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Research Article

Optimization of biodiesel production from candlenut oil via simultaneous reaction using a bifunctional CeO_2.CaO catalyst

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Abstract. The biodiesel synthesis process with a high FFA content can be accomplished in a single stage using solid catalysts that function simultaneously as base and acid catalysts. In this study, CeO_2.CaO was used as a bifunctional catalyst for biodiesel synthesis from candlenut seed oil. CeO2.CaO catalyst with a weight ratio of CeO2 : CaO (1:4) was synthesized through a physical mixing process. The effects of the methanol-to-oil molar ratio, catalyst loading, and reaction temperature on the resulting biodiesel yield were investigated. Biodiesel was synthesized in a three-necked flask with a mole ratio of methanol to oil (8:1, 10:1, 12:1). CeO2.CaO catalyst was added with a concentration of 2% w/w, 4% w/w, and 6% w/w to the weight of candlenut oil. Heating was carried out at 50°C, 60°C, and 70°C with stirring using a magnetic stirrer at 200 rpm for 1 hour. The FTIR analysis shows peaks corresponding to the O-Ca-O and O-Ce-O groups, indicating the formation of the CeO_2.CaO catalyst. BET analysis provides data on the catalyst's surface area (9.536 m^2/g), pore diameter (5.876 nm), and pore volume (0.028 cm^3/g). SEM-EDX analysis reveals that the catalyst has a mesoporous structure, which is beneficial for transesterification reactions. TPD analysis indicates that the bifunctional CeO_2.CaO catalyst possesses strong acidic and basic properties. The optimum operating conditions to achieve a high FAME yield were a methanol-to-oil molar ratio of 10.3:1, 5.39% w/w catalyst loading, and a reaction temperature of 60°C. Based on the catalyst reusability assessment, the CeO_2.CaO bifunctional catalyst demonstrated favorable stability, retaining catalytic performance over multiple cycles. After four consecutive reaction cycles, the catalyst maintained an overall biodiesel yield exceeding 75%, indicating its potential for repeated use in transesterification processes.

Keywords: Bifunctional catalyst, biodiesel, process optimization, cerium oxide, calcium oxide

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1. Introduction

The current era of energy crisis is urging researchers and governments to limit the use of fossil fuels because their reserves are dwindling and are also causing environmental damage (Hussain *et al*., 2021; Martins *et al.*, 2018; Munfarida *et al.,* 2020; Widayat, *et al.,,* 2023). Researchers are beginning to see a glimmer of hope from biodiesel, which can be produced from vegetable oils that are abundant in nature (Vilas Bôas & Mendes, 2022). Seeing the massive potential of biodiesel, various countries, both developed and developing, have begun to encourage massive biodiesel production, which is estimated to reach 36.5 million tons in 2025 and 277 million tons in 2050 (Mishra & Goswami, 2018; Rouhany & Montgomery, 2019). This biodiesel is very spectacular because it has a high cetane number and flash point with low sulfur content, making its emission gas safe to be released into the air (Alsultan *et al.,* 2021; Hartono & Cahyono, 2020; Wu *et al.,* 2020). Biodiesel has the potential to be an environmentally friendly alternative energy due to its renewability and lower emissions (Gebremariam & Marchetti, 2018; Syazwani *et al.,* 2019).

One of the non-edible oils that can be used for biodiesel synthesis is candlenut seed oil. Candlenut (*Aleurites moluccana Wild*) is one of the promising raw materials for biodiesel production because the seeds have an oil content of about 55 - 66% by weight and can also grow in various places, including infertile soils such as sandy soils, saline soils, and gravelly soils (Shaah *et al.*, 2022). Candlenut oil contains α-eleostearic acid, a toxic compound that makes candlenut oil non-food (non-edible oil). Candlenut seed oil has a high FFA (Free Fatty Acid) content of about 5.4%, so to be used in the transesterification process, it must go through an esterification process to reduce the free fatty acid content to below 2% (Hadiyanto, *et.al,* 2020; Siregar *et al.*, 2024).

The high oil content of candlenut seeds, which are classified as non-edible oil, makes many researchers conduct research related to the manufacture of biodiesel from candlenut seeds to encourage the development of renewable energy. Pham *et al.* (2018) produced biodiesel from candlenut seeds using a two-step co-solvent process with an acid catalyst in the form of H_2SO_4 and a base catalyst in the form of KOH. This process has the disadvantage of using co-solvent, which requires additional separation and purification to remove residual solvent from the

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final product. In addition, the catalyst used is still homogeneous, so the catalyst is difficult to separate from the product, cannot be reused, and can produce hazardous waste. Shaah *et al*. (2022) used the non-catalytic supercritical methanol transesterification method to produce biodiesel without a catalyst. This method requires high temperatures and pressures to achieve supercritical methanol conditions, requiring expensive and high-risk specialized equipment. In addition, side reactions such as the decomposition of triglycerides, methanol, and biodiesel products can occur at supercritical conditions. Juwono *et al.* (2023), conducted a photocatalytic process of candlenut seeds with ZnO nanocatalyst. This method requires a strong light source (usually UV light), which requires higher energy consumption and operational costs. In addition, photocatalytics often have lower conversion efficiency than conventional methods, such as transesterification, because they are greatly affected by the distribution and intensity of UV light. Siregar *et al.* (2024), synthesized biodiesel using an acid catalyst in the form of H_2SO_4 and a base catalyst in the form of NaOH/CaO/Ca. Widayat, *et.al.,* (2023) used heterogen catalyst for biodiesel production viaesterification and trans esterification simultaneous reaction. The esterification and transesterification processes are still inefficient because they require many processes.

The biodiesel synthesis process in candlenut seeds with high FFA content requires a two-stage reaction, i.e. esterification and transesterification. This two-stage reaction is less effective because it requires many processes. A one-stage reaction is needed to overcome this problem. Solid-solid catalysts that work simultaneously are needed as base and acid catalysts. The use of heterogeneous catalysts has several advantages, such as being more environmentally friendly, easier to separate from liquid products, reusable, modified to increase activity, and longer service life (Faruque *et al.*, 2020). Several researchers have synthesized acid-base bifunctional catalysts for biodiesel production in one reaction stage, including CeO_2.MgO (Manríquez-Ramírez *et al.,* 2013), CeO_2.CaO (Wong *et al.*, 2015), ZrO_2.CaO (H. Li *et al.,* 2022), Mgo-CaO/SiO_2 (Widayat, *et.al.,* 2023) and V_2O_5.CaO (Mulyatun *et al.*, 2023). Alkaline earth metal catalysts, including CaO, MgO, and SrO, demonstrate effective catalytic performance in biodiesel production, which is attributed to their strong Lewis base characteristics, leading to high yields (T *et al.*, 2024). Calcium oxide (CaO) is frequently utilised as a catalyst because it can be modified, providing a high surface area. Additionally, it is cost-effective, as it can be derived from natural materials such as limestone, eggshells, seashells, and bones. Nonetheless, a significant limitation of CaO is the possibility of deactivation due to the leaching of Ca^{2+} ions by free fatty acids (FFAs) (Mazaheri *et al.*, 2021; Mohd Johari, *et.al.*, 2024). A combination of calcium oxide and cerium oxide has been shown to decrease CaO leaching during biodiesel synthesis with high free fatty acid content (Zhang *et al.*, 2018). This study employed CeO_2.CaO as a bifunctional catalyst for the synthesis of biodiesel from candlenut oil. Process optimization will be conducted to find the best variables (methanol-to-oil molar ratio, catalyst loading, and reaction temperature) in the synthesis of biodiesel from candlenut seed with CeO_2.CaO catalyst.

2. Materials and Methods

2.1 Materials

The raw materials used for catalyst synthesis are limestone and cerium nitrate hexahydrate ($Ce(NO_3)_3.6H_2O$, 99%, Merck, Germany). The candlenut seeds used were from East Nusa Tenggara, Indonesia. Biodiesel synthesis was carried out using 96% methanol. N-hexane was used to regenerate the catalyst that had been used. KOH and phenolphthalein were used to analyze the FFA content in the sample.

2.2 Raw Material Preparation

Limestone is crushed and then sieved using a sieve shaker with a size of 200 mesh. The limestone is then calcined using a furnace at 750°C for 4 hours to release the CO_2 and leave CaO (Zhang *et al*., 2018). CaO produced from calcination will be used for the synthesis of CeO_2.CaO catalyst.

Candlenut seeds were washed with warm water to remove dirt and then dried in the sun to dry the seeds. Extraction of candlenut oil using the pressing method will use a screw press machine which can produce large amounts of oil in a short time (Shaah *et al.,* 2022). The pressed oil was filtered and cooled, and its free fatty acid content was checked.

2.3 Synthesis CeO_2.CaO Catalyst

The CeO_2.CaO bifunctional catalyst was synthesized via a solid-state mixing method, employing a weight ratio of 1:4 (CeO_2:CaO). Cerium nitrate hexahydrate ($Ce(NO_3)_3{\cdot}6H_2O$) and calcium oxide (CaO) powders were thoroughly homogenized through manual grinding in an agate mortar to ensure uniform particle distribution. The resulting mixture was subjected to thermal treatment in a muffle furnace at 600 °C for 4 hours to facilitate phase interaction and enhance catalytic activity (Mulyatun *et al*., 2023). Prior to catalytic application, the physicochemical properties of the catalyst were characterized using Fourier Transform Infrared Spectroscopy (FTIR), Brunauer–Emmett–Teller (BET) surface area analysis, Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy (SEM-EDX), and Temperature-Programmed Desorption (TPD) to evaluate its structural, morphological, and surface characteristics.

2.4 Catalyst Characterization

Fourier Transform Infrared Spectroscopy (FTIR) was employed to identify the functional groups on the catalyst surface and investigate the chemical bonds and surface interactions (Mulyatun *et al*., 2023). FTIR analysis was performed using a Perkin-Elmer UATR Spectrum instrument, which is widely used for laboratory-scale characterization. The Brunauer–Emmett–Teller (BET) analysis was conducted using a Quantachrome Autosorb-iQ instrument to determine the specific surface area and pore diameter of the bifunctional catalyst, which are essential for classifying the pore structure and catalytic potential. Scanning Electron Microscopy coupled with Energy-Dispersive X-ray Spectroscopy (SEM-EDX) was carried out to examine the surface morphology and elemental composition of the catalyst, providing insights into the homogeneity of the material. This analysis was performed using a JEOL JSM-6510LA SEM-EDX instrument, operated at an accelerating voltage of 20 kV and a probe current of 1.00000 nA. Additionally, Temperature-Programmed Desorption (TPD) analysis was conducted to evaluate the acidic and basic properties of the catalyst, which are critical factors influencing the efficiency of bifunctional catalytic reactions.

2.5 Biodiesel Production

Biodiesel synthesis was conducted in a laboratory-scale glass reactor system consisting of a three-necked round-bottom

Table 1
Design of Experiment

Run Number	Methanol to Oil Mole Ratio	Catalyst Loading (% wt oil)	Operation Temperature (°C)	Biodiesel Yield (%)
1.	12	2	50	Y1
2.	8	6	50	Y2
3.	12	6	50	Y3
4.	8	2	70	Y4
5.	12	2	70	Y5
6.	8	6	70	Y6
7.	12	6	70	Y7
8.	6,6364	4	60	Y8
9.	13,3636	4	60	Y9
10	10	0,6364	60	Y10
11	10	7,3636	60	Y11
12	10	4	43,2	Y12
13	10	4	76,8	Y13
14	10	4	60	Y14
15	10	4	60	Y15
16	12	2	50	Y16

flask equipped with a reflux condenser to maintain a closed system and prevent methanol loss. The transesterification reaction was initiated by mixing methanol and oil in the reactor at varying molar ratios of 8:1, 10:1, and 12:1. A bifunctional catalyst, serving a crucial role in facilitating both esterification and transesterification reactions, was introduced at concentrations of 2 wt.%, 4 wt.%, and 6 wt.%. To investigate the influence of thermal conditions on reaction efficiency, the reaction was carried out at three different temperatures: 50 °C, 60 °C, and 70 °C. Experimental conditions were optimized using Response Surface Methodology (RSM) with a Central Composite Design (CCD) approach (Nguyen, *et.al*., 2023). A summary of the experimental design matrix is presented in Table 1. Each reaction was maintained for 1 hour under continuous stirring at 200 rpm using a magnetic stirrer to ensure homogeneous mixing. Upon completion, the catalyst was separated from the reaction mixture via centrifugation at 5000 rpm for 5 minutes. The liquid product was further subjected to phase separation using a separating funnel for 24 hours to ensure complete separation of the biodiesel and glycerol layer (Al-Saadi *et al*., 2020).

2.6 Catalyst Reusability Test

Catalyst recovery was performed by washing the spent catalyst with an n-hexane solution to remove residual organic compounds and reaction by-products. Following the washing step, the catalyst was dried in an oven at 70 °C for 6 hours to eliminate any remaining solvent and moisture (Mulyatun *et al*., 2023). o evaluate the reusability and stability of the catalyst, recycling experiments were conducted under identical reaction conditions: a methanol-to-oil molar ratio of 10:1, catalyst loading of 4 wt.%, and a reaction temperature of 60 °C. These experiments aimed to assess the catalytic performance over successive reaction cycles.

2.7 Biodiesel Characterization

A series of physicochemical analyses were performed to ensure that the produced biodiesel complied with the Indonesian National Standard (SNI) 7182:2015. The density of biodiesel was determined using a pycnometer, and its value was calculated according to Equation (1) (Buchori *et al*., 2020):

$$\boldsymbol{\rho} = \frac{(\textbf{mass of pycnometer+sample}-(\textbf{mass of pycnometer})}{\textbf{volume of pycnometer}} \quad (1)$$

The kinematic viscosity was measured using an Ostwald viscometer by recording the time required for the biodiesel to flow between two designated points. The viscosity was then

calculated using Equation (2), where η_x represents the viscosity of the sample (mm^2/s), η_a the viscosity of distilled water (mm^2/s), ρ_x the density of the sample (kg/m^3), ρ_a the density of distilled water (kg/m^3), t_x the flow time of the sample (s), and t_a the flow time of distilled water (s) (Buchori *et al.*, 2020):

$$\eta_x = \frac{\rho_x \cdot t_x}{\rho_a \cdot t_a} \times \eta_a \quad (2)$$

The free fatty acid (FFA) content was analyzed via acid-base titration using potassium hydroxide (KOH) as the titrant. In this procedure, 5 mL of biodiesel was mixed with 5 mL of methanol and two drops of phenolphthalein indicator. The mixture was titrated with 0.1 N KOH until a stable pink endpoint was achieved. The FFA content was calculated using Equation (3), where MW is the molecular weight of fatty acids (g/mol), V is the volume of KOH used (mL), N is the normality of KOH (N), and m is the mass of the biodiesel sample (g) (Susilowati *et al.*, 2019).

$$\%FFA = \frac{MW \times V \times N}{m \times 1000} \times 100\% \quad (3)$$

The overall yield of biodiesel was determined based on the mass ratio between the obtained biodiesel product and the initial mass of candlenut oil used as the feedstock, and it was calculated using Equation (4). (Prameswari *et al.*, 2023). Additionally, the composition of fatty acid methyl esters (FAMEs) in the biodiesel was identified using Gas Chromatography–Mass Spectrometry (GC-MS) analysis, conducted with a SHIMADZU QP 2010S instrument equipped with a DB-1 capillary column. The FAME yield was quantified based on the chromatographic area data and calculated by equation (5) (Mulyatun *et al.*, 2024).

$$\text{Yield overall } (\%) = \frac{\text{mass of biodiesel}}{\text{mass of candlenut oil}} \times 100\% \quad (4)$$

$$\text{Yield FAME}(\%) = \%\text{GC area FAME} \times \frac{\text{m biodiesel}}{\text{m candlenut oil}} \quad (5)$$

3. Results and Discussion

3.1 Characteristics of candlenut oil

Candlenut seeds are one of the raw materials used to make biodiesel, which has a high oil content and is not edible. According to the Free Fatty Acid (FFA) analysis, candlenut oil showed an initial FFA content of 2.287%. This suggests a pretreatment step like esterification is required to lower the FFA level and prevent soap formation during transesterification. In the simultaneous reaction system, free fatty acids (FFAs) were transformed into fatty acid methyl esters (FAMEs) through esterification, while the triglyceride components underwent transesterification to produce biodiesel and glycerol. To identify the feedstock composition, Gas Chromatography-Mass Spectrometry (GC-MS) analysis was conducted to identify

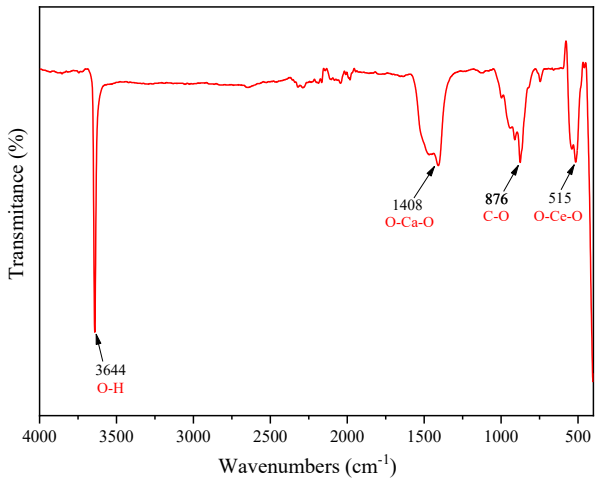


Fig. 1. FTIR spectrum of CeO_2.CaO

the primary fatty acid components of candlenut oil. Table 2 is presenting of type of fatty acid. These components are essential to determine the quality and fuel characteristics of the produced biodiesel. The linoleic acid was dominant of type fatty acid in candlenut oil about 62.821%.

Oils generally contain both saturated and unsaturated fatty acids. Saturated fatty acids can be identified by the absence of double bonds in their hydrocarbon chains, which results in a linear molecular structure. In contrast, unsaturated fatty acids contain one or more double bonds, which introduce kinks in the molecular configuration and affect their physicochemical properties. (Li *et al.*, 2019). Saturated fatty acids usually have a higher melting point than unsaturated fatty acids (Devi & Khatkar, 2016). GC-MS results show that candlenut oil contains saturated fatty acids, including hexadecanoic acid (palmitic acid) and octadecanoic acid (stearic acid). Candlenut oil also

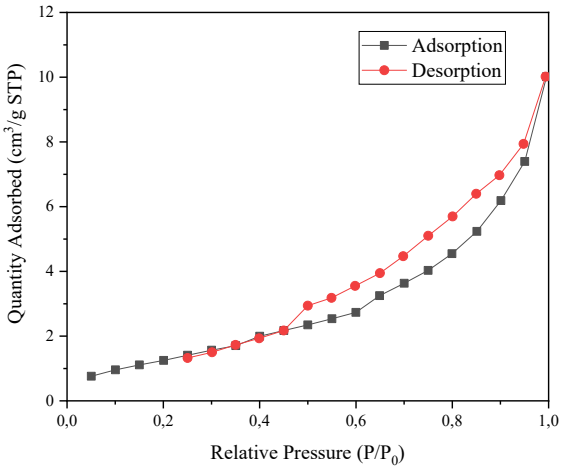


Fig. 2. Adsorption-desorption curve of CeO_2.CaO catalyst

Table 2
Composition of candlenut oil

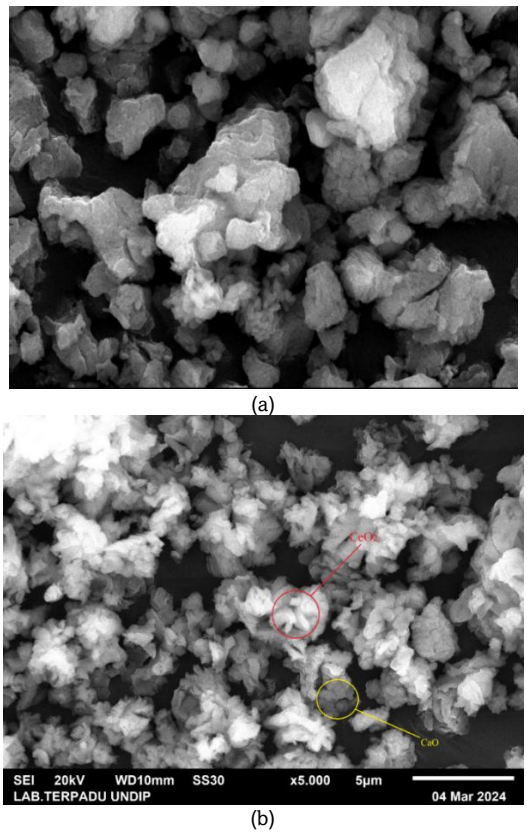
Compound	Trivial Name	Molecular formula	Area%
Hexadecanoic acid	Palmitic Acid	$C_{17}H_{34}O_2$	30.194
9,12-Octadecanoic acid	Linoleic Acid	$C_{19}H_{34}O_2$	67.821
Octadecanoic acid	Stearic Acid	$C_{19}H_{34}O$	1.985

contains unsaturated fatty acids in 9,12-octadecanoic acid (linoleic acid).

3.2 Characteristics of CeO_2.CaO catalyst

FTIR analysis was carried out to see functional groups in the CeO_2.CaO bifunctional catalyst. Fig. 1. shows the results of the FTIR analysis. The peak at a wavelength of 876 cm^{-1} refers to the C-O group of CO_3^{2-} which shows the presence of $CaCO_3$ on the catalyst (Maneerung *et al.*, 2016). $CaCO_3$ can be formed due to the high affinity of Ca-O (Kesserwan *et al.*, 2020). At a wavelength of 1408 cm^{-1}, an O-Ca-O group is formed, which indicates the presence of CaO (Mekonnen & Yesuf, 2024). Hydroxyl (O-H) groups, i.e. $Ca(OH)_2$ are seen at a wavelength of 3644 cm^{-1}. The presence of hydroxyl (O-H) groups on the catalyst surface is due to the adsorption of water molecules. Additionally, the thermal decomposition of nitrate precursors in the presence of water vapor may form calcium hydroxide ($Ca(OH)_2$) via a subsequent hydrolysis reaction. (Maneerung et al., 2016). The peak formed at 515 cm^{-1} indicates the presence of the O-Ce-O group, which indicates the presence of CeO_2 on the catalyst (Prabaharan *et al.,* 2016).

BET analysis results show that the average surface area of CeO_2.CaO catalyst is 9.536 m^2/g. A large surface area is triggered by high porosity in the catalyst. High porosity can form due to the presence of $CaCO_3$, which releases CO_2 during high-temperature calcination (Mulyatun *et al.*, 2023). The average pore diameter of the bifunctional catalyst is 5.876 nm, while the pore diameter of CeO_2.CaO catalyst is in the 2-50 nm range, classified as mesoporous. Mesoporous catalysts are excellent for transesterification reactions that require many reactants. (Zhang *et al.*, 2018). Based on BET analysis, the average pore volume of the catalyst is 0.028 cm^3/g. The $CaCO_3$ calcination process will release CO_2 gas, so pores appear in the catalyst (Mulyatun *et al.*, 2023). Increased catalyst pores will increase the pore volume of the catalyst.



(a)

(b)

Fig. 3. SEM analysis of (a) CaO (b) CeO_2.CaO with 5,000x magnification

The adsorption-desorption curve of CeO_2.CaO bifunctional catalyst is shown in Fig. 2. The nitrogen adsorption-desorption isotherm demonstrated Type IV characteristics based on the IUPAC classification, indicating the formation of a mesoporous structure. Furthermore, the observation of a Type H3 hysteresis loop, which closes at a relative pressure exceeding 0.4 (P/P_0 > 0.4), provides additional confirmation of the presence of slit-shaped mesopores in the bifunctional CeO_2·CaO catalyst. (Kingkam et al., 2024). The pore size of mesoporous materials ranges from 2-50 nm. Closed loops at P/P_0 between 0.4 - 0.5 indicate that the pore diameter is more than 2 nm (Mulyatun *et al.,* 2024). The BET analysis also shows that the bifunctional catalyst CeO_2.CaO has a mesopore size of 5.876 nm, more than 2 nm. Mesoporous catalysts have several advantages because of their large surface area and interconnected pore networks, which promote reactant molecule diffusion toward the active sites. Triglyceride molecules may pass through the internal pore channels of the mesoporous structure and interact with the catalytic sites in transesterification reactions, increasing conversion rates and reaction efficiency (Nayebzadeh & Hojjat, 2020).

The physical mixing method effectively yielded the CeO_2.CaO catalyst, as confirmed by the SEM analysis results presented in Figure 3. The presence of cerium oxide is identifiable by its sharp, needle-like structures, in which both CeO_2 and CaO are uniformly distributed and exhibit relatively consistent sizes and shapes. It can be seen that the CeO_2.CaO catalyst has macro and meso pore sizes, significantly supporting transesterification reactions. Triglyceride molecules will penetrate the macropores to reach the active side of the catalyst (Zheng *et al.*, 2017). The presence of mesopores can increase the surface area of the catalyst, and the pores will increase so that the active side of the catalyst will also be greater (Qian *et al.,* 2022).

Assessing bifunctional catalysts' acidic and basic properties is crucial for determining their potential efficacy in promoting simultaneous esterification and transesterification reactions. Temperature-programmed desorption (TPD) profiles demonstrate the strength of acid and base sites: desorption peaks below 300 °C are generally attributed to weak acidic or basic sites, peaks between 400–500 °C correspond to sites of moderate strength, whereas peaks exceeding 500 °C signify the presence of strong acidic or basic sites (Gil, 2023).

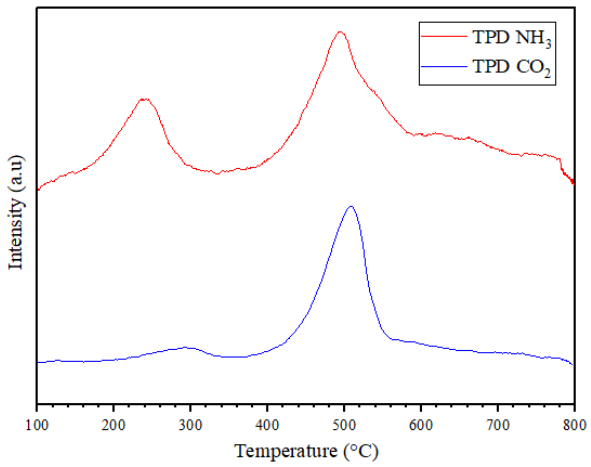


Fig. 4. TPD NH_3 and TPD CO_2 result

Table 3
ANOVA process optimization

Source	SS	DF	MS	F	P
Model	2616.71	9	290.75	165.31	< 0.0001
A-Mole ratio of methanol : oil	42.11	1	42.11	23.94	0.0027
B-Catalyst loading	1540.40	1	1540.40	875.81	< 0.0001
C-Reaction temperature	1.46	1	1.46	0.8310	0.3971
AB (Interaction)	15.41	1	15.41	8.76	0.0253
AC (Interaction)	44.84	1	44.84	25.50	0.0023
BC (Interaction)	1.88	1	1.88	1.07	0.3408
A^2 (Squared)	797.14	1	797.14	453.22	< 0.0001
B^2 (Squared)	558.01	1	558.01	317.26	< 0.0001
C^2 (Squared)	175.07	1	175.07	99.54	< 0.0001
Residual	10.55	6	1.76		
Lack of fit	10.51	5	2.10	47.56	0.1096
Pure error	0.0442	1	0.0442		
Cor Total	2627.27	15			

R^2	Adjusted R^2	Predicted R^2	Adeq Precision
0.9960	0.9900	0.9660	37.9726

Fig. 4 displays the results of the TPD-NH3 and TPD-CO2 analyses. TPD-CO_2 provides data on the total base site density of 1.1971 mmol/g. Based on Figure 4 illustrates the observation of two distinct CO_2 desorption peaks within the temperature ranges of 200–300 °C and 400–600 °C, suggesting the existence of both weak and strong basic sites on the surface of the CeO_2·CaO catalyst. The strong basicity can be assigned to the abundant existence of surface oxygen species linked to the Ca–O bond. Moreover, the synergistic interaction between CaO and CeO_2 improves the overall basicity of the catalyst, which facilitates simultaneous processes of esterification and transesterification reactions (Zhang *et al.*, 2018). Figure 4 further discusses the NH_3-TPD profile of the catalyst, revealing two distinct desorption peaks within the temperature ranges of 150–300 °C and 400–700 °C, which are indicative of weak and strong acid sites, respectively. The total acid site density was identified to be 1.7202 mmol/g, which indicates a significnat presence of acidic sites on the catalyst surface. The combination of CaO with transition metal oxides like ZnO, CeO_2, ZrO_2, and W-Mo has been reported to modify the surface acidity of the catalyst, which may improve its bifunctional catalytic performance by adjusting the distribution and intensity of acid sites (Basumatary *et al.*, 2023). The presence of metal oxides in CaO, for example CeO_2 can encourage the esterification and transesterification reaction of non-edible oil simultaneously. From the previous study, the TPD-NH_3 analysis of CeO_2.CaO catalyst reveal the presence of both basic and acidic active sites, with measured site densities of 2.985 mmol/g and 1.042 mmol/g, respectively. Basic sites improve nucleophilic interactions and facilitate effective catalysis in processes involving multi-step or concurrent reactions, while acidic sites are generally linked to the activation of electrophilic species. The synergistic interaction between these sites emphasises CeO_2·CaO applicability as a heterogeneous catalyst in simultaneous reaction systems. These findings corroborate the present investigation, reinforcing the bifunctional nature of the CeO_2·CaO catalyst system.

3.3 Process Optimization

The experimental data obtained were then processed using Design Expert software with the Central Composite Design (CCD) process optimization method to see the optimum parameters. The number of runs in this study was 16 times with 2 center points. The model obtained is a quadratic equation as equation (6).

$$\text{FAME Yield} = 79.27 + 1.76X_1 + 10.62X_2 - 0.3271X_3 + 1.39X_1X_2 - 2.37X_1X_3 + 0.485X_2X_3 - 9.28X_1^2 - 7.76X_2^2 - 4.35X_3^2 \quad (6)$$

The dependent variable in the equation is FAME yield, while X_1, X_2, and X_3 are independent variables, i.e. the methanol-to-oil molar ratio, catalyst loading, and reaction temperature. X1.X2, X1.X3, and X2.X3 describe the interaction between the three variables. The terms X_1^2, X_2^2, and X_3^2 represent the quadratic effects of the respective independent variables, illustrating the non-linear relationships between each factor and the response within the experimental design.

Based on Table 3., it can be seen that the F value obtained is 165.31, indicating that the model is significant. The P value in the model is less than 0.05, indicating that the model is significant (Njoku & Otisi, 2023). A significant P value is also shown in variables B, AB, AC, BC, A^2, B^2, and C^2. The F value on Lack of Fit is 47.56, indicating that lack of fitness is insignificant. Lack of Fit, which is not significant, indicates that the model used is appropriate. The R^2 value obtained is 0.9960, where the value is close to 1. This shows that the model is good at predicting the response.

Biodiesel production from candlenut oil with CeO_2.CaO catalyst was carried out by varying the methanol-to-oil molar ratio, catalyst loading, and reaction temperature. The methanol-to-oil molar ratio was varied from 8:1, 10:1, and 12:1. The catalyst loading was varied from 2% w/w, 4% w/w, and 6% w/w. The reaction temperature was varied from 50°C, 60°C, and 70°C.

Fig. 5(a). shows the three-dimensional plot of the interaction between the methanol-to-oil molar ratio (A) and catalyst loading (B) on FAME yield. The three-dimensional surface response shows that the Fatty Acid Methyl Ester yield increases as the methanol-to-oil molar ratio increases up to 10:1. The FAME yield decreased when it reached a mole ratio of 12:1. The increase in the amount of catalyst added to the reaction caused the FAME yield to increase as well. Al-Muhtaseb *et al.* (2021) produced biodiesel from loquat oil using a bifunctional CeO_2.CaO catalyst. The study showed that the optimal condition to achieve the highest yield of 90.14% was at a methanol-to-oil molar ratio of 9:1 and a catalyst loading of

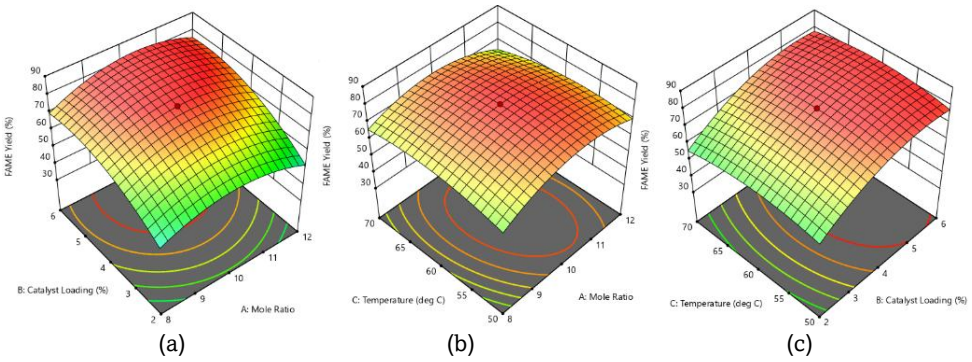


Fig. 5. Optimization graph of: (a) methanol : oil molar ratio vs catalyst loading (b) methanol : oil molar ratio vs temperature (c) catalyst loading vs temperature

4%w/w. These results align with the research, where the optimal methanol-to-oil molar ratio for simultaneous reactions is ± 10:1 with a catalyst loading of ± 6% w/w. Esterification and transesterification reactions are reversible so that excess methanol can drive the reaction towards the product. However, too much methanol can saturate the catalyst's active sites, thus inhibiting triglyceride protonation into carbonyl groups (Mulyatun et al., 2024). The more catalysts used in the reaction, the greater the number of active sites contributing to biodiesel formation (Al-Muhtaseb *et al.*, 2021).

The 3D response surface between the methanol-to-oil molar ratio (A) and reaction temperature (C) is shown in Fig. 5(b). Based on the figure, it can be seen that the yield of FAME increases at an increase in the methanol-to-oil molar ratio up to 10:1 and an increase in temperature up to 60°C. There is a decrease in FAME yield when the methanol-to-oil molar ratio reaches 12:1 and the temperature is 70°C. Similar results have been found in biodiesel production using neem oil and heterogeneous copper-doped zinc oxide nanocatalysts by Gurunathan and Ravi (2015). Previous studies reported that the optimal operating conditions for biodiesel synthesis were achieved at a methanol-to-oil molar ratio of 10:1 and a reaction temperature of 55 °C, resulting in a FAME yield of 97.18%. These findings are consistent with the present study, which also identified a methanol-to-oil molar ratio of 10:1 and a reaction temperature around 60 °C as optimal for biodiesel production from non-edible oils. The transesterification reaction is reversible; increasing the methanol concentration drives the reaction equilibrium toward the product side, enhancing biodiesel formation. However, excessive methanol can lead to a catalyst dilution effect and reduce the FAME yield due to reduced solubility and limited interaction between reactants and active sites. (Mulyatun *et al.*, 2024). The reaction rate is significantly influenced by the reaction temperature, which is a critical parameter affecting molecules' kinetic energy. Molecular interactions are generally accelerated and reaction rates are enhanced due to increased temperature. Nevertheless, the rapid evaporation of methanol can reduce its effective concentration in the reaction mixture and potentially decrease the overall conversion efficiency when temperatures are excessively high (Lani *et al.*, 2022).

Fig. 5(c). shows the interaction plot between catalyst loading and reaction temperature on FAME yield. An increase in catalyst loading causes an increase in FAME yield. The FAME yield also increased at an increase in temperature up to 60°C. The increase in temperature up to 70°C causes a decrease in FAME yield obtained. Wong et al. (2015) effectively produced biodiesel from palm oil with a CeO_2·CaO catalyst, attaining a maximum yield of 95% with a catalyst loading of 5% w/w at a reaction temperature of 65 °C. The results align closely with the current study, which determined optimal conditions at approximately 6% w/w catalyst loading and a temperature of about 60 °C. The overall reaction efficiency is improved by increasing the catalyst concentration because it typically increases the number of available active sites, encouraging greater contact between reactants and catalytic surfaces (Mulyatun *et al.*, 2022).

The kinetic energy of the reactant molecules and the reaction temperature are directly proportional; as the temperature rises, molecular collisions become more intense and frequent, speeding up the reaction rate. However, when the reaction temperature exceeds methanol's boiling point, significant vaporisation may occur, resulting in a decrease in the effective concentration of methanol in the reaction medium and, as a result, reducing the overall efficiency of the transesterification process (Al-Muhtaseb *et al.*, 2021).

Based on optimization using CCD in Design Expert software, it was found that the optimum parameters for

Table 4
FAME components of biodiesel product (variable 4)

Component	Molecular Formula	Area%
Hexadecanoic acid, methyl ester	$C_{17}H_{34}O_2$	44.07
11,14-Eicosadienoic acid, methyl ester	$C_{21}H_{38}O_2$	6.25
9,12-Octadecadienoic acid, methyl ester	$C_{19}H_{34}O_2$	10.71
13-Octadecenoic acid, methyl ester,	$C_{19}H_{36}O_2$	9.29
9,12,15-Octadecatrienoic acid, methyl ester	$C_{19}H_{32}O_2$	6.33
Octadecanoic acid, methyl ester	$C_{19}H_{38}O_2$	15.53
9-Octadecenoic acid, methyl ester	$C_{19}H_{36}O_2$	5.48

Table 5.
Characteristics of biodiesel

	FAME Yield (%)	Calorific Value (Cal/g)	Density (g/cm^3)	Viscosity (cSt)	FFA (%)
SNI 7182:2015	96.5	-	0.85-0.89	2.3-6	-
Variable 1 (8:1, 2%w/w, 50°C)	46.546	9240.630	0.900	3.6	0.182
Variable 2 (12:1, 2%w/w, 50°C)	49.554	9132.810	0.900	4.0	0.201
Variable 3 (8:1, 6%w/w, 50°C)	61.846	9101.330	0.900	2.6	0.238
Variable 4 (12:1, 6%w/w, 50°C)	73.841	9099.030	0.890	1.8	0.148
Variable 5 (8:1, 2%w/w, 70°C)	48.306	9170.570	0.900	4.3	0.128
Variable 6 (12:1, 2%w/w, 70°C)	45.279	9107.570	0.890	5.0	0.147
Variable 7 (8:1, 6%w/w, 70°C)	68.982	9263.260	0.890	4.1	0.240
Variable 8 (12:1, 6%w/w, 70°C)	68.068	9228.920	0.910	2.7	0.217
Variable 9 (6.6364:1, 4%w/w, 60°C)	49.317	9024.410	0.900	2.5	0.292
Variable 10 (13.3636:1, 4%w/w, 60°C)	57.001	9094.020	0.900	3.8	0.200
Variable 11 (10:1, 0.6364%w/w, 60°C)	39.014	9215.680	0.900	3.9	0.237
Variable 12 (10:1, 7.3636%w/w, 60°C)	75.875	9188.390	0.870	1.1	0.132
Variable 13 (10:1, 4%w/w, 43.2°C)	68.085	9145.420	0.900	1.9	0.073
Variable 14 (10:1, 4%w/w, 76.8°C)	66.116	9044.000	0.890	2.0	0.166
Variable 15 (10:1, 4%w/w, 60°C)	79.104	8984.850	0.880	2.1	0.149
Variable 16 (10:1, 4%w/w, 60°C)	79.402	8105.850	0.880	1.9	0.130
Suggested Operating Condition from Optimization Process (10.3:1, 5.39%w/w, 60°C)	83.673	8892.610	0.88	2.5	0.145

biodiesel production from candlenut oil were at a methanol-to-oil molar ratio of 10.3:1, catalyst loading of 5.39%w/w, and temperature of 60°C. These optimum conditions are estimated to produce a FAME yield of 83.1125% with a desirability value of 0.959. The desirability value shows that from the FAME yield target (85%) there is a 95.9% possibility that the target can be achieved. Biodiesel production was conducted under the suggested operating conditions obtained from the experimental data optimization. The accuracy and dependability of the optimization strategy were confirmed by the final FAME yield of 83.673%, which closely matched the value predicted by the optimization model. Moreover, the biodiesel's physicochemical characteristics, notably its density and kinematic viscosity, conformed to the Indonesian National Standard (SNI), as shown in Table 5. The results demonstrate that the optimized process conditions improve biodiesel yield while ensuring the final product's quality complies with regulatory standards for commercial fuel applications.

3.4 Characteristics of biodiesel

The constituent components of biodiesel can be determined by GC-MS (Gas Chromatography Mass Spectrometry) analysis. The data presented are the GC-MS results from variable 4 with the highest %GC Area FAME like on Table 4.. GC-MS analysis revealed the presence of FAME compounds in the final product, with the main components in biodiesel being methyl palmitate (44.07%) and methyl stearate (15.53%). This proves that the bifunctional CeO_2.CaO catalyst is successfully used for simultaneous esterification-transesterification reactions and produces methyl esters.

Calorific value, density, viscosity, and %FFA analyses of biodiesel were also carried out to determine the product characteristics. The value of the analysis results was then compared with the value of the Indonesian National Standard (SNI) 7182: 2015 to determine the success of the CeO_2.CaO catalyst in producing biodiesel products. The results of biodiesel characterization can be seen in can be seen in Table 5.

Fatty Acid Methyl Esters (FAME) yield is a primary quality indicator in biodiesel production, as it reflects the extent of conversion and directly correlates with fuel purity. According to the Indonesian National Standard (SNI 7182:2015), biodiesel must contain a minimum of 96.5% FAME to be deemed suitable for commercial use. In this study, the obtained FAME yield did not meet the SNI threshold, suggesting incomplete conversion or the presence of residual impurities. A high FAME content typically signifies lower contaminants such as unreacted glycerol, methanol, and free fatty acids, which are detrimental to fuel performance and stability.

Contaminants contained in biodiesel can reduce engine performance and even damage the engine. High FAME content can minimize the presence of unsaturated fatty acids, which are more susceptible to oxidation (Tomić et al., 2019). High FAME content can also reduce the risk of fuel degradation and increase its shelf life.

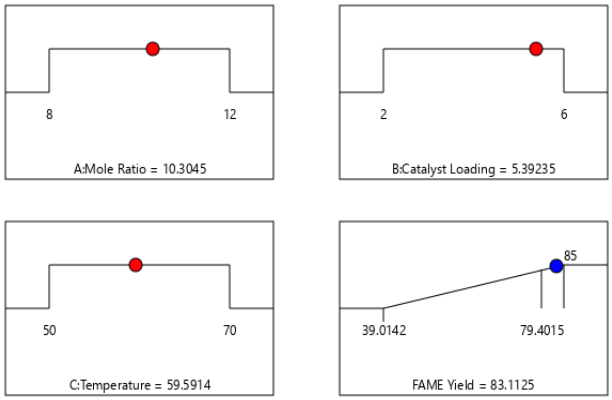


Fig. 6. Optimization of simultaneous reaction operating conditions

Fatty Acid Methyl Ester (FAME) yield is a key parameter in determining biodiesel quality. According to the Indonesian National Standard (SNI) 7182:2015, high-quality biodiesel must contain at least 96.5% FAME. The results of this study show that the overall FAME yield obtained was below the SNI standard. A high FAME content indicates good biodiesel quality; the higher the ester percentage, the lower the concentration of impurities like methanol, glycerol, or free fatty acids left over from the production process (Tomić *et al.*, 2019). The short reaction duration of only 1 hour in this study may have led to the substandard FAME yield, as it was not sufficient for the reactants to interact with the active sites of the catalyst effectively. In a study by Al-Muhtaseb *et al.* (2021), biodiesel synthesis from loquat oil using a CeO_2.CaO catalyst over a 60-minute reaction period resulted in a FAME yield of only 79.62%, supporting the findings of this research.

The calorific value indicates how much heat can be released during combustion or the fuel's energy capacity. The calorific value of biodiesel from candlenut oil shows results of 9000 Cal/g. Cahyono *et al.* (2018) tested the calorific value of biodiesel from candlenut oil and obtained a value of 9387 Cal/g. This aligns with the research conducted, where the calorific value of biodiesel from candlenut oil is approximately 9000 Cal/g. A large calorific value indicates that the fuel is more efficient (Karmakar *et al.*, 2018). A low calorific value of biodiesel will require more biodiesel mass to burn.

Another parameter to determine biodiesel quality can be seen from its density value. Based on SNI 7182:2015, the density requirement that must be met for biodiesel is between 0.85 - 0.89 g/cm^3 at 40°C. The results showed that some variables met the requirements, but nine variables did not meet the requirements, i.e., variables 1, 2, 3, 5, 8, 9, 10, 11, and 13. The lowest density value produced was 0.87 g/cm^3, while the highest value obtained was 0.91 g/cm^3. The density value is related to the calorific value of biodiesel, where the higher the density, the higher the calorific value (Ozcanli *et al.,* 2013). The high-density value of biodiesel can be caused by glycerol in the biodiesel (Elgharbawy et al., 2021). Glycerol has a relatively high density of 1.26 g/cm^3. If glycerol is not completelFy separated from biodiesel, the density of biodiesel will increase. Biodiesel density higher than the quality requirement will cause an increase in particulate matter and NOx emissions (Yildiz *et al.*, 2022).

Viscosity is a parameter that must be considered when determining biodiesel quality. The requirements determined by SNI 7182: 2015 for biodiesel viscosity are 2.3 - 6 cSt. The results showed that most of the variables met the specified requirements, but several variables did not meet the requirements, i.e., variables 4, 12, 13, 14, 15, and 16. The lowest viscosity value obtained was 1.1 cSt, while the highest was 5.0 cSt. Low-viscosity will complicate fuel distribution, making it difficult to burn and potentially causing leaks in the pipe (Gülüm & Bilgin, 2017). The viscosity of biodiesel is less than the quality standard, which can also reduce combustion efficiency because the fuel will flow faster and the contact time with engine components will be reduced (Ferreira *et al.*, 2021).

Free fatty acid (FFA) levels can be a parameter for the success of esterification reactions in biodiesel production. If the FFA level in biodiesel is low or less than 2%, it indicates that the conversion reaction of FFA into biodiesel is successful. The research showed that the FFA content in all variables had decreased from the initial candlenut oil FFA content of 2.287%. The decrease in FFA levels showed that the bifunctional catalyst CeO_2.CaO successfully carried out simultaneous reactions, which included esterification and transesterification. Too high FFA content in biodiesel indicates a high amount of free fatty acids that can cause corrosion in diesel engines (Oni *et al.*, 2022).

3.5 Catalyst reusability

In this study, the catalyst was reused 4 times in simultaneous reactions to see the reusability of the CeO_2.CaO catalyst. The operating condition used was the 15th run condition (center point), which was at a methanol-to-oil molar ratio of 10:1, 4%w/w catalyst loading, and a temperature of 60°C. After the reaction, the catalyst was separated from the product, washed with n-hexane several times, and dried in an oven for 6 hours before being used in the next cycle. Fig. 7. illustrates the reusability of the CeO_2.CaO catalyst.

Based on Fig. 7., it can be seen that after reusing the catalyst 4 times, the overall yield can be maintained above 75%. Run 15 produced an overall yield of 89.3328%, then after reuse, the overall yield continued to decrease to 87.5135% after being used again for the first time, 83.6182% for the second time, 79.3382% for the third time, and 75.1719% for the fourth times. CaO-based catalysts can deactivate due to the leaching of CaO into the reaction medium. In addition, a decrease in yield can occur due to the adsorption of fatty acids, glycerol, or glycerides (triglycerides, diglycerides, and monoglycerides) on the active sites (Zhang *et al.*, 2018). Based on the catalyst reusability testing conducted, it can be seen that the bifunctional CeO_2.CaO catalyst has good stability. Reusability is an important factor in heterogeneous catalysts, which can later be developed for industrial needs.

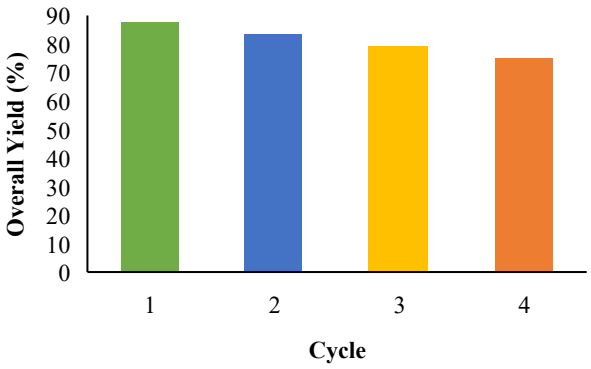


Fig. 7. Biodiesel yield in the catalyst reusability test

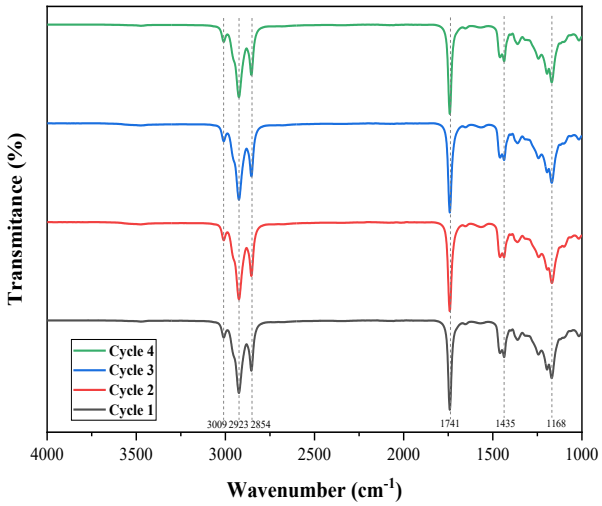


Fig. 8. FTIR analysis of biodiesel products in the catalyst reusability test

The CeO_2.CaO catalyst retained its ability to produce high-quality biodiesel after three regeneration cycles. The FTIR analysis results of biodiesel produced using both fresh and regenerated catalysts are shown in Figure 8. Based on these results, no significant changes were observed in the functional groups of the biodiesel product. The peaks between 1400 and 1600 cm^{-1} indicate bending vibrations of the aliphatic CH_2 and CH_3 groups. The peak at 1168 cm^{-1} corresponds to the bending vibration of the C-O ester group (Ali *et al.*, 2018). The strong peak at 1741 cm^{-1} represents the stretching vibration of the C=O carbonyl group, which is present in the methyl ester (Rosset & Perez-Lopez, 2019). The peaks observed at wavelengths 2923 and 2854 cm^{-1} correspond to the symmetric/asymmetric stretching vibrations of C-H from the alkyl groups CH_2 and CH_3 (Popovicheva *et al.*, 2017). The regeneration of the CeO_2.CaO catalyst for three cycles successfully maintained the quality of the produced biodiesel. Stable functional groups associated with the methyl ester are demonstrated in the FTIR results, with consistent intensities across each cycle. This also suggests that the catalyst is stable after regeneration.

Figure 9 displays the XRD patterns of both the fresh and regenerated catalysts. Distinctive peaks of CaO are noted at 2θ = 32.41°, 37.54°, and 53.44° (JCPDS file No. 37-1947), whereas the peaks associated with CeO_2 are found at 2θ = 28.72°, 33.41°, 47.61°, and 56.40° (JCPDS file No. 37-1497). The XRD analysis of the CeO_2.CaO catalyst reveals the presence of distinct crystalline phases of CaO and CeO_2 without forming new species or binary phases such as $CaCeO_3$ (Zhang *et al.,* 2018). The decrease in peak intensity observed in the regenerated catalyst is likely due to contamination by residual oil, methyl esters, and glycerol that were not completely removed (Sjöström, *et al.,* 2019).

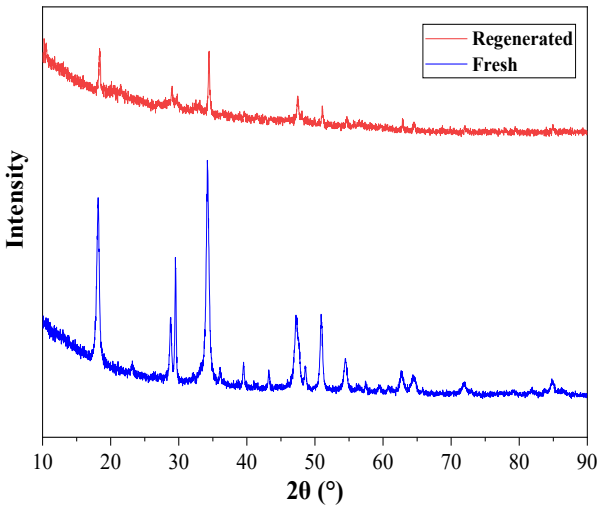


Fig. 9. XRD analysis of fresh and regenerated catalyst

4. Conclusion

The acid-base bifunctional catalyst CeO_2.CaO was successfully synthesized via a physical mixing method. Characterization results confirmed the homogeneous distribution of CeO_2 and CaO phases within the catalyst. The synthesized catalyst exhibited both acidic and basic active sites and a mesoporous structure, making it well-suited for facilitating transesterification reactions. The reusability catalyst test demonstrated that the catalyst maintained an overall biodiesel yield above 75% after four cycles, indicating good catalytic stability. The optimal operating conditions for biodiesel production from candlenut oil using the CeO_2.CaO catalysts were determined to have a methanol-to-oil molar ratio of 10.3:1, catalyst loading of 5.39% w/w, and a reaction temperature of 60°C.

Acknowledgments

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