₂O₃ assisted by ultrasonic waves needs to be done. This research was conducted to find the best yield with a catalyst variation of 3–5% w/w oil with a reaction time of <1 hour at 60 °C with a mole ratio of oil: methanol 1:12. The analysis will be represented by characterization and comprehensive understanding.

2. Materials and methods

This research was a laboratory experimental research that aimed to synthesize biodiesel from waste cooking oil. The materials for this research were waste cooking oil from collector (small fried food restaurant) in Malang, active natural zeolite from Chemistry Laboratory of Universitas Negeri Malang (natural zeolite was obtained from Malang, Indonesia), aquadest, KOH 0.01 N & 0.1 N, alcohol 95%, Phenolphthalein indicator, methanol p.a., H₂SO₄ p.a, MgSO₄ anhydrous, oxalic acid p.a., NaOH p.a., AlCl₃.6H₂O p.a., iodine p.a., and ethyl acetate p.a.. The research tools were a condenser, a 1600 RPM hot plate, a magnetic stirrer, analytical balance (Durasclae DAB 200), an Ostwald viscometer, a 10 mL pycnometer, a set of glass ware (consisted of reflux, three-neck flask, Beaker, Erlenmeyer, Biuret), Fourier Transform Infra-Red (FTIR) (Shimadzu IRPRESTIGE 21), gas chromatography-mass spectroscopy (GC-MS) (Shimadzu QP2010PLUS), oven (Mettler), furnace (RMF QUARTECH 2800), scanning electron microscopy (SEM) (FEI Inspect-S50), thermometer 110 °C, Ultrasonic cleaner (Delta D68H), X-Ray Diffraction (XRD) (PanAnalytical E'xpert Pro).

2.1. Synthesis of Na₂O/γ-Al₂O₃

The synthesis of Na₂O/γ-Al₂O₃ catalyst was carried out by synthesis of γ-Al₂O₃ and then the synthesis of Na₂O/γ-Al₂O₃. First, the γ-Al₂O₃ catalyst was prepared by: the γ-Al₂O₃ catalyst was prepared by 50.001 grams of AlCl₃.6H₂O (merck) dissolved in 83 mL of distilled water. Then, it was stirred with a magnetic stirrer at a temperature of 100 °C for 4 hours. Then NH₄OH was added until the pH reached ±9. The obtained precipitate was filtered and then washed with distilled water and washed 4 times with ethanol. The solids were dried at 80 °C for 48 hours. It was then calcined at a temperature of 500 °C for 2 hours. Second, the preparation of Na₂O/γ-Al₂O₃ catalyst was prepared by: mixing γ-Al₂O₃ with NaOH which has been dissolved in distilled water with a mole ratio (variations of study were 1:1, 1:2, and 1:3). Then, the mixture was dried at a temperature of 130 °C for 3 hours. Then, it was calcined at a temperature of 450 °C for 3 hours with a heating rate of 10 °C/minute. Next, the catalyst was characterized by XRD and SEM. Crystal size from the obtained XRD can be calculated by Scherrer equation [24] with the Equation:

$$\text{crystal size} = \frac{k \times \lambda}{\beta \cos \theta} \quad (1)$$

which k = Scherrer constant (0.9), λ = wavelength of X-ray, and β = FWHM (full width at Half Maximum).

2.2. Preparation of waste cooking oil

The preparation was refining of waste cooking oil. The refining of waste cooking oil was carried out as follow: [2] (1) waste cooking oil was heated at 90 °C with stirring of 1000 rpm, (2) active natural zeolite was mixed about 30% of oil weight, (3) stirring was constant for 90 minutes, and (4) oil was separated from the zeolite. Refined oil was identified using the FTIR instrument and Free Fatty

Acid (FFA) test. For FFA test, the procedures were: 1 gram of the oil and 5 mL of ethanol 95% were put into Erlenmeyer. The mixture was then heated in waterbath for 1 minute. The mixture was then added phenolphthalein indicator and titrated with KOH 0.01 N. The equation for FFA test was:

$$\text{FFA} = \frac{\{\text{Normality (N)} \times \text{Volume (mL)}\} \text{ of KOH} \times 265,687 \frac{\text{g}}{\text{mol}}}{\text{mass of sample} \times 1000} \times 100\% \quad (2)$$

2.3. Transesterification of waste cooking oil

Transesterification of waste cooking oil was carried out in the following way: the refined oil was put into a three-neck flask. Then, it was added with a certain volume of methanol in a ratio of 1:12. The two materials were mixed and catalyst was added with various variations of the molar ratio (1:1, 1:2 and 1:3) and the concentrations were 3%, 4%, and 5% by weight of the oil. The mixture was stirred with a magnetic stirrer and put into the ultrasonic reactor for 15 minutes at a temperature of 65 °C. Then, the mixture put into a separating funnel and left for ± 24 hours. The top layer was taken and anhydrous MgSO_4 was added, filtered with Whatman filter paper Number 41. Next, the product was put into the oven to remove the remaining methanol at 70 °C for 3 hours. Mass of the product (synthesized methyl ester) was then weighed by analytical balance. After that, identification of the functional groups used FTIR and identification of the components used GC-MS. The calculation of the biodiesel yield was calculated according to Santoso's research [25] by Eq 3:

$$\text{Yield} = \frac{\text{mass of synthesized methyl ester}}{\text{mass of theoretical methyl ester}} \times 100\% \quad (3)$$

The characterization carried out was density, viscosity, acid number, [25] and Thin-Layer Chromatography test [26]. The characterization procedures were:

2.3.1. Density

Density measuring used a pycnometer and the calculation used Eq 4:

$$\text{density } (\rho) = \frac{\text{sample mass in pycnometer (g)} - \text{mass of pycnometer (g)}}{\text{volume of pycnometer (mL)}} \quad (4)$$

2.3.2. Viscosity

Viscosity measuring used a Ostwald viscometer and the calculation used Eq 5:

$$\frac{\eta_{\text{aquadest}}}{\eta_{\text{sample}}} = \frac{\rho_{\text{aquadest}} \times t_{\text{aquadest}}}{\rho_{\text{sample}} \times t_{\text{sample}}} \quad (5)$$

2.3.3. Acid number

1.00 g of oil was put into a 100 mL Erlenmeyer and then 5.00 mL of alcohol was added. The

mixture was heated in a boiling water bath for 10 minutes. The mixture was then added to the phenolphthalein indicator and then it was titrated with 0.1N KOH. The calculation of acid number used Eq 6:

$$\text{acid number} = \frac{\left\{ \text{volume (mL)} \times \text{Normality (N)} \times \text{molecular weight} \left(\frac{\text{g}}{\text{mol}} \right) \right\} \text{of KOH}}{\text{sample mass (g)}} \quad (6)$$

3. Results and discussion

3.1. Characterization of $\text{Na}_2\text{O}/\gamma\text{-Al}_2\text{O}_3$

In this study, the catalyst used for transesterification is NaOH which was impregnated into $\gamma\text{-Al}_2\text{O}_3$ catalyst. Then, the mixture calcined, so that it NaOH changes into Na_2O . The synthesis produces a $\text{Na}_2\text{O}/\gamma\text{-Al}_2\text{O}_3$ catalyst with various mole ratios of 1:2, 1:1 and 1:3. The step aims to determine the effect of basicity given by NaOH in the transesterification reaction of waste cooking oil. The catalyst was characterized by XRD and SEM (Figure 1).

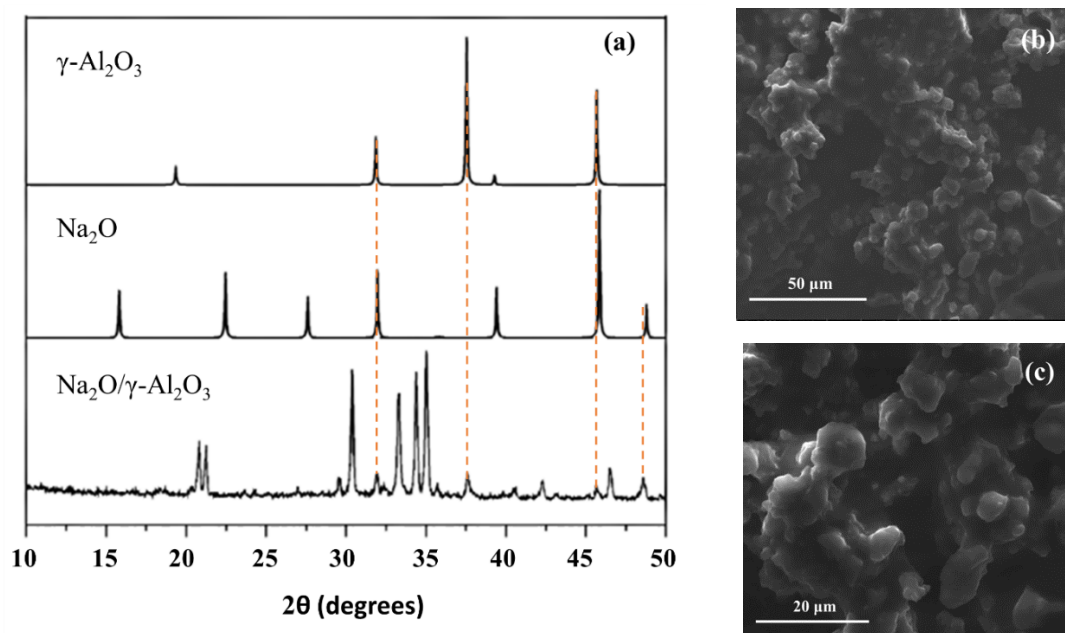


Figure 1. (a) XRD result of $\text{Na}_2\text{O}/\gamma\text{-Al}_2\text{O}_3$, and microstructure of $\text{Na}_2\text{O}/\gamma\text{-Al}_2\text{O}_3$ with magnification: (b) 2000x, (c) 5000x.

Based on Figure 1(a), the results of data analysis showed that there has been a difference of 2θ angle between $\text{Na}_2\text{O}/\gamma\text{-Al}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3$ standard, namely the appearance of a peak at 2θ angle which was typical for XRD Na_2O standards. The XRD peaks of Na_2O are at $2\theta = 28.01, 32.30, 54.89$ and 57.50° are due to Na_2O (ICSD-180570) [27]. This was in accordance with the results of this study which showed a peak of $2\theta = 33.19^\circ$ with a weak intensity. The XRD peaks of $\gamma\text{-Al}_2\text{O}_3$ were at $2\theta = 12.35^\circ, 19.89^\circ, 20.38^\circ, 24.88^\circ, 35.02^\circ, 35.95^\circ, 36.06^\circ, 38.35^\circ$ and 62.37° [28]. This was also in accordance with the results of the study which showed that there were peaks of $2\theta = 20.67^\circ, 35.05^\circ$ and 61.98° and also the similarity of peaks between the XRD results of the study and the standard

XRD of γ -Al₂O₃. The analysed peaks can be able to determine the crystal size with using Scherrer equation. The result of Scherrer equation for this catalyst showed that crystal size of Na₂O/ γ -Al₂O₃ was about 30.59 nm. Therefore, the peaks correlated to less than 100 nm, and it was relatively known nanoparticle size of Na₂O/ γ -Al₂O₃. In addition, the synthesis of Na₂O/ γ -Al₂O₃ catalyst was calcined from 450 to 500 °C, suggesting the transformation phase of boehmite to γ -Al₂O₃. In the future, the combination of the XRD, XPS, and FT-IR analysis is needed to reveal the efficient stable transformation of γ -Al₂O₃.

The microstructure can be analyzed through characterization with SEM at 2000x and 5000x magnification. The results of the microstructure analysis can be seen in Figure 1(b) and 1(c). The results of SEM characterization at 2000x magnification showed that the surface of the sample contained clumps like crystals but they were not clearly visible. The 5000x magnification was more clearly visible than the 2000x magnification which indicated the presence of Na₂O. The presence of crystals that look like Na₂O grains with fairly large and inhomogeneous particle sizes. The results of the analysis showed that Na₂O grain were evenly formed on the surface of γ -Al₂O₃ and had a fairly large and inhomogeneous particle size. Furthermore, the results of SEM-EDX analysis showed that Na₂O had been impregnated into γ -Al₂O₃. Therefore, the SEM results can strengthen the results of XRD analysis that the catalyst in this study is a Na₂O/ γ -Al₂O₃ catalyst.

3.2. Results of preparation of waste cooking oil

The results of the study provide the characteristics of waste cooking oil before and after being refined. The color originally changed from brownish to yellow color (in Figure 2(a) and 2(b)). This was because the oxidized compounds have been adsorbed and retained in the activated zeolite cavity. In addition to changes in the color of the oil, the refined oil also experienced a decrease in acid and free fatty acid numbers as shown in Table 1. The results of the FTIR characterization of refined oil can be seen in Figure 2(c). These results indicate the presence of triglycerides which were characterized by the stretching vibrations of C=O, C-O, O-H, C-H alkanes, C-H alkenes, and CH₂ bonds. The wave number and absorption intensity data can be seen in Table 2. In this study, the results of refinement showed that there was a reduction in fatty acids in the oil. The obtained free fatty acid was less than 2% as requirement to transesterification process [29], the refined oil can be able as raw materials in transesterification. If the FFA is more than 2%, the transesterification will form a soap, as known as saponification [30]. As competitive reaction, it will probably occur a hydrolysis reaction [2].

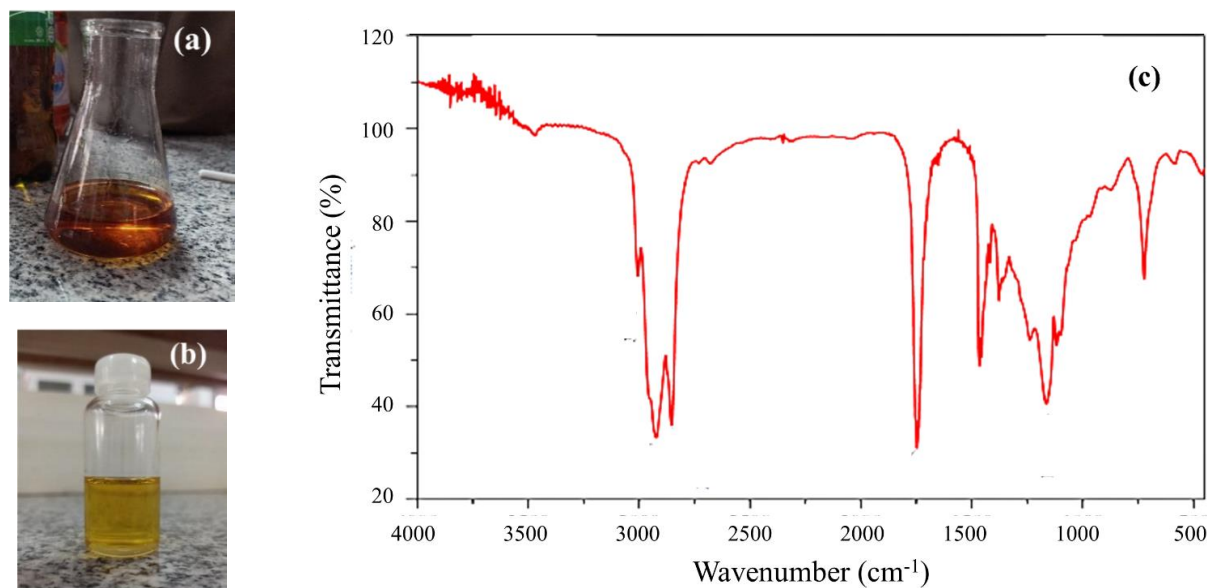


Figure 2. Oil: (a) before refinement, (b) after refinement, and (c) FTIR result.

Table 1. Characteristics of waste cooking oil before and after refining.

Parameter	Before refining	After refining
Density (g/cm ³)	0.9260	0.9261
Acid number (mg KOH/g)	1.98	1.73
Viscosity (cSt)	35.69	36.71
Free fatty acid (FFA) (%)	0.94	0.82

Table 2. Analysis of IR spectrum of waste cooking oil.

Stretching vibration-	Wave number (cm ⁻¹)	Absorption intensity	Wavenumber (cm ⁻¹) [31]
C-H alkene	3007.02	strong, sharp	3008.28
C-H alkane	2924.04	strong, sharp	2925.80
	2852.72	Strong, sharp	2854.60
C=O ester	1747.51	strong, sharp	1746.26
C-O	1161.53	strong, sharp	1163.12
CH ₂	721.38	strong, sharp	722.80

3.3. Results of transesterification of waste cooking oil

The biodiesel synthesis was carried out from waste cooking oil which had been refined using zeolite 30% by weight of oil. This was done with the aim that the color of the oil becomes clearer and reduces free fatty acid of the oil. The free fatty acid of the oil after being refined was 0.82%, so that the transesterification process can be continued. The transesterification process was carried out using a Na₂O/γ-Al₂O₃ catalyst with a variation of the mole ratio of the catalyst 1:1, 1:2, 1:3 and the concentration of the catalyst with variations of 3%, 4% and 5% by weight of oil. It aims to determine

the best condition of biodiesel synthesis. In this study, biodiesel was formed through a transesterification process using a mole ratio of oil: methanol, which is 1:12 with ultrasonic wave at a temperature of 65 °C.

The result of transesterification formed two layers, the top layer was methyl ester (biodiesel) and the bottom layer was glycerol (Figure 3(a)). In this study, the transesterification process was assisted by ultrasonic wave for 15 minutes, so that the reaction rate increased. Increasing the reaction rate can result in the formation of higher methyl esters in a shorter time that compared to the process without using ultrasonic wave [32].

The yield of transesterification from waste cooking oil in this study can be seen in Figure 4. Based on Figure 4, the results of transesterification assisted by ultrasonic waves using a 1:1 mole ratio catalyst with a concentration of 3% have a higher yield than the catalyst with a mole ratio of 1:2 and 1:3. However, at 1:1 catalyst the yield decreased from 83.51%, 75.59% and 60.94% yields. The decrease in yield indicated that the amount of the used catalyst was in excess. This was because the use of excess catalyst can result in saponification. The presence of soap in the transesterification reaction can complicated the formation of the product, so the product was difficult to separate from glycerol, and the results did not show a significant increase [33]. Therefore, the best $\text{Na}_2\text{O}/\gamma\text{-Al}_2\text{O}_3$ catalyst used for the transesterification reaction was at a concentration of 3% with a catalyst ratio of 1:1 mole ratio. In addition, the presence of ultrasonic waves can shorten the reaction time to less than 30 minutes [34].

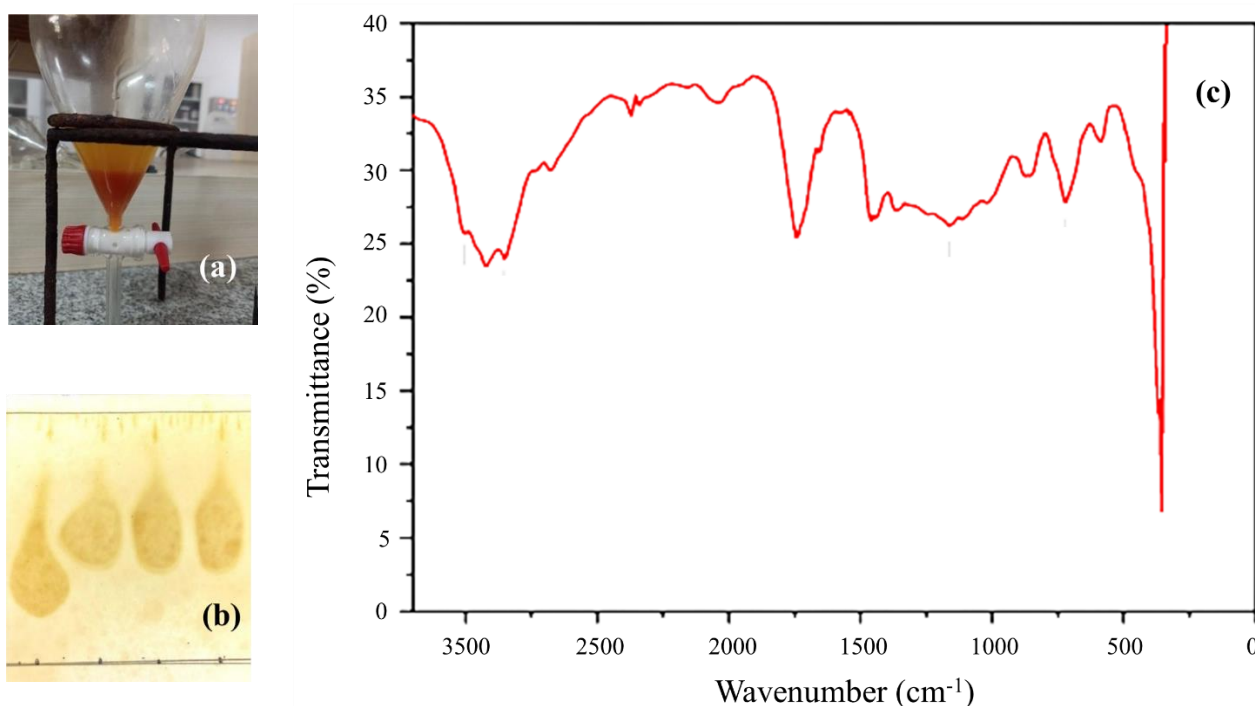


Figure 3. Results of waste cooking oil for: (a) transesterification of, (b) thin layer chromatography test, and (c) FTIR test.

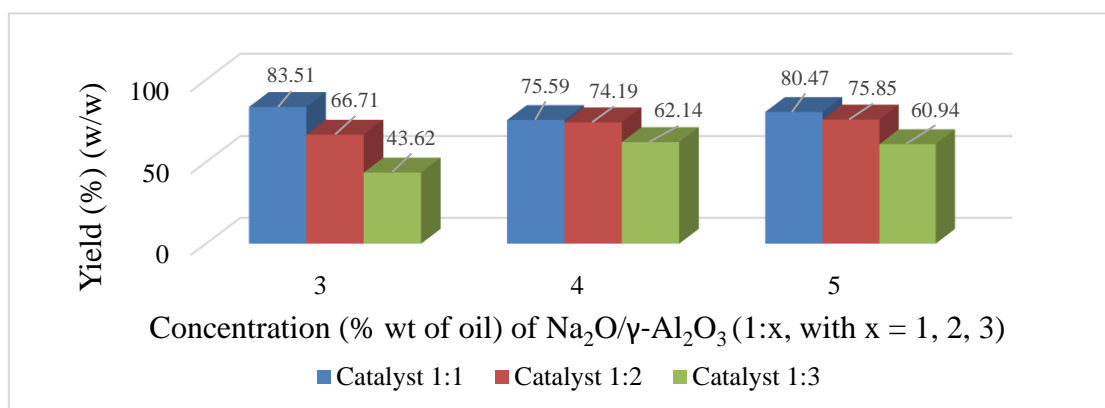


Figure 4. Effect of catalyst concentration on yield of transesterification results.

The product resulting from the transesterification reaction was carried out by the Thin-Layer Chromatography (TLC) test (see Figure 3(b)). The test aims to determine that the result of transesterification is biodiesel instead of oil. Based on Figure 3(b), the produced spot from oil and some samples from the transesterification have different R_f value. R_f value of oil was 0.32 and R_f value of biodiesel was 0.5, so it can be concluded that biodiesel synthesis was successful.

The transesterification yield was characterized to determine whether the resulting product was suitable, namely in the form of biodiesel with the standard quality requirements of SNI Biodiesel. The data from the characterization results were listed in Table 3. Based on the results of the characterization of biodiesel that was in accordance with Indonesian National Standard (SNI) for Biodiesel, it can be concluded that this biodiesel meets the quality requirements as biodiesel and can be investigated further.

Table 3. The synthesized biodiesel characterization results.

Parameter	Research results	SNI 7182:2015
Density (g/m ³)	0.886	0.850–0.890
Viscosity (cSt)	3.191	2.3–6.0
Free fatty acid (mg-KOH/g)	0.39	max 0.8

The trans-esterified product was further identified using the FTIR instrument. It aims to determine the functional groups present in the product. The IR spectrum of the trans-esterified product was shown in Figure 3(b). Based on the IR spectrum, there were six typical absorption bands as shown in Table 4. Based on Table 4, the indications of the detected absorption bands were the presence of CH alkene bond stretching vibrations, CH alkane bond stretching vibrations, typical bond stretching vibrations of C=O as ester, vibration CO bond stretching, and CH₂ bond stretching vibrations. Based on the results of the IR spectrum analysis, it can be seen that the trans-esterification product has a C=O functional group as R-COOR as an ester.

Table 4. IR interpretation of the synthesized biodiesel.

Stretching vibration-	Wavenumber of the study (cm ⁻¹)	Absorption intensity	Wavenumber (cm ⁻¹) [35]
C-H alkene	3008.33	Strong, sharp	3008.9
C-H alkane	2924.09	Strong, sharp	2925.76
	2854.65	Strong, sharp	2855.76
C=O ester	1743.65	Strong, sharp	1743.54
C-O	1165.00	weak, sharp	1172.42
CH ₂	725.23	Strong, sharp	722.75

Furthermore, GC-MS analysis was carried out to determine the components present in biodiesel. Based on the results of the GC analysis, there were 8 peaks on the chromatogram as shown in Figure 5a, and MS results of the sample in Figure 5(b). Then the peaks were analyzed by MS to produce an MS spectrum (Table 5).

Table 5. Mass spectrum analysis of the biodiesel of waste cooking oil.

Retention time (minutes)	Content (%)	C content (hydrocarbon)	Compound
7.202	1.39	(C13:0)	Methyl Laurate
8.744	2.26	(C15:0)	Methyl Miristate
10.021	0.80	(C17:1)	Methyl Palmitoleate
10.176	30.90	(C17:0)	Methyl Palmitate
11.270	16.61	(C19:2)	Methyl Linoleate
11.323	38.54	(C19:1)	Methyl Elaidate
11.436	8.62	(C19:0)	Methyl Stearate
12.599	0.88	(C21:0)	Methyl Arachidate

MS spectrum peaks were compared with library data. The first peak (retention time of 7.202 minutes) had fragments with m/z 43.74, 101, 143, 171, 214, 253, 281, 331, and 405. Based on data from the NIST17.L library, the first peak has a similarity percentage of 98% with the methyl laurate compound which was 1.39%. The second peak (retention time of 8.744 minutes) had fragments with m/z 43.74, 101, 143, 171, 199, 242, 281, 326, 355, and 405. Based on data from the NIST17.L library, the second peak has a 99% similarity percentage with the methyl myristate compound as much as 2.26%. The third peak (retention time of 10.021 minutes) had fragments with m/z 55.87, 123, 155, 194, 236, 268, 315, 355, 403, and 477. Based on data from the NIST17.L library, the third peak has a 99% similarity percentage with methyl palmitoleate as much as 0.80%. The fourth peak (retention time of 10.176 minutes) had fragments with m/z 43, 74, 101, 143, 185, 227, 270, 297, 327, 355, and 401. Based on data from the NIST17.L library, the fourth peak has a 99% similarity percentage with methyl palmitate compounds as much as 30.90%. The fifth peak (retention time of 11.270 minutes) has fragments with m/z 31, 67, 109, 150, 187, 220, 262, 294, 355, 389, 429, and 470. Based on library data NIST17.L, the fifth peak has a 99% similarity percentage with methyl linoleic compounds as much as 16.61%. The sixth peak (retention time of 11.323 minutes) had fragments with m/z 55, 97, 137, 180, 222, 264, 296, 255, 389, 429, and 470. Based on data from the NIST17.L library, the sixth

peak has a 99% similarity percentage with methyl elaidate compounds as much as 38.54%. The seventh peak (retention time of 11.436 minutes) had fragments with m/z 74, 143, 199, 255, 298, 355, 415, 460, and 503. Based on NIST17.L library data, the seventh peak has a 99% similarity percentage with methyl stearate compounds as much as 8.62%. The eighth peak (retention time of 12.599 minutes) had fragments with m/z 39, 74, 109, 143, 207, 241, 283, 326, 377, 429, and 470. Based on the NIST17 library data, the eighth peak has 99% similarity with methyl arachidate compound as much as 0.88%.

This study was clear for the identification and characterization of the synthesized biodiesel. Recent studies for the best condition compare to this study as listed in Table 6. Based on Table 6, this study has more effective transesterification than previous study because of ultrasonic wave (for 15 minutes). Besides, $\text{Na}_2\text{O}/\gamma\text{-Al}_2\text{O}_3$ catalyst needs to low amount for the transesterification of waste cooking oil.

Table 6. Comparison study to the synthesized biodiesel of waste cooking oil.

Catalyst	alcohol to oil molar ratio/temperature ($^{\circ}\text{C}$)/catalyst (%wt)/time (h)/reactor	Yield (%)	Ref.
$\text{CaO-K}_2\text{O}$	15:1/65/8/5/ultrasonic wave	92.37	[5]
$\text{SrO-ZnO/Al}_2\text{O}_3$	10:1/75/15/5	95.7	[36]
$\text{CaO/Al}_2\text{O}_3$	12:1/65/3/3/	30.91	[37]
$\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$	12:1/65/10/3	98.6	[38]
$\text{KOH/Al}_2\text{O}_3$	12:1/65/7/2	73.7	[39]
$\text{K/Al}_2\text{O}_3$,	17:1/70/8.25/7	82.01	[40]
$\text{NaOH/Al}_2\text{O}_3$	7:1/70/1.5/4	92	[41]
$\text{K/Fe}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$	9.73/65/4.6/7.84	99	[42]

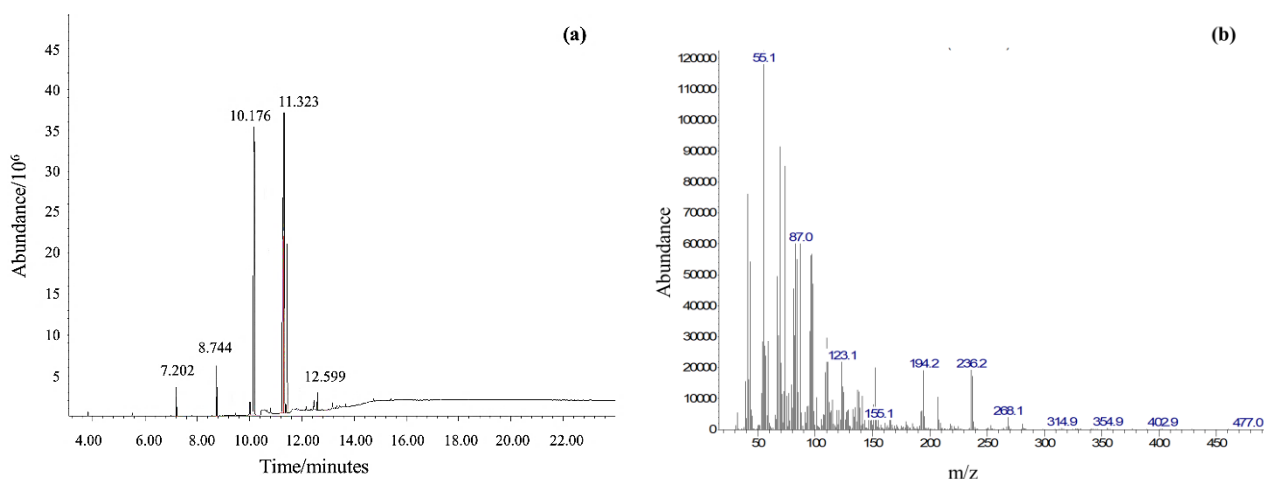


Figure 5. Results of the synthesized biodiesel: (a) Gas Chromatogram, and (b) Mass Spectra.

4. Conclusions

Based on the research, The results showed that the refined waste cooking oil using FTIR was known that there was still a carbonyl group indicating the presence of triglycerides. FFA content of

waste cooking oil after esterification was 0.40%, so that the transesterification reaction could be carried out. The XRD results of the catalyst showed a conformity with the reference and it was determined by the Scherrer formula that the crystal size of catalyst was 30.59 nm. The best condition of biodiesel synthesis from waste cooking oil was obtained, namely with the catalyst concentration of 3% with a mole ratio of 1:1 of $\text{Na}_2\text{O}:\gamma\text{-Al}_2\text{O}_3$ of ultrasonication, 65 °C, and molar ratio of methanol: oil (12:1), the yield was 83.51%. The best conditions correlate to the best yield, so it is understood that the results will probably be higher than this study in the future [43]. The results of the characterization of viscosity, density, acid number and Free Fatty Acid of biodiesel were in accordance with Standar Nasional Indonesia (SNI) for Biodiesel (SNI 7182:2015). The TLC test showed that there was a difference in R_f between waste cooking oil and biodiesel so it could be concluded that the biodiesel synthesis was successful. The FTIR results showed that the transesterification product was an ester and further identified using GC-MS, the biodiesel component of the transesterification product contained 38.54% methyl elaidate, 30.90% methyl palmitate, 16.61% methyl linoleate, 8.62% methyl stearate, 2.26% methyl myristate, 1.39% methyl laurate, 0.88% methyl arachidate, and 0.80% methyl palmitoleate.

Acknowledgments

The authors would like to thank LPPM UM, who provided PNBPN research funds.

Conflict of interest

The authors declare no conflict of interest.

Author contributions

Aman Santoso contributed with conceptualization and formal analysis. Thitania Nur Kusumah contributed with investigation, methodology and writing—original draft. Sumari Sumari, Anugrah Ricky Wijaya, and Siti Marfuah contributed with writing—original draft and writing—review & editing. Rini Retnosari, Ihsan Budi Rachman, and Muhammad Roy Asrori contributed with writing—review & editing.

References

1. Rosa L, Davis KF, Rulli MC, et al. (2017) Environmental consequences of oil production from oil sands. *Earth's Future* 5: 158–170. <https://doi.org/10.1002/2016EF000484>
2. Sumari S, Santoso A, Asrori MR (2021) A review: Synthesis of biodiesel from low/off grade crude palm oil on pretreatment, transesterification, and characteristics. *Orbital Electron J Chem* 13: 385–91. <http://dx.doi.org/10.17807/orbital.v13i4.1632>
3. Fajriyati M, Sri I, Akhmad R, et al. (2021) Mango seed kernel oil extraction with ethanol: Optimization of oil yield and polyphenol. *Chem Ind Chem Eng Q* 27: 207–214. <https://doi.org/10.2298/CICEQ200128039M>

4. Asrori MR, Santoso A, Sumari S (2022) Initial defect product on immiscible mixture of palm oil: Ethanol by amphiphilic chitosan/Zeolite LTA as optimization of microemulsion fuel. *Ind Crops Prod* 180: 114727. <https://doi.org/10.1016/j.indcrop.2022.114727>
5. Santoso A, Wijaya AR, Rahmadani A, et al. (2021) Effect of CaO_K₂O heterogeneous catalyst concentration and reaction temperature on trans-esterification of waste cooking oil with ultrasonic wave. *AIP Conference Proceedings* 2330: 70009. <https://doi.org/10.1063/5.0043404>
6. De Feo G, Di Domenico A, Ferrara C, et al. (2020) Evolution of waste cooking oil collection in an area with long-standing waste management problems. *Sustainability* 12: 1–16. <https://doi.org/10.3390/su12208578>
7. Singh D, Sharma D, Soni SL, et al. (2021) A comprehensive review of biodiesel production from waste cooking oil and its use as fuel in compression ignition engines: 3rd generation cleaner feedstock. *J Cleaner Prod* 307: 127299. <https://doi.org/10.1016/j.jclepro.2021.127299>
8. Karthikeyan C, Karuppuchamy S (2017) Synthesis of novel CuO–Al₂O₃ catalyst for biodiesel production. *Adv Sci Eng Med* 9: 1011–1016. <https://doi.org/10.1166/ase.2017.2080>
9. Haryono H, Natanael LC, Rukiah R, et al. (2018) Kalsium oksida mikropartikel dari cangkang telur sebagai katalis pada sintesis biodiesel dari minyak goreng bekas. *Jurnal Material dan Energi Indonesia* 8: 8–15. Available from: <https://jurnal.unpad.ac.id/jmei/article/view/17865>.
10. de Oliveira KG, de Lima RRS, de Longe C, et al. (2022) Sodium and potassium silicate-based catalysts prepared using sand silica concerning biodiesel production from waste oil. *Arabian J Chem* 15: 103603. <https://doi.org/10.1016/j.arabjc.2021.103603>
11. de Oliveira KG, de Lima RRS, Moura HM de A, et al. (2022) Tangerine peel ashes applied as green catalyst: A biorefinery-based approach for biodiesel production. *Biofuels, Bioprod, Biorefin* 16: 548–561. <https://doi.org/10.1002/bbb.2327>
12. Vádrine JC (2017) Heterogeneous catalysis on metal oxides. *Catalysts* 7: 341. <https://doi.org/10.3390/catal7110341>
13. Martínez SL, Romero R, Natividad R, et al. (2014) Optimization of biodiesel production from sunflower oil by transesterification using Na₂O/NaX and methanol. *Catal Today* 220–222: 12–20. <https://doi.org/10.1016/j.cattod.2013.08.022>
14. Benjapornkulaphong S, Ngamcharussrivichai C, Bunyakiat K (2009) Al₂O₃-supported alkali and alkali earth metal oxides for transesterification of palm kernel oil and coconut oil. *Chem Eng J (Amsterdam, Neth.)* 145: 468–474. <https://doi.org/10.1016/j.cej.2008.04.036>
15. Ibrahim ML, Nik Abdul Khalil NNA, Islam A, et al. (2020) Preparation of Na₂O supported CNTs nanocatalyst for efficient biodiesel production from waste-oil. *Energy Convers Manage* 205: 112445. <https://doi.org/10.1016/j.enconman.2019.112445>
16. Feng R, Hu X, Yan X, et al. (2017) A high surface area mesoporous γ -Al₂O₃ with tailoring texture by glucose template for ethanol dehydration to ethylene. *Microporous Mesoporous Mater* 241: 89–97. <https://doi.org/10.1016/j.micromeso.2016.11.035>
17. Sulaiman NF, Wan Abu Bakar WA, Ali R (2017) Response surface methodology for the optimum production of biodiesel over Cr/Ca/ γ -Al₂O₃ catalyst: Catalytic performance and physicochemical studies. *Renewable Energy* 113: 697–705. <https://doi.org/10.1016/j.renene.2017.06.007>
18. Han H, Guan Y (2009) Synthesis of biodiesel from rapeseed oil using K₂O/ γ -Al₂O₃ as nano-solid-base catalyst. *Wuhan Univ J Nat Sci* 14: 75–79. <https://doi.org/10.1007/s11859-009-0116-x>

19. Rasyid R, Sabara Z, Ainun Pratiwi H, et al. (2018) The production of biodiesel from a traditional coconut oil using NaOH/ γ -Al₂O₃ heterogeneous catalyst. *IOP Conf Ser Earth Environ Sci* 175: 12025. <http://dx.doi.org/10.1088/1755-1315/175/1/012025>
20. Sumari, Murti M, Santoso A, et al. (2022) Sono-Transesterification of Kapok seed oil with CaO:BaO-(x:y)/Active natural zeolite catalyst. *J Renewable Mater* 10: 3659–3670. <https://doi.org/10.32604/jrm.2022.022995>
21. Pukale DD, Maddikeri GL, Gogate PR, et al. (2015) Ultrasound assisted transesterification of waste cooking oil using heterogeneous solid catalyst. *Ultrason Sonochem* 22: 278–286. <https://doi.org/10.1016/j.ultsonch.2014.05.020>
22. Maddikeri GL, Gogate PR, Pandit AB (2014) Intensified synthesis of biodiesel using hydrodynamic cavitation reactors based on the interesterification of waste cooking oil. *Fuel* 137: 285–92. <https://doi.org/10.1016/j.fuel.2014.08.013>
23. Sumari, Fajaroh F, Santoso A, et al. (2018) Performance of activated natural Zeolite/Cu as a catalyst on degradation of glycerol into ethanol assisted by ultrasonic. *J Phys Conf Ser* 1093: 012036. <https://doi.org/10.1088/1742-6596/1093/1/012036>
24. Sinaga Z, Joniwarta J (2020) Analisis ukuran kristal dan sifat magnetik melalui proses pemesinan milling menggunakan metode karakterisasi xrd, mechanical alloying, dan ultrasonik tekanan tinggi pada material barium hexaferrite (Baf₆O₁₉). *J Kajian Teknik Mesin* 5: 9–14. <https://doi.org/10.52447/jktm.v5i1.2372>
25. Santoso A, Aghnia Hanindita CF, Sumari, et al. (2019) Synthesis of biodiesel from low-quality crude palm oil with heterogeneous catalyst CaO-ZnO. *IOP Conf Ser Mater Sci Eng* 515: 12082. <http://dx.doi.org/10.1088/1757-899X/515/1/012082>
26. Plata V, Gauthier-Maradei P, Romero-Bohórquez AR, et al. (2015) Characterization of insoluble material isolated from Colombian palm oil biodiesel. *Biomass Bioenergy* 74: 6–14. <https://doi.org/10.1016/j.biombioe.2014.12.024>
27. Kumar S, Kishore B, Munichandraiah N (2016) Electrochemical studies of non-aqueous Na–O₂ cells employing Ag-RGO as the bifunctional catalyst. *RSC Adv* 6: 63477–63479. <http://dx.doi.org/10.1039/C6RA13596J>
28. Salahudeen N, Ahmed AS, Al-Muhtaseb AH, et al. (2015) Synthesis of gamma alumina from Kankara kaolin using a novel technique. *Appl Clay Sci* 105–106: 170–177. <https://doi.org/10.1016/j.clay.2014.11.041>
29. Helwani Z, Ramli M, Saputra E, et al. (2020) Impregnation of CaO from eggshell waste with magnetite as a solid catalyst (Fe₃O₄/CaO) for transesterification of palm oil off-grade. *Catalysts* 10: 164. <https://doi.org/10.3390/catal10020164>
30. Santoso A, Sumari, Salim A, et al. (2018) Synthesis of methyl ester from chicken oil and methanol using heterogeneous catalyst of CaO-MgO as well as characterization its potential as a biodiesel fuel. *J Physic Conf Ser* 1093: 12035. Available from: <https://iopscience.iop.org/article/10.1088/1742-6596/1093/1/012035>.
31. Rafati A, Tahvildari K, Nozari M (2019) Production of biodiesel by electrolysis method from waste cooking oil using heterogeneous MgO-NaOH nano catalyst. *Energy Sources, Part A* 41: 1062–1074. <https://doi.org/10.1080/15567036.2018.1539139>

32. Ho WWS, Ng HK, Gan S, et al. (2015) Ultrasound-assisted transesterification of refined and crude palm oils using heterogeneous palm oil mill fly ash supported calcium oxide catalyst. *Energy Sci Eng* 3: 257–269. <https://doi.org/10.1002/ese3.56>
33. Avhad MR, Marchetti JM (2015) A review on recent advancement in catalytic materials for biodiesel production. *Renewable Sustainable Energy Rev* 50: 696–718. <https://doi.org/10.1016/j.rser.2015.05.038>
34. Stavarache C, Vinatoru M, Nishimura R, et al. (2003) Conversion of vegetable oil to biodiesel using ultrasonic irradiation. *Chem Lett* 32: 716–717. <https://doi.org/10.1246/cl.2003.716>
35. Kamaranzaman MFF, Kahar H, Hassan N, et al. (2020) Analysis of biodiesel product derived from waste cooking oil using fourier transform infrared spectroscopy. *Mater Today Proc* 31: 329–332. <https://doi.org/10.1016/j.matpr.2020.06.088>
36. Al-Saadi A, Mathan B, He Y (2020) Biodiesel production via simultaneous transesterification and esterification reactions over SrO–ZnO/Al₂O₃ as a bifunctional catalyst using high acidic waste cooking oil. *Chem Eng Res Des* 162: 238–248. <https://doi.org/10.1016/j.cherd.2020.08.018>
37. Shohaimi NAM, Marodzi FNS (2018) Transesterification of waste cooking oil in biodiesel production utilizing CaO/Al₂O₃ heterogeneous catalyst. *Malays J Anal Sci* 22: 157–165. <https://doi.org/10.17576/mjas-2018-2201-20>
38. Nohhakim MAHL, Shohaimi NAM, Ibrahim ML, et al. (2021) Transesterification of waste cooking oil utilizing heterogeneous K₂CO₃/Al₂O₃ and KOH/Al₂O₃ catalysts. *Malays J Chem* 23: 74–83. <https://doi.org/10.55373/mjchem.v23i2.1000>
39. Kamarullah SH, Razak ZKA, Shohaimi NAM, et al. (2021) Production of biodiesel from waste cooking oil using potassium hydroxide supported on alumina catalyst. *Malays J Anal Sci* 25: 596–604. Available from: https://mjas.analis.com.my/mjas/v25_n4/pdf/Hanum_25_4_5.pdf.
40. Ghavami K, Akhlaghian F, Rahmani F (2022) Potassium compounds-Al₂O₃ catalyst synthesized by using the sol-gel urea combustion method for transesterification of sunflower and waste cooking oils. *Biomass Convers Biorefin* 12: 1139–1152. <https://doi.org/10.1007/s13399-020-00731-z>
41. Hajyheidar T, Tahvildari K (2015) Efficient synthesis of biodiesel from waste cooking oil catalysed by Al₂O₃ impregnated with NaOH. *J Chem Pet Eng* 49: 143–151. <https://dx.doi.org/10.22059/jchpe.2015.1806>
42. Yazdani F, Akia M, Khanbolouk F, et al. (2019) Novel heterogeneous base nanocatalysts supported on a spray dried gamma alumina applying optimized production of biodiesel from waste cooking oil. *Biofuels* 12: 1275–1281. <https://doi.org/10.1080/17597269.2019.1613749>
43. Sumari S, Fajaroh F, Yahmin, et al. (2019) Effect of temperature synthesis on structural behaviours of NaY zeolite using local sand as a silica source. *IOP Conf Ser Mater Sci Eng* 515: 012036. <https://doi.org/10.1088/1757-899X/515/1/012036>



AIMS Press

© 2022 the Author(s), licensee AIMS Press. This is an open access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/4.0>)