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Synthesis and Characterization of ZnO/CaO Nanocatalysts and Utilization in Biodiesel Transesterification Reaction from Waste Cooking Oil

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Abstract: The increase in global energy demand has led to increased consumption of fossil fuels, resulting in increasingly depleted energy reserves. In addition, the use of fossil fuels has various negative environmental impacts, including air pollution, global warming, and greenhouse gas emissions. Therefore, the development of environmentally friendly, sustainable alternative energy sources is needed. One renewable energy source with development potential is biodiesel. This study aims to synthesize biodiesel from waste cooking oil through a transesterification reaction using ZnO/CaO nanocatalysts. The novelty of this research lies in the synthesis of ZnO/CaO nanocatalysts via a combination of sol-gel and impregnation methods, which are expected to increase the catalysts' surface area, stability, and catalytic activity. The CaO catalyst was synthesized using the sol-gel method and modified with ZnO through a wet impregnation method using Zn acetate precursor at various concentrations of 0%, 1%, 2%, and 3%. FTIR and XRD characterizations confirmed the success of ZnO impregnation on CaO, while PSA analysis showed a decrease in particle size from 107.85 nm on CaO to 79.28 nm on 1% ZnO/CaO, which has the potential to increase catalytic activity. The transesterification reaction was carried out at 65°C for 2 hours, using a methanol-to-oil molar ratio of 1:9 and a catalyst loading of 3% of the oil weight. The resulting biodiesel was then analyzed using GC-MS, and it was found that ZnO modification increased the methyl ester area percentage from 92.74% in CaO to 99.61% in ZnO/CaO 1%. In addition, the highest biodiesel yield using 1% ZnO/CaO produced a density of 853.8 kg/m³, a viscosity of 2.30 mm²/s (cSt), a water content of 0.02%, and an acid number of 0.43 mg-KOH/g.

Keywords: Biodiesel; Nanocatalyst; Transesterification; Waste Cooking Oil; ZnO/CaO.

Introduction

Global energy demand continues to increase and is projected to rise by 45% with an average growth rate of 1.6% per year until 2030[1]. This increase causes fossil energy reserves to become increasingly depleted, while its use has negative impacts on the environment, such as air pollution, global warming and greenhouse gas emissions [2]. The transportation sector even contributes around 21% of total global CO_2 emissions due to the use of fossil fuels [3]. Therefore, it is necessary to develop alternative energy that is environmentally friendly and sustainable, one of which is biodiesel.

Biodiesel is a renewable fuel that is biodegradable, environmentally friendly, and produces lower emissions [4]. Biodiesel can be produced from various sources, including waste cooking oil, which has the potential to pollute the environment if not used properly [5]. Biodiesel is produced by transesterification with a catalyst. Homogeneous catalysts have the disadvantage of being separated and reused [6], so that heterogeneous catalysts are more widely developed because they are easier to separate and can be reused [7].

CaO catalyst is a heterogeneous base catalyst that has high catalytic activity [8], but it has weaknesses in the form of hygroscopic properties and is easily leached by Ca^{2+} ions, which can reduce the stability of the catalyst [9]. Therefore, modification was carried out with other metal oxides, such as ZnO, which has good thermal and chemical stability [10].

Previous research shows that the ZnO/CaO catalyst is able to increase biodiesel yield up to 97.2% [11] and at Zn/CaO with a concentration of 1 wt% produced a yield of 96% [6]. However, commonly used synthesis methods such as coprecipitation have been reported to cause an increase in particle size due to agglomeration upon the addition of ZnO [12], and calcination still has limitations in controlling particle size down to the micrometer scale [13]. This condition has the potential to reduce the number of active sites on the catalyst and reduce the efficiency of the transesterification reaction, which can reduce the surface area and activity of the catalyst [14].

The sol-gel method is capable of producing nanocatalysts with smaller particle sizes and larger surface areas [15]. This method is capable of producing CaO nanocatalysts with biodiesel yields of up to 97.61% [16]. Then, further research reported the success of the combination of sol-gel and impregnation with KOH to improve catalyst performance [17]. The application of the sol-gel method to the synthesis of ZnO-modified CaO nanocatalysts via impregnation, and its use in biodiesel production from used cooking oil, remain very limited. This combination of methods has the potential to produce catalysts with smaller particle sizes, more homogeneous ZnO distribution, and better stability than the previously widely used coprecipitation and calcination methods.

Based on the description, this study developed ZnO/CaO nanocatalysts through a combination of sol-gel and ZnO impregnation methods as an alternative approach to

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overcome the limitations of previous synthesis methods in controlling particle size and preventing agglomeration. This approach is expected to produce catalysts with smaller particle sizes, greater stability, and high catalytic activity for the transesterification of used cooking oil. In addition to evaluating the characteristics of the resulting catalyst, this study examined the effect of ZnO modification on biodiesel quality. The results of this study are expected to contribute to the development of more effective heterogeneous catalysts for biodiesel production and to support the use of used cooking oil as a sustainable, renewable energy source.

Research Methods

Tools and Materials

The equipment that will be used in this study are analytical scale, spatula, 500 mL three-neck flask, reflux condenser, thermometer, hot plate magnetic stirrer, burette, 250 mL Erlenmeyer flask, 250 mL volumetric flask, dropper pipette, beaker glass, oven, furnace, vial bottle, porcelain cup, pH paper, desiccator, filter paper, separatory funnel, water hose, clamp, stand, centrifuge, FTIR (Shimadzu IR Prestige 21), XRD (PANalytical X'Pert PRO), GC-MS (Shimadzu QP2010 SE), and PSA (Biobase BK-802N). The materials that will be used are waste cooking oil, PP indicator, Ca nitrate tetrahydrate, Zn acetate dihydrate, NaOH, ethylene glycol, KOH, distilled water, methanol, and 96% ethanol.

Preparation of Waste Cooking Oil

Waste cooking oil is filtered using filter paper to remove impurities, then heated at 110°C for 30 minutes to remove water content [6]. Next, the free fatty acid (FFA) and water contents were measured. FFA levels were determined using a titration method. 5 g of oil sample was mixed with 25 mL of warm ethanol, phenolphthalein indicator was added, and then titrated with 0.1 N NaOH solution until a stable pink color was formed [18]. The maximum FFA content allowed for the transesterification process is 3%. Moisture content was analyzed using the oven method at 130°C, with weighing before and after heating according to ASTM D6751 standards, with a maximum limit of 0.05% [19].

Synthesis of ZnO/CaO Nanocatalyst

The CaO nanocatalyst was synthesized using the sol-gel method. Calcium nitrate tetrahydrate was dissolved in distilled water, then mixed with ethylene glycol and stirred using a magnetic stirrer. A 1 M NaOH solution was added gradually until a white gel formed, and the mixture was then left to stand overnight. The gel was separated by centrifugation, washed with distilled water and ethanol, and then dried at 120°C for 4 hours. The dried sample was then ground and calcined at 850°C for 1 hour to produce the CaO nanocatalyst [20][21].

The CaO nanocatalyst was then impregnated with Zn acetate. The Zn acetate solution was mixed with CaO and stirred at room temperature for 4 hours. The mixture was dried at 120°C for 6 hours and calcined at 850°C for 2 hours [22]. The concentration of ZnO was varied by 0%, 1%, 2%, and 3% to evaluate the effect of ZnO addition on the catalyst characteristics and its performance in the biodiesel transesterification reaction based on previous research reports showing that ZnO modification at low concentrations was able to increase the catalytic activity of the CaO catalyst.

Biodiesel Synthesis from Waste Cooking Oil

Biodiesel synthesis was carried out through a transesterification reaction at 65°C for 2 hours with a methanol:oil mole ratio of 9:1 and a ZnO/CaO catalyst of 3% by weight of the oil. The reaction conditions were selected based on preliminary studies and previous literature reporting favorable biodiesel conversion using ZnO/CaO-based catalysts. In the initial stage, the catalyst was mixed with methanol and stirred using a magnetic stirrer for 30 minutes at room temperature. Next, waste cooking oil was added to the mixture and the reaction proceeded according to the specified conditions. After the reaction was complete, the mixture was centrifuged at 4000 rpm for 10 minutes. The biodiesel was then washed with distilled water and dried at 110°C to remove residual water and methanol [13]. A CaO catalyst without ZnO modification was used as a control sample to evaluate the effect of ZnO impregnation on catalyst characteristics and biodiesel quality.

Characterization and Data Analysis

Catalyst characterization was performed using FTIR, XRD, and PSA. FTIR spectra were used to identify functional groups and interactions between ZnO and CaO. XRD diffraction patterns were used to confirm the crystal phase and to calculate the crystallinity percentage and crystallite size using the Scherrer equation. PSA analysis was used to determine the distribution and particle size of the catalyst. The resulting biodiesel was analyzed using GC-MS to identify the methyl ester components formed, while physical property testing, including density, viscosity, water content, and acid number, was used to evaluate the quality of the biodiesel produced.

Results and Discussion

Waste Cooking Oil Quality Analysis

Waste cooking oil quality analysis is based on two main parameters: free fatty acid (FFA) and water content. FFA levels are analyzed using the acid-base titration method, while water content is analyzed using the gravimetric method [23]. The analysis results showed that the FFA content was 1.278% and the water content was 0.128%, both of which were still below the maximum limits as biodiesel raw materials, namely 3% [24] and 0,5% respectively [25].

A low FFA value indicates that waste cooking oil is suitable for use in the transesterification process. High FFA levels can cause a saponification reaction on the base catalyst, producing soap, thus reducing biodiesel yield and complicating the product separation process [26].

Apart from that, low water content is also important to prevent the hydrolysis reaction of triglycerides into free fatty acids and glycerol [27] and reduce biodiesel yield [28]. Thus, the waste cooking oil meets the requirements for use

as a raw material for biodiesel and is suitable for the transesterification process.

XRD

XRD characterization was performed in the 2θ angle range of 10°-90° to identify the phase, crystallinity, and crystal size of the catalyst. The diffraction patterns obtained were compared with ICDD standard data to identify the phases formed. Sharp diffraction peaks indicate a high degree of crystallinity in the material [6]. In addition, the catalyst crystallite size was calculated using the Debye-Scherrer equation. The diffraction patterns of CaO and ZnO/CaO catalysts with various concentrations are presented in Figure 1, while the peak positions are shown in Table 1.

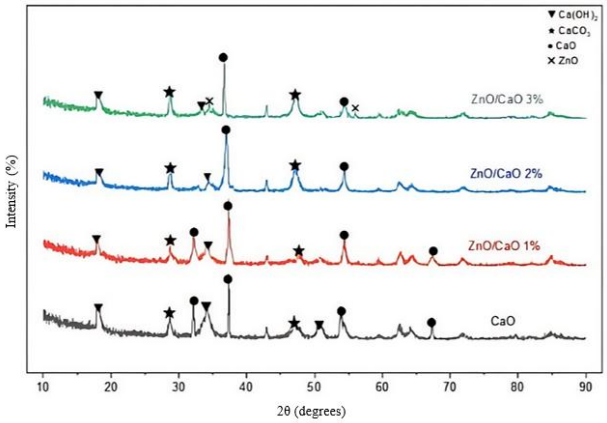

Figure 1. XRD results of CaO, ZnO/CaO 1%, ZnO/CaO 2%, and ZnO/CaO 3%

Table 1. Comparison of XRD peaks with the ICDD database

Peak 2θ (degrees)				ICDD
CaO	ZnO/ CaO 1%	ZnO/ CaO 2%	ZnO/ CaO 3%	
18.00	18.03	18.05	18.07	(96-152-9753)
34.09	34.13	34.16	34.17	$Ca(OH)_2$
50.82				
28.66	28.74	28.73	28.75	(96-900-7287)
47.12	47.21	47.22	47.25	$CaCO_3$
32.20	32.21	37.42	37.45	(96-900-6732)
37.36	37.39	54.44	54.42	CaO
53.88	54.39			
67.42	67.44			
-	-	-	34.52	(96-210-7060)
			56.44	ZnO

XRD diffraction shows that the CaO catalyst has a 2θ peak at 37.36°, indicating the cubic phase of CaO. The addition of ZnO causes a shift in the CaO diffraction peak to a higher 2θ angle. This shift indicates an interaction between Zn^{2+} and the CaO crystal lattice, leading to changes in lattice parameters and increased lattice strain. This interaction indicates that ZnO is not only physically deposited on the CaO surface but also affects its crystal structure. This structural modification has the potential to increase the number of active base sites that play a crucial role in the formation of methoxide ions during the transesterification reaction, thereby enhancing catalytic activity in biodiesel synthesis [29].

At 2% and 3% ZnO/CaO concentrations, some CaO peaks decreased, indicating the possibility of new phase formation or interactions between phases. At 3% ZnO/CaO concentration, new peaks appeared at 34.52° and 56.44°, indicating the formation of a hexagonal ZnO phase. This indicates that at high concentrations, ZnO is not fully dispersed but forms a separate phase, while at low concentrations, ZnO is evenly dispersed [30].

In addition, the $Ca(OH)_2$ and $CaCO_3$ phases were detected, which were formed due to the reaction of CaO with H_2O and CO_2 in the air [31]. Increasing the concentration of ZnO tends to increase the formation of $CaCO_3$ by increasing the surface reactivity of the catalyst [12].

The decrease in crystallinity in 1% ZnO/CaO indicates that ZnO is evenly dispersed on the CaO surface, thus inhibiting crystal growth and producing a more irregular structure [6]. This condition is generally beneficial because it can increase the number of crystal defects that function as catalytically active sites. Conversely, the increase in crystallinity in 2% and 3% ZnO/CaO indicates the onset of ZnO particle agglomeration. This agglomeration can reduce the specific surface area and partially cover the CaO active sites, potentially decreasing the effectiveness of the catalyst in the transesterification reaction[22]. The results of the % crystallinity calculation are shown in Figure 2.

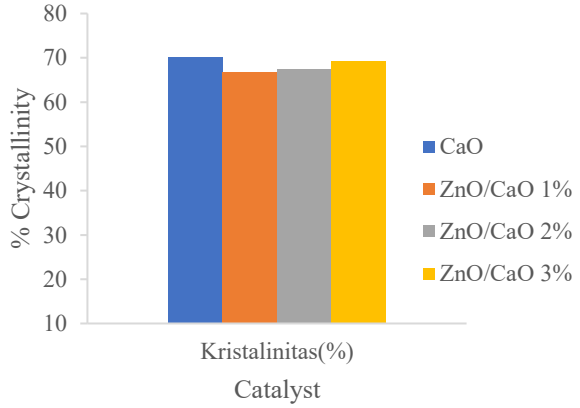

Figure 2. Crystallinity of CaO, ZnO/CaO 1%, ZnO/CaO 2%, and ZnO/CaO 3% catalysts

Then the crystal size calculation is carried out using the Debye-Scherrer equation with the formula:

$$D = \frac{K\lambda}{\beta \cos\theta}$$

Table 2. Average size of nanocatalyst crystals

Catalyst	Crystal size (nm)
CaO	23.75
ZnO/CaO 1%	17.67
ZnO/CaO 2%	20.20
ZnO/CaO 3%	22.52

It was observed that the crystallite size decreased with the addition of 1% ZnO, then increased again at 2% and 3% concentrations. The smallest crystallite size was obtained for 1% ZnO/CaO, at 17.67 nm. The smaller crystallite size not only increases the surface area but also shortens the diffusion path of the reactants to the active site. Thus, the interaction

between triglycerides, methanol, and the catalyst becomes more effective. The same study showed that the crystallite size of CaO decreased from 21.14 nm to 12.51 nm after impregnation with ZnO [22].

FTIR

FTIR characterization was performed to identify functional groups and chemical interactions in the catalyst through changes in absorption bands. Analysis was performed on CaO and ZnO/CaO catalysts (1%, 2%, and 3%) at a wavelength range of 400-4000 cm^{-1}. The FTIR spectra are presented in Figure 3, and their analysis is presented in Table 3.

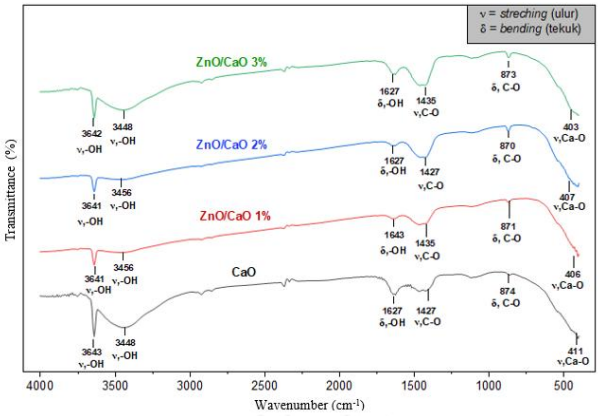

Figure 3. Spektra FTIR CaO, ZnO/CaO 1%, ZnO/CaO 2%, dan ZnO/CaO 3%

Table 3. FTIR spectra analysis results

Interpretation of functional groups	Wavenumber (cm^{-1})				Reference
	CaO	ZnO/ CaO 1%	ZnO/ CaO 2%	ZnO/ CaO 3%	
O-H stretching vibration	3643,3448	3641, 3456	3641, 3456	3642, 3448	3448-3648 [32]
Bending vibration O-H	1627	1653	1627	1627	1600-1650 [33]
C-O asymmetric stretching vibration	1427	1435	1427	1435	1400-1550 [22]
C-O bending vibration	874	871	870	873	713-877 [32]
Ca-O stretching vibration	411	406	407	403	400-600 [34]

The FTIR results show an absorption band at around 3641-3643 cm^{-1} which is related to the stretching vibration of the -OH group of $Ca(OH)_2$, as well as a broad band at 3448-3456 cm^{-1} which indicates the presence of adsorbed water on the catalyst surface [32]. The intensity of the -OH band decreased after the addition of ZnO, which indicates a reduction in the formation of $Ca(OH)_2$ due to the impregnation process [12]. This condition is favorable because $Ca(OH)_2$ has a lower basicity than CaO. With the reduction of the hydroxide phase, more strong base sites of CaO remain available to activate methanol to form methoxide ions, the main active species in the transesterification reaction.

The absorption bands at 1427-1435 cm^{-1} and around 870-875 cm^{-1} indicate the presence of carbonate groups due to the carbonation process of CaO by CO_2 [22]. In addition, the band in the range of 403-411 cm^{-1} which is related to the Ca-O vibration shifts to a lower wave number after the addition of ZnO, which indicates the interaction between CaO and ZnO and the possibility of the formation of a mixed oxide system. [30].

PSA

A Particle Size Analyzer (PSA) was used to determine the particle size and size distribution, as well as the homogeneity of the CaO and ZnO/CaO catalyst samples. Characterization was performed on CaO nanocatalysts as a standard catalyst and 1% ZnO/CaO with the highest biodiesel yield. The characterization results with PSA are shown in Figure 4.

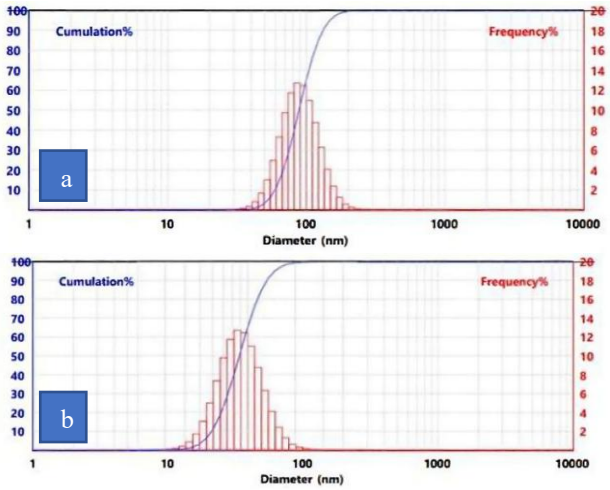

Figure 4. Size distribution based on particle number, a) CaO and b) ZnO/CaO 1%

The PSA characterization results show that the CaO catalyst has an average particle size of 107.85 nm with a Polydispersity Index (PI) value of 0.1, which indicates a relatively homogeneous particle distribution [35]. The D10, D50, and D90 values were 59.3 nm, 88.66 nm, and 132.56 nm, respectively. This relatively large particle size is thought to result from agglomeration during calcination, which triggers sintering and reduces surface area and catalytic activity [22]. This finding is consistent with previous studies reporting that increasing the calcination temperature decreases catalyst activity due to agglomeration [36]. The particle size of CaO reaches 175 nm due to a similar process [37]. After modification with ZnO, the particle size

decreased to 79.28 nm with a PI value of 0.2, and D10, D50, and D90 values of 45.20 nm, 67.98 nm, and 89.25 nm, respectively. The decrease in particle size from 107.85 nm to 79.28 nm after ZnO impregnation indicates that ZnO can inhibit particle growth and aggregation during calcination. Smaller particle size increases the surface area-to-volume ratio, thereby increasing the number of active sites available for the transesterification reaction. These PSA results are consistent with the XRD data, which show the smallest crystal size in the 1% ZnO/CaO sample. The agreement between the two characterization results indicates that the increase in biodiesel yield on the 1% ZnO/CaO catalyst is not only influenced by changes in the crystal structure, but also by an increase in surface area and better dispersion of active sites. These results are supported by studies reporting that the addition of ZnO can suppress sintering and reduce the particle size of AuNPs during heating, from 4.0 ± 1.0 nm to 2.5 ± 0.9 nm [38].

Biodiesel Synthesis

Biodiesel synthesis is carried out through a transesterification reaction between methanol and triglycerides to form methyl esters and glycerol as by-products [39]. The reaction took place at a temperature of 65°C for 2 hours using a three-necked flask equipped with a thermometer and condenser to maintain temperature stability and prevent methanol from evaporating [40]. The reaction apparatus circuit is shown in Figure 5.

Figure 5. Transesterification reaction apparatus

The transesterification reaction was carried out using heterogeneous catalysts CaO and ZnO/CaO, with ZnO varying from 1-3%. The catalyst plays a role in providing an alternative reaction pathway with lower activation energy, thereby increasing the reaction rate [41]. Before use, the catalyst was activated at 130°C for 2 hours to remove moisture. The reaction was carried out using a catalyst loading of 3% by weight of oil and a methanol:oil molar ratio of 9:1.

The initial reaction stage begins with mixing the catalyst and methanol to form methoxide ions, which then react with triglycerides. Next, waste cooking oil is added, and the reaction proceeds at 65°C for 2 hours, which is the optimal condition for reducing the oil's viscosity and increasing interphase contact [42]. The transesterification reaction mechanism is shown in Figure 6.

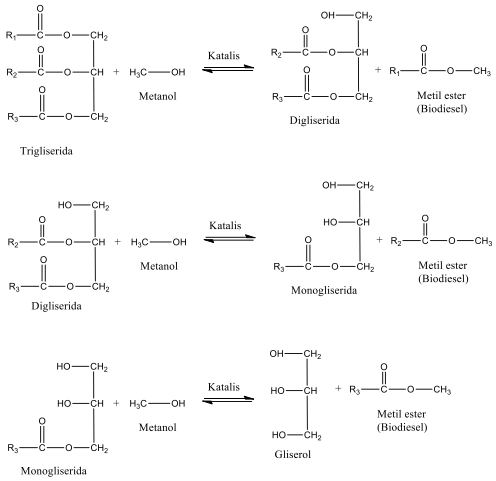

Figure 6. Transesterification reaction mechanism [43]

The transesterification reaction consists of three stages of reversible reactions that occur successively, namely, triglycerides are converted into diglycerides, diglycerides are converted into monoglycerides, and finally, monoglycerides are converted into glycerol [28]. In the initial stage, triglycerides react with methanol to form diglycerides (DG) and a fatty acid methyl ester (FAME). DG then reacts further with methanol, producing monoglycerides (MG) and a second FAME molecule. In the final stage, MG is converted to glycerol and a third FAME molecule [43]. After the reaction, the mixture was separated using centrifugation at 4000 rpm for 10 minutes [40]. After centrifugation, three layers formed: the topmost layer was methanol, the middle layer was biodiesel, and the bottom layer was a mixture of catalyst and glycerol. The separation results are shown in Figure 6.

Figure 6. Separation of biodiesel using a centrifuge

After separating the biodiesel, a purification process is carried out by repeatedly washing with aqueous until the wash water is clear and the pH is neutral. The biodiesel washing process is shown in Figure 7.

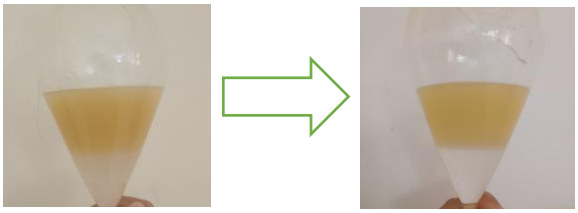

Figure 7. Results of washing biodiesel with aqueous solutions

Biodiesel washing aims to remove impurities, such as residual catalyst, glycerol, and methanol still present in the biodiesel. Afterwards, the biodiesel is heated to 110°C to evaporate any remaining water and methanol. Following the purification process, the biodiesel is weighed to determine the percent yield. The results of the percent yield can be seen in Table 4.

Table 4. Biodiesel yield percentage

Sample	Yield (%)
CaO	64.93
ZnO/CaO 1%	79.35
ZnO/CaO 2%	70.39
ZnO/CaO 3%	66.48

Based on Table 4, the use of CaO catalyst resulted in a biodiesel yield of 64.93%. After ZnO impregnation, the yield increased significantly, reaching a maximum of 79.35% ZnO/CaO. These results indicate that the addition of ZnO can increase catalyst activity. This increase is due to the interaction between CaO and ZnO, where CaO provides strong base sites [13], while ZnO increases catalyst stability [44] by reducing sintering and leaching of Ca^{2+} , which can trigger soap formation. [34]. In addition, decreasing the particle size from 107.85 nm to 79.28 nm increases the catalyst surface area, thus increasing the number of active sites available for triglyceride and methanol adsorption. This finding is consistent with the XRD characterization which shows that 1% ZnO/CaO has the smallest crystallite size compared to other catalysts. Smaller crystallite and particle sizes allow for more effective contact between the reactants and the catalyst surface, thereby increasing reaction efficiency. This condition accelerates the formation of methoxide ions which act as active species in the transesterification reaction, thereby increasing the conversion of triglycerides to methyl esters [44].

The increase in methyl ester content in 1% ZnO/CaO indicates that the addition of small amounts of ZnO can increase the stability and catalytic activity of CaO. However, at higher ZnO concentrations (2% and 3%), the methyl ester content decreases. This phenomenon is thought to be caused by particle agglomeration and partial coverage of CaO active sites by ZnO, thus reducing the access of reactants to the catalyst surface. In addition, excess ZnO can cause a decrease in the number of basic sites that play an important role in the formation of methoxide ions during the transesterification reaction because ZnO has a lower basicity than CaO. This condition leads to less optimal methoxide formation and reduced catalytic activity. In addition, increased side reactions such as saponification also contribute to the decreased yield because soap formation can inhibit the separation of biodiesel and glycerol [45]. These results indicate that an optimal ZnO concentration improves catalyst performance, whereas excessive ZnO addition decreases catalytic activity due to reduced accessibility of active sites and increased particle agglomeration.

The highest and lowest yields were then analyzed using GC-MS to determine the compound composition and methyl ester content (% FAME). The GC-MS characterization results are shown in Figures 8 and 9.

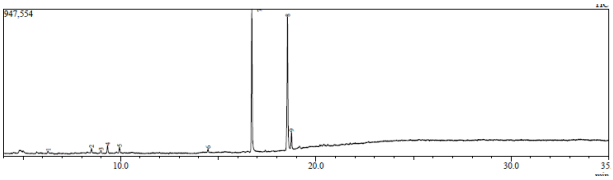

Figure 8. GC-MS chromatogram of CaO nanocatalyst biodiesel

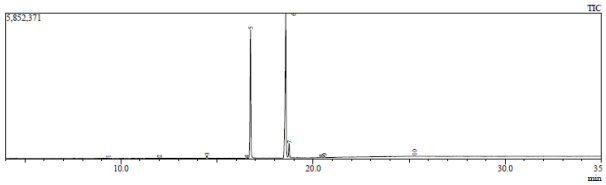

Figure 9. GC-MS chromatogram of 1% ZnO/CaO nanocatalyst biodiesel

Figures 8 and 9 show the peaks of methyl ester compounds and other compounds resulting from transesterification contained in the samples. In the figure, in both samples, the two highest peaks are Hexadecanoic acid, methyl ester (methyl palmitate) and 9-Octadecanoid acid, methyl ester (methyl oleate). The results of GC-MS analysis of biodiesel resulting from transesterification with CaO nanocatalyst are listed in Table 5 and ZnO/CaO 1% in Table 6.

Table 5. GC-MS test results of biodiesel with CaO nanocatalyst

Compound name	Chemical formula	Retention time	% Area
Tetradecanoic acid, methyl ester	$C_{15}H_{30}O_2$	14.473	0.83
Hexadecanoic acid, methyl ester	$C_{17}H_{34}O_2$	16.719	42.02
9-Octadecenoic acid, methyl ester	$C_{19}H_{36}O_2$	18.547	44.41
Octadecanoic acid, methyl ester	$C_{19}H_{38}O_2$	18.749	5.48
Total FAME (%)			92.74

Table 6. GC-MS test results of biodiesel with ZnO/CaO 1% nanocatalyst

Compound name	Chemical formula	Retention time	% Area
Dodecanoic acid, methyl ester	$C_{13}H_{26}O_2$	11.994	0.14
Tetradecanoic acid, methyl ester	$C_{15}H_{30}O_2$	14.474	0.89
9-Hexadecenoic acid, methyl ester, (Z)-	$C_{17}H_{32}O_2$	16.529	0.17
Hexadecanoic acid, methyl ester	$C_{17}H_{34}O_2$	16.745	40.12
9-Octadecenoic acid (Z)-, methyl ester	$C_{19}H_{36}O_2$	18.578	53.12

Octadecanoic acid, methyl ester	$C_{19}H_{38}O_2$	18.753	4.55
9-Octadecenoic acid, methyl ester, (E)-	$C_{19}H_{36}O_2$	20.419	0.26
Eicosanoic acid, methyl ester	$C_{21}H_{42}O_2$	20.600	0.36
Total FAME (%)			99.61

The results of GC-MS analysis showed that the biodiesel produced using the CaO catalyst contained four main types of methyl esters, namely methyl myristate, methyl palmitate, methyl oleate, and methyl stearate, with a total FAME content of 92.74%. This value does not meet the EN 14214 standard (≥96.5%). In addition, non-FAME compounds such as aldehydes (7.27%) were still detected, which originated from the oxidative degradation of fatty acids during the use of waste cooking oil [46].

The low FAME content in CaO is associated with its hygroscopic nature and easy deactivation through Ca^{2+} dissolution, reaction with FFA to form soap, and carbonation and hydration, which reduce the number of active base sites [47]. As a result, the conversion of triglycerides into methyl esters is not optimal.

In contrast, the use of 1% ZnO/CaO catalyst produced eight types of methyl esters with a total FAME content of 99.61%, which has met the EN 14214 standard. The non-FAME compounds detected were very small (<0.5%), indicating a more effective conversion. These results are in line with previous studies that reported an increase in methyl ester content after modification of CaO with ZnO from 13.62% to 90.12% [48].

Biodiesel quality analysis

The resulting biodiesel was analyzed for quality based on ASTM (American Society for Testing and Materials) standards to ensure quality, safety, and performance. Test parameters included density, kinematic viscosity, acid number, and water content. The biodiesel quality test results are shown in Table 5.

Table 5. Biodiesel quality test results

	Parameters			
Sample	Density (kg/m^3)	Kinematic viscosity (mm^2/s or cSt)	Acid number (mg-KOH/g)	Water content (%)
CaO	857.73	2.35	0.56	0.08
ZnO/ CaO 1%	853.8	2.30	0.43	0.02
ZnO/ CaO 2%	855.87	2.32	0.47	0.04
ZnO/ CaO 3%	860.32	2.38	0.63	0.07
Standard	850-890 (ASTM D 1298)	1.9-6.0 (ASTM D 445)	max 0.50 (ASTM D 664)	max 0.05 (ASTM D 6751)

Biodiesel quality test results showed that all samples had densities in the range of 853.8-860.32 kg/m^3, thus meeting the ASTM D1298 standard (850-890 kg/m^3). The increase in density with increasing ZnO content is associated with changes in the methyl ester composition and the possible presence of heavy compounds such as glycerol or soap [49][50].

The kinematic viscosity values are in the range of 2.30-2.38 mm^2/s and meet the ASTM D445 standard (1.9-6.0 mm^2/s). Viscosity is influenced by the structure of the fatty acids, where longer and more saturated carbon chains tend to increase viscosity [49].

The acid value ranged from 0.43 to 0.63 mg KOH/g. Biodiesel with 1% and 2% ZnO/CaO catalysts met ASTM D664 standards (<0.5 mg KOH/g), with the lowest value at 1% ZnO/CaO (0.43 mg KOH/g). These results indicate that adding ZnO at the optimum concentration increases the conversion of FFA to methyl esters. The higher values at 3% CaO and ZnO/CaO are thought to be due to incomplete reactions and side reactions such as hydrolysis [51].

The biodiesel moisture content ranged from 0.02% to 0.08%, with 1% and 2% ZnO/CaO meeting the ASTM D6751 standard (<0.05%). The lowest value was obtained at 1% ZnO/CaO (0.02%), indicating a more optimal reaction. Conversely, the increased moisture content at 3% CaO and ZnO/CaO indicated an incomplete reaction or a suboptimal purification process [52].

Conclusion

Based on the research results, the catalyst characterization showed that CaO has a cubic phase with a main peak at 2θ around 37°, and the addition of ZnO causes a peak shift, indicating an interaction between Zn^{2+} ions and the CaO crystal lattice. At 1% and 2% ZnO variations, ZnO is well dispersed in the CaO matrix, while at 3%, a separate ZnO phase begins to form. FTIR results confirmed the presence of -OH groups, carbonate, and Ca-O vibrations that shift due to interaction with ZnO. PSA analysis showed that the particle size decreased from 107.85 nm (CaO) to 79.28 nm (ZnO/CaO 1%), potentially increasing surface area and catalyst activity. The catalyst performance showed that using 1% ZnO/CaO produced the highest biodiesel yield (79.35%) compared to CaO (64.93%). The GC-MS results showed an increase in methyl ester content from 92.74% (CaO) to 99.61% (1% ZnO/CaO), meeting the EN 14214 standard. In addition, the quality of biodiesel produced using 1% ZnO/CaO met the ASTM standard for density, viscosity, water content, and acid number. These findings indicate that the ZnO/CaO catalyst has the potential to be a promising alternative heterogeneous catalyst for waste cooking oil-based biodiesel production, thus supporting the development of more sustainable renewable fuels while increasing the utilization of waste as a value-added raw material. Furthermore, the combination of sol-gel and impregnation methods used in the catalyst synthesis shows potential for further development on a larger scale due to its relatively simple process and its ability to produce a catalyst with characteristics that support the transesterification reaction. However, this study has not evaluated the catalyst stability during repeated use or the feasibility of the process on a larger scale. All experiments were conducted under identical operating conditions to ensure procedural consistency, with

a focus on evaluating the effects of varying ZnO concentrations on catalyst characteristics and biodiesel performance. Therefore, experimental replication and statistical analysis have not been performed in this study and could be part of further research. In addition, future research needs to focus on testing catalyst reusability, optimizing ZnO concentration and reaction conditions, and studying the process scale to support industrial-level applications.

Author's Contribution

N.V. Marta: The author of this article, responsible for compiling the content and analyzing the research data. A.P. Purnamasari: The supervisor who provided direction, guidance, and input throughout the writing process.

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