



Biodiesel Produced from Sunflower Oil via Heterogeneous Catalysts of Calcium Oxide Prepared from Eggshells Loaded on Barium Oxide

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Abstract: In recent years, interest in converting vegetable oils into biodiesel as an environmentally friendly alternative to fossil fuels has increased. Sunflower oil is a vegetable oil that has great potential for biodiesel production. This work explores the use of eggshell-derived calcium oxide along with barium oxide as a heterogeneous catalyst for sunflower oil-based biodiesel generation. The aim of this study was to evaluate the efficiency and feasibility of this catalyst combination in biodiesel synthesis. Experimental tests are conducted to analyze the reaction parameters, including the reaction time, catalyst loading, and temperature, to optimize the biodiesel production process. The properties of the resulting biodiesel are analyzed and compared with standard specifications to assess its quality. The use of heterogeneous catalysts derived from BaO/CaO has shown promising results in transesterification reactions for sunflower oil. The findings of this study provide valuable insights into the potential implementation of these catalyst systems for environmentally friendly biodiesel production.

Keywords: Biodiesel, Eggshells, BaO, Heterogeneous catalyst, Transesterification, Sunflower oils.

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1. INTRODUCTION

The depletion of fossil fuel resources and associated environmental problems have spurred the quest for renewable energy sources, such as biodiesel. Biodiesel is a renewable energy source that can replace conventional diesel fuel. Biomass products are made from biomass sources such as vegetables or animal fats. (Bhatia, 2014, Speight, 2022).

Biodiesel, derived from vegetable oils, is considered a sustainable alternative because of its renewable nature, biodegradability, and reduced emissions. Sunflower oil, which is abundant in many regions, is a viable feedstock for biodiesel production (Bhatia, 2014, Speight, 2022). Studies have estimated that the life cycle emission of greenhouse gases from biodiesel can reach 75% lower than that of petroleum diesel, leading to a reduced carbon footprint (Chen et al., 2018, Gupta et al., 2022, Xu et al., 2022). Moreover, biodiesel has positive impacts on engine performance and longevity. It has higher lubricity than petroleum diesel does, which can improve the lubrication of

engine components and reduce wear and tear (Dharma et al., 2016). Transesterification is defined as a chemical reaction that transforms fats and oils into fatty acid methyl esters (biodiesel) (Bhatia, 2014, Couto et al., 2011).

Conventional catalytic processes for the production of biodiesel use homogeneous catalysts, which often require additional purification steps and generate large amounts of waste water (Smith and Notheisz, 1999, Di Serio et al., 2008, Rizwanul Fatah et al., 2020). Heterogeneous catalysts have emerged as a promising alternative to overcome these limitations. Catalysts play a critical role in biodiesel production by accelerating transesterification, increasing conversion efficiency, allowing milder reaction conditions, facilitating continuous production and enabling catalyst reuse (Maheshwari et al., 2022, Neupane, 2022). A variety of catalysts, including enzymatic, base and acidic catalysts, are used in the synthesis of biodiesel. Each type of catalyst has a different mechanism of action and a range of advantages and disadvantages (Mandari and Devarai, 2022, Changmai et al., 2020, Di Serio et al., 2008, Ma, 1999).

The production process is more efficient when heterogeneous catalysts are used since they are easily separated from biodiesel and are insoluble in the reaction mixture (Yan et al., 2010). Heterogeneous catalysts facilitate the transesterification reaction by providing active sites on their surface for the reaction to occur. These active sites promote the interaction between triglycerides and alcohol, leading to the formation of fatty acid methyl esters (FAMES). The catalysts can be tailored to increase their activity, selectivity, and stability in biodiesel production (Védrine, 2017, Yan et al., 2010, Zabeti et al., 2009). In recent years, several heterogeneous catalysts have been extensively studied for their potential applications in biodiesel synthesis (Mahdi et al., 2023, Rizwanul Fattah et al., 2020, Laskar et al., 2018, Roschat et al., 2016). One widely investigated heterogeneous catalyst is based on solid acids. These catalysts are typically composed of an acidic material supported on a solid substrate, such as silica or alumina. Solid acid catalysts offer numerous advantages, including high activity, reusability, and resistance to water and impurities.

The unique features and high catalytic activity of alkali earth metal oxide catalysts have demonstrated considerable potential in the generation of biodiesel (Sulaiman et al., 2020). These catalysts, including calcium oxide, magnesium oxide, strontium oxide and barium oxide, offer several advantages in the transesterification process because they exhibit strong basicity, which is essential for the transesterification reaction (Li et al., 2022, Sulaiman et al., 2020, Roschat et al., 2016, Anastopoulos et al., 2013b, Verziu et al., 2011). Research has demonstrated that alkaline earth metal oxide catalysts exhibit high catalytic activity, leading to faster reaction rates and higher biodiesel yields. Triglycerides are easily converted to fatty acid methyl esters (FAMES) via the use of these catalysts (Ma, 1999, Leung et al., 2010, Rizwanul Fattah et al., 2020). The strong basic sites on the catalyst surface promote the breaking of ester bonds, resulting in efficient transesterification reactions. Furthermore, alkali earth metal oxide catalysts are relatively inexpensive, readily available, and environmentally friendly. CaO, for example, can easily be derived from calcium-rich sources, such as limestone, also known as quicklime, and is one of the most widely used alkali earth metal oxide catalysts in biodiesel production. CaO has strong basic properties, allowing it to efficiently catalyze the transesterification reaction. It provides active sites on its surface for the interaction between triglycerides and alcohol, promoting the formation of fatty acid methyl esters (FAMES) and glycerol (Kesic et al., 2016). Similarly, MgO and SrO can be obtained from abundant sources, further increasing their economic viability (Rasouli and Esmaeili, 2019, Hu et al., 2023, Verziu et al., 2011).

As has been demonstrated in numerous studies, CaO catalyst has been demonstrated to effectively

catalyze the transesterification of high-grade or vegetable oil. In order to further enhance the catalytic properties of BaO, an attempt was made to combine it with CaO. It has been demonstrated that barium oxide catalysts display catalytic activity in transesterification processes, attributed to their high basicity (Ghanbari Zadeh Fard et al., 2019, Hanif et al., 2022, Ivanova et al., 2012, Martinez-Guerra and Gude, 2014, Olutoye et al., 2016, Sahani et al., 2019, Singh et al., 2019, Yusuff et al., 2021, Chew et al., 2017, Patil, 2012, Al-Abbasi et al., 2023). The transesterification of palm cooking oil using barium-containing titanates, including Ba-TiO₃ and Ba₂NiTi₅O₁₃, as well as their Na-doped analogues, was investigated by Chew et al. (Chew et al., 2017). The efficacy of microwave irradiation in biodiesel production from waste cooking oil was evaluated through a microwave-assisted catalytic transesterification process utilising BaO and KOH (Patil, 2012).

Recently, we have successfully synthesized BaO nanoparticles via the sol-gel method and examined their catalytic performance on the transesterification of sunflower oil (Al-Abbasi et al., 2023). To date, no studies have been conducted on the transesterification of sunflower oil using barium oxide nanoparticles supported by CaO from natural resources. Continuing our previous study of the chemistry of metals and their use in various industrial applications (Belkher, 2019, Khalifa, 2018, Al-Abbasi et al., 2023, Al-abbasi et al., 2022, Al-abbasi et al., 2012, Al-abbasi and Kassim, 2011), this research aimed to investigate the efficiency of CaO, BaO and CaO/BaO catalysts in converting sunflower oil into biodiesel while also analyzing the reaction parameters that can impact biodiesel yield, including reaction time, catalyst loading, and temperature. Analyses were carried out on the generated biodiesel to determine its density, kinematic viscosity, and acid value.

2. EXPERIMENTAL SECTION

2.1 Materials

All the chemicals were utilized just as received and required no additional purification. Citric acid (> 99.5%), barium nitrate (> 96%) and EDTA (> 99%) were used. Sunflower oil (SFO) was provided by Sabha city local market. Chicken eggshells were collected as waste from the house used.

2.2 Preparation

2.2.1 Preparation of the Eggshell Waste-Derived CaO Catalyst

The CaO catalyst can be produced via calcination, in which the dried eggshells are calcined for four hours at 1000 °C. The product was obtained as a white powder. The calcined samples were kept in a closed vessel.

2.2.2 Preparation of BaO nanoparticles

The sol-gel approach was used for generating BaO, and the procedure was described in our recent publication (Al-Abbasi et al., 2023, Salim et al., 2022).

2.2.3 Preparation of BaO/CaO NPs

The sol-gel technique, which is similar to BaO synthesis, was used to produce BaO/CaO (Al-Abbasi et al., 2023). A 1:1:1:1.5 molar ratio of calcium oxide from calcined egg shells, barium nitrate, EDTA, and citric acid was combined with deionized water. The end product was dried overnight at 60 °C to produce a dense black gel. After that, the gel was calcined at 1000 °C until it became a white powder.

2.2.4 Biodiesel preparation

$$\text{Yield (\%)} = \frac{\text{Weight of biodiesel product}}{\text{weight of SFO oil}} \times 100 \quad (1)$$

2.3 Characterization Methods

Infrared data were collected in the 400–4000 cm⁻¹ wavenumber range using a Bruker (Germany). An NEX QC-JSM-6290LV analyzer was used to carry out the EDXRF analysis. High-performance liquid chromatography (HPLC) analyses were performed with a KNAUER AZURA HPLC instrument with a DAD 6.1 UV-Vis detector and a Eurospher II 100-5 C18 column. The flow rate was 1 mL/min, the column temperature was maintained at 40 °C, and the UV detector wavelength was set at 205 nm. The mobile phase was composed of polar mixtures of water and acetonitrile.

2.4. Physical Properties of Biodiesel

2.4.1 Acid Value Test

The acid content was calculated via the following formula (Eq. 2):

$$pH = \frac{(b-a) \times (x) \times N}{W} \quad (2)$$

where N is the standard alkali's normality, W is the sample weight (g), x is the molar mass of KOH, b is the standard alkali used for the sample's titration (mL), and a is the standard alkali used for the blank's titration (mL).

2.4.2 Determination of water content

The glass beaker was washed well with distilled water and dried in a desiccator. W₁ was weighed, 10 ml of oil was placed in the beaker, W₂ was

Previously published papers (Salim et al., 2022, Al-Abbasi et al., 2023) described the process of preparing biodiesel. Typically, methanol was added along with the selected catalyst (BaO, CaO, or BaO/CaO) in a two-necked flask connected to a refluxing apparatus, and sunflower oil was added. After the transesterification reaction was complete, the mixture was centrifuged at 5000 rpm for 15 minutes to remove the catalyst particles. This was followed by washing the solution with hot distilled water. The yield was calculated via Equation (1):

weighed, the cup was placed in the desiccator for 15 minutes, W₃ and the cup were returned to the desiccator for another 15 minutes, the weight was taken as W₄, the cup was returned to the dryer for another 15 minutes, and the weight was taken. W₅, the weight level means that the oil does not contain any moisture. The moisture content is estimated from the following law:

$$\text{Water ratio} = \frac{W_i - W_f}{W_i} 100\% \quad (3)$$

3. RESULTS AND DISCUSSION

3.1 Thermal Decomposition of Eggshell Powder

The thermal decomposition of eggshell powder refers to the process by which eggshell powder decomposes when subjected to high temperatures. Carbon dioxide (CO₂) gas and calcium oxide (CaO) are the products of the thermal decomposition of calcium carbonate (CaCO₃). This reaction proceeds in accordance with the following equation:



The temperature at which this decomposition occurs typically ranges between 900 °C and 1000 °C. Overall, the thermal decomposition of eggshell powder provides a means to separate the calcium carbonate component and obtain calcium oxide, which has utility in a range of industries (Figure 1).

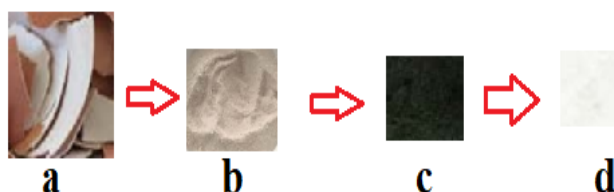


Figure 1: a) Raw eggshells, b) powdered eggshells, c) 1-hour calcined eggshell, and d) CaO oxide powder.

3.2 Characterization of the BaO Catalyst

Characterization of the synthesized catalyst was performed via techniques such as energy-disper-

sive X-ray spectroscopy (EDXRF) and infrared (IR) spectroscopy. EDXRF analysis was used to determine the CaO, BaO and CaO/BaO catalysts after synthesis and calcination (Titus et al., 2019, Scimeca et al., 2018). The results of the EDXRF analysis are shown in Figure 2, and the compositions of the samples are presented in Table 1. The observed and calculated values for the metal oxide catalysts used were similar, as shown in Table 1. On the basis of the EDXRF analysis, the CaO catalyst from the eggshell was determined to be composed of 72.3% w/w CaO, 89.3% w/w BaO, 19.4% w/w CaO and 64.0% w/w BaO. Thus, eggshell material can be utilized as a raw material for CaO catalyst synthesis. The spectrum depicted in Figure 2 shows the EDXRF readings for Ca ($K\alpha = 3.692$ keV, $K\beta = 4.012$ keV), which are consistent with findings from previous research (Wicaksono and Kusumaningtyas, 2019, Lignon et al., 2017). However, the results of earlier studies (Al-Abbasi et al., 2023) were compatible with the EDXRF values for Ba $K\alpha$ (31.81 and 32.19 KeV), Ba $L\alpha$ (4.46 and 4.83 KeV), Ba $L\beta$ (4.93 and 5.16 KeV), and Ba $k\beta$ (36.37 and 73.35 KeV) at high Z (Renukadevi et al., 2020).

Figure 3 displays the FT-IR pattern of the prepared 1:1 BaO/CaO catalyst, the obtained BaO, and the

eggshell-derived CaO over the 400–4000 cm^{-1} range. The interpretation of the FTIR spectra of BaO would be similar to the interpretation mentioned above for CaO. The existence of peaks between 500 and 600 cm^{-1} , which are suggestive of the M-O stretch, which is the stretching vibration of the metal-oxygen bond, may indicate the presence of characteristic peaks associated with the metal-oxide structure in the spectrum. (Manauwar Ali and Nusrat, 2021, Jitjamnong et al., 2019, Al-abbasi et al., 2010, Almutaleb and Alabbasi, 2023).

Furthermore, the bending vibrations of the oxygen atoms in the lattice may be represented by peaks in the 600–900 cm^{-1} range (Manauwar Ali and Nusrat, 2021, Renukadevi et al., 2020, Sundharam et al., 2017). Water absorption on the synthesized catalyst surface was linked to two absorption bands at 3640 cm^{-1} and 1400 cm^{-1} , which correspond to the OH bond stretching and bending modes of vibrations, respectively (Jitjamnong et al., 2019, Boro et al., 2011, Al-Abbasi et al., 2023). It was determined that the bending mode of the OH group of physically adsorbed moisture on the surface was responsible for the wider band at approximately 3423 cm^{-1} (Boro et al., 2011, Ma-nerung et al., 2016, Al-Abbasi et al., 2023).

Table 1: Elemental analysis of the metal oxide catalysts.

Catalyst	Ca % (Calc.)	Ba % (Calc.)
BaO	- (/)	89.3 (89.6)
CaO	72.3 (71.4)	- (/)
BaO/CaO	19.4 (19.1)	64.0 (65.6)

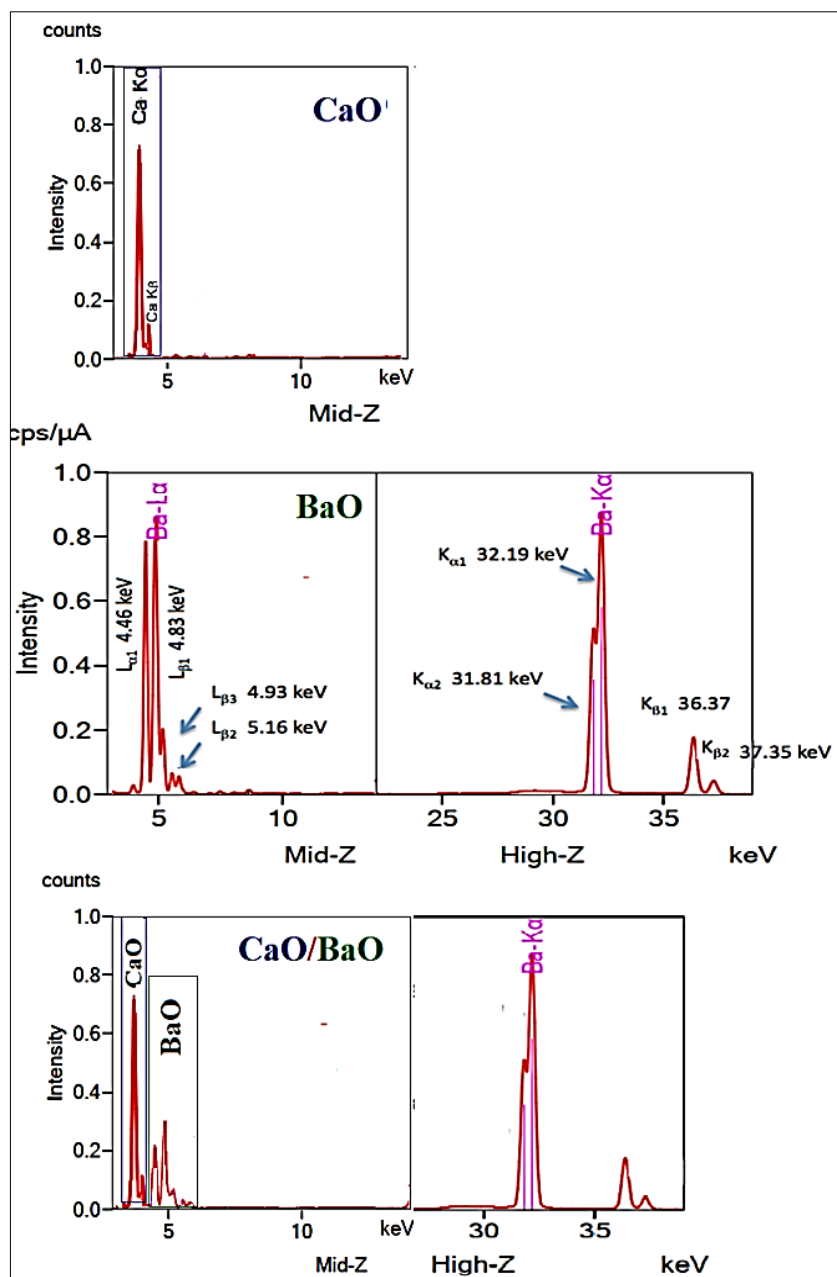


Figure 2: Catalyst EDX signals.

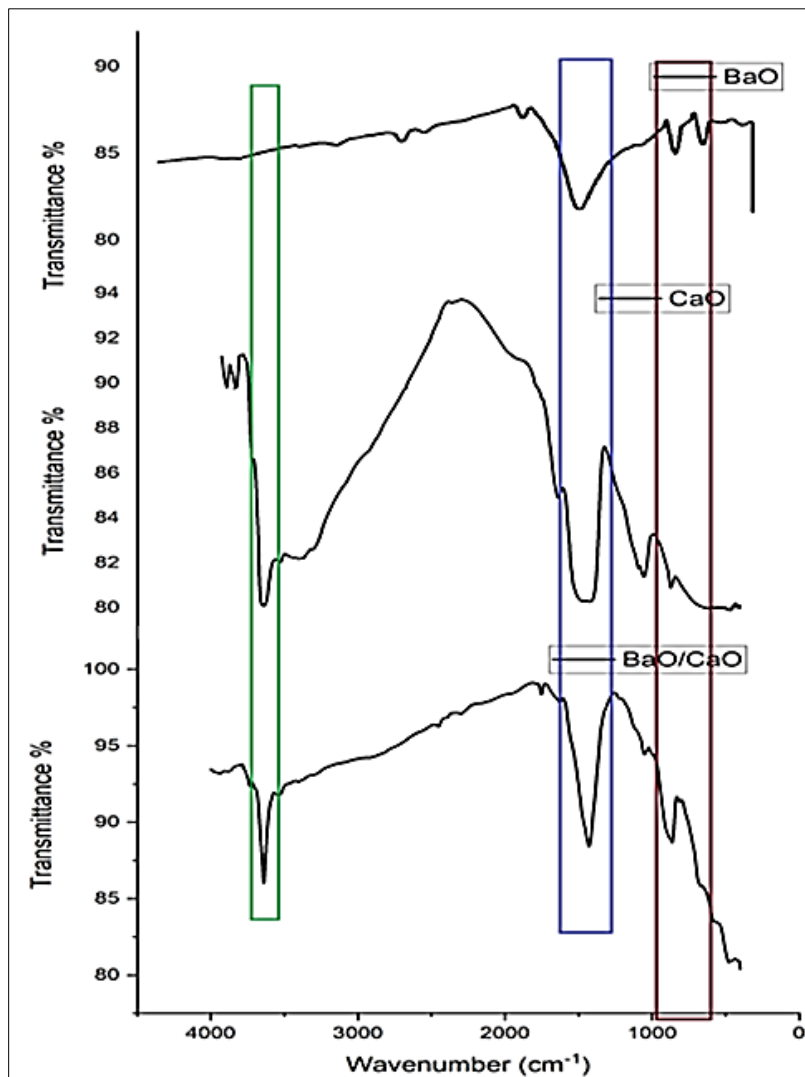


Figure 2: IR spectra of prepared catalyst.

3.2. Characterization of Prepared Biodiesel

The chemical constitution of the biodiesel was ascertained via high-performance liquid chromatography (HPLC). Retention time information was used to identify a number of FAMES. The biodiesel HPLC spectrum revealed seven primary signs (Figure 4).

Software for library matching was used to assess each signal. Linoleic, oleic, palmitic, and stearic acids are the most common fatty acids (Salim et al., 2022, Anastopoulos et al., 2013a, Anastopoulos et al., 2013b, Al-Abbasi et al., 2023).

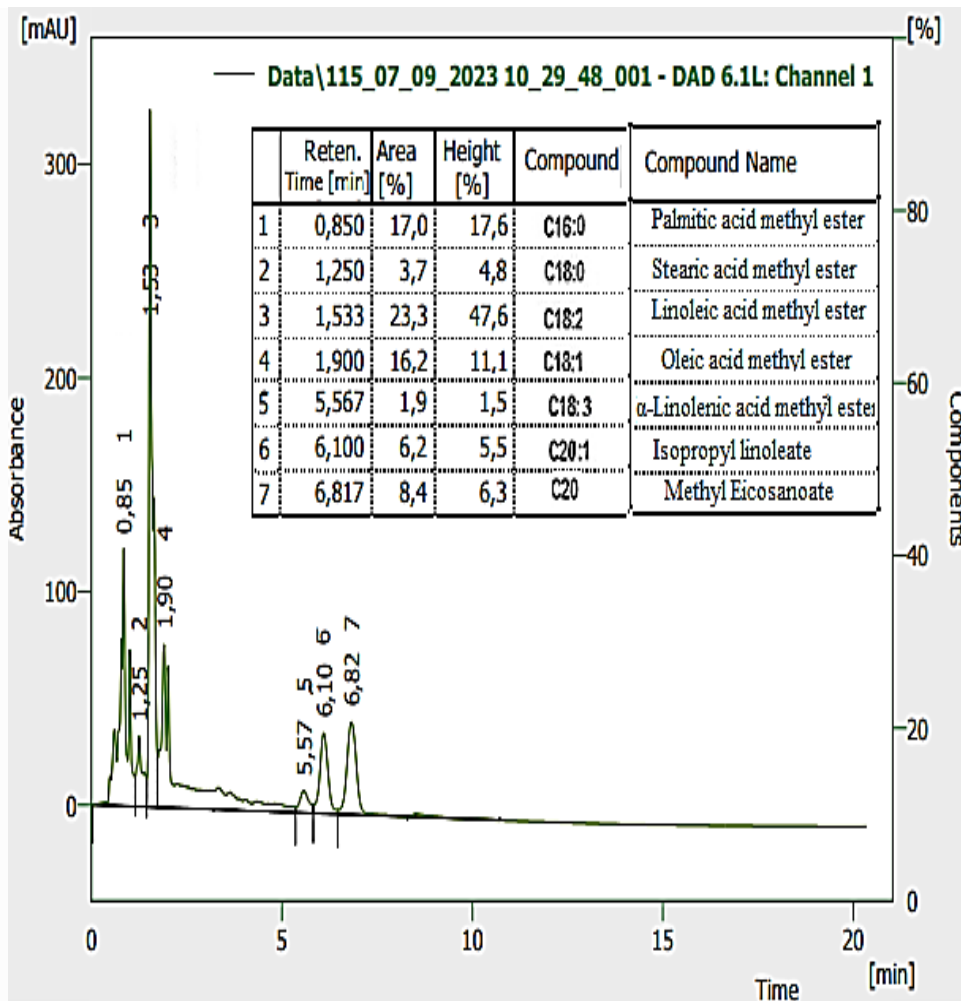


Figure 4: HPLC chromatogram from an experimental run.

The infrared (IR) spectra of biodiesel can provide information about its molecular structure and functional groups. The mid-infrared (4000–400 cm^{-1}) IR spectra, which correspond to the molecular vibrational frequencies, are shown in Figure 5. Carbonyl (C=O) stretching, ester (C-O-C) stretching, and methylene (CH_2) bending are often encountered as functional groups in biodiesel.

By analyzing the FTIR spectra of the FAME fuel in Figure 5, various functional groups present in the fuel can be identified. The absorption peak at approximately 1740–1760 cm^{-1} indicates the presence of carbonyl (C=O) stretching vibrations, which are characteristic of esters. Peaks attributed to C-H vibrations are found between 2800 and 3000 cm^{-1} (Wembabazi et al., 2015, Al-Abbasi et al., 2023). Additional biodiesel peak signals were detected at a wavenumber of 1099 cm^{-1} (C-O), which was similar to what was previously reported (Wembabazi et al., 2015, Yuan et al., 2014, Siatis et al., 2006).

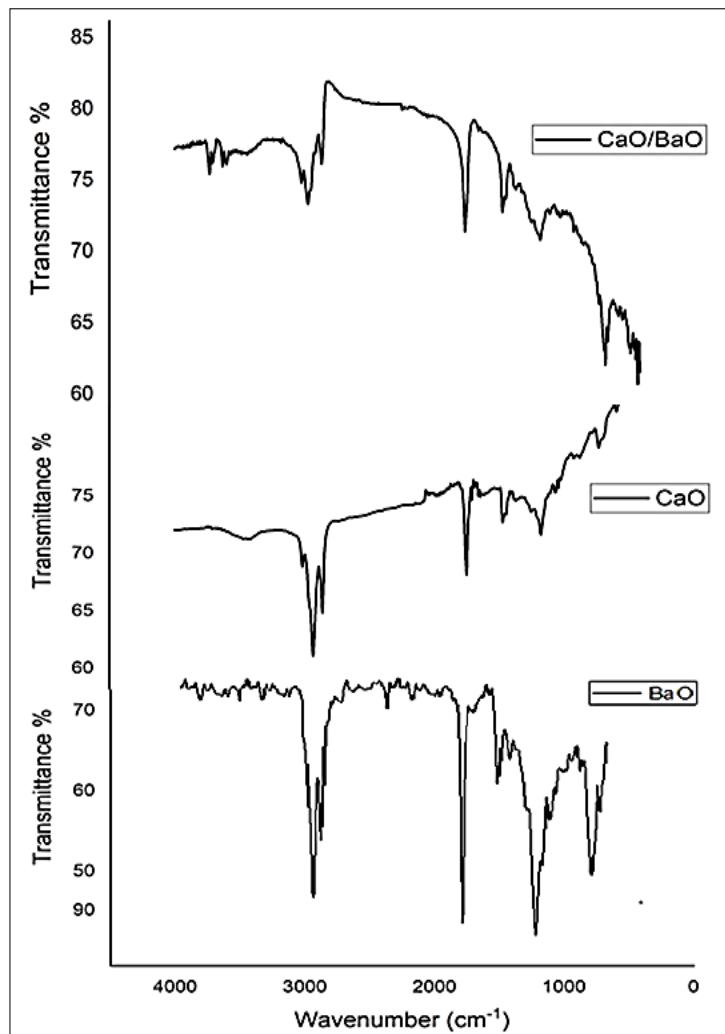


Figure 5: FT-IR spectra of the FAME samples.

3.3 Transesterification Optimization Conditions

Researchers have identified key factors that influence the transesterification process: the methanol-to-oil ratio, catalyst concentration, temperature and reaction time. These factors were varied at different levels to determine their individual and combined effects on biodiesel yield. Initially, in our

previously published research, the methanol-to-oil ratio was optimized by the use of barium oxide. The ideal methanol-to-oil ratio was found to be 20:1 according to tests conducted to determine the effect on biodiesel yield (Al-Abbasi et al., 2023). Thus, in this continued research, the methanol-to-oil ratio was fixed at 20:1 in all the runs (Table 2).

Table 2: FAME yield optimization values.

Exp. No	Time (min)	Temp (°C)	Cata. (W%)	Yield (%)		
				BaO	CaO	CaO/BaO
1	60	70	4.7	61.3	80.2	83.04
2	120	70	4.7	66.8	80.58	83.87
3	180	70	4.7	72.53	81.25	85.95
4	240	70	4.7	78.38	86.03	87.77
5	180	65	4.7	63.24	79.12	82.5
6	180	75	4.7	68.45	66.01	62.65
7	180	70	1.58	68.15	74.67	78.28
8	180	70	3.15	70.67	76.98	82.48
9	180	70	4.7	72.53	81.25	85.95
10	180	70	6.3	74.82	83.2	88.48

3.4.1. Temperature

The reaction rate, yield, and selectivity of the transesterification process are directly influenced

by the temperature at which the reaction is carried out.

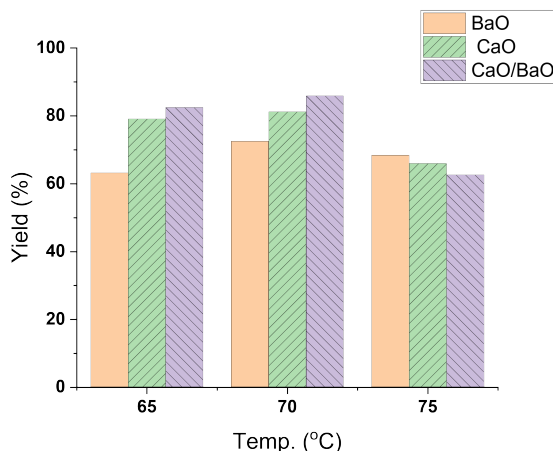


Figure 6: FAME yield change with temperature.

Research has shown that increasing the temperature generally enhances the reaction rate of transesterification (Figure 6). This is because higher temperatures increase the kinetic energy of the reactant molecules, leading to an increased frequency of collisions and, subsequently, a higher rate of reaction. However, there is an optimal temperature range for transesterification reactions. The reaction rate may begin to decline after this optimum range because of the thermal degradation of the reactants or the production of undesirable byproducts. The transesterification procedure was carried out at three different temperatures—65, 70, and 75 °C—to examine the effect of temperature on the FAME yield. During the optimization process, the following parameters were maintained constant: a time interval of 180 minutes, a catalyst quantity of 4.7%, and a methanol/oil ratio of 20:1. The efficiency of methyl ester conversion is illustrated in Figure 6. With all the tested catalysts, the highest conversion efficiencies of 72.53%, 81.25%, and 87.77% were achieved at

70 °C for BaO, CaO, and BaO/CaO catalysts, respectively.

3.4.2. Effect of catalyst concentration

An experiment was carried out with a 12:1 methanol-to-oil ratio at 65 °C for three hours. This result is exemplified in Figure 7, where a lower catalyst concentration of 1.58% offers lower biodiesel yields of 68.15%, 74.67%, 78.28% and 83.49% for the BaO, CaO, and BaO/CaO catalysts, respectively. Increasing the catalyst concentration to 6.3% also increased the FAME yield by 74.82%, 83.2%, 88.48% and 92.45% for the BaO, CaO, and BaO/CaO catalysts, respectively. Several studies have examined how the concentration of alkali earth catalysts affects the transesterification reaction. (Anastopoulos et al., 2013b, Arun et al., 2017, Kouzu et al., 2008, Roschat et al., 2016, Verziu et al., 2011). Increasing the catalyst concentration often results in increased reaction rates and conversions (Antunes et al., 2008).

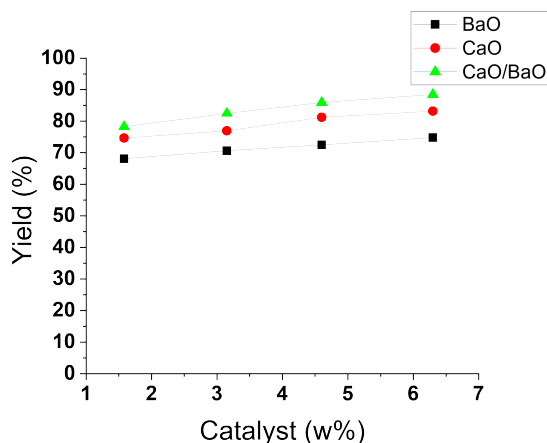


Figure 7: FAME yield under catalyst concentration optimization.

3.4.3. The effect of time

The reaction time can significantly affect the transesterification reaction. Figure 8 shows that longer reaction times (up to 240 min) led to higher conversion rates and improved biodiesel yields by all

the used catalysts, whose yield started to decrease after 180 min, indicating that an optimal reaction time exists for this catalyst to achieve maximum conversion.

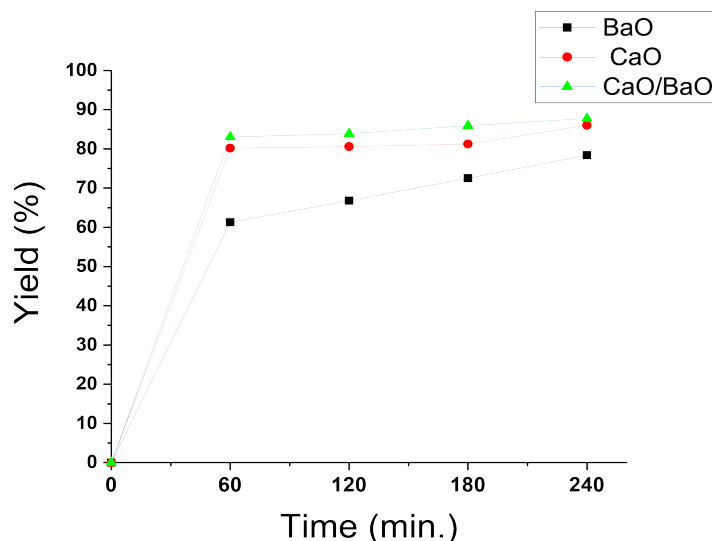


Figure 8: FAME yield under time optimization.

A longer reaction time can generally lead to higher conversion rates and better yields. However, the relationship between reaction time and reaction kinetics is complex and may depend on various factors, such as reaction conditions, catalyst type, reactant concentrations, and temperature (Anastopoulos et al., 2013b, Arun et al., 2017, Verziu et al., 2011).

3.5 Physicochemical Properties of Biodiesel

The physicochemical properties of biodiesel refer to the characteristics and behavior of biodiesel from a physical and chemical perspective. The characteristics of the biodiesel were evaluated according to ASTM 6750.820 - 0.8452. The biodiesel quality was evaluated on the basis of the ASTM-global biodiesel standards (Table 3).

The biodiesel density refers to the mass of biodiesel per unit volume. The estimated densities were 0.904, 0.909 and 0.908 g/cm³. The density of fuel is affected by a number of parameters, such as unsaturation, which causes the density to increase with unsaturation, and chain length, which causes the fuel density to decrease with chain length. (Salim et al., 2022). Viscosity measures the

fluidity or thickness of biodiesel. It affects the fuel's ability to atomize and vaporize during combustion, as well as its flow characteristics in fuel delivery systems. The estimated viscosities at 100°C were 5.58, 3.601 and 3.577 cST for BaO, CaO and CaO/BaO, respectively, which are comparable to the international standards (Keera et al., 2018, Salim et al., 2022).

The acid content and water content are important parameters used to assess the quality of biodiesel. The quantity of free fatty acids in biodiesel fuel is recognized as the acid value of biodiesel. The estimated acid concentrations were 1.052, 0.974 and 1.066 mg KOH/g for biodiesel produced by the BaO, CaO and CaO/BaO catalysts, respectively, which are higher than the ASTM international standards. The presence of free fatty acids is considered to indicate high acidity. The water content of biodiesel refers to the amount of water present in the biodiesel fuel. The estimated water percentages were 0.001, 0.01 and 0.1 for biodiesel produced by the BaO, CaO and CaO/BaO catalysts, respectively, which are comparable to the ASTM-6750.820 - 0.8452 standards.

Table 3: Physicochemical properties of the biofuel.

ASTM Test	Unit	Standard ASTM-6750. 820 -0.8452	Results			
			Sunflower oil	BaO	CaO	CaO/BaO
Specific Grav- ity15@ °C)60°F)	-	820 - 845.2	0.923	0.904	0.909	0.908
Density 15@ °C	kg/L	820 - 845.2	0.92	0.902	0.907	0.908
Kinematic Vis- cosity 100@ °C	cST	1.9 - 6.0	6.39	5.58	3.601	3.557
Water Content	%	< 0.05	0.32	0.1	0.01	0.012
Acid Value	mg/g	0.50	0.432	1.105	0.974	1.066

4. CONCLUSION

This research aimed to provide valuable insights into the conversion of sunflower oil into biodiesel via the use of heterogeneous CaO, BaO and CaO/BaO catalysts. Thus, the catalytic activities of three different catalysts, CaO, BaO, and CaO/BaO, for the production of biodiesel as heterogeneous catalysts were investigated. Chicken eggshell waste was calcined at 1000 °C to yield a CaO catalyst for the synthesis of biodiesel. The tested catalysts were characterized by EDXRF and IR spectroscopy and then evaluated for successful transesterification with methanol. In addition, IR spectroscopy and HPLC were used to investigate the biodiesel that was produced. The influences of the reaction time, reaction temperature, and catalyst concentration on the biofuel yield were explored. The addition of eggshell CaO to BaO resulted in an increase in yield to approximately 87.7% compared with that of the BaO catalyst (78.38%) under the same experimental conditions: a reaction time of 4 h, a reaction temperature of 70°C, a methanol-to-oil ratio of 20:1, and a catalyst loading of 4.6 wt%. The ability of the tested catalysts to transcribe was in the order of BaO < CaO < CaO/BaO. The generated biodiesel was tested against relevant international standards, indicating that it fits certain criteria and is therefore a biocompatible substitute for regular diesel. The use of discarded eggshells was one of the key benefits of this study. Future research can examine the effects of additional natural sources of calcium oxide, such as bone and eggshells, on the transesterification of plant-based oils.

5. CONFLICT OF INTEREST

No conflict of interest.

6. ACKNOWLEDGMENTS

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