Jurnal Akademika Kimia, 14(1): 40-50, February 2025
ISSN (online) 2477-5185 | ISSN (print) 2302-6030
http://jurnal.fkip.untad.ac.id/index.php/jak/
OPEN ACCESS

Optimization of Palm Bunch Ash-Based Catalysts for the Transesterification of Waste Cooking Oil into Biodiesel

***Fillah M. Sakhi, Aman Santoso, & Sumari**
Program Studi Kimia/FMIPA – Universitas Negeri Malang, Malang – Indonesia 94119

Received 09 January 2025, Revised 30 January 2025, Accepted 20 February 2025
doi: 10.22487/j24775185.2025.v14.i1.pp40-50

Abstract

The increasing dependence on fossil fuels to meet fuel needs has caused several problems, such as air pollution, greenhouse effects, unpleasant odors, and loud noises. This research aims to design an alternative fuel in the form of biodiesel by applying a heterogeneous catalyst based on palm bunch to synthesize biodiesel through transesterification. The research stages include activating the active sites of palm bunches through calcination at temperatures of 400 °C, 500 °C, and 600 °C; refining waste cooking oil; esterification; and transesterification. The active components of palm bunch ash (PBA) were characterized using XRF and alkalinity testing. XRF results indicated that PBA contains active basic compounds such as K_2O *and CaO, crucial in catalytic activity. Physical-chemical property testing revealed that the synthesis achieved the highest yield of 93.744 %. The results of the physical-chemical characteristic tests produced the best density with an average of 0.888* $g\ mL^{-1}$*, and the lowest viscosity with an average of 3.79 cSt at 40 °C with an iodine number of 80.116* $g\ I_2\ 100\ g^{-1}$*, a saponification number of 170.57* $mg\ KOH\ g^{-1}$*, and a refractive index of 1.445. The catalyst demonstrated stable performance up to three reuses with yields ranging from 80–90 %. FTIR spectra showed strong absorption bands at 1172–1165* cm^{-1}*, indicating* $C\text{-}O\text{-}CH_3$ *stretching from methyl esters. GC-MS analysis showed that the biodiesel consists of various fatty acid methyl esters (FAME), with the main component being methyl oleate, which appears at a retention time of 37.096 minutes with an area of 40.31 %. So it is shown that PBA catalysts have an excellent potential for commercial applications as they can reduce dependence on fossil fuels by utilizing household waste.*

Keywords: Heterogeneous catalyst, palm bunch ash, waste cooking oil, FAME

Introduction

The depletion of fossil fuels as the primary energy source has made studying new and renewable energy (EBT) increasingly crucial. The development of EBT is targeted to reach 23 % by 2025. To achieve this, proactive measures are being taken, such as eliminating fossil fuel subsidies, regional market integration, and developing alternative fuels such as biodiesel.

Biodiesel is composed of fatty acid methyl esters (FAME) formed from the transesterification reaction between triglycerides (vegetable oil or animal fat) with methanol and a base catalyst (Yucel & Turkay, 2002). It contains 75 % paraffin hydrocarbons, aromatic hydrocarbon derivatives, and 25 % alkyl benzene and naphthalene derivatives. These characteristics resemble petrodiesel, enabling it to be used as a blend in fossil diesel fuel (Galadima & Muraza, 2020).

Biodiesel can be synthesized from waste cooking oil (WCO) triglycerides. WCO is a waste product from repeated frying that has undergone chemical degradation, such as hydrolysis and oxidation (Hambali et al., 2007; Nuryanti et al., 2023). Repeated heating of WCO significantly increases the free fatty acid content, much higher than new cooking oil (Widyaningsih et al., 2023). According to Aworanti et al. (2023), the free fatty acid content in waste cooking oil reaches 14.25 %, while Suroso (2013) reports a higher figure of 18 % (Posada et al., 2007; Sujadi et al., 2016). The high free fatty acid content can trigger saponification reactions, leading to the formation of soap and emulsions that are difficult to separate. Therefore, several pretreatment processes, such as esterification, are required to reduce the free fatty acid content, ensuring the resulting biodiesel is high quality (Japir et al., 2017). Biodiesel synthesis is processed through transesterification reactions using a heterogeneous base catalyst, palm bunch ash (PBA). The transesterification reaction is carried out in methanol solvent, with the main product being biodiesel, and the byproduct is glycerol (Attari et al., 2022; Joshi et al., 2017).

Catalysts play a crucial role in accelerating reactions by reducing the activation energy of the reaction (Berchmans & Hirata, 2008). Heterogeneous catalysts have several advantages, including reusability, easy operating procedures,

---

*Correspondence:
Fillah M. Sakhi
e-mail: fillahmuftisakhi26@gmail.com

easy product separation, and minimal wastewater generation (Zheng et al., 2017). Heterogeneous catalysts are developed and processed into ash using waste materials such as eggshells, snail shells, and animal bones (Boey et al., 2009). In this study, palm bunches were selected as a heterogeneous catalyst in transesterification reactions to produce biodiesel. A palm bunch contains various minerals, primarily potassium. The calcination process converts potassium into potassium oxide (K_2O). K_2O reacts with methanol to form active methoxide, which converts triglycerides in waste cooking oil into methyl esters and glycerol.

Due to its high potassium content and strong pore structure, this ash has potential as a catalyst. The highest metal oxide in PBA, K_2O, is a strong base, providing O_2^- or OH^- ions. These ions break the ester bonds in triglyceride molecules. In the reaction mechanism, the base ions from K_2O help form methoxide ions ($CH3O^-$) from methanol, which then attack the carbonyl group of triglycerides. This reaction produces new esters and exchanges fatty acid positions, yielding methyl esters and glycerol (Chi, 1999). This reaction forms methyl esters more quickly than esterification reactions using acid catalysts. Esterification is necessary to reduce high levels of free fatty acids (FFA) and prevent saponification reactions. The esterification process also reduces water content, as high water content can cause hydrolysis reactions that reduce biodiesel yield (Patil et al., 2018).

This study aims to synthesize biodiesel as a renewable alternative to replace fossil fuels using household and palm oil waste, making the research environmentally friendly.

Methods

Tools and materials

The tools used in this research were beaker glasses 100 mL (Iwaki), burettes 50 mL (Iwaki), volumetric flasks (Iwaki), stands and clamps, three-neck boiling flasks 50 mL (Iwaki), erlenmeyer flask (Pyrex), glass funnel (Pyrex), porcelain crucible, digital balance (Shimadzu ATX224), volumetric pipette (Iwaki), separating funnel (Pyrex), watch glass (Pyrex), thermometer 100 °C, condenser (Iwaki), hot plate, magnetic stirrer, furnace (Thermo), oven (Memmert, Type: UN 55), oswald viscometer, pycnometer (Iwaki), ultrasonic water bath (Branson 1510), cleveland cup, filter paper, and, universal indicator paper. The instruments were XRD (PANalytical Type: X'Pert PRO), XRF (PANalytical Type: Minipal 4), GC-MS (Shimadzu QP2010 Plus), FTIR (Shimadzu Type: IRPrestige 21), SEM-EDX (FEI, Type: Inspect-S50), and SAA (QuadraSorb Station 2 version 5). The materials used in this study were waste cooking oil, palm bunch waste, methanol p.a. (Merck), 96 % alcohol, 0.1 N KOH (Merck), alcoholic KOH (Merck), 0.5 N HCl (Smartlab), 1 % H_2SO_4, demineralized water, 3 M HCl, n-hexane (Smartlab), acetone (Smartlab), chloroform (Merck), KI solution (Smartlab), 0.1 N $Na_2S_2O_3$, starch solution, phenolphthalein indicator (PP), universal indicator, and distilled water.

Activation of the Active Site of Palm Bunch Catalyst

A sample of palm bunch waste was obtained from South Blitar plantation. Sample preparation in this research refers to the procedure by Santoso et al. (2018). A sample palm bunch waste was washed with clean water until all dirt and dust were removed. The samples were dried and chopped under the sun for two days, followed by drying in an oven at 110 ℃ for 24 hours. The samples are ground using a mortar and sieved using a 100-mesh sieve. Each sample is calcined at varying temperatures of 400 ℃, 500 ℃, and 600 ℃ for 4 hours.

Refining of Waste Cooking Oil (WCO)

Waste cooking oil is obtained from snack frying in Malang City. The first step is to prepare 500 g of waste cooking oil in a 1000 mL beaker. The oil is mixed with zeolite, which amounts to 50 % of the oil weight, which is 250 g. The mixture is stirred at 80 ℃ at 1000 rpm for 3 hours. The mixture is separated into oil and zeolite. The acid value and % FFA of the refined oil are tested.

Esterification

Refined oil is weighed to a total of 200 grams. The oil is heated to a temperature of 80 ℃. A 1 % H_2SO_4 catalyst solution (2 mL) is mixed with methanol (51) to a total of 47.28 mL. This mixture is then added to the heated oil. The mixture is refluxed at 60 ℃ - 65 ℃ for 5 hours. After the reaction process, the upper layer (organic phase) and lower layer (water phase) are separated. The organic layer is washed with warm water, and the acid number and % FFA are tested.

Transesterification with the Reflux Method

The esterification oil was weighed at 25 mL and then heated to 80 °C. The palm bunch ash (PBA) catalysts were weighed at 3 %, 5 %, 7 %, and 9 % respectively. Methanol (15 1) at 14.1 mL was mixed with the ash catalyst. The mixture is refluxed at 60 °C – 65 °C for 2 hours. After the reaction, the mixture is separated by centrifugation for 30 minutes at 3000 rpm. The methyl ester is separated from the glycerol using a glass funnel and washed with warm water. The washed methyl ester is then heated to 150 °C to remove residual catalyst and glycerol, and then added as much as necessary of anhydrous $MgSO_4$ to the methyl ester, followed by centrifugation for 30 minutes at 3000 rpm. The synthesized methyl ester is weighed for yield and subjected to physical and chemical property testing.

Results and Discussion

Activation and Characterization of Heterogeneous Catalysts from Palm Bunch Waste

The catalyst was prepared by thermal calcination of dry palm oil waste ash, as shown in **Figure 1**. The calcination process was carried out in a furnace at temperatures of 400 °C, 500 °C, and 600 °C for four hours to remove volatile organic compounds and convert metal elements into active oxide forms. The temperature selection was done gradually to study the effect of activation temperature on the formation of basic sites.

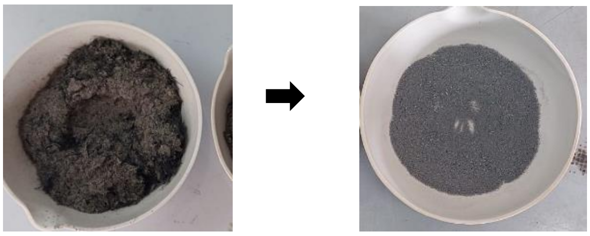

Figure 1. The palm bunch was heated with calcined

Calcination at higher temperatures accelerates the decomposition of carbonate compounds into oxides, while increasing the crystallinity of the catalyst and the availability of active surface area (Jiang et al., 2023; Okoye et al., 2019).

Based on analysis using X-ray Fluorescence (XRF) instrumentation, palm bunch ash calcined at temperatures of 400 °C, 500 °C, and 600 °C contains the metal oxide components as shown in **Table 1**.

Table 1. XRF Result Metal Oxide Content in PBA

Metal Oxide	Calcination Temperature		
	400 °C (%)	500 °C (%)	600 °C (%)
K_2O	50.5	51.7	48.5
CaO	17.1	18.5	18.2
SiO_2	17.4	15.4	17.0
Other	15	14.4	16.3

The high K_2O and CaO content indicates the potential alkalinity of the catalyst, as both oxides are known to be active centers in transesterification reactions. These two oxides can provide O^{2-} and OH^- ions that support the mechanism of methoxide formation from methanol (Maneechakr & Karnjanakom, 2021). Other components such as SiO, Al_2O_3, and Fe_2O_3 were detected in significant amounts, which can affect the texture and structural strength of the catalyst.

High levels of SiO2 (15.4 %) are generally chemically inert, but they can function as a thermal and mechanical support matrix in heterogeneous catalyst systems. Other compounds such as Fe2O3, MnO, CuO, and ZnO were also found in small amounts. They did not contribute significantly to basic activity but could affect the texture, thermal stability, or mechanical strength of the catalyst (Zabeti et al., 2009).

The number of basic sites on the catalyst is expressed in moles of basic sites per gram. The basic strength of the catalyst surface refers to the catalyst's ability to convert adsorbed neutral acids into their conjugates electrically. The basicity value of the catalyst is determined by acid-base titration, as shown in **Table 2**.

Table 2. Results of alkalinity testing using the acid-base titration method

Calcination Temperature (°C)	Basicity (mmol/g)
400	15.48
500	15.62
600	15.66

The results of the basicity test using the fatty acid titration method showed that the average basicity of palm kernel shell ash catalyst was 15.58 mmol/g. This value indicates many basic sites that activate methanol molecules in the transesterification reaction. For comparison, in Mulyani et al. (2024), which tested the basicity of CaO metal oxide without doping, the value obtained was 23.5 mmol/g. This level of basicity is closely related to the dominant content of CaO and K_2O, where K_2O contributes as a strong base and CaO as a moderate base, both working synergistically to enhance catalytic activity. Comparing catalysts calcined at 400 °C, 500 °C, and 600 °C shows that 600 °C produces the highest number of basic sites, consistent with carbonate degradation and the formation of pure metal oxides. The choice of calcination temperature significantly influences the basicity of the catalyst (Boey et al., 2009). The dominance of strong base oxides such as K_2O and CaO is due to the deprotonation process, which directly contributes to forming Lewis base active sites capable of generating strong nucleophiles from methanol, particularly methoxide ions (CH_3O^-). These methoxide ions act as nucleophiles that attack the carbonyl ester groups in triglycerides, leading to transesterification reactions (Khatibi et al., 2021).

Characterization of Waste Cooking Oil

The waste cooking oil used in this study was obtained from household frying residues that had been repeatedly used to fry various types of food. The cooking oil was characterized to determine its initial quality before further processing. Several parameters were tested, including free fatty acid (FFA) content, acid value, viscosity, density, and constituent compound content based on GC-MS and FT-IR analysis. The characterization results are presented in **Table 3**.

Table 3. Results of characterization of WCO

Characterization	Result
FFA (%)	8.116
Acid Value (mg KOH/g sample)	16.911
Density (g/mL)	978
Viscosity (cSt)	13.949

The FFA content test using the alkalimetric titration method yielded a value of 8.116 %, indicating that this oil has undergone degradation. This figure is very high when compared to the recommended content for transesterification raw materials (< 2 %) (Rusdi et al., 2024). This is consistent with the acid number, significantly higher than the SNI standard at 16.911 mg KOH/g oil. This value indicates that the used cooking oil has undergone physical-chemical changes due to triglyceride hydrolysis, oxidation, decomposition, and oligomerization caused by repeated frying (Mustafa et al., 2023; Wiege et al., 2020). The acid number significantly affects oil quality, as a higher acid number indicates poorer oil quality. High levels of FFA and acid number can lead to side reactions such as soap formation/saponification when directly reacted with a basic catalyst. Therefore, pretreatment is required, such as esterification using an acid catalyst to reduce FFA levels (Santoso et al., 2023). Viscosity was calculated using the Poiseuille equation and water as the reference fluid, yielding a value of 50 cST (40 °C). This indicates that the oil experienced increased viscosity due to polar compounds forming from thermal and oxidative degradation. This value is influenced by changes in the degree of unsaturation of the fatty acid chain, where the double bonds decrease, making the oil more saturated and flow more difficult (Santos et al., 2005; Wiege et al., 2020). Furthermore, the measured density value of 0.999 g/ml is still within the general range of vegetable oils.

Characterization of Methyl Esters

As shown in Figure 2, the synthesis result of FAME must be ensured to meet applicable standards; therefore, physical and chemical properties are tested based on the parameters listed in SNI 7182: 2015. These parameters include density, kinematic viscosity, acid number, free fatty acid content, refractive index, saponification number, and iodine number. Each parameter serves a specific function in assessing the chemical stability, combustion performance, and corrosion potential of the fuel on the engine. The test results are then compared with the SNI quality limits to evaluate the compliance of the produced biodiesel. The test results are presented in **Table 4.**

Density indicates the amount or ratio of a substance in a unit volume. This test is influenced by fatty acid composition, namely the length of the ester carbon chain and the degree of fatty acid saturation. The longer the carbon chain, the greater the molecular mass (Verduzco et al., 2012). Density measurements were conducted using the pycnometric method at 40 °C. Based on **Table 1**, the sample with the highest calcination temperature (600 °C) produced biodiesel with a lower density than the other calcination temperatures. This change in density indicates a more stable and responsive catalyst pore structure as a result of optimal calcination, so the transesterification process runs more smoothly. In contrast, the biodiesel density at 400 °C showed a fluctuating pattern. This indicates that the active sites have not reached their peak and still contain residues or amorphous structures that are not yet uniform, thus affecting the reaction efficiency and composition after producing biodiesel (Verduzco et al., 2012).

(a) (b) (c)

Figure 2. FAME results with PBA catalyst at various temperature variants (a) 400 °C, (b) 500 °C, (c) 600 °C

Table 4. Test Results of Physical and Chemical Properties of FAM

Calcined Temp.	Conc.	Parameter Uji							
		Yield (g)	Density (g/ml)	Viscosity (cSt)	Acid Value (mg KOH/g)	FFA (%)	Index of Bias	Saponification Numbers (mg KOH/g)	Iod Numbers (g I_2/100 g)
SNI 7182:2015		-	850-890	2.3-6.0	Max. 0.5	Max. 0.2	1.445 – 1.462	-	Max. 115
400°C	3%	90.668	894	7.04	0.548	0.263	1.451	160.13	71.242
	5%	91.876	903	3.76	0.543	0.261	1.446	169.73	70.014
	7%	90.676	898	6.64	0.545	0.262	1.450	164.89	65.638
	9%	91.848	899	5.27	0.544	0.261	1.450	165.95	79.900
500°C	3%	92.580	904	5.70	0.544	0.261	1.448	168.58	73.833
	5%	93.744	902	4.33	0.548	0.263	1.446	172.62	80.953
	7%	93.676	880	4.02	0.546	0.262	1.445	167.25	77.550
	9%	93.568	880	3.33	0.547	0.263	1.446	172.90	70.014
600°C	3%	91.472	898	4.08	0.544	0.261	1.445	169.56	80.953
	5%	92.928	880	3.94	0.549	0.263	1.446	171.67	79.624
	7%	92.296	878	3.59	0.545	0.262	1.446	166.52	92.065
	9%	92.048	897	3.75	0.546	0.262	1.445	174.56	67.826

The following test parameter is viscosity. Viscosity is important to study because it is related to performance and directly affects injection efficiency, fuel atomization, and the formation of the air-fuel mixture in the combustion chamber. Viscosity values were calculated using the Poiseuille equation, and water was used to compare fluids. Test results based on **Table 1**, at calcination temperatures of 500 °C and 600 °C, show viscosity values within the standard range of SNI 7182: 2015 (2.3 - 6.0 cSt). In contrast, samples at 400 °C with 3 % and 5 % catalyst dosage had viscosity values that exceeded the maximum limit of 7.04 cSt and 6.64 cSt, respectively, indicating an imperfect transesterification reaction or high residual triglyceride content.

Based on thermodynamics, a calcination temperature that is too low limits the active surface area of the catalyst, and imperfect oxide structures are formed, reducing the catalytic base activity. This can produce products with longer carbon chains, thus increasing the product's viscosity. Catalysts calcined at 500 °C and 600 °C have more stable and uniformly distributed base sites that can encourage the formation of many double bonds and produce lower viscosity (Knothe & Steidley, 2011).

The acid number of the biodiesel produced (0.543 - 0.549 mg KOH g^{-1}) already exceeded SNI 7182: 2015 (≤ 0.5 mg KOH g^{-1}), the deviation was still not too far from the tolerance limit, considering that the method used was manual titration with a minimal titrant volume. This confirms that the transesterification reaction was effective at all combinations of calcination temperatures (400 °C - 600 °C) at various doses. Neither temperature nor dosage variation showed a significant trend; the difference between values was only ± 0.005 mg KOH g-1, because the concentration of active strong bases (metal oxides) in the catalyst ash was sufficient even at the lowest temperature to neutralize free fatty acids (FFA). The remaining FFA content (0.261 - 0.263 %) is still within the practical limits often used in industry, although it slightly exceeds the 0.20 % figure often used as a reference for raw material quality. This indicates that a small amount of free fatty acids remains post-reaction, but the amount is not significant enough to destabilize the product or cause biodiesel quality degradation (Santoso et al. 2018).

The resulting iodine number is considered to meet the saturation criteria. It is still below the maximum limit of 115 g I_2/100 g according to SNI 7182: 2015, which is in the range of 71 - 107 g I_2/100 g for all changes in calcination temperature and catalyst dose (Sumari et al., 2021). The iodine number indicates the degree of unsaturation of compounds in biodiesel, especially the number of double bonds in fatty acids. With a catalyst dose of 5 - 7 % and calcination temperatures of 400 °C and 500 °C, the highest value (107.209 g I_2/100 g) was obtained, close to the maximum limit but still safe. This indicates that the structure of unsaturated fatty acids is generally maintained during the transesterification process under these conditions. Overall, the 400 °C - 500 °C condition with a 5 - 7 % dosage is still in the optimal balance and remains safe from the oxidation limit according to SNI.

Analysis of FAME Components with FTIR and GC-MS

The results of the FT-IR spectra analysis are shown in **Figure 3**, which shows several absorption peaks and a variety of characteristic bands presented in **Table 5**. The absorption peaks of the biodiesel fingerprint region are 400 - 1500 cm^{-1}, indicating the presence of functional groups related to the catalyst from palm bunch ash (Phetrungnapha et al., 2023).

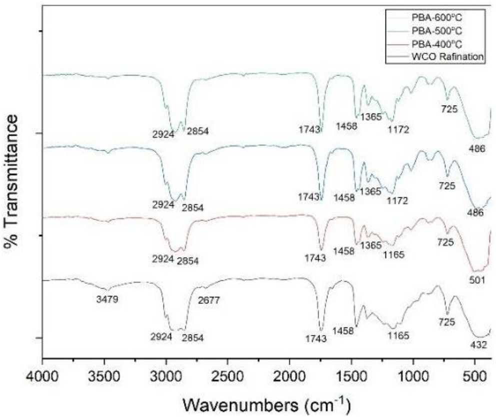

Figure 3. FTIR Spectrum of FAME and WCO

Table 5. Analysis IR spectrum

Wavenumbers (cm-1)	Absorption Intensity	Signature Band
3479	weak-broad	stretching vibration of O-H (carboxylic acid)
3001	medium-sharp	stretching vibration of C-H sp^2 (=C-H)
2924-2854	strong-sharp	stretching vibration of C–H sp^3 (–CH_2/CH_3)
1743	strong-sharp	stretching vibration of C=O ester
1458	medium-sharp	rocking vibration of CH_2 / CH_3
1365	medium-sharp	stretching vibration of –CH_3 bend to O (–O–CH_3)
1172-1165	strong-sharp	stretching vibration of C-O ester
725	medium-sharp	rocking vibration of $(CH_2)n$
501-432	strong-broad	metal–O stretching vibration –O / Si–O

In the WCO spectra at wave number 3479 cm^{-1}, there is a peak with weak intensity and very wide, showing the characteristic O-H bond stretching vibrations for carboxylic acid compounds, which indicates that WCO still contains free fatty acids, which, in the ATS spectra, do not appear. At wave number 3001 cm^{-1}, there is one peak with medium intensity and sharp, which shows the characteristic of C-H sp^2 (=C-H) bond stretching vibrations. This indicates that both WCO and FAME ATS compounds have unsaturated hydrocarbon groups, namely alkene. In the wave number region of 2924 cm^{-1} - 2854 cm^{-1}, two peaks with strong and sharp intensity show the characteristic C-H sp^3 ($-CH_2/CH_3$) bond stretching vibrations, which indicate that there are saturated hydrocarbon groups, namely alkane compounds (Santoso et al., 2018). Typical methyl esters display a peak at a wave number of 1740 cm^{-1} with a strong and sharp intensity that shows a typical C=O stretching vibration in ester compounds. This peak vibrates asymmetrically and is characteristic of FAME.

At wave number 1365 cm^{-1}, which has a medium-sharp intensity, there is symmetrical bending of the ($-CH_3$) group, which indicates the presence of the $-OCH_3$ methoxy group in FAME. This indicates the attachment of the alkyl group of the alcohol to the triglyceride fatty acid. Followed by the appearance of C-O stretching vibrations with strong and sharp intensity that appeared at wave numbers 1172 cm^{-1} - 1165 cm^{-1}.

This shows that the compound has a C-O bond in the ester group. The peak of 1170 cm^{-1} shows the $O-CH_3$ stretch, characteristic of FAME (Fereidooni et al., 2021).

GC-MS identified the fatty acid composition of the biodiesel. Peak identification was done by comparing each peak's retention time and mass band against the mass spectra data in the library (NIST12.LIB) (Agunbiade & Adewole, 2014).

The product analyzed synthesized a five wt% % palm bunch ash catalyst with a calcination temperature of 500 °C. **Figure 4** shows the chromatogram of the synthesized biodiesel along with the FAME distribution.

The GC-MS chromatogram in Figure 4 shows eight peaks, indicating the constituent compounds present in the biodiesel product. Table 6 shows eight compound peaks with the highest area (Saleem et al., 2022).

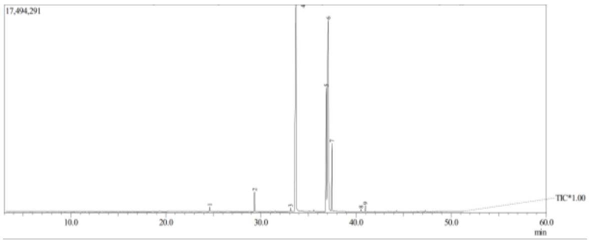

Figure 4. GC-MS Results Chromatogram of FAME in PBA-500-5%

Table 6. Retention Time and Area of FAME Product PBA-500-5 %

Retention Time (minutes)	% Area
24.616	0.38
29.326	1.57
33.141	0.28
33.688	37.18
36.879	14.13
37.096	40,31
37.472	5.67
40.986	0.49

The constituent components of biodiesel for each retention time in **Table 6** were analyzed for fragmentation to determine the constituent compounds of the biodiesel product. The mass spectra of biodiesel with the highest area with retention times of 37.096 and 33.688 minutes are shown in **Figures 5 and 6**.

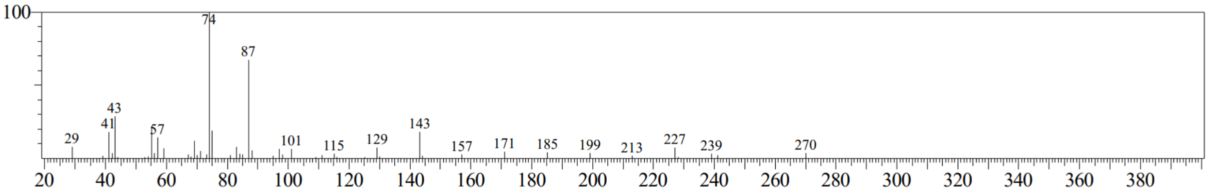

Figure 5. Mass Spectrum of Biodiesel with a Retention Time of 37.096 minutes.

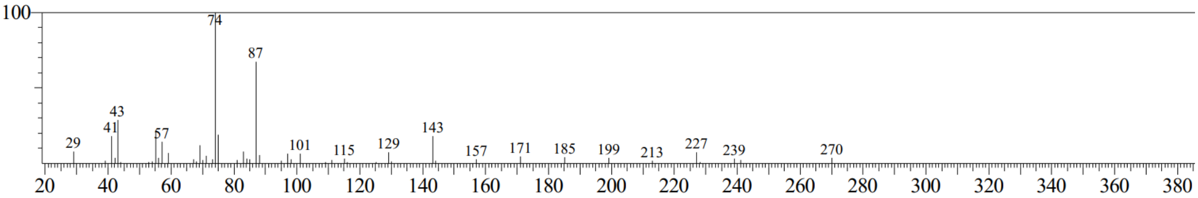

Figure 6. Mass Spectrum of Biodiesel with a Retention Time of 33.688 minutes.

Figure 5 is the mass spectrum of the product compound with the highest area at the retention time of 37.096 minutes, which has a similarity index of 95 % with the NIST12.LIB library No. 10.438. The suspected compound is methyl oleate ($C_{19}H_{36}O_2$). The mass spectrum was analyzed for fragmentation patterns to support the assumption that the compound was methyl oleate. Methyl oleate is an ester form of oleic acid with a molecular weight of 296 m/z. This compound undergoes a fragmentation pattern based on the cleavage rule at the branch point, with a break as seen in **Figure 7**. In the mass spectrum of the methyl oleate compound, the molecular ion remains detectable, albeit with low intensity. The m/z 296 molecular ion of methyl oleate has two fragmentation pathways typical for long-chain esters. The first fragmentation involves the release of the methanol (CH_3OH) group from the ester group and produces an ion of mass m/z 264.

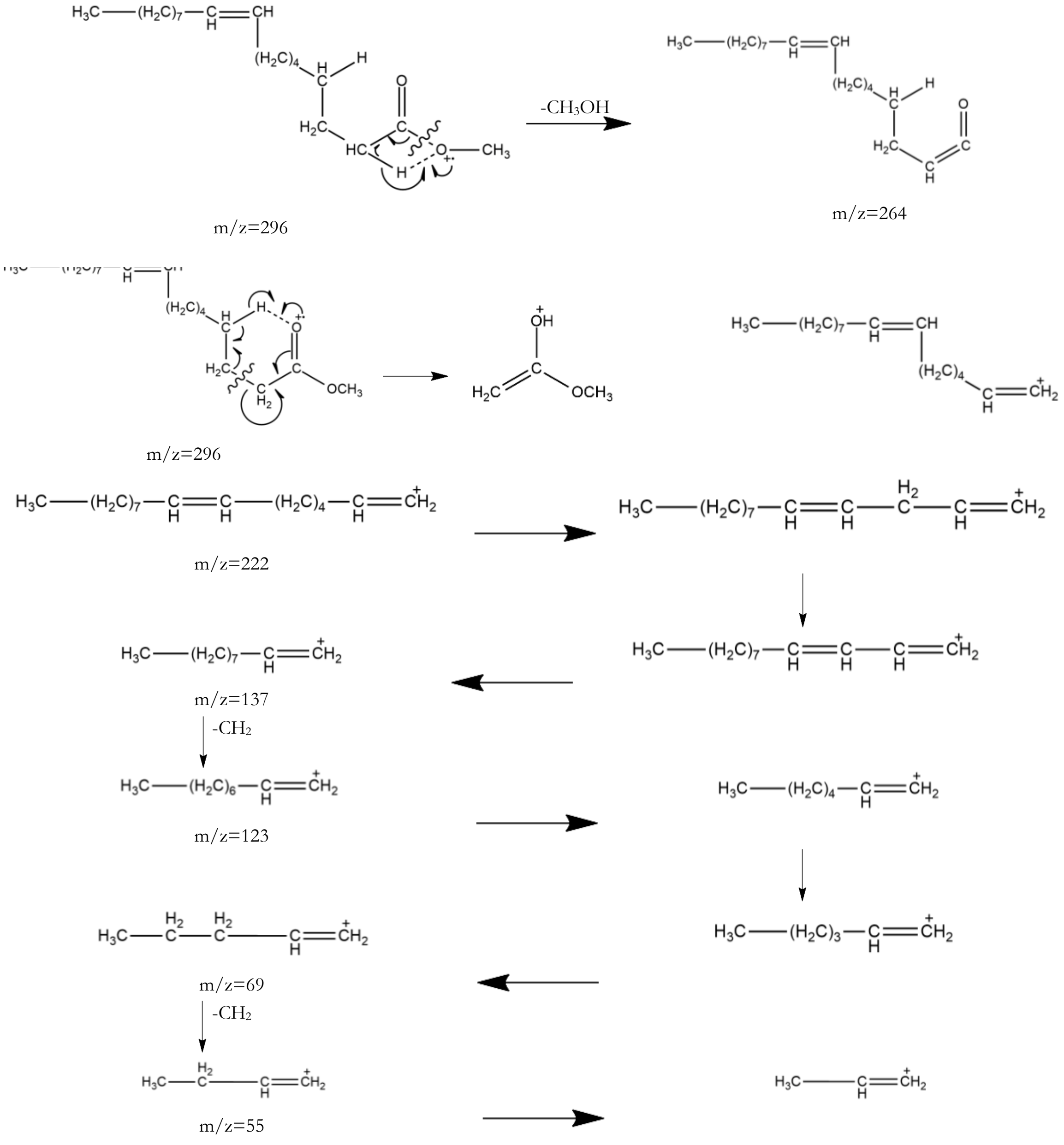

Figure 7. Fragmentation pattern of the compound at retention time 37.096 minutes

The second typical fragmentation pattern is through the McLafferty rearrangement mechanism, which produces two main fragments, namely m/z 74 mass ion and m/z 222 mass ion, which are the remaining unsaturated hydrocarbon chain of methyl oleate (Ismiyarto et al., 2006).

Furthermore, the series of fragments m/z = 137, 123, 97, 83, 69, 55, and 41 shows a typical fragmentation pattern, where each peak has a difference of 14, which indicates the sequential release of the $-CH_2$ group. Based on the fragmentation pattern in the mass spectrum, it can be proved that the compound formed is methyl oleate with the structure shown in **Figure 8**.

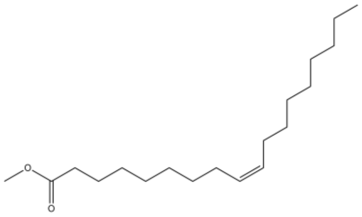

Figure 8. Methyl oleate structure ($C_{19}H_{36}O_2$)

The second highest peak at a retention time of 33.688 minutes, shown in Figure 6, shows a reasonably high intensity and indicates the presence of methyl palmitate compounds ($C_{17}H_{34}O_2$). It has a similarity index of 95 % with the NIST12.LIB library No. 9775. The fragmentation pattern formed is also consistent with the characteristics of methyl esters of saturated fatty acids, including the appearance of typical fragmentation peaks such as m/z 239 due to the release of methanol (CH_3OH), as well as fragment m/z 74, which shows typical ester rearrangement (Hädeler, 2025). The mass spectrum was analyzed for fragmentation patterns based on the cleavage rules listed in **Figure 9**.

Fragmentation of methyl palmitate shows typical ester identification characteristics, starting with the McLafferty rearrangement mechanism, which produces a stable fragment m/z 74 through γ-hydrogen transfer and β-γ bond breaking. This fragment then undergoes the release of the $-OCH_3$ group, producing ion m/z 43, an acylium ion ($CH_2{=}CO^+$). This pattern confirms the presence of long-chain saturated ester groups in the compound structure (Torres et al., 2020)

Other chromatogram peaks were identified similarly, resulting in the biodiesel product compound components, retention times, and concentrations shown in **Table 7**.

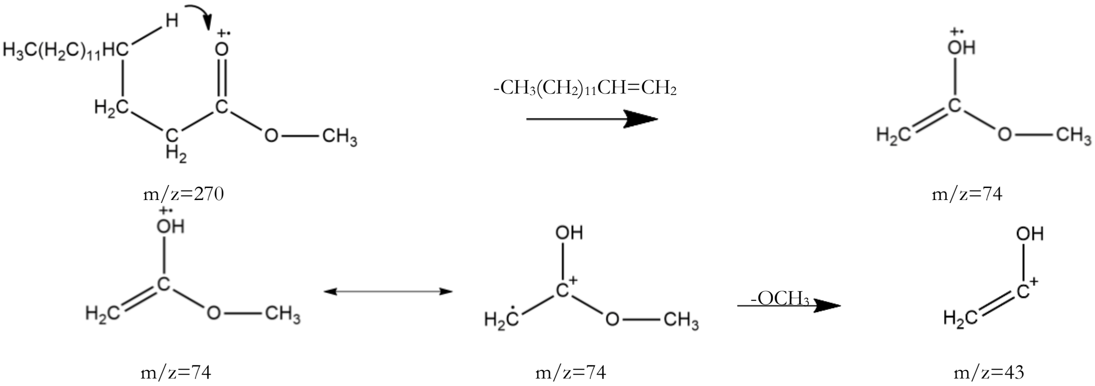

Figure 9. Fragmentation pattern of the compound at retention time 33.688 minutes

Table 7. FAME Content of Biodiesel

Retention time	Compund	Rumus Molekul	Luas Area (%)
24.616	Methyl dodecanoate (methyl laurate)	$C_{13}H_{26}O_2$	0.38
29.326	Methyl tetradecanoate (methyl myristate)	$C_{15}H_{30}O_2$	1.57
33.141	Methyl 9-hexadecenoate (methyl palmitoleate)	$C_{17}H_{32}O_2$	0.28
33.688	Methyl hexadecanoate (methyl palmitate)	$C_{17}H_{34}O_2$	37.18
36.879	Methyl 9,12-octadecadienoate (methyl linoleate)	$C_{19}H_{34}O_2$	14.13
37.096	Methyl 9-octadecenoate (methyl oleate)	$C_{19}H_{36}O_2$	40.31
37.472	Methyl octadecanoate (methyl stearate)	$C_{19}H_{38}O_2$	5.67
40.986	Methyl eicosanoate (methyl arachidate)	$C_{21}H_{42}O_2$	0.49

Catalyst Reusability Test

The Heterogeneous base catalytic biodiesel synthesis has the advantage of being reusable. The palm bunch ash catalyst used in the transesterification reaction cycle was reused with the addition of 5 wt% % catalyst, a methanol: oil ratio of 15:1, and a reaction temperature of 65 °C, with a time of 3 hours. After each cycle, the solid catalyst was separated from the mixture and washed with n-hexane and acetone. It was then re-calcined at 500 °C for further use (Niju et al., 2014). The results showed that the catalyst could maintain its activity and be reused up to four cycles. Data on the characteristics of biodiesel with reused catalysts are presented in **Table 8**.

The results show that the catalyst can maintain its catalytic properties in the second and third uses. The biodiesel yield decreased from ± 92 % (first cycle) to 91 % and 90 %, indicating that the catalytic activity remains functionally maintained. The acid number of the product remained below 0.55 mg KOH/g.

The results show that the catalyst can maintain its catalytic properties in the second and third uses. The biodiesel yield decreased from ± 92 % (first cycle) to 91 % and 90 %, indicating that the

catalytic activity remains functionally maintained. The acid number of the product remained below 0.55 mg KOH/g.

Table 8. Physical and chemical properties of reused catalyst FAME

Characteristics	Reuse		
	2	3	4
Yield (g)	91.216	90.988	81.060
Density (g/ml)	881	895	911
Viscosity (cSt)	4.02	3.93	4.45
FFA (%)	0.263	0.263	0.263
Acid Value (mg KOH/g)	0.548	0.548	0.548
Index of Bias	1.456	1.459	1.459
Saponification Numbers (mg KOH/g)	209.604	213.303	214.322
Iod Numbers (g I2/100 g)	95.175	100.056	92.291

The decrease in yield in the fourth reuse (81.060 %) was likely caused by residues such as glycerol, mono-diglycerides, and methanol on the active surface of the catalyst. In addition, the gradual dissolution of light alkali metals (K^+/Ca^{2+}) into the liquid phase also reduced the fundamental strength of the catalyst. However, catalyst activity can be partially restored through washing with n-hexane and acetone and recalcination at the appropriate temperature for 4 hours. This treatment removes organic contaminants and reactivates the basic sites, resulting in biodiesel yields nearly equivalent to the initial cycle (± 90 %). With relatively stable performance and simple recovery, this catalyst shows excellent potential for application in biodiesel production, requiring cost efficiency and minimal waste.

Conclusions

The synthesis of biodiesel using calcined palm bunch ash (PBA) catalyst at 600 °C produced the best biodiesel (conversion rate of 92 % ± 1), with an average kinematic viscosity of 3.79 cSt at 40 °C and a density of 0.888 g mL^{-1}, both within the limits specified by SNI/EN 14214. In contrast, the iodine number of 80.116 g I2 100 g^{-1} ensures oxidative stability, and the saponification number of 170.57 mg KOH g^{-1} confirms the dominance of the C16 –C18 chain, as well as a refractive index of 1.445. GC-MS analysis shows the central peak of methyl oleate at tR ≈ 37.096 minutes with an area of 40.31 %, indicating unsaturated components as the most significant fraction, while FT - IR shows a single peak of C–O–CH3 (≈ 1172 – 1165 cm^{-1}) characteristic of ester compounds. These results confirm that the transesterification process at the highest calcination temperature produces high-quality biodiesel suitable for use as fuel.

Acknowledgment

The author would like to express sincere gratitude to Prof. Dr. Aman Santoso, M.Si., the principal supervisor, for his ideas, guidance, and continuous support throughout this research, and to Prof. Dr. Sumari, M.Si., the co-supervisor, for his valuable input and assistance.

References

Agunbiade, F. O., & Adewole, T. A. (2014). Methanolysis of carica papaya seed oil for the production of biodiesel. *Journal of Fuels*, *2014*(1), 1–6.

Attari, A., Mayvan, A. A., & Alisaraie, A. T. (2022). Process optimization of ultrasonic-assisted biodiesel production from waste cooking oil using waste chicken eggshell-derived CaO as a green heterogeneous catalyst. *Biomass and Bioenergy*, *158*(January). 106357

Aworanti, O. A., Agbede, O. O., Popoola, A. O., Ogunsola, A. D., Agarry, S. E., Adekunle, O. J., Ogunkunle, O., Laseinde, O. T., Odesanmi, A. A., & Alade, A. O. (2022). Synthesized heterogeneous nano-catalyst from cow teeth for fatty acid methyl esters production through transesterification of waste vegetable frying oil and methanol: Characterization and optimization studies. *Engineering Reports*, *5*(5), 1–25.

Berchmans, H. J., & Hirata, S. (2008). Biodiesel production from crude Jatropha curcas L. seed oil has a high content of free fatty acids. *Bioresource Technology*, *99*(6), 1716–1721.

Boey, P. L., Maniam, G. P., & Hamid, S. A. (2009). Biodiesel production via transesterification of palm olein using waste mud crab (Scylla serrata) shell as a heterogeneous catalyst. *Bioresource Technology*, *100*(24), 6362–6368.

Chi, L. (1999). The production of methyl esters from vegetable oil/fatty acid mixtures. *Thesis*, University Of Toronto, Ontario, Canada.

Fereidooni, L., Abbaspourrad, A., & Enayati, M. (2021). Electrolytic transesterification of waste frying oil using Na^+/zeolite–chitosan biocomposite for biodiesel production. *Waste Management*, *127*(May), 48–62.

Galadima, A., & Muraza, O. (2020). Waste materials for production of biodiesel catalysts: Technological status and prospects. *Journal of Cleaner Production*, *263*(August), 121358.

Hädeler, J. (2025). Natural abiotic iron-mediated formation of C1 and C2 compounds from environmentally important methyl-substituted substrates and their implication for nature. *Dissertation*, Ruprecht Karls University

Heidelberg, Heidelberg, Germany.

Hambali, E., Mujdalifah, S., Tambunan, A. H. Prattiwiri, A. W., & Hendroko, R. (2007). *Teknologi Bioenergi*. Tangerang: PT AgroMedia Pustaka.

Ismiyarto, Halim, S. A., & Wibawa, P. J. (2006). Identification of fatty acid compotition in turi seed oil (Sesbania grandifora (L) Pers). *Jurnal Kimia Sains dan Aplikasi*, *IX*(1), 1–3.

Japir, A. A. W., Salimon, J., Derawi, D., Bahadi, M., Al-Shuja'A, S., & Yusop, M. R. (2017). Physicochemical characteristics of high free fatty acid crude palm oil. *Oilseeds and Fats, Crops and Lipids*, *24*(5), 1-9.

Jiang, S., You, Z., & Tang, N. (2023). Effects of calcination temperature and calcination atmosphere on the performance of CO_3O_4 catalysts for the catalytic oxidation of toluene. *Processes*, *11*(7), 1-14.

Joshi, S., Gogate, P. R., Moreira, P. F., & Giudici, R. (2017). Intensification of biodiesel production from soybean oil and waste cooking oil in the presence of heterogeneous catalyst using high speed homogenizer. *Ultrasonics Sonochemistry*, *39*(November), 645–653.

Khatibi, M., Khorasheh, F., & Larimi, A. (2021). Biodiesel production via transesterification of canola oil in the presence of Na–K doped CaO derived from calcined eggshell. *Renewable Energy*, *163*(January), 1626–1636.

Knothe, G., & Steidley, K. R. (2011). Kinematic viscosity of fatty acid methyl esters: Prediction, calculated viscosity contribution of esters with unavailable data, and carbon-oxygen equivalents. *Fuel*, *90*(11), 3217–3224.

Maneechakr, P., & Karnjanakom, S. (2021). Systematic production of biodiesel fuel from palm oil over porous $K_2O.CaO$ catalyst derived from waste chicken eggshell via RSM/kinetic/thermodynamic studies. *Journal of Environmental Chemical Engineering*, *9*(6), 106542.

Mulyani, Y., Nurhayati, & Awaluddin, A. (2024). Effect of acidity , basicity , and heterogeneous CaO/silica gel catalyst from biomass waste on biodiesel yield from crude palm oil. *Al Kimiya: Jurnal Ilmu Kimia Dan Terapan*, *11*(2), 121–131.

Mustafa, K., Oko, S., & Sirajuddin, S. Z. (2023). Utilization of red onion skin extract as a natural antioxidant to reduce free fatty acid levels in used cooking oil. *International Journal of Multidisciplinary Reseacrh and Publications, 6*(6), 264–267.

Niju, S., Begum, K. M. M. S., & Anantharaman, N. (2014). Modification of egg shell and its application in biodiesel production. *Journal of Saudi Chemical Society*, *18*(5), 702–706.

Nuryanti R., Anggraini, I. F., Sari D. K., & Sonya. (2023). Uji kualitas bahan bakar biodiesel dari minyak jelantah (penggorengan pecel lele) dengan parameter uji spesific gravity 60/60 °f astm d-1298, distilasi astm d-86, viskositas kinematik astm d-445, flash point pm astm d-93, pour point astm d-97 dan cetane. *Jurnal Cakrawala Ilmiah*, *3*(1), 229–236.

Okoye, P. U., Wang, S., Xu, L., Li, S., Wang, J., & Zhang, L. (2019). Promotional effect of calcination temperature on structural evolution, basicity, and activity of oil palm empty fruit bunch derived catalyst for glycerol carbonate synthesis. *Energy Conversion and Management*, *179*(January), 192–200.

Patil, A. D., Baral, S. S., Dhanke, P. B., Madankar, C. S., Patil, U. S., & Kore, V. S. (2018). Parametric studies of methyl esters synthesis from thumba seed oil using heterogeneous catalyst under conventional stirring and ultrasonic cavitation. *Materials Science for Energy Technologies*, *1*(2018), 106–116.

Phetrungnapha, A., Wiengnak, N., & Maikrang, K. (2023). Removal of free fatty acid from waste cooking oil using an adsorbent derived from cassava peels. *Korean Journal of Chemical Engineering*, *40*(9), 2253–2262.

Posada, L. R., Shi, J., Kakuda, Y., & Xue, S. J. (2007). Extraction of tocotrienols from palm fatty acid distillates using molecular distillation. *Separation and Purification Technology*, *57*(2), 220–229.

Rusdi, H. O., Kusumaningrum, I. K., Nareswari, T. J., Fauziah, P. N., Maharani, R. N., & Natasya, S. (2024). Separation and determination of free fatty acids in corn oil and palm oil by liquid-liquid extraction and acidi-alkalimetric titration. *Walisongo Journal of Chemistry, 7*(1), 98-106.

Saleem, M., Jamil, F., Qamar, O. A., Akhter, P., Hussain, M., Khurram, M. S., Al-Muhtaseb, A. H., Inayat, A., & Shah, N. S. (2022). Enhancing the catalytic activity of eggshell-derived cao catalyst and its application in biodiesel production from waste chicken fat. *Catalysts*, *12*(12), 1-14.

Santos, J. C. O., Santos, I. M. G., & Souza, A. G. (2005). Effect of heating and cooling on rheological parameters of edible vegetable oils. *Journal of Food Engineering*, *67*(4), 401–405.

Santoso, A., Sumari, Asrori, M. R., & Januarti, W. (2023). Biodiesel characterization study from castor oil (Jatropha curcas L) with CaO/K_2O catalyst. *Jurnal IPTEK Media Komunikasi Teknologi*, *27*(2), 95–106.

Santoso, A., Sumari, S., Sukarianingsih, D., & Sari, R. M. (2018). Optimization of Synthesis of Biodiesel from Jatropha curcas L. with Heterogeneous Catalyst of CaO and MgO by Transesterification Reaction Using Microwave. *Journal of Physics: Conference Series*, *1093*(September), 1-8.

Santoso, A., Sumari, Salim, A., & Marfu'ah, S. (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. *Journal of Physics: Conference Series*, *1093*(September), 1-9.

Sujadi, Hasibuan, H. A., Rahmadi, H. Y., & Purba, A. R. (2016). Komposisi asam lemak dan bilangan iod minyak dari sembilan varietas kelapa sawit DxP komersial di PPKS. *Jurnal Penelitian Kelapa Sawit*, *24*(1), 1–11.

Sumari, Santoso, A., & Asrori, M. R. (2021). A review: Synthesis of biodiesel from low/off grade crude palm oil on pretreatment, transesterification, and characteristics. *Orbital: the Electron Journal of Chemistry*, *13*(4), 385–391.

Suroso, A. S. (2013). Kualitas minyak goreng habis pakai ditinjau dari bilangan peroksida, bilangan asam dan kadar air. *Jurnal Kefarmasian Indonesia, 3*(2), 77-88.

Torres A., Fuentes B., Rodríguez, K. E., Brito, A., & Díaz, L. (2020). Analysis of the content of fatty acid methyl esters in biodiesel by fourier-transform infrared spectroscopy: method and comparison with gas chromatography. *Journal of the American Oil Chemists' Society, 97*(6), 651–661.

Verduzco, R. L. F., Rodríguez-Rodríguez, J. E., & Jaramillo-Jacob, A. D. R. (2012). Predicting cetane number, kinematic viscosity, density and higher heating value of biodiesel from its fatty acid methyl ester composition. *Fuel*, *91*(1), 102–111.

Widyaningsih, F., Irwanto, R., & Panjaitan, D. (2023). Characterization of Oil Palm Sap (Elaeis guineensis Jacq. Results of Zero Waste Based Waste Treatment). *Jurnal Kesehatan Masyarakat dan Gigi*, *5*(2), 195–202.

Wiege, B., Fehling, E., Matthäus, B., & Schmidt, M. (2020). Changes in physical and chemical properties of thermally and oxidatively degraded sunflower oil and palm fat. *Foods*, *9*(9), 1-14.

Yucel, O. S., & Turkay, S. (2002). Variables affecting the yields of methyl esters derived from in situ esterification of rice bran oil. *Journal of the American Oil Chemists' Society*, *79*(6), 611–614.

Zabeti, M., Wan Daud, W. M. A., & Aroua, M. K. (2009). Activity of solid catalysts for biodiesel production: A review. *Fuel Processing Technology*, *90*(6), 770–777.

Zheng, Y., Zhang, W., Li, Y., Chen, J., Yu, B., Wang, J., Zhang, L., & Zhang, J. (2017). Energy related CO_2 conversion and utilization: Advanced materials/nanomaterials, reaction mechanisms and technologies. *Nano Energy*, *40*(October), 512–539.