



## Research article

# Optimization and characterization of biodiesel from waste cooking oil using modified CaO catalyst derived from snail shell

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## ABSTRACT

Currently, research has diverted toward generating renewable fuels due to the unreliable supply and rising cost of conventional fuels. Biodiesel is renewable fuel commonly obtainable via a simple process. Biodiesel was produced via the transesterification of waste cooking oil (WCO) using heterogeneous catalysts. The aim of this study was to synthesize a ZnO and TiO<sub>2</sub>-supported CaO catalyst from a snail shell for the transesterification of waste cooking palm oil to produce biodiesel. Sol-gel and wet-impregnated methods were adopted to synthesize ZnO and catalyst, respectively. The physicochemical properties of waste cooking oil and biodiesel were characterized in accordance to AOAC and ASTM standard methods. The FTIR and XRD analyses were carried out to characterize the biodiesel and the prepared catalysts. The result of this study revealed that CaO catalyst derived from snail shell, resulted to a WCO-derived biodiesel yield of 80%. The CaO catalyst modified with ZnO and TiO<sub>2</sub>, further led to an increased biodiesel of 90% and 95%, respectively. The result of this study showed that the optimum conditions associated with highest biodiesel yield over the synthesized catalysts were at 3% catalyst weight, 65 °C, a 6:1 methanol-to-oil ratio and 3-h reaction time. The FTIR spectra also proved successful formation of biodiesel. Biodiesel was successfully synthesized from WCO, and the CaO catalyst synthesized from snail shells and modified with ZnO and TiO<sub>2</sub>, showed potential to substitute for costly catalysts derived from chemical reagents for biodiesel production.

## 1. Introduction

Sustainable development and the role of energy in the development process are important topics that have gotten a lot of attention in recent decades. Since the beginning of time, fossil fuels have been the primary source of energy [1,2]. Unfortunately, due to significant worldwide population expansion and urbanization, these fossil fuel reservoirs are rapidly depleting [3]. The global energy crisis has sparked initiatives around the world to investigate alternate and potentially sustainable energy sources [4]. The U.S. energy information administration, in its international energy outlook report, indicated that the world's total energy consumption is significantly increasing [5]. However, numerous studies showed that the combustion of non-renewable fossil fuels contributes approximately 52% of CO<sub>2</sub> emissions, which is the major source of greenhouse gases and its leads to global warming [6]. Nowadays, various renewable resources such as wind, geothermal, solar, wave energy, and biofuel are considered as alternative fossil fuels [3,7]. Among these alternative fuels, biodiesel (BD) is promoted as a supplementary fuel for diesel engines [8].

These is due to its clean combustion, biodegradability, less toxicity, lower CO<sub>2</sub> and CO emission, greater ability to blend with other

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energy sources, and renewability [9,10]. Furthermore, among renewable fuels, BD has one of the highest energy returns [11]. It delivers around 90% more energy than the energy invested in its production, whereas ethanol only provides about 25% net energy [12]. BD is produced by transesterification of vegetable oil using a heterogeneous catalyst [13]. However, homogeneous catalysts have excellent catalytic activity in the synthesis of BD [14]. Separating these catalysts from BD, however, necessitates washing with water, which results in the loss of fatty acid alkyl esters, increased energy consumption, and enormous amounts of waste water [15]. Moreover, these catalysts cause reactor corrosion and are difficult to recover, thus increasing the overall BD production cost [16]. Various heterogeneous catalysts for BD generation, such as zeolite, CaO@La<sub>2</sub>O<sub>3</sub>, lipase/GO-Fe<sub>3</sub>O<sub>4</sub>, Cu/ZnO, WO<sub>3</sub>-ZrO<sub>2</sub>, and SO<sub>4</sub><sup>2-</sup>ZrO<sub>2</sub>, alkali earth metal oxides, KF/YAl<sub>2</sub>O<sub>3</sub>, and sodium aluminate were developed [17,18]. However, only selective heterogeneous catalysts like CaO was utilized in the BD production which is due to the expensive raw material for catalysts synthesis, lower reusability, environmental pollution of the catalysts synthesis process, lower thermal stability, and higher toxicity [19,20]. Heterogeneous catalysts make the BD synthesis process easier since they might be reused multiple times without losing catalytic activity, making the process more cost-effective [21,22]. The wise use of waste material as a heterogeneous catalyst can minimize overall BD production costs. Because of its abundance in nature, low cost, and high level of activity, CaO is a common type of heterogeneous catalyst for BD production [23,24].

Calcium oxide (CaO) is one such heterogeneous catalyst that can be obtained from river snail shells [20]. Calcium oxide can be synthesized from river snail shells by calcination at 700–900 °C for 4 h, and its subsequent use as a catalyst for biodiesel production [25,26]. Snail shells (SS) are rich in CaO and contain about 97.14%. Also, it includes SiO<sub>2</sub> (0.628%), SrO (0.457%), Fe<sub>2</sub>O<sub>3</sub> (0.409%), etc. [20]. The other main difficulty in the BD sector is feedstock, since producing biodiesel from edible vegetable oils is not cost-effective and causes food shortages. Since the production of biodiesel from non-edible raw materials is a topic under intense research, studies on other sources of triglycerides that do not compete with the food business must be created [15]. Non-edible vegetable oil, animal fat, and WCO are promising feedstocks for BD production [27,28]. Production BD from WCO's is also environmentally friendly because it recycles used cooking oil and provides clean, renewable energy that might help partially replace imports of petrochemical oil [29,30]. Economic, environmental, and waste management strategies are the main reasons for using WCO for BD production [27,29]. Moreover, the production of BD from WCO will not only avoid the competition for the same oil resources for food and fuel but also solve the problems associated with its disposal [31,32]. Lack of inexpensive feedstock and poor catalysts for the transesterification processes are the main complaints about the BD industry. Currently, much of the BD production is concentrated on edible vegetable oil, which is inefficient and causes a food crisis. Since the majority of the catalysts used today are expensive, scarce, toxic, and ineffective for BD conversion, a stable and affordable catalyst is required. The main goal of this study is to eliminate the discrepancy caused by the shortage of affordable feedstock for BD production and minimize the use of non-renewable fossil fuels. Moreover, the study focused on the preparation of heterogeneous catalysts from waste material (SS) for the production of BD. The BD production from WCO is one of the major ways of recycling the oil, retarding the environmental pollution associated with its disposal, and decreasing emissions of greenhouse gas from fossil fuels that cause global warming. The heterogeneous catalyst driven from SS showed extraordinary potential to substitute the toxic, expensive, and non-recyclable chemical catalyst. Therefore, the aim of this study was to introduce more reactive, economical, efficient, thermally stable, and non-toxic heterogeneous catalysts from biomass for the transesterification of WCO. Additionally, it is important to explore for less expensive feedstock, such as WCO, as an alternative renewable energy source (BD) and to eventually replace petrochemical diesels.

## 2. Experimental section

### 2.1. Study area and sample collection

Waste cooking oil (WCO) and snail shell (SS) were collected from hotel and around the Sore River, respectively, in the Ilubabara Zone of South-Western, Ethiopia. All the experimental activities were conducted in the department of Chemistry, College of Natural and Computational Sciences at Mattu University.

### 2.2. Chemicals and instruments

The chemicals such as zinc acetate, sodium hydroxide, titanium isopropoxide, isopropyl alcohol, were products of BDH, CDH (India), and Fisher (UK). All the solvents, including ethanol (99%), chloroform (99%), and methanol (99.99%), were from Blulax, India. Glacial acetic acid, potassium iodide, sodium bisulphate, hydrochloric acid (98%), ammonium chloride, ammonium hydroxide, Hanus solution, ferric chloride, sodium thioselphate, and potassium hydroxide were all from Sigma Aldrich UK. The chemicals and reagents used for this study were all of analytical grade. The functional group identification of WCO and BD were recorded using Infrared, Spectrum FTIR (PerkinElmer) spectroscopy. The crystal structure of the synthesized catalyst materials were investigated using X-ray diffraction (Drawell XRD-700, UK) at Jimma University, Jimma, south western Ethiopia.

### 2.3. Catalyst preparation

The collected SS were washed with distilled water, dried in an oven at 120 °C for 10 h. A 35 g of the dried SS were powdered using an electrical grinder [33]. The powder material (20 g) was calcined at 400–1000 °C for 1–6 h. The resulting CaO catalyst (13.5 g) was kept in an airtight container for further use.

#### 2.4. Preparation of ZnO

2 g of zinc acetate dihydrate and 8 g of sodium hydroxide were dissolved in 15 mL and 10 mL of distilled water, respectively. Each solution was stirred for 5 min at a steady speed. After thoroughly mixing, the sodium hydroxide solution was mixed with the zinc acetate solution and stirred continuously for 5 min with a magnetic stirrer. The solution, which contained sodium hydroxide solution as well as zinc acetate, was then dropped wise using a burette filled with 100 mL ethanol. The resultant solution was then dropwise added with ethanol via a 100 mL burette, until a white precipitate was generated [34].

#### 2.5. Preparation of TiO<sub>2</sub>

Titanium oxide nanoparticles were synthesized via the sol-gel method using titanium isopropoxide, de-ionized water, and isopropyl alcohol as starting materials. About 15 mL of titanium isopropoxide, 100 mL of isopropyl alcohol were mixed and the solution was agitated for 10 min. Then, 10 mL of deionized water was added to the mixed solution drop by drop. The entire solution was then agitated continuously for 2 h. The gel was dried in a hot-air oven at 60 °C before being calcined at 400 °C for 3 h [35].

#### 2.6. Preparation of catalyst

A wet impregnation approach with a slight modification was carried out to synthesize a catalyst [3,33]. The CaO from the SS was separately mixed with ZnO and TiO<sub>2</sub> in a mass ratio of 1:1 in a separate flask. The mixtures were immersed in distilled water (10 mL). Then, the solution was stirred continuously for 3 h at room temperature, and the product was dried for 24 h at 80 °C. The dried powder was calcined for 1–6 h at 400–1000 °C, and the resulting samples were denoted as CaO/TiO<sub>2</sub> and CaO/ZnO. The calcination procedure and conditions were adopted from Mersi S et al. [36] with slight modification.

#### 2.7. Transesterification reaction

The transesterification process was conducted according to the method reported by Khan H et al., 2020 [37], with minor modifications. In a 250 mL two-necked flat-bottom flask equipped with a reflux condenser, 20 g of the purified WCO was added, then stirred at 600 rpm for all test runs. To evaporate water and other volatile contaminants, the oil was pre-heated at 105 °C for 5 min in a heating mantle. The set-range of methanol-to-oil ratio (3:1–12:1), temperature (60–85 °C), catalyst load (1–108 6% wt.), and reaction time (1–6 h) were all evaluated in the experiment for optimization. The used catalyst, after centrifugation, was regenerated by treatment with methanol. To reuse or regenerate the catalyst, it was treated with methanol after centrifugation. The filtrate mixture was then placed in a separating funnel for 10 min for layer separation. The biodiesel make up the top layer and glycerol were found in the lower layer [28]. Then, the mixture was separated using a separatory funnel, and the surplus methanol was removed by distillation. After continuous stirring the water was left to settle for 48 h. At this point, the process was complete, and the clear crystal product (biodiesel) was obtained. The resulting biodiesel were stored in desiccator for further analysis and resulting yield was calculated using the following equation.

#### 2.8. Characterization of the synthesized catalyst and biodiesel

The physicochemical characteristics of WCO and BD, such as acid value (AV), refractive index (RI), iodine value (IV), saponification value (SV), density, free fatty acid (FFA), moisture content, and pH, were analyzed following the AOAC official method (969.17) [38]. The density, flash point, pour point, cetane number, and cloud point measurements of the ethyl esters produced were subjected to ASTM D-6751 fuel characterization standards [39]. The XRD analysis of the catalyst and FTIR analysis of the BD were conducted at Jimma University, Institute of Technology, Department of Material Sciences and Engineering.

#### Ethical approval

Whether the study was conducted using experimental animals in compliance with the code of ethics or not, ethical approval is required. However, for this investigation, the SS was not removed directly from the snail. However, the snail had previously removed its shell, which had accumulated at the sampling site.

#### 2.9. Statistical analysis

The physicochemical properties of oil and BD were recorded in triplicate and expressed as a mean ± standard deviation. Then the obtained data were entered into an Excel sheet, and the graphical data were drawn using Origin software version 8.

### 3. Result and discussion

#### 3.1. Physicochemical characteristics of WCO

The physicochemical characteristics such as moisture content, pH, density, conductivity, RI, AV, FFA, SV, IV, and PV were

evaluated using the AOAC official standard method (Table 1). The oxidative breakdown of oil is accelerated by repeated heating of the oil, creating reactive oxygen species and decreasing the frying oil's natural antioxidant content [40]. WCO had a higher moisture content, densities, RI, AV, FFA, SV, IV, and PV than purified waste cooking oil (PWCO), but a lower pH. The frying process alters the physicochemical properties of oil, indicating that it has been degraded [41,42]. The low moisture content in PWCO samples revealed that they can improve the storability and suitability [43]. The RI of PWCO ( $1.33 \pm 0.33$ ) is lower than both WCO ( $1.45 \pm 0.12$ ) and un-fried palm oil, which indicates the oxidation of unsaturated bonds during cooking [44]. The AV, SV, PV, FFA (%), and IV of WCO were greater than those of PWCO. The greater AV ( $9.41 \pm 0.19$  mg KOH/g) in WCO was an indication of the oil's being highly degraded due to excessive heating during food cooking [26], but in PWCO the AV was comparable with normal palm oil. The increase in AV and FFA in WCO may be attributed to the formation of monomeric acids with lower molecular weight [45,46]. The AV of WCO was ( $9.41 \pm 0.19$  mg KOH/g) and PWCO was ( $5.61 \pm 0.56$  mg KOH/g), but both WCO and PWCO oil had greater AV than the reported AOAC and Malaysian crude palm oil standard (CPOMS) [38,47]. Similarly, the FFA content of WCO was higher than PWCO and AOAC standard. This indicates that the glycerides in it are degrading, which causes rancidity [36]. The SV indicates the molecular weight of the fatty acid in the oil [48]. The results of this study also showed that WCO ( $208.18 \pm 0.40$  mg KOH/g) had a greater SV than the PWCO ( $190.6 \pm 0.81$  mg KOH/g), but both WCO and PWCO oil were in good agreement with the reported AOAC standard [38]. The IV of WCO ( $76.14 \pm 0.34$ ) was greater than the PWCO ( $65.53 \pm 0.00$  g I<sub>2</sub>/100 g), but both are lower than unfried palm oil and the AOAC standard. The IV of unsaturated fatty acids is increased, the effect of polymerization is enhanced [49]. The PV test is the most extensively used method for evaluating oil oxidation. The PV of WCO ( $11.30 \pm 0.22$  meq O<sub>2</sub>/kg) was higher than that of PWCO ( $8.00 \pm 0.01$  meq O<sub>2</sub>/kg). However, both the WCO and PWCO are in good agreement with the AOAC standard. Furthermore, a rise in PV shows the rancidity or degree of oxidation of the fat or oxidative oil, not its stability [50].

### 3.2. XRD diffraction of the synthesized catalysts

The XRD pattern of the calcined SS and the normal CaO are almost similar in 2 theta value (Fig. 1). The intensity peaks of the two CaO catalysts were determined at temperatures of 900 °C at 2 theta values of 26.3°, 28.13°, 33.5°, 37.3°, 47.1°, and 53.8°. The result matched the reported data for CaO (JCPDS file no. 48–1467) [25,51], confirming the formation of CaO. The intense and sharp peak of the calcined SS revealed the crystalline nature of the catalyst [52]. The findings strongly support the previous study report [53]. The powder XRD patterns of ZnO show intensified and narrowed peaks at 2θ angle of 31.6°, 34.52°, 37.3°, 47.31°, 66.21°, and 67.6°. When ZnO was impregnated with CaO, some shift in the peak at 2 theta was observed. This indicates that the formation of CaO/ZnO and the peak of CaO 2θ at 26.3° shifted to 37.3°. This might be due to the effect of ZnO on the structure and formation of CaO/ZnO [54]. As shown in Fig. 2, the diffraction peaks at 2θ = 25.64°, 38.26°, 48.40°, 63.00°, 69.26°, and 75.16°, respectively, are crystal planes of anatase TiO<sub>2</sub>, while the peaks located at 2θ = 27.74°, 36.42°, 41.58°, 44.40°, 54.64°, 56.56°, 63.09°, 69.26°, and 69.83° are diffraction peaks of rutile TiO<sub>2</sub>. The results agree with the JCPDS card no-211,272 (anatase TiO<sub>2</sub>) and the XRD pattern of TiO<sub>2</sub> nanoparticles in other literature [55]. TiO<sub>2</sub> in the anatase phase showed a strong diffraction peaks at 27.74° [56]. Addition of TiO<sub>2</sub> to CaO were improved the catalytic property by increasing the surface area and strength of basic sites, hence increased the catalytic performance of CaO–TiO<sub>2</sub> [57]. The intensity of the XRD peaks in the sample indicates that the formed nanoparticles are crystalline. When the calcined SS (CaO) mixed with TiO<sub>2</sub>, the XRD patterns changed [58]. The XRD results of the catalyst indicated that the introduction of alkaline earth metal influenced the crystal structure of BiVO<sub>4</sub> and lead to the formation of a mixed crystal phase structure [59]. Additional peaks were observed, indicating that the TiO<sub>2</sub> affected the crystalline structure of CaO from the SS and showed the formation of CaO/TiO<sub>2</sub>.

### 3.3. Optimization of the synthesized biodiesel

#### 3.3.1. Effect of calcination temperature

The effect of calcination temperature on BD yield is depicted in Fig. 2. Calcination was carried out at several temperatures, from 400 to 1000 °C, to activate the catalyst. CaO/TiO<sub>2</sub> catalysts converted more BD (95%) at 500 and 600 °C calcination temperatures, while CaO and CaO/ZnO catalysts converted 80 and 90% at 900 and 500 °C calcination temperatures, respectively (Fig. 2). With increasing calcination temperatures, the percentage yield of BD on the CaO catalyst increases. This could be because it enhances the

**Table 1**  
Physicochemical properties of waste cooking and purified waste cooking oil.

Physicochemical	Normal Palm oil	WCO	PWCO	AOAC and CPOMS [38,47]
Moisture (%)	0.20 ± 0.23	0.90 ± 1.02	0.30 ± 0.55	≤0.3
pH at 25 °C	6.50 ± 0.04	4.70 ± 0.09	6.0 ± 0.31	5–7
Density (g/cm <sup>3</sup> ) 25 °C	0.72 ± 0.12	0.80 ± 0.06	0.49 ± 0.54	0.840
RI (at 25 °C (nD))	1.46 ± 0.93	1.45 ± 0.12	1.33 ± 0.33	1.469
Acid value (mg KOH/g)	4.01 ± 0.80	9.41 ± 0.19	5.61 ± 0.56	≤5.00
% FFA (mg KOH/g)	1.50 ± 1.03	5.27 ± 0.75	3.05 ± 0.40	≤1.304
Saponification value (mg KOH/g)	190.10 ± 0.53	208.18 ± 0.40	190.6 ± 0.81	≥180
Iodine value (g I <sub>2</sub> /100 g)	90.02 ± 0.23	76.14 ± 0.34	65.53 ± 0.00	80–100
Peroxide value (meq O <sub>2</sub> /kg)	10.04 ± 0.17	11.30 ± 0.22	8.00 ± 0.01	2–10

Key: WCO = waste cooking oil, PWCO = purified waste cooking oil.

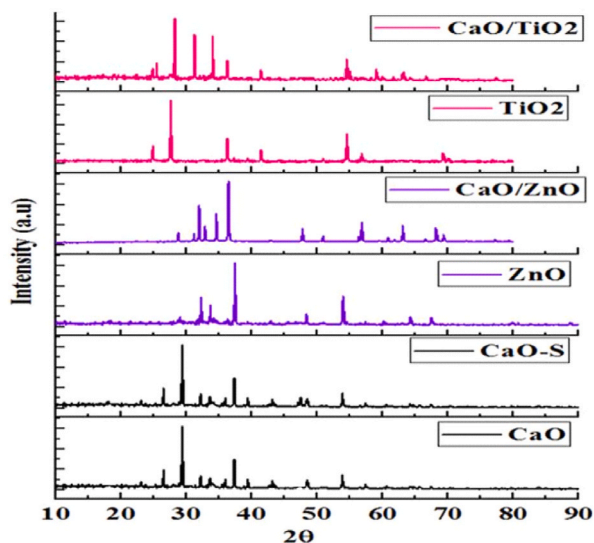


Fig. 1. XRD diffraction of the synthesized catalysts.

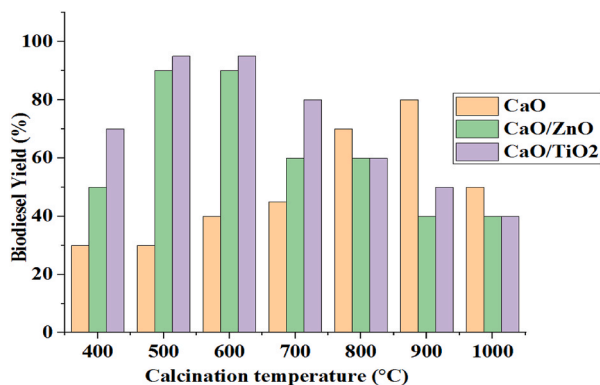


Fig. 2. Effect of calcination temperature on biodiesel yield recorded under optimized condition: 6:1 methanol to oil ratio, 3%wt. Catalyst load, 3 h and a temperature of 65 °C.

surface area of the catalyst, stimulates the creation of active basic sites, and facilitates the reaction of methoxide during the transesterification process. During the transesterification reaction, the presence of active basic sites at their optimal strength on the catalyst surface creates the highly reactive methoxide species [20,57]. However, increasing the calcination temperature of the catalyst from 400 to 600 °C increases the BD yield, while simultaneously decreased after 600 °C. This might be due to the enhancement of the catalyst surface area, which leads to a decrease in the catalytic activity. This study is in line with the previous report from Sinaga M et al. and Mohamed M et al. [36,57], which showed catalyst calcination above 600 °C verifies the surface of the catalyst, makes the particle larger, forms a smooth surface, and decreases the catalyst activity. The CaO nano-catalyst had the highest biodiesel conversion (98.2%). The optimal conditions for such a high conversion yield were a methanol to oil ratio of 1:8, a reaction temperature of 65 °C, a reaction time of 76 min, and a catalyst loading of 4 wt% [60]. The variation in BD percentage yield could be attributed to WCO's transesterification condition (microwave-assisted transesterification).

In addition to that, high calcination temperatures lead to a decline in alkali ion concentration [18]. The lower BD amount observed on the synthesized catalyst at a lower calcination temperature (400 °C) is possible due to the excessively porous nature of the catalyst surface. According to the findings of this study, the calcination temperature should be optimized in order to obtain an effective catalyst for the transesterification reaction, and CaO/TiO<sub>2</sub> may have optimal active site strength at 500 and 600 °C, allowing for effective conversion of BD from WCO. Similar study reported from Mardhiah M et al. [24], stated that 76.67% of the oil was successfully converted into BD using an 800 °C calcined CaO–TiO<sub>2</sub> catalyst. It was discovered that the calcination temperature of the catalyst and the amount of catalyst had a significant effect on the conversion of oil. The difference on the BD production might be due to the oil type and catalyst source.

### 3.3.2. Effect of reaction time (h) on biodiesel yield

The effect of reaction time on BD yield is shown in Fig. 3. In this study, the effect of reaction time on BD yield was investigated from 1 to 5 h and the results revealed that increasing the reaction time increased BD yield. However, this is only true for the first 3 h and decreases after that for all synthesized catalysts. This may be due to the deterioration and hydrolysis of biodiesel starting to occur, further increasing the reaction time. The reversible reaction may occur after reaching equilibrium, lowering the yield and increasing the probability of saponification rather than esterification [57]. A 95% conversion from CaO/TiO<sub>2</sub> was recorded in 3 h reaction time, but the maximum conversion of oil to BD from CaO and CaO/ZnO catalysts was 90% and 80%, respectively. In a nutshell, optimum BD yield was obtained with reaction parameters such as a methanol to oil ratio of 6:1, catalyst loading of 3 wt%, and a reaction time of 3 h.

### 3.3.3. Effect of temperature on biodiesel yield

Fig. 4 depicts a gradual increase in conversion with an optimized time of 3 h at various temperatures, a catalyst amount of 3% wt., and a methanol to oil ratio of 6:1. To increase the BD yield, raise the temperature to 55–65 °C. However, the percentage conversion was reduced after 65 °C. This might be due to the evaporation of methanol from the reservoir rather than it reacting with the oil. A similar study reported from Birla et al., 2012 [18] and stated that when the reaction was above the boiling point of methanol, the solvent vaporized and remained in the vapor phase in the reactor, causing a reduction in BD yield. The study revealed that an appropriate temperature is required to synthesize BD and maximum conversion of oil to BD (95%, 90%, and 80%, respectively) was recorded in the 3% wt. Of CaO/TiO<sub>2</sub>, CaO/ZnO, and CaO at the boiling point of the methanol (65 °C, respectively).

### 3.3.4. Effect of methanol to oil on biodiesel yield

One of the major factors influencing BD yield is the methanol-to-oil ratio. For effective conversion of oil to BD, 3 mol of methanol are required for 1 mol of glyceride [61]. Various methanol-to-oil ratios were tested in this study to determine the best molar ratio for converting oil to BD. The amount of methanol must be increased to maintain equilibrium in the forward reaction. As a result, under optimal conditions of temperature (65 °C), catalyst loading (3% wt.), reaction time (3 h), and 6:1 methanol to oil ratio produced the highest BD yield (Fig. 5). This study is consistent with the previous report from Laskar et al., 2018 [20], stated that, under optimized conditions, a 6:1 methanol to oil ratio was suitable for BD synthesis. Increase the methanol amount does not increase the BD yield it will reduce the product and dissolve the glycerol, which would reverse the reaction.

### 3.3.5. Effect of catalyst load on biodiesel yield

The catalyst amount for BD synthesis was investigated under optimized conditions of 65 °C, 3 h reaction time, and a methanol to oil ratio of 6:1. Fig. 6 shows an increase in the amount of catalyst, increasing the BD yield up to 3% wt., and then a constant decrease. The maximum conversion was recorded at 3% wt. In all the synthesized catalysts. In a similar study reported by Birla et al., 2012 [18], the reduced conversion of oil to BD with excess catalyst may be attributed to an increase in the viscosity of the reaction mixture. Increase the catalyst concentration does not increase the BD yield however, it did raise the production costs of the catalyst, make the separation process more complicated after the BD conversion and decrease the BD purity. Another similar study report from Gupta J et al., 2019 [33], suggests that with an increase in catalyst amount, the reaction mixture may become more viscous, which resists and, hence, results in a decline in BD yield. Compared to CaO modified with ZnO lower catalytic activity and BD conversion compared to CaO modified with ZnO. The activity of CaO/TiO<sub>2</sub> catalyst was due to the photocatalytic properties, higher crystallinity, and average pore size of TiO<sub>2</sub> enhanced the BD yield. A thorough analysis of the catalyst revealed that the substitution of Ti and Ca ions in the calcium lattice caused by the addition of TiO<sub>2</sub> to CaO increased the catalytic activity [57]. However, further advanced instrumental analysis were required to analyses the pore size, the surface morphology, and crystallinity of the synthesized catalyst.

### 3.3.6. Effect of catalyst reusability on biodiesel yield

The ability to reuse catalyst not only reduces costs but also makes the complex separation process more stable, efficient, and recyclable. A catalyst was necessary for BD synthesis. From an economic point of view, more reusable catalyst is required, particularly

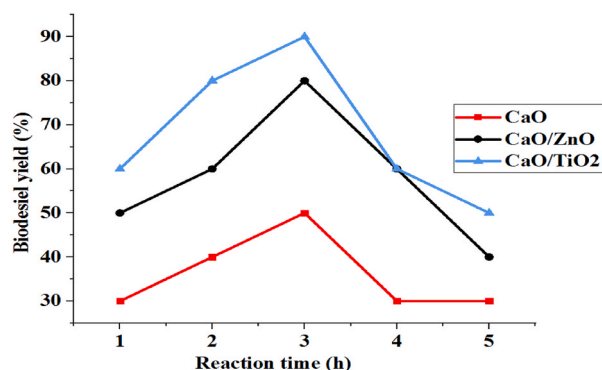


Fig. 3. Effect of reaction time (h) on biodiesel yield with 6:1 methanol to oil ratio, 3%wt. Catalyst load at 65 °C.

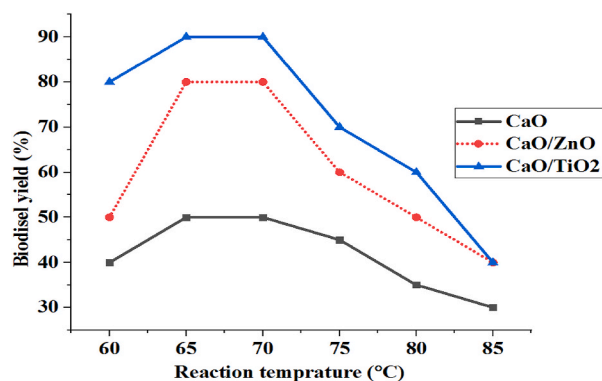


Fig. 4. Effect of reaction temperature on biodiesel yield with 3 h reaction time, 3%wt. Catalyst load and methanol to oil ratio of 6:1.

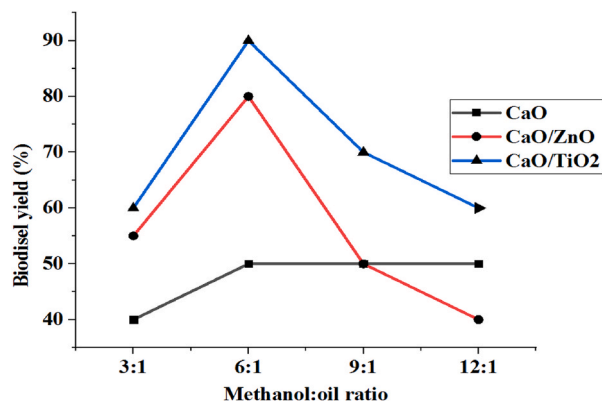


Fig. 5. Effect of methanol to oil on biodiesel yield with 3 h reaction time and 3%wt. Catalyst load at 65 °C.

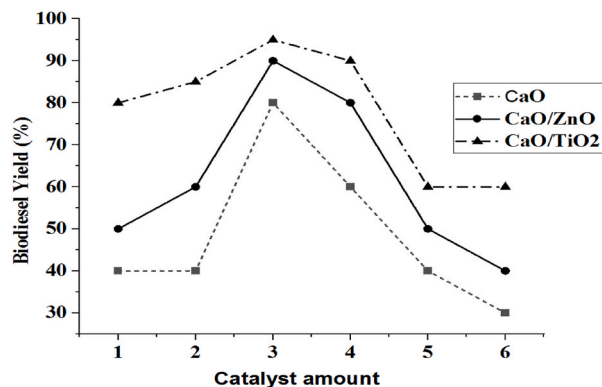


Fig. 6. Effect of catalyst load on biodiesel yield with 6:1 methanol/oil for 3 h at 65 °C.

for industrial applications. To evaluate the reusability, the solid catalyst was separated through filtration followed by centrifugation. The catalyst's reusability was tested under optimized conditions of temperature (65 °C), reaction time (3 h), catalyst load (3% wt.), and methanol to oil ratio (6:1) (Fig. 7). In this study, the catalyst was reused five times to evaluate the effectiveness, lifetime, and stability of the synthesized catalyst. All the synthesized catalysts decrease their synthesizing efficiency from the first cycle to the fifth cycle. However, the CaO/TiO<sub>2</sub> catalyst remains the same up to three cycles (i.e., 95% BD conversion). CaO/ZnO catalysts convert oil to BD with 90%, 90%, 50%, and 40% efficiency from the first to fifth cycles, respectively. The CaO catalyst from SS converts 80% of oil to BD in the first run and then decreases when the reusability of the catalyst increases. Therefore, the CaO/TiO<sub>2</sub> catalyst was more economical to synthesize BD due to its high stability, lifetime, and effective conversion ability of oil to BD. The study also compared with various literature reports in Table 4.

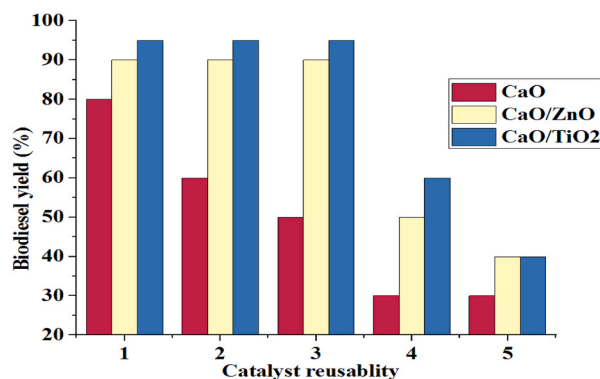


Fig. 7. Effect of catalyst reusability on biodiesel yield with 3%wt catalyst load, methanol: oil of 6:1 for 3 h at 65 °C.

### 3.3.7. Effect of calcination time

The effect of calcination time on BD yield was evaluated at optimized conditions of reaction time of 3 h, methanol to oil ratio of 6:1, 3% wt. Catalyst load, and temperature of 65 °C (Table 2). The maximum Bd (80%) was obtained after 3 h of operation with the SS driver CaO catalyst. However, the SS modified with ZnO and TiO<sub>2</sub> exceeded the yield of BD by 90% and 95%, respectively, at 3 h. The study results reveal that increasing the calcination time on the catalyst does not increase the BD yield. This indicated that an appropriate calcination time should be required to obtain a greater BD yield. All synthesized catalysts remain constant for 3–4 h and then decrease, particularly the CaO from SS modified with ZnO and TiO<sub>2</sub> catalysts. The study result is also compared with various study reports [17,62,63], and it is more economical, efficient, cost-effective, and time-saving (Table 2).

### 3.4. Physicochemical properties of biodiesel

To evaluate the quality of the synthesized BD, some physicochemical properties, such as moisture content, RI, density, AV, PV, SV, CN, cloud point, pour point, flash point, and IV, were measured (Table 3). The moisture content of the obtained BD was lower than the ASTM standard, which indicates the quality of as synthesized BD. High moisture content in BD causes a number of issues, including water accumulation and the growth of microorganisms during transportation and storage [64]. This was formed might be due to the improper treatment of the BD after preparation. The RI is a major optimized parameter that is related to molecular weight, fatty acid chain length, unsaturation, and conjugation [65]. This is formed due to the improper treatment of the BD after processing. The RI of BD from WCO was  $1.46 \pm 0.01$ , which is comparable with the ASTM D-6751 standard. These results are in good agreement with Khanam T et al., 2021 [66] and reported that pure BD possesses an RI in the range of 1.45. Because injection systems, pumps, and injectors must deliver a precise amount of fuel to ensure effective combustion, density is a crucial fuel attributes [67]. To ensure optimal air-to-fuel ratios during complete combustion, the density values must be kept within acceptable norms. With high-density BD or its combination, incomplete combustion and particulate matter emissions are possible [68]. In these studies, the density of BD was  $0.88 \pm 1.03 \text{ g/cm}^3$ , which is in the range of ASTM fuel characterization ( $0.82\text{--}0.90 \text{ g/cm}^3$ ) [69]. The AV of BD can play an important role in identifying the formation of FFA [70]. An increase in the acid value indicates enhancement of the fatty acid, which breaks down into shorter-chain acids. The AV of BD was shown in Table 3, and the obtained BD was 0.62 mg KOH/g, which is consistent with the ASTM standard. The highest amount of AV reported was 0.8 mg KOH/g [71]. The lower AV in the BD indicates the purity of BD and the formation of FAME in a greater amount. A higher AV in the fuel supply system and the internal combustion engine might cause severe corrosion [7,72]. The degree of unsaturation in oils and BD was indicated by the iodine value. IV is an important parameter for studying the chemical stability and rancidity of BD. IVs are useful for determining the overall degree of saturation of the oil, which is important for viscosity and cloud points. The lower the IV, the better the fuel will be as BD.

The IV of BD from WCO was  $60.00 \pm 0.30 \text{ g I}_2/100 \text{ g}$  which is within the range of ASTM standards ( $80\text{--}106 \text{ g I}_2/100 \text{ g}$ ). This study, in contrast with the previous report, which stated that the IV was  $104 \text{ g I}_2/100 \text{ g}$  in the oils. The disagreement may be due to the oil type

Table 2

Effect of calcination time on biodiesel yield with methanol: oil of 6:1, reaction time of 3 h, catalyst load (3%wt.), and temperature at 65 °C.

Calcination time(h)	Biodiesel yield (%)		
	SS-CaO (900 °C)	CaO/ZnO (500 °C)	CaO/TiO <sub>2</sub> (500 °C)
1	40	60	80
2	40	70	80
3	80	90	95
4	80	90	95
5	80	70	80
6	50	60	60

Key: SS: snail shell.



**Table 3**

Physicochemical properties of biodiesel with methanol: oil of 6:1, reaction time of 3 h, catalyst load (3%wt.), and temperature at 65 °C.

Physicochemical properties	Result (Mean ± SD)	Standard [ASTM D6751]
Moisture (%)	0.03 ± 0.50	0.050
RI (at 25 °C nD)	1.46 ± 0.01	1.45
pH	5.40 ± 0.21	6.99
Density (g/cm <sup>3</sup> at 25 °C)	0.88 ± 1.03	0.82–0.90
Cloud point (°C)	1.10 ± 0.40	-3–12
Pour point (°C)	2.10 ± 1.09	-5–10
Flash point (°C)	160.00 ± 2.01	130
Acid value (mg KOH/g)	0.62 ± 0.23	≤0.8
%FFA (mg KOH/g)	0.30 ± 0.56	2.5
Iodine value (g I <sub>2</sub> /100 g)	60.00 ± 0.30	80–106
Saponification value (mg KOH/g)	162.35 ± 0.47	150.1
PV (meq O <sub>2</sub> /kg)	3.00 ± 0.59	8
Cetane number	89.06 ± 1.70	≥50

**Key:** BPWCO = Biodiesel from purified waste cooking oil, PV = peroxide value.

**Table 4**

Comparison of various solid catalysts for transesterification reaction.

Optimization condition						
Catalyst	MEOH: Oil	Temp. (°C)	Catalyst (%wt.)	Time (h)	Conversion (%)	Reff.
CaO from egg shell	6:1	65	4	3	75.85	[81]
KOH load SS	9:1	65	6	3.5	96	[33]
KF/CaO	8:1	65	5	2	95	[3]
Pyrolyzed rice husk	20:1	110	5	3	98.17	[82]
Li loaded egg shell	10:1		5	4	94	[83]
TiO <sub>2</sub> -ZnO	6:1	60	0.02	5	92.2	[62]
Scallop shell	6:1	65	5	–	86	[84]
KBr loaded eggshell	12:1	65	3	–	82.48	[63]
CaO/dolomite	6:1	65	5	3	90	[85]
CaO/Al <sub>2</sub> O <sub>3</sub>	12:1	65	4	5	98.6	[86]
CaO/Fe <sub>3</sub> O <sub>4</sub>	15:1	65	1.3	2	95	[87]
CaO/mesoporous	16:1	60	5	8	95.2	[88]
Biochar -CaO/Al <sub>2</sub> O <sub>3</sub>	18:1	65	3	3.25	98.3	[89]
KI loaded oyster shell	6:1	60	3.5		85	[16]
CaO from SS	6:1	65	3	3	80	R
TiO <sub>2</sub> loaded Shell	6:1	65	3	3	95	R
ZnO loaded Shell	6:1	65	3	3	90	R

**Key:** MEOH; Methanol, R; Current work result.

and the amount of catalyst utilized during the study [73]. Oils with IVs greater than 125 are classified as drying oils, those with IVs less than 110 are classified as nondrying oils, and those with IVs between 110 and 140 are classified as semidrying oils [70]. Based on this evidence, the obtained BD was synthesized from non-drying oil and was in good agreement with the standard fuel characterization. The SV of BD from WCO was shown in Table 3. SV indicates the average molecular weight of triglycerides in the oil and is expressed in milligrams of potassium hydroxide per g of oil. The lower the SV, the larger the molecular weight of fatty acids in the glycerides [44]. The SV of the obtained BD from WCO was 162.35 ± 0.47 mg KOH/g, which is higher than ASTM fuel characterization but lower than the previous report from H. Ibrahim [74], which reported that BD from sweet orange seed oil has a SV of 292 mg KOH/g. The disagreement may be due to the oil type, material, and amount of catalyst used. The amount of PV of fats indicates the primary oxidation and rancidity in oil. The PV increased with increasing moisture content [75,76]. The PV determination measures the presence of oxidative moieties (i.e., the portion of a molecule bearing characteristic oxidative properties) in a sample. Hydroperoxides, which are generated when oxygen from the air combines with fatty esters, are the most common oxidative moiety identified in BD. This is frequently the initial step in BD oxidative breakdown cycle. The PV of the obtained BD was lower (3 meq O<sub>2</sub>/kg) than the ASTM-D6751 Standard, which is 8. The low PV and AV were good for BD. As it tends to be seen that the cetane number of BD obtained is 89.06 ± 1.70, which is more than the minimum limits provided by ASTM and EN standards. BD from vegetable oils with high amounts of saturates (which means low IVs) will have a higher cetane number (CN), while BD from vegetable oils with high amounts of unsaturated (high IVs) will have a lower CN [70]. Unsaturation in the fatty acid chain is the most significant cause of lower CNs. The cetane number is a critical quantity to determine for assessing ignition delay because it is directly related to the engine igniting [77]. It depends on the product's makeup; for example, BD with more saturated ingredients has a higher cetane number, allowing for a faster ignition time. In general, the efficacy of the BD prepared from WCO was comparable to that of ASTM standards and previously reported literature [78].

### 3.5. FTIR characterization of waste cooking oil and biodiesel

In the FTIR characterization of WCO and BD were depicted in Fig. 8. The FTIR spectra of WCO showed a broad peak in the region at 3500–3300  $\text{cm}^{-1}$  assigned for the  $\text{OH}$  stretching of fatty acid which was formed during repetitive frying. The small, intense bands in the region of 2950  $\text{cm}^{-1}$  are assigned to  $\text{sp}^3$  carbon stretching of the terminal methyl group. The peak at 2800  $\text{cm}^{-1}$  is assigned for  $\text{CH}_2$  stretching. The medium peak at 1650  $\text{cm}^{-1}$  indicates carbonyl stretching ( $\text{C}=\text{O}$ ) and the strong, intense peak at 1100  $\text{cm}^{-1}$  is attributed to  $\text{C}-\text{O}$  ( $\text{CH}_3\text{O}^-$ ) stretching. The medium peak at 1470  $\text{cm}^{-1}$  indicates  $\text{CH}$  bending of  $\text{sp}^3$  carbon (alkane) [79,80]. The FTIR spectra of BD showed intense bands in the region of 2950–3000  $\text{cm}^{-1}$  was assigned to  $\text{sp}^3$  carbon stretching for the terminal methyl group of FFA chain. The medium peak at 2800  $\text{cm}^{-1}$  was assigned for aliphatic  $\text{CH}_2$  stretching. The medium peak at 16,001,700  $\text{cm}^{-1}$  was assigned to carbonyl stretching of the ester functional group ( $\text{C}=\text{O}$ ). The strong, intense peaks at 980–1100  $\text{cm}^{-1}$  indicate  $\text{C}-\text{O}$  ( $\text{CH}_3\text{O}^-$ ) stretching of the ester. The medium peaks at 1480  $\text{cm}^{-1}$  indicate  $\text{CH}$  bending of  $\text{sp}^3$  carbon (alkane) [80]. In general the BD was synthesized from wco as revealed from the FTIR spectral data.

### 3.6. Effect of catalyst reusability vs. weight loss

The effect of repetitive use of catalyst on weight loss was also investigated at optimization conditions of calcination time (3 h), catalyst load (3% wt.), and calcination temperature (500  $^\circ\text{C}$  for  $\text{CaO}/\text{TiO}_2$  and  $\text{CaO}/\text{ZnO}$  and 800  $^\circ\text{C}$  for  $\text{CaO}$  catalysts (Fig. 9). The result of this study demonstrated that increasing the catalyst's reusability decreased the weight of all the synthesized catalysts. However,  $\text{CaO}$  from the SS decreases slightly from the first cycle to the second (3–2.8% wt.).

The  $\text{CaO}$  catalyst mixed with  $\text{TiO}_2$  and  $\text{ZnO}$  decreases the catalyst amount from 3 to 2 and 2.5, respectively. The weight losses in the catalyst were observed due to inappropriately separation of the catalyst during centrifugation (filtration) or some amount of catalyst dissolved in the BD and glycerol. Generally, in order to produce BD from WCO using those as synthesized catalysts, a greater amount is required, particularly for industrial applications.

## 4. Conclusion

The potential to produce BD from waste cooking oil was economical and reduced environmental pollution associated with petroleum-based diesel. Apart from BD production, these environmentally friendly waste-derived heterogeneous catalysts have the potential to be effective catalysts in a variety of chemical transformations. The study shows that a waste material can be converted into a valuable product while using minimal energy during the transesterification reaction. The result of the physiochemical properties demonstrates that the oil is adequate for BD production, and the BD properties meet the majority of the ASTM standards. Thus, the BD prepared from WCO was used as a potential alternative for petroleum fuel. Moreover, the waste snail shell contains a high percentage of  $\text{CaO}$  when it is calcined, which can be used as a substitute catalyst for BD production. In comparison to other methods of catalyst preparation the heterogeneous catalyst formulation from snail shells is less expensive. The results obtained from this study showed that the heterogeneous catalyst driven from a SS is efficient, active, and cost-effective for converting waste cooking oil to BD. Furthermore, the  $\text{CaO}$  was prepared from SS and modified with  $\text{ZnO}$  and  $\text{TiO}_2$ . To investigate the effectiveness and efficacy of the prepared catalyst optimization parameter, the conversion efficiency is increased with a lower catalyst load, a lower methanol-to-oil ratio, and a shorter time. Compared to all the synthesized catalysts, SS modified with  $\text{TiO}_2$  showed a maximum BD yield of 95% with a 3 h reaction time, a methanol to oil ratio of 6:1, and a catalyst load of 3% wt. Upon using the synthesized catalyst, PWCO could possibly be converted to BD and serve as an alternative feedstock for BD synthesis. The as synthesized heterogeneous catalyst, particularly  $\text{CaO}/\text{TiO}_2$ , had extraordinary performance to convert PWCO to BD with a short reaction time, a lower methanol to oil ratio, and a minimum amount of catalyst load. Based on the result of this study, researchers should focus on a low-grade feedstock like WCO, affordable and efficient heterogeneous catalysts such as  $\text{CaO}/\text{ZnO}$  and  $\text{CaO}/\text{TiO}_2$ , as a novel approach to replace non-economical catalysts, and a better BD

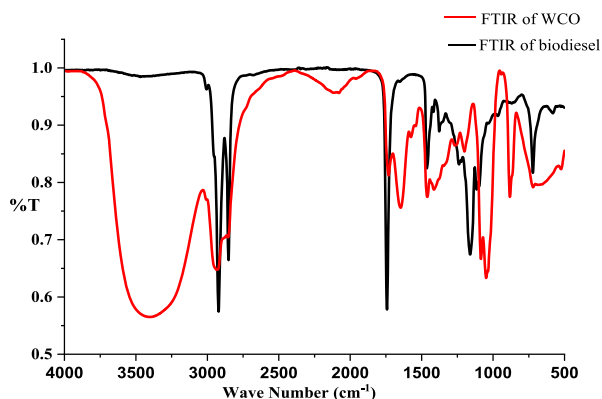


Fig. 8. FTIR characterization of the synthesized waste cooking oil and biodiesel.

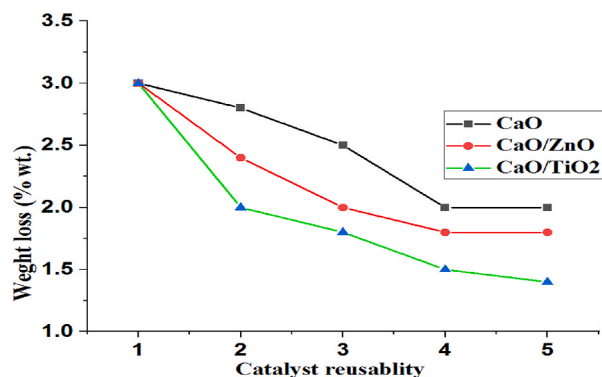


Fig. 9. Effect of catalyst reusability vs. weight loss (%wt.).

yield that can be used as a practical energy source in the near future. However, previous catalysts used in the BD industry were not cost effective, were unstable to reuse, the catalyst raw material was expensive, and the separation process was more complicated. To create an efficient and cost-effective catalyst, the catalyst stability, reusability, calcination temperature, reaction time, and methanol to oil ratio parameters should be optimized. The result of this study revealed that CaO catalyst derived from SS resulted in a WCO-derived biodiesel yield of 80%. The CaO catalyst modified with ZnO and TiO<sub>2</sub> further led to increased biodiesel of 90% and 95%, respectively. The result of this study showed that the optimum conditions associated with the highest biodiesel yield over the synthesized catalysts were 3% catalyst weight, 65 °C, a 6:1 methanol-to-oil ratio, and a 3-h reaction time. The photocatalytic activity, stability, and surface morphology of the synthesized CaO/TiO<sub>2</sub> required further investigation through advanced instrumental characterization such as thermogravimetric analysis (TGA) for thermal stability, scanning electron microscopy (SEM) for surface morphology, and energy dispersive X-ray (EDX) spectroscopy for chemical characterization of a catalyst.

#### Author contribution statement

Welela Meka Kedir, Kokob Teshome Wondimu, Getabalew Shifera Weldegrum: Conceived and designed the experiments; performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

#### Data availability statement

Data will be made available on request.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

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