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Synthesis of Calcium Glyceroxide Catalyst from Pensi Shells for CPO-Based Biodiesel Production

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Abstract

The synthesis of a calcium glyceroxide catalyst derived from pensi shells for biodiesel production using crude palm oil (CPO) has been successfully conducted. The catalyst was prepared via the wet impregnation method by reacting CaO with glycerol in methanol as a solvent for 5 hours at 65°C, with catalyst-to-glycerol ratios of 1:1, 1:1.5, and 1:2. The glycerol used was obtained from crude glycerol, a by-product of biodiesel transesterification. CaO was derived from the calcination of pensi shells at 1000°C. The synthesized catalyst was tested for activity in biodiesel production from CPO. The test parameters included catalyst concentrations of 1.5%, 2%, and 2.5%, reaction times of 2 hours and 4 hours, and oil-to-methanol molar ratios of 1:5. The biodiesel yield for a 2-hour reaction time at catalyst concentrations of 1.5%, 2%, and 2.5% was 56.32%, 54.80%, and 50.19%, respectively. For a 4-hour reaction time at the same concentrations, the biodiesel yields were 40.28%, 60.73%, and 65.98%, respectively. Catalyst characterization was performed using XRD, XRF, SEM, and FTIR to support the activity test data. SEM analysis visually confirmed the bonding between CaO and glycerol. XRD results revealed the highest peaks at 2θ angles of 37.621° for CaO and 34.101° for $Ca(OH)_2$, indicating a bond formation between CaO and glycerol. XRF analysis determined a CaO concentration of 96.21%. FTIR analysis identified the presence of glycerol through dominant -OH and C-O groups. The quality of the resulting biodiesel was tested against SNI (Indonesian National Standard) parameters. The analysis showed the highest methyl ester content (95.6%) at a reaction time of 4 hours. The highest oxidation stability (10.77 hours) was observed at a reaction time of 2 hours. Additional results included an acid number of 0.1%, total glycerol content of 0.279%-b, free glycerol content of 0.018%-b, and viscosity at 40°C of 3.559 mm^2/s. The quality test results demonstrated that several parameters met SNI biodiesel standards.

1. Introduction

Catalysts play a crucial role in biodiesel production. Typically, homogeneous base catalysts such as KOH and NaOH are used in biodiesel synthesis. However, these catalysts have significant drawbacks, including high chemical costs and the inability to regenerate for reuse, which increases production costs and limits their practicality [1, 2].

To address these challenges, various studies have focused on developing heterogeneous catalysts using materials rich in calcium carbonate ($CaCO_3$). For instance, Anindita *et al.* [3] synthesized CaO/K_2O catalysts from limestone, achieving a FAME yield of 65.2%. Alam *et al.* [4] successfully synthesized CaO catalysts from duck eggshells, producing biodiesel with a yield of 78.4% in 3 hours. Similarly, Syahputri and Broto [5] developed CaO catalysts from chicken eggshells, yielding 78.2% biodiesel in 130 minutes.

Despite these advancements, the 2023 SNI quality standard for methyl esters requires a minimum purity of

96.5%. Catalysts derived solely from CaO often yield suboptimal biodiesel and require prolonged reaction times. This limitation arises because CaO tends to bind with the glycerol formed during the initial stages of transesterification, reducing its catalytic efficiency. By impregnating CaO with glycerol, a heterogeneous calcium glyceroxide catalyst can be synthesized. This modification enhances catalytic activity, as the CaO is saturated with glycerol beforehand, preventing it from binding glycerol during the reaction and thereby accelerating the reaction rate [6, 7].

In this study, pensi shells, a natural resource abundant in West Sumatra, serve as a source of calcium carbonate ($CaCO_3$) for producing CaO. The glycerol used originates from the by-product of the transesterification process. This approach aims to develop a catalyst capable of producing biodiesel that meets the SNI methyl ester quality standard.

2. Experimental

2.1. Tools and Instruments

The materials used in this study included pensi shells sourced from a traditional market in Padang City, crude glycerol, and CPO obtained from PT. Padang Raya Cakrawala and chemicals such as methanol, ethanol, phosphoric acid, and hydrochloric acid (HCl) supplied by CV. Novalindo. Catalyst characterization was conducted using XRD (X'Pert Pro Powder Pw3040/60 PANalytical), XRF (PANalytical Epsilon 3), FTIR (PerkinElmer Frontier Optica), and SEM (Hitachi Tabletop Microscope TM 3000). Biodiesel quality testing adhered to SNI 7182:2015 standards, while oxidation stability testing followed the Rancimat method (EN 15751).

2.2. Synthesis of Calcium Glyceroxide Catalyst

The pensi shell, used as the raw material for CaO, was cleaned with running water and 0.1 M HNO_3 to remove impurities. It was then dried in an oven at 105°C for 5 hours. After drying, the shell was ground and sieved using a 60-mesh sieve to achieve a uniform particle size. The sieved shell was calcined at 1000°C for 5 hours to produce CaO. Wet impregnation was performed using CaO-to-glycerol molar ratios of 1:1, 1:1.5, and 1:2. CaO and crude glycerol were dissolved in 100 mL of CH_3OH and heated under reflux at 65°C for 5 hours. The resulting mixture was filtered and washed with 96% C_2H_5OH. The solid product was dried at 80°C until its weight stabilized. The calcium glyceroxide catalyst was characterized using SEM to examine morphology and compositional uniformity, XRD to identify bonds formed, XRF to determine CaO content, and FTIR to identify functional groups [8, 9, 10].

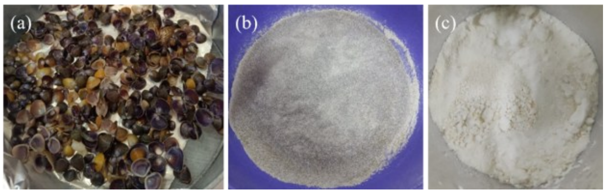

Figure 1. (a) Initial shell, (b) before calcination, and (c) after calcination

2.3. Crude Glycerol Purification

The purpose of refining crude glycerol was to remove residual alcohol, catalyst, and water, as well as to neutralize its pH. The purification process involved microfiltration, neutralization, and washing. Crude glycerol was first filtered through a 60-mesh sieve to remove traces of catalyst and solid particles. The filtered glycerol was then heated at 105°C for 10 minutes. Due to its high pH of 10, neutralization was necessary, which was achieved by adding HCl until the pH reached 2. The mixture was then transferred to a separating funnel, where three layers formed: the upper layer contained free fatty acids, the middle layer was glycerol-rich, and the bottom layer consisted of the base catalyst neutralized by the acid, along with the acid waste. The glycerol-rich layer was separated and washed with ethanol to enhance the purity of the glycerol and remove any remaining impurities. The washed glycerol was heated for 10 minutes at 105°C to evaporate any residual water or alcohol [11, 12].

2.4. CPO Refining

CPO, as a raw material for biodiesel production, was first purified using the glycerolysis method. This method involved reacting glycerol with CPO to reduce the free fatty acids content of the CPO, making it suitable for biodiesel production. At this stage, glycerol was mixed with a KOH catalyst and stirred at high speed at 65°C. N- hexane was then added to facilitate solubility. Once the mixture reached the desired solubility, it was added to the heated CPO, and the reaction time began once mixing occurred. After the reaction was complete, the mixture was transferred to a separating funnel. Separation occurred over 2-4 hours. The top layer was the glycerolysis product, while the bottom layer consisted of unreacted glycerol [13, 14, 15].

3. Results and Discussion

3.1. Calcium Glyceroxide Catalyst

The pensi shell, used as a raw material in this study for $CaCO_3$ extraction, was first cleaned and ground using a blender. After grinding, the shell was sieved through a 60-mesh sieve to obtain a homogeneous powder. The powder was calcined at 1000°C for 5 hours to produce CaO [2].

Figure 2. Calcium glyceroxide catalyst synthesis process

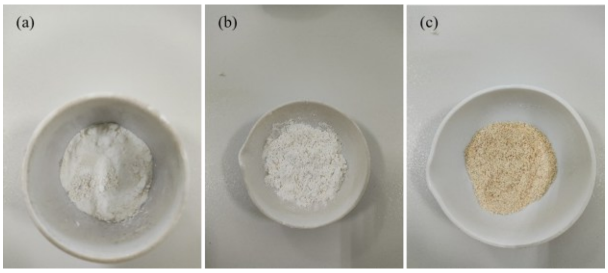

Figure 3. Calcium glyceroxide catalyst variations: (a) CaO:glycerol ratio of 1:1, (b) ratio of 1:1.5, and (c) ratio of 1:2

Figure 1 shows that the pensi shell is blackish before calcination, while it becomes white and homogeneous after calcination. This color change occurs because the pensi shell, before calcination, contains $CaCO_3$, which includes carbon elements that cause its black appearance. After calcination, the process is followed by synthesizing the calcium glyceroxide catalyst. The synthesis was carried out using the reflux method, where CaO was reacted with glycerol at 65°C for 5 hours with methanol as the solvent. Three catalyst synthesis variations were explored, with CaO to glycerol ratios of 1:1, 1:1.5, and 1:2. The synthesis process is illustrated in Figure 2.

After calcination, the calcium glyceroxide catalyst, bound to glycerol, is obtained. The purpose of reacting CaO with glycerol is to prevent CaO from binding glycerol during the initial stages of the transesterification reaction, which could otherwise slow down the biodiesel formation rate. The glycerol used in this reaction is raw glycerol, which serves the additional purpose of utilizing the glycerol by-product from the transesterification process.

Figure 3 shows the result of the calcium glyceroxide catalyst synthesis, highlighting a noticeable color change in the catalyst. A significant color change is observed in the catalyst variation with a CaO:glycerol ratio of 1:2, where the catalyst appears brownish. This change occurs because the originally white CaO binds with the raw glycerol, leading to the observed color transformation.

3.2. Catalyst Characterization

3.2.1. SEM Analysis

The SEM images in Figure 4 illustrate the microstructure of the mixture of glycerol and calcium oxide synthesized using the reflux method. This analysis offers valuable insights into the material's physical characteristics, including surface area, porosity, and potential reactivity.

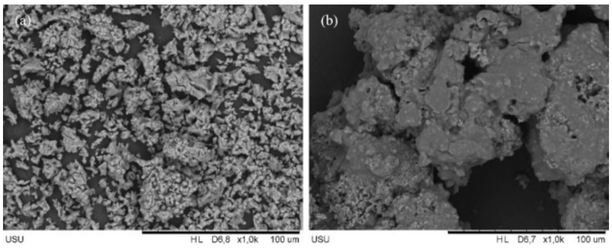

Figure 4. SEM analysis of (a) CaO catalyst without glycerol and (b) calcium glyceroxide catalyst synthesized with glycerol

The SEM analysis was performed at a magnification of 1,000 times (×1.0k) with a field of view width of 100 micrometers, providing a detailed visualization of the catalyst's microstructure. In Figure 4(a), the particle structure appears less homogeneous and more varied, whereas in Figure 4(b), the particles are observed to form aggregates. This aggregation indicates that CaO has successfully interacted with glycerol, forming the calcium glyceroxide catalyst. The particle surface appears rough and porous, a characteristic that increases the catalyst's surface area. This enhanced surface area is crucial for catalytic activity, providing more sites for chemical reactions.

3.2.2. XRD Analysis

XRD characterization was conducted to identify the crystal phases present in the catalyst sample and confirm that the catalyst possesses the desired crystal structure without any undesired phases [16]. This analysis aimed to determine whether the catalyst contains pure CaO and $Ca(OH)_2$, the latter being a compound formed from the interaction between CaO and glycerol during synthesizing the calcium glyceroxide catalyst.

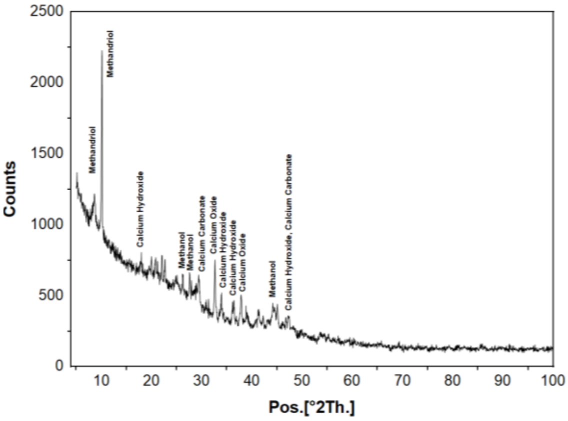

Figure 5. XRD pattern of the catalyst

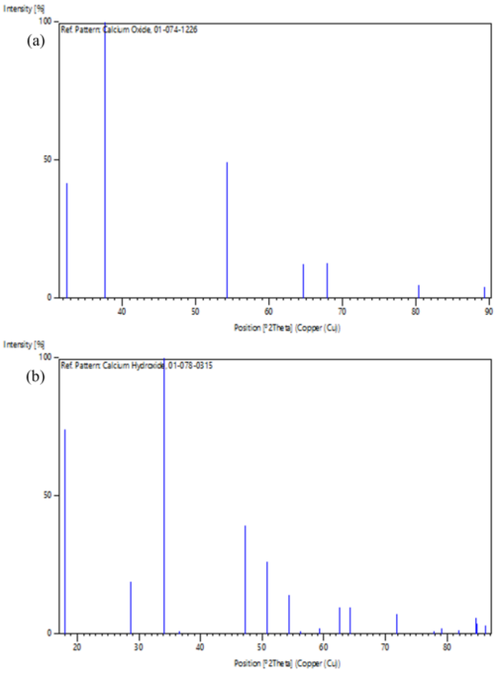

Figure 6. XRD patterns of (a) CaO and (b) $Ca(OH)_2$ peaks

Table 1. Oxide compounds resulting from XRF analysis of the catalyst

Element	Concentration (%)	Compound	Concentration (%)	Compound	Concentration (%)
Al	0.147	Al_2O_3	0.24	Al_2O_3	0.24
P	0.153	P_2O_5	0.298	P_2O_5	0.298
Cl	3.468	Cl	2.82	CaO	96.217
Ca	95.712	CaO	96.263	TiO_2	0.001
Ti	0.001	Ti	0.001	V_2O_5	0.005
V	0.004	V	0.003	Cr_2O_3	0.004
Cr	0.005	Cr	0.003	MnO	0.009
Mn	0.01	Mn	0.007	Fe_2O_3	0.074
Fe	0.078	Fe_2O_3	0.074	SrO	0.171
Sr	0.219	Sr	0.144	ZrO_2	0.002
Zr	0.002	Zr	0.001	Ag_2O	0.092
Ag	0.107	Ag	0.086	BaO	0.04
Ba	0.055	Ba	0.035	CeO_2	0
C	0	C	0	Sm_2O_3	0
Sm	0	Sm	0	Eu_2O_3	0
Eu	0	Eu	0	Yb_2O_3	0.006
Yb	0.008	Yb	0.006	Lu_2O_3	0.023
Lu	0.032	Lu	0.02	Cl	2.819

Figure 5 displays the overall peaks of compounds in the catalyst, with Methandriol showing the highest peak. Other peaks correspond to methanol, CaO, $Ca(OH)_2$, and $CaCO_3$. The presence of $Ca(OH)_2$ confirms calcium glyceroxide formation from the CaO-glycerol reaction, while the CaO peak indicates unreacted CaO, and the $CaCO_3$ peak suggests incomplete calcination. Figure 6 details the CaO and $Ca(OH)_2$ peaks, with CaO at 37° 2θ (100% intensity) and $Ca(OH)_2$ at 18.06° 2θ (74%) and 34.1° 2θ (100%), matching reference patterns (JCPDS-01-072-1266 for CaO and JCPDS-01-078-4315 for $Ca(OH)_2$).

3.2.3. XRF Analysis

XRF catalyst characterization provides several benefits, including identifying and measuring the concentration of elements in the catalyst to ensure it meets the desired specifications [17]. Additionally, XRF can be used to analyze the catalyst at various synthesis stages, confirming that the process produces the catalyst with the intended elemental composition.

Table 1 shows the concentration of various elements and oxides in the catalyst sample, expressed as percentages (%). The data indicate that the catalyst sample predominantly comprises calcium (Ca) at 96.26% and CaO at 96.21%, with significantly high concentrations. Other elements and oxides are present in much smaller amounts, as shown in Figure 7.

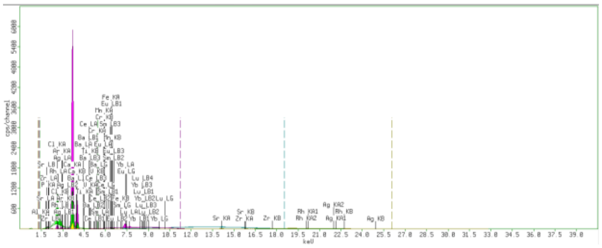

Figure 7. XRF analysis results

3.2.4. FTIR Analysis

The FTIR spectrum (Figure 8) reveals several prominent peaks highlighting the interaction between glycerol and the catalyst, confirming its adsorption and possible chemical bonding. The peak at 3233.86 cm^{-1} is attributed to O−H vibrations from the hydroxyl group (OH) in glycerol, suggesting hydrogen bonding or interactions with the CaO surface, indicating that glycerol remains adsorbed on the catalyst. Peaks at 2934.62 cm^{-1} and 2823.28 cm^{-1} correspond to C−H vibrations from the methylene ($-CH_2$) and methyl ($-CH_3$) groups, confirming that the carbon structure of glycerol is preserved without significant degradation [17]. The peak at 1586.26 cm^{-1}, associated with O−H deformation vibrations, further supports the interaction of glycerol with CaO, possibly through surface hydroxylation. Additionally, the peak at 1424.14 cm^{-1} corresponds to symmetric C−O vibrations, suggesting that glycerol may be chemically adsorbed on the CaO surface, potentially forming a calcium glyceroxide intermediate that enhances catalytic activity.

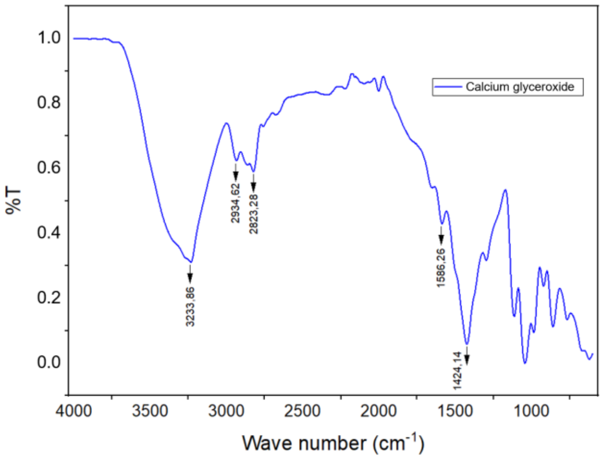

Figure 8. FTIR spectra of calcium glyceroxide catalyst

Table 2. Catalyst activity test results

Reaction time (hour)	Catalyst type (CaO: Glycerol)	Catalyst concentration (%)	Biodiesel yield (%)	Average	
		1.5	56.17		
	1:1	2	30.94	46.62	
		2.5	52.75		
		1.5	45		
2	1:1.5	2	65.46	51.20	53.77
		2.5	43.13		
		1.5	67.79		
	1:2	2	68.01	63.50	
		2.5	54.71		
		1.5	40		
	1:1	2	51.7	52.53	
		2.5	65.89		
		1.5	50.84		
4	1:1.5	2	68	61.33	55.67
		2.5	65.17		
		1.5	30		
	1:2	2	62.5	53.13	
		2.5	66.9		

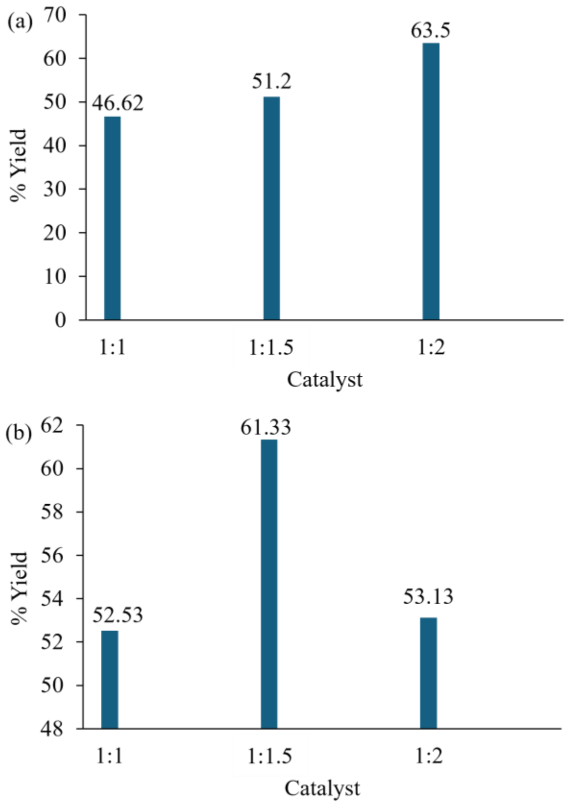

Figure 9. The relationship between catalyst type and biodiesel yield (%) at reaction times (a) 2 hours and (b) 4 hours

3.3. Biodiesel Production Using Calcium Glyceroxide Catalyst

CPO from glycerolysis is converted into biodiesel through the transesterification method using the previously synthesized catalyst. The transesterification process is conducted with various molar ratios of CaO catalyst to glycerol, specifically at catalyst concentrations of 1.5%, 2%, and 2.5%, reaction times of 2 hours and 4 hours, and a methanol to CPO molar ratio of 1:5. Table 2 presents the results of the activity test of the calcium glyceroxide catalyst in the biodiesel formation from CPO obtained via glycerolysis.

3.4. Effect of Catalyst Concentration

The observed data shows a linear relationship between the catalyst ratio and biodiesel yield percentage. The highest yield, 68.01%, was achieved at a CaO:glycerol ratio of 1:2 with a catalyst concentration of 2% and a reaction time of 2 hours. For a reaction time of 4 hours, the highest yield of 68% was obtained at a 1:1.5 catalyst ratio with a 2% catalyst concentration. In both cases, a 2% catalyst concentration was optimal, effectively balancing the reaction rate and yield. The catalyst concentration impacts the reaction results by influencing factors such as reaction rate, yield, and efficiency. Higher concentrations typically accelerate the reaction rate due to more active sites available, leading to higher yields up to an optimal point. Conversely, lower concentrations may slow the reaction, resulting in lower yields. Additionally, catalyst efficiency is crucial—too little catalyst may hinder the reaction, while excessive amounts may be wasteful and economically inefficient.

3.5. Effect of Reaction Time on Catalyst Performance

Figure 9 shows that, at a reaction time of 2 hours, the highest yield (68.01%) was achieved at a CaO:glycerol ratio of 1:2 and a catalyst concentration of 2%. The yield varied significantly with different catalyst concentrations, suggesting that reaction time considerably affected catalyst concentration. At a reaction time of 4 hours, the highest yield (68%) was achieved at a CaO:glycerol ratio of 1:1.5 and a catalyst concentration of 2%. The overall yield was higher than the 2-hour reaction time, with average yields of 53.77% at 2 hours and 55.67% at 4 hours. This indicates that a longer reaction time leads to better conversion of reactants. The 2-hour reaction time showed variability in yield based on catalyst concentration, suggesting that the reaction had not yet reached its optimum point, whereas the 4-hour reaction time generally produced higher yields, indicating a more complete conversion and better catalyst performance.

3.6. Biodiesel Quality Test Results

Biodiesel as a fuel must meet certain standards to ensure it does not damage engines or negatively impact the environment. In Indonesia, these standards are outlined in SNI 7182:2015. This study conducted a quality test using the synthesized catalyst to assess the quality of the biodiesel produced. The results of the quality test, based on various parameters from SNI 7182:2015, are presented in Table 3.

Based on the results of the biodiesel quality tests according to SNI Biodiesel 7182:2015, it can be concluded that while most parameters meet the standards, two parameters—density and total glycerol—did not meet the required values at a reaction time of 2 hours. This indicates that a reaction time of 2 hours is not optimal for producing biodiesel from CPO using the calcium glyceroxide catalyst derived from pensi shells.

Table 3. Biodiesel quality test results from CPO using the calcium glyceroxide catalyst

Parameter	SNI	Unit	Reaction time	
			2 hours (1:2)	4 hours (1:2)
Acid number	Max 0.5	mg-KOH/g	0.2	0.1
Total glycerol	Max 0.24	%mass	0.279	0.229
Free glycerol	Max 0.02	%mass	0.019	0.018
Oxidation stability	Min 6	Hour	10.77	10.37
Ester content	Min 96.5	%mass	97.34	97.85
Density	850-890	kg/m^3	895	878
Viscosity	2.3-6.0	mm/s (cSt)	3.559	3.732

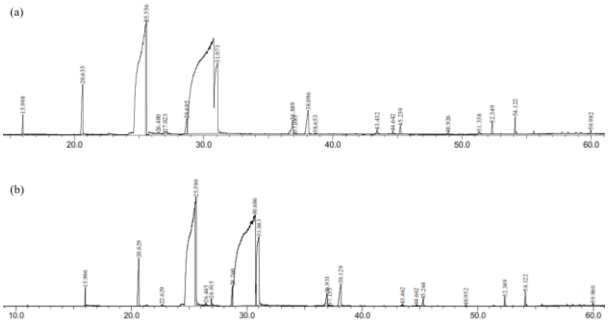

Figure 10. GC-MS analysis results of biodiesel using the catalyst (1:2) at reaction times of (a) 2 hours and (b) 4 hours

Table 4. Methyl ester compounds analysis results with GC-MS

No.	Compound name
1.	Dodecanoic acid
2.	Tetradecanoic acid
3.	Pentadecanoic acid
4.	Hexadecanoic acid
5.	cis-10-Heptadecenoic acid
6.	Heptadecanoic acid
7.	9,12-Octadecadienoic acid
8.	8-Octadecenoic acid
9.	Octadecanoic acid
10.	cis-13-Eicosenoic acid
11.	Heptadecanoic acid, 8-oxo-
12.	Eicosanoid acid
13.	Docosanoic acid
14.	Tricosanoic acid
15.	Tetracosanoic acid

The GC-MS results (Figure 10) show a series of peaks corresponding to different compounds, with retention time on the x-axis and signal intensity on the y-axis. The retention time represents the time each compound takes to pass through the GC column and be detected by MS, with shorter retention times indicating earlier elution. The peak area and height reflect the relative abundance of each compound. Key compounds such as fatty acid methyl esters—Hexadecanoic Acid and 9-Octadecenoic acid (Z)- are predominant in biodiesel, suggesting the presence of methyl esters commonly found in high-quality biodiesel. The substantial presence of methyl oleate and methyl palmitate indicates that the transesterification process is progressing effectively, producing biodiesel with desirable properties.

4. Conclusion

The calcium glyceroxide catalyst synthesized from pensi shells demonstrated high effectiveness in the transesterification process for biodiesel production. The highest biodiesel yield of 68.01% was achieved with a CaO:glycerol ratio of 1:2 and a catalyst concentration of 2%. Catalyst characterization results, including SEM, XRD, XRF, and FTIR, confirmed the catalyst's composition and interactions. SEM showed uniformity in CaO and glycerol particles, while XRD identified CaO as a pure substance and revealed the formation of $Ca(OH)_2$ from the interaction of CaO and glycerol. XRF analysis indicated that calcium (Ca) and calcium oxide (CaO) dominated the catalyst composition, with concentrations of 96.26% and 96.21%, respectively. FTIR analysis detected O–H vibrations from the glycerol hydroxyl group and C–H vibrations from the methylene ($-CH_2$) and methyl ($-CH_3$) groups of glycerol, as well as interactions between CaO and glycerol. Lastly, biodiesel quality tests revealed that the biodiesel met the SNI 7182:2015 standards for parameters such as acid number, total glycerol, free glycerol, oxidation stability, ester content, density, and viscosity.

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