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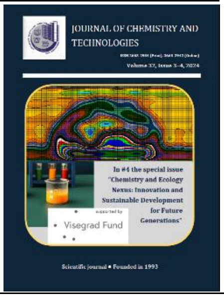

UDC 665.1

# SYNTHESIS OF NEW CaO-MgO CATALYST FROM EGGSHELLS: EXPLORING THE INFLUENCE OF CATALYST SIZE VARIATIONS ON BIODIESEL FORMATION YIELD

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## Abstract

**This scientific research delves into the viability of synthesizing a novel heterogeneous catalyst, leveraging the synergistic combination of eggshell-derived calcium monoxide (CaO) and magnesium oxide (MgO). The study meticulously characterizes variously synthesized catalyst samples employing an array of sophisticated analytical techniques including X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and Brunauer-Emmett-Teller (BET) analysis. Through these analyses, the intricate relationship between size variations and the resultant properties of the catalysts is thoroughly elucidated, providing invaluable insights into their structural and morphological features. Subsequent to characterization, the catalysts are rigorously evaluated in the transesterification reaction of waste cooking oil to biodiesel. This pivotal phase of the investigation aims to discern the catalyst that exhibits the highest biodiesel yield. FTIR analysis identified 1100 °C as the optimal temperature for converting eggshell-derived $CaCO_3$ to CaO. XRD confirmed the formation of CaO and the desired CaO-MgO catalyst. SEM showed that catalyst morphology varies with size, while BET analysis indicated that surface area is influenced by these size changes. Biodiesel yield was found to be sensitive to catalyst size variations.**

*Keywords:* Heterogeneous catalyst; eggshells; CaO; MgO; transesterification; waste cooking oil; biodiesel.

# СИНТЕЗ НОВОГО CaO-MgO-КАТАЛІЗАТОРА З ЯЄШНОЇ ШКАРАЛУПИ: ДОСЛІДЖЕННЯ ВПЛИВУ РОЗМІРУ ЧАСТИНОК КАТАЛІЗАТОРА НА ВИХІД БІОЛОГІЧНОЇ МОДЕЛІ

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## Анотація

**Дане наукове дослідження розглядає перспективи синтезу нового гетерогенного каталізатора, який складається з синергетичної комбінації оксиду кальцію (CaO) та оксиду магнію (MgO), отриманих з яєчної шкаралупи. У дослідженні ретельно охарактеризовано синтезовані зразки каталізаторів із застосуванням низки складних аналітичних методів, включаючи рентгеноструктурний аналіз (XRD), інфрачервону спектроскопію з перетворенням Фур'є (FTIR), растрову електронну мікроскопію (SEM) та аналіз Брунауера-Еммета-Теллера (BET). За допомогою цих методів з'ясований складний взаємозв'язок між варіаціями розмірів і властивостями каталізаторів, що дає безцінну інформацію про їхні структурні та морфологічні особливості. Після визначення характеристик каталізатори ретельно оцінюються в реакції переетерифікації відпрацьованої кулінарної олії в біодизель. Цей ключовий етап дослідження спрямований на виявлення каталізатора, який демонструє найвищий вихід біодизеля. ІЧ-Фур'є аналіз показав, що 1100 °C є оптимальною температурою для перетворення $CaCO_3$, отриманого з яєчної шкаралупи, на CaO. Рентгеноструктурний аналіз підтвердив утворення CaO і бажаного CaO-MgO каталізатора. SEM показав, що морфологія каталізатора змінюється залежно від розміру, а BET-аналіз показав, що зміна розміру впливає на площу поверхні. Вихід біодизеля виявився чутливим до зміни розміру каталізатора.**

*Ключові слова:* Гетерогенний каталізатор; яєчна шкаралупа; CaO; MgO; переетерифікація; відходи кулінарної олії; біодизель.

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## Introduction

In the backdrop of rapid economic expansion and societal evolution coupled with burgeoning population dynamics, the pressing issues of environmental degradation and unsustainable consumption of fossil fuels have propelled a surge in research endeavors aimed at unveiling viable, eco-conscious alternatives [1; 2]. Amidst this pursuit, biodiesel emerges as a beacon of promise, captivating the scientific community owing to its akin physicochemical attributes to traditional diesel fuel, alongside its capacity for mitigating hazardous gas emissions [3].

Biodiesel is derived from a variety of biomass sources including vegetable oils, animal fats, or oils. Through the process of transesterification, typically employing methanol or ethanol, these resources undergo a metamorphosis, yielding a renewable and biodegradable elixir. This eco-friendly fuel mirrors the properties of traditional fuels while offering a greener solution [4–6].

The allure of biodiesel from waste cooking oils (WCO) lies not only in its commendable environmental credentials but also in its economic viability, with production costs markedly diminished compared to virgin vegetable oils [7]. Nevertheless, the burgeoning production of WCO, necessitated by stringent reuse and disposal protocols, has ushered in a slew of challenges concerning resource management [8; 9]. At the forefront of biodiesel synthesis techniques, transesterification reigns supreme, with the conventional alkali catalysis method being commonplace, albeit recent strides in heterogeneous catalyst research spotlight the potential of diverse alternatives [10–12].

Within the realm of heterogeneous catalysts, calcium oxide (CaO) emerges as a stalwart contender, often harnessed for its catalytic prowess in biodiesel production, sourced sustainably from a plethora of natural reservoirs including eggshells, crab shells, and snail shells. The integration of metal ions or amalgamation with other metal-laden materials further augments its catalytic efficacy, accentuating its appeal for biodiesel synthesis [13–15]. Meanwhile, magnesium oxide (MgO) stands out as a promising catalyst, endowed with high catalytic activity and economic feasibility, signaling a paradigm shift towards the exploration of heterogeneous catalysts for biodiesel production [16].

In a bid to refine biodiesel production methodologies, researchers embark on a quest for optimization, leveraging the merits of heterogeneous catalysts based on CaO to achieve enhanced yields while minimizing environmental footprints [17]. In recent times, there has been a surge of interest among researchers in the realm of biodiesel technology towards a catalyst amalgamating calcium oxide (CaO) and magnesium oxide (MgO). This interest stems from its perceived advantages, notably its cost-effectiveness and the anticipated superior catalytic efficacy it promises to offer. The strategic combination of these two compounds is seen as a potential game-changer in the field, with the potential to significantly enhance the efficiency and viability of biodiesel production processes. This catalyst presents a compelling proposition, as it not only addresses the economic concerns associated with catalyst procurement but also holds promise for delivering enhanced performance outcomes, thereby driving innovation and progress in the biodiesel industry [18].

This pioneering scientific endeavor delves into the feasibility of fabricating cost-effective and highly efficient heterogeneous catalysts, specifically employing calcium monoxide (CaO) derived from eggshells in conjunction with magnesium oxide (MgO). The synthesized catalyst samples underwent comprehensive characterization employing a multifaceted approach encompassing X-ray diffraction (XRD), Fourier-transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), and Brunauer-Emmett-Teller (BET) analysis. This meticulous characterization aimed to unravel the intricate interplay between catalyst size variations and their resultant properties. Subsequent to characterization, these catalysts were put to the test in the transesterification reaction of waste cooking oil into biodiesel, with the overarching objective of pinpointing the catalyst capable of yielding the highest biodiesel output.

## Experimental part

*Catalyst CaO-MgO preparation protocol:*

The fabrication of the desired catalyst involved a meticulous sequence of steps:

*Preparation of calcium oxide CaO:*

Chicken eggshells were procured from a fast-food establishment, thoroughly cleaned with distilled water after removing the inner membrane, and subsequently dried in an oven at 100 °C for 6 hours. The dried shells were finely ground into powder using a ceramic mortar. The resulting powder underwent sieving via an electric sieve to obtain particles of four distinct sizes: 63 µm, 90 µm, 125 µm, and 250 µm. These diverse-sized precursor materials underwent calcination at 850 °C, 950 °C, and 1100 °C to find the optimum calcination temperature that converts the calcium carbonate $CaCO_3$ present in the chicken eggshells into calcium oxide CaO through the following reaction:

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_2(g)$$

*Addition of magnesium oxide MgO:*

Following the determination of the optimal calcination temperature for our process, a minute quantity (2 % wt) of magnesium oxide MgO was introduced to the obtained calcium oxide to yield the desired catalyst. The two oxide powders were meticulously mixed and subjected to magnetic stirring in ethanol at 60 °C for 2 hours, followed by placement in an oven at 70 °C to eliminate excess ethanol. Upon drying, the resultant mixture was milled for 6 hours using a ceramic mortar to ensure proper dispersion of its constituents and then calcined at 850 °C.

*Preparation of biodiesel:*

We employed waste sunflower cooking oil for the transesterification reaction. This oil had undergone multiple daily uses before being meticulously filtered with filter paper to eliminate impurities. Subsequently, it was subjected to heating at 100 °C for duration of 2 hours to effectively eliminate any residual water content.

*Characterizations:*

X-ray diffraction (XRD) analysis was conducted to ascertain the phase identification of the calcined eggshells and to explore the phase formation of the elaborated catalysts. Scans were meticulously recorded across a Bragg angle range from 10° to 90° utilizing PANalytical EMPYREAN diffractometer operating at room temperature. Fourier transform infrared spectroscopy (FTIR) was employed to scrutinize the structural properties of the calcined eggshells, the prepared catalysts, and the biodiesel. FTIR spectra were meticulously registered within the wavenumber range spanning from 400 to 4000 $cm^{-1}$ utilizing a PerkinElmer spectrophotometer. The surface characteristics of the examined catalysts, encompassing surface area and pore volume, were quantified through Brunauer-Emmett-Teller (BET) analysis using ASAP 2020 Plus 2.00 instrument. Scanning electron microscopy (SEM) was utilized to explore the morphology of the catalysts under examination, employing a TS5136XM TESCAN VEGA machine operating at low vacuum conditions.

## Results and discussion

*FTIR results:*

In our quest to ascertain the optimal temperature, Fourier transform infrared spectroscopy (FTIR) analysis was conducted on four samples of varying sizes, subjected to a range of thermal treatments at 850°C, 950°C, and 1100°C. Fig. 1 (a, b, c, and d) presents the FTIR spectra of the samples at different temperatures. At room temperature, the FTIR spectra of the analyzed samples consistently revealed characteristic bands at 712 $cm^{-1}$ and 873 $cm^{-1}$ which could be dedicated to asymmetric CO stretching mode of calcium carbonate. However, the peak located at 1412 $cm^{-1}$ is referred to the stretching vibration of calcite $CaCO_3$. As the temperature escalated, a gradual attenuation in the intensity of these typical $CaCO_3$ peaks ensued, concomitant with the emergence of a distinctive absorption peak around 400 $cm^{-1}$. This new peak, attributed to the Ca-O vibration of calcium monoxide CaO, suggests the conversion of the utilized $CaCO_3$ precursor to CaO [19]. The optimum temperature was found to be 1100 °C.

The four prepared catalysts having respective sizes of 63 µm, 90 µm, 125 µm, and 250 µm, have been the subject of FTIR analysis in order to investigate their structural features. As can be seen from Fig. 2, the FTIR spectra of the samples under probe exhibited similar shape with some variations in peak intensities contingent upon sample size, implying their potential for similar performance. Notably, the absorption peak observed at 405 $cm^{-1}$ referred to the presence of metal oxide Ca-O, derived from the transformation of $CaCO_3$ in the eggshells. The distinctive bands appeared at 470 $cm^{-1}$ and 875 $cm^{-1}$, respectively, are attributed to Mg-O vibration mode [20] and Ca-O stretching mode, respectively, thus affirming the formation of the CaO-MgO binary system. Moreover, a prominent peak located at 3641 $cm^{-1}$ is an indicative of O-H stretching vibration of calcium hydroxide $Ca(OH)_2$. This intense peak stemmed from atmospheric moisture post-calcination, owing to calcium mono oxide inherent hydrophobic nature [21].

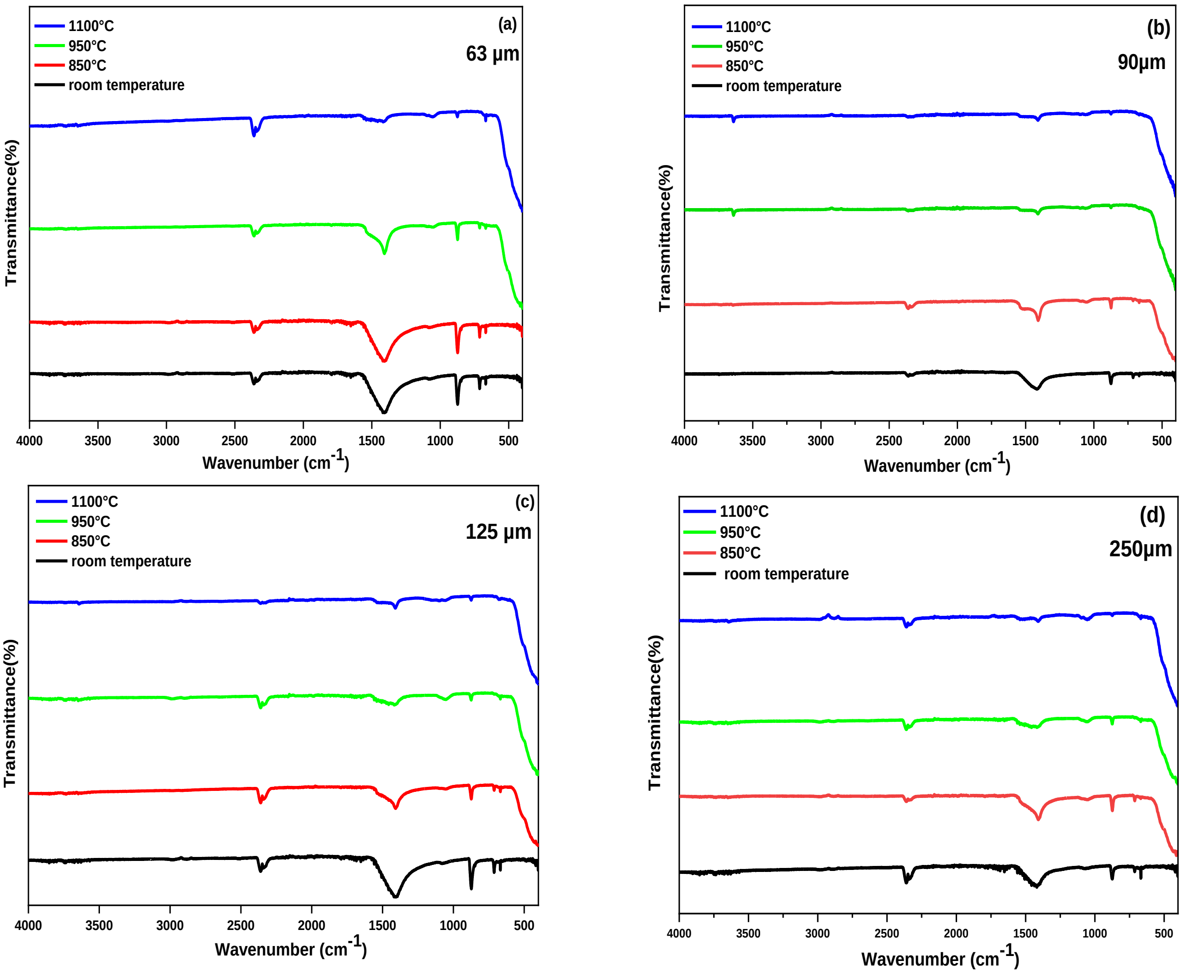


**Fig. 1. FTIR spectra of the eggshell samples of different sizes calcined at different temperatures a: 63 μm shell sample, b: 90 μm shell sample, c: 125 μm shell sample, and d: 250 μm shell sample**

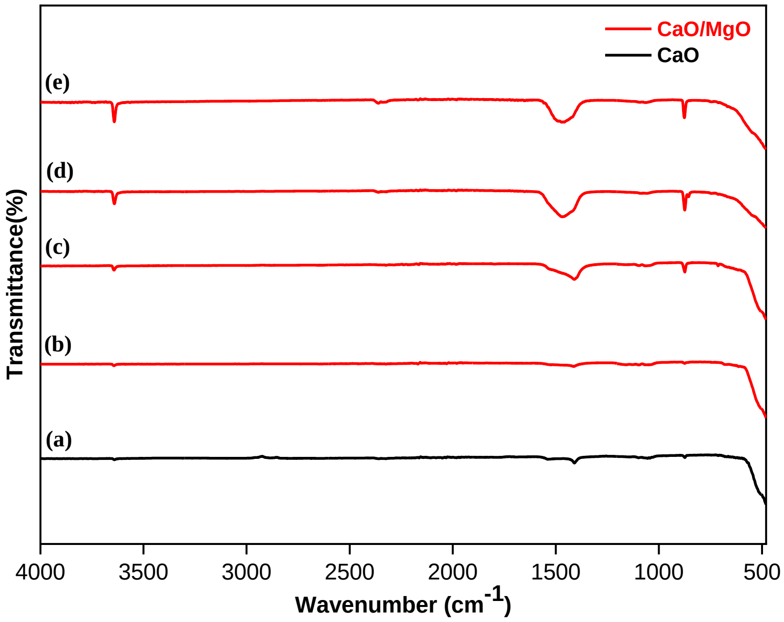


**Fig. 2. FTIR spectra of the studied samples: a: the pure CaO, b: CaO-MgO catalyst with 63 μm size, c: CaO-MgO catalyst with 90 μm size, d: CaO-MgO catalyst with 125 μm size, and e: CaO-MgO catalyst with 250 μm size**

*XRD results:*

X-ray diffraction (XRD) is emerging as a key technique for analyzing catalysts, providing a deep insight into the crystal structure of the material by accurately measuring the X-ray diffraction angles resulting from the deflection of atoms in the crystal lattice. In our study, XRD analysis serves as the cornerstone for assessing the phase identification of chicken eggshell samples of varying sizes subjected to calcination at 1100 °C. Illustrated in Fig. 3 are the XRD patterns of the examined samples, meticulously compared against the ICCD-PDF database. Notably, all acquired diffractograms manifest prominent signals at Bragg angle 2θ of 32.2°, 37.3°, 53.8°, 64.22°, and 67.41°, indicative of the (111), (200), (220), (311) and (222) planes of calcium monoxide (CaO) crystallized within a centered cubic crystal lattice and Fm-3m (225) group space (ICDD-PDF file No. 00-037-1497) [22]. This revelation underscores that precursor grain size has no significant influence on the optimal temperature, a conclusion consonant with the findings of FTIR tests.

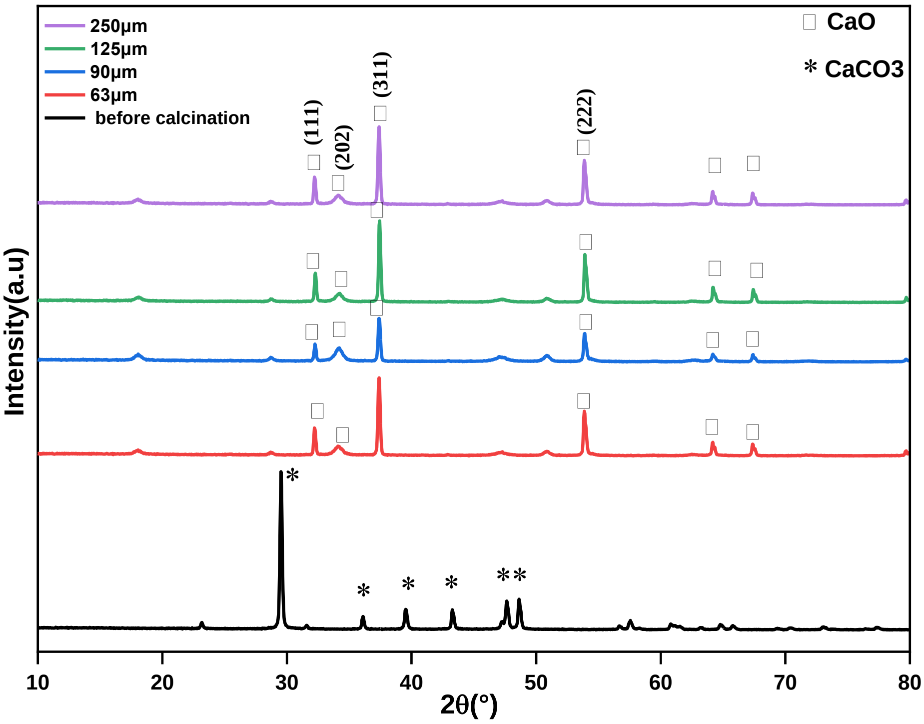


**Fig. 3. XRD patterns of the eggshell samples of different sizes calcined at 1100 °C**

The catalysts prepared and calcined at 850 °C underwent XRD analysis to further elucidate their structural characteristics. The XRD diffraction patterns depicted in Fig. 4 revealed distinct peaks at 2θ = 32.2°, 37.3°, 53.8°, 64.22°, 67.41°, and 79.7°, corresponding precisely to the (111), (200), (220), (311), (222) and (400) planes of CaO, crystallized within a centered cubic crystal structure with an Fm-3m (225) space group (ICDD-PDF file No. 00-037-1497) [22]. Additionally, discernible peaks at 2θ = 42.99° and 62.64°, attributed to the (200) and (220) planes, respectively, signify the presence of the magnesia phase MgO, also crystallized in a centered cubic structure with an Fm-3m (225) space group (ICDD-PDF file No. 00-045-0946) [23]. These findings strongly indicate the successful formation of a CaO-MgO catalyst. Furthermore, the detection of low-intensity peaks at 2θ = 18°, 29°, 34°, and 54° suggests the presence of $CaCO_3$ traces within the samples [24], likely due to the heightened sensitivity of CaO to moisture absorption from atmospheric water.

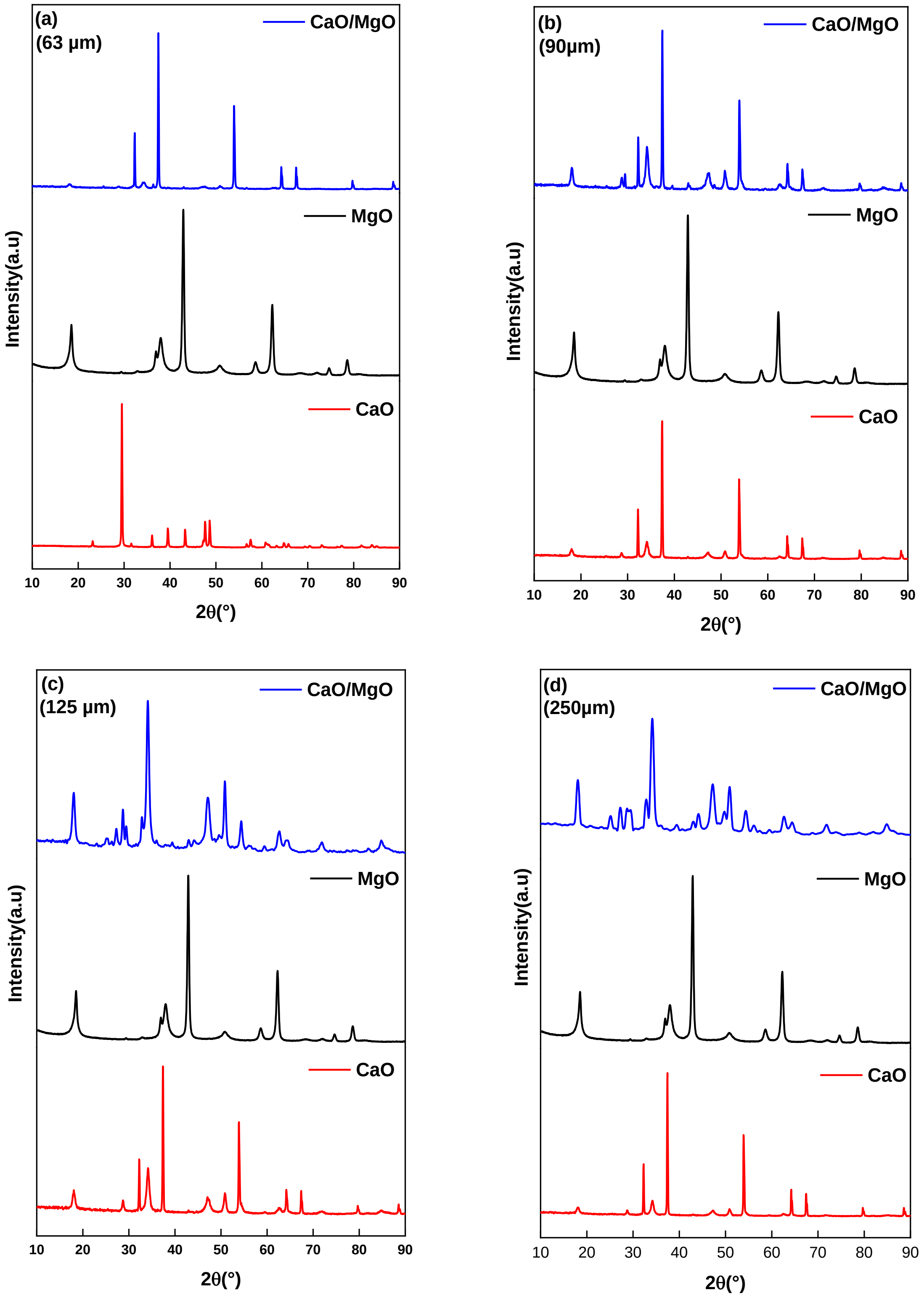


**Fig. 4. XRD patterns corresponding to CaO-MgO catalyst of different sizes calcined at 850 °C: a: CaO-MgO catalyst with 63 µm size, b: CaO-MgO catalyst with 90 µm size, c: CaO-MgO catalyst with 125 µm size, and d: CaO-MgO catalyst with 250 µm size**

*SEM outcomes:*

The morphology of synthesized materials plays a pivotal role in determining their physicochemical properties and, consequently, their suitability for various industrial applications. To delve into this aspect, we conducted scanning electron microscopy SEM analysis to scrutinize the morphology of the catalysts under study, each featuring different sizes. Fig. 5 shows SEM images of the analyzed materials. The images reveal distinct microstructural characteristics: Sample (a) displays a densely packed arrangement comprising agglomerated particles with irregular shapes and non-uniformity. In contrast, the microstructures of the remaining samples (b, c, d) exhibit particles of varied shapes and sizes, punctuated by a substantial presence of pores and voids. This porous morphology holds promise for enhancing the catalytic performance of the materials under examination.

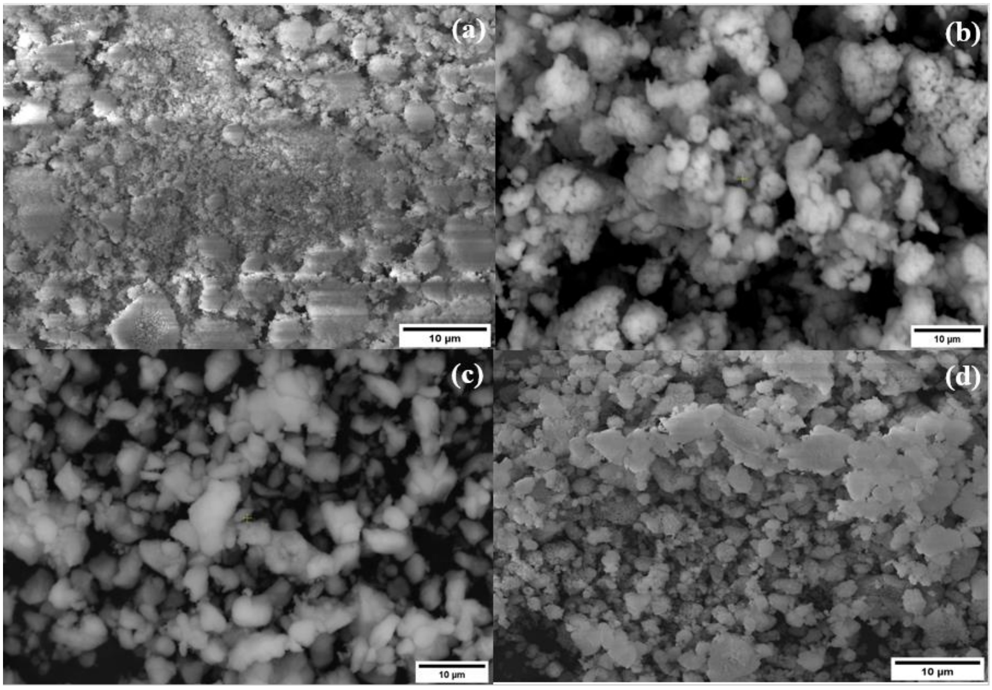
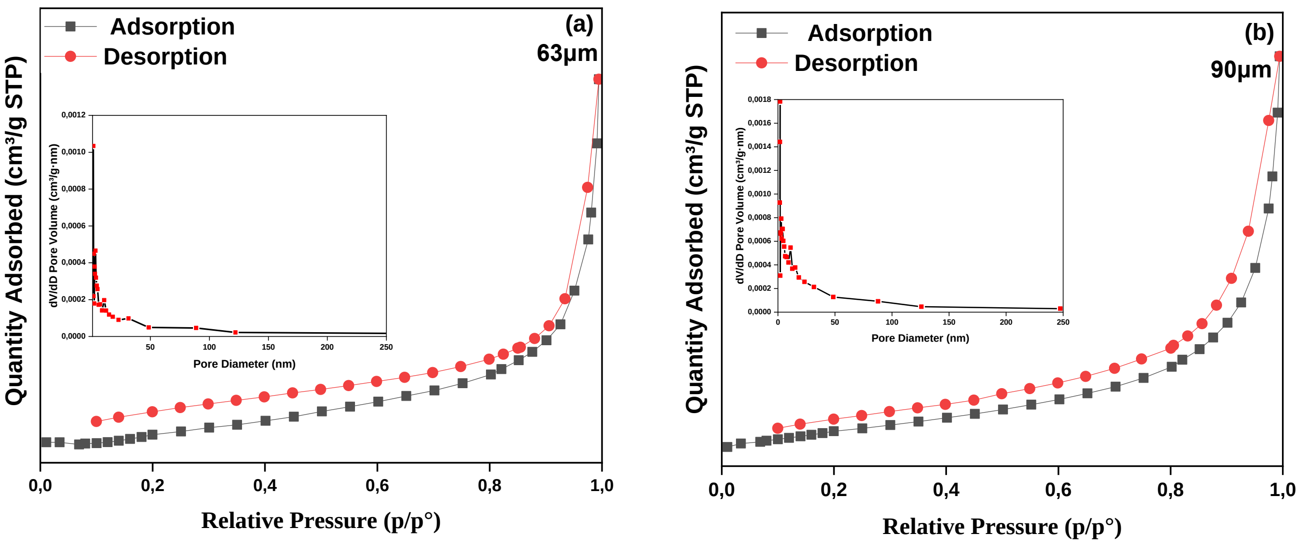


**Fig. 5. SEM images of the obtained CaO-MgO catalysts of different sizes: a : CaO-MgO catalyst with 63 µm size, b: CaO-MgO catalyst with 90 µm size, c: CaO-MgO catalyst with 125 µm size, and d: CaO-MgO catalyst with 250 µm size**

*BET results*

The nitrogen adsorption-desorption isotherms for the samples under investigation are depicted in Fig. 6. Utilizing the Brunauer-Emmett-Teller (BET) method, we assessed the specific surface area and pore volume of catalysts of varying sizes, as aforementioned. The BET specific surface area values obtained for samples (a), (b), (c), and (d) were 2.5239 $m^2/g$, 6.1978 $m^2/g$, 12.6272 $m^2/g$, and 13.7002 $m^2/g$, respectively. According to the literature, the specific surface area decreases with increasing particle size. However, it can also be influenced by other factors such as pore structure, shape, roughness, material composition, impurities, and calcination conditions [25].



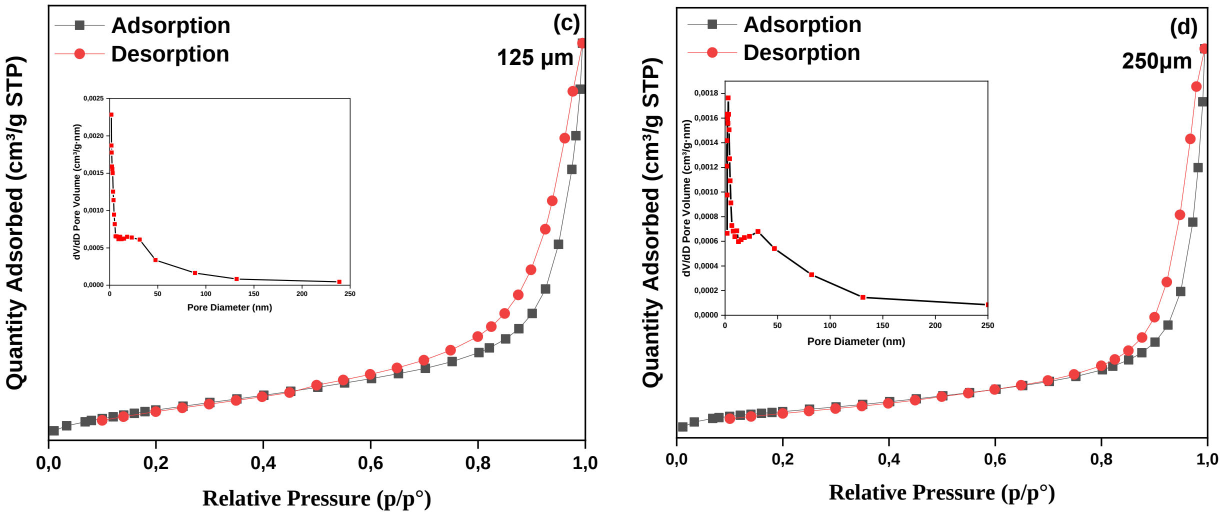


**Fig. 6. Adsorption-desorption isotherms of investigated catalysts of different sizes: a: CaO-MgO catalyst with 63 µm size, b: CaO-MgO catalyst with 90 µm size, c: CaO-MgO catalyst with 125 µm size, and d: CaO-MgO catalyst with 250 µm size**

*Biodiesel production results:*

Bioesterification stands as a pivotal process in the conversion of oils into biodiesel. Within the scope of this study, the triglyceride in the waste cooking oil undergoes a transformative reaction with ethanol, facilitated by the studied catalyst CaO-MgO. This reaction yields fatty acid methyl esters, colloquially known as biodiesel, alongside glycerol. The chemical equation governing this conversion can be succinctly represented as follows:

Triglyceride + Alcohol → Biodiesel + Glycerol

The yield of biodiesel formation can be calculated using the following equation [3]:

$$\boldsymbol{Biodiesel\ yield}\ (\%) = \frac{\boldsymbol{Weight\ of\ biodiesel}}{\boldsymbol{Weight\ of\ waste\ cooking\ oil}} \times \mathbf{100}$$

FTIR spectra, as depicted in Fig. 7, show the alterations in functional groups in the waste cooking oil associated with biodiesel formation. Absorption bands at 3006 $cm^{-1}$, 2921 $cm^{-1}$, and 2854 $cm^{-1}$ are dedicated to CH, $CH_2$, and $CH_3$ functional groups vibrations as well as flexion vibrations detected at 1454 $cm^{-1}$ and 1157 $cm^{-1}$. However, a pronounced absorption peak at 1742 $cm^{-1}$ indicates the presence of C=O and C-O groups, characteristic of the ester formation during the transesterification process in biodiesel production. Furthermore, a peak at 717 $cm^{-1}$ signifies the presence of methylene groups -$(CH_2)_n$-. Noteworthy changes in peak characteristics, particularly in the range of 1157-1171 $cm^{-1}$ in biodiesel, signify the degradation of glycerol structure, reduction of $CH_2$-O groups due to humidity, and formation of O-$CH_3$ functional groups [8]. These transformations underscore the comprehensive impact of the transesterification process on the molecular composition and functional groups of the resulting biodiesel.

The efficiency of biodiesel formation, contingent upon catalyst sizes of 63 µm, 90 µm, 125 µm, and 250 µm, exhibits respective yields of 78%, 77%, 70%, and 22%. This discernible trend underscores that as the catalyst size increases; its catalytic efficacy diminishes in the conversion of the targeted waste cooking oil into biodiesel.

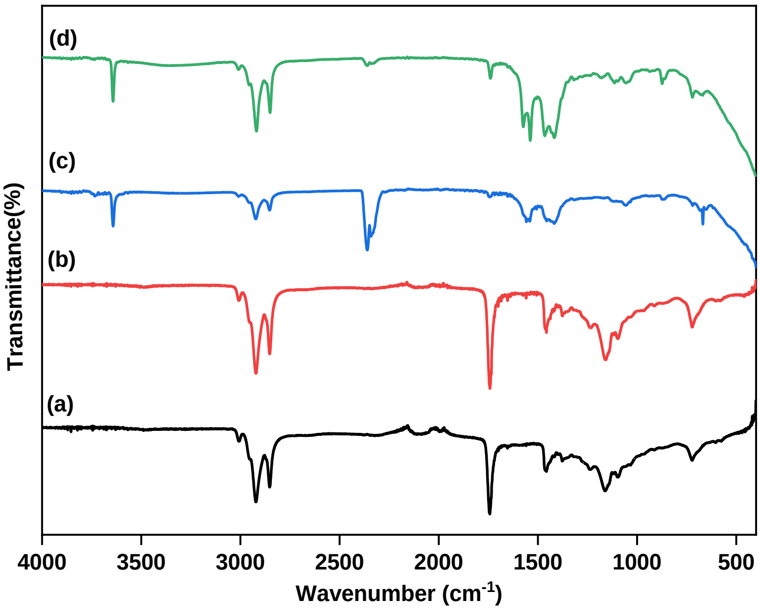


**Fig. 7. FTIR spectra of the obtained biodiesel samples: a: biodiesel prepared on 63 µm CaO-MgO catalyst, b: biodiesel prepared on 90 µm CaO-MgO catalyst, c: biodiesel prepared on 125 µm CaO-MgO catalyst, and d: biodiesel prepared on 250 µm CaO-MgO catalyst.**

## Conclusion

This scientific contribution explores the potential of synthesizing an effective and economical heterogeneous catalyst, CaO-MgO, through the combination of calcium oxide (CaO) derived from discarded eggshells and magnesium oxide (MgO). The catalyst samples underwent comprehensive analysis using X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and Brunauer-Emmett-Teller (BET) techniques to elucidate the impact of size variations on their properties especially their catalytic activity to convert waste cooking oil to biodiesel. In the light of the above reasoning, we can draw the following conclusions:

- FTIR analysis demonstrated that 1100 °C was the optimal temperature for converting $CaCO_3$ in eggshells to CaO, and confirmed both the formation of the CaO/MgO system and biodiesel production.
- XRD analyses confirm the successful formation of the calcium mono oxide from eggshells as well as the formation of the desired CaO-MgO catalyst.
- SEM results indicate that the morphology of the catalyst is influenced by size variations.
- BET findings revealed that the specific surface area varies with the changes in the catalyst size.
- The biodiesel yield varies with catalyst size, with the highest yield achieved using the smallest catalyst size of 63 µm.

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