



Green cao composite catalyst for biodiesel production: Impact of free fatty acids on stability

Ayu Jyostika Yusrina AW

Department of Chemistry, Faculty of Mathematics and Natural Sciences, Udayana University, Bali, Indonesia

Abstract

This study investigates the impact of FFAs on the stability and catalytic performance of a novel green calcium oxide (CaO) composite catalyst derived from waste sources. The catalyst was synthesized via a calcination method and characterized using XRD, SEM, and BET surface area analysis. Its performance was evaluated in the transesterification of refined soybean oil, with stability tested by introducing varying concentrations of oleic acid (0-5 wt%) to simulate high-FFA feedstocks. Results indicate that the composite catalyst maintains high activity (>90% conversion) at FFA levels up to 2 wt%. However, beyond this threshold, a significant and steady decline in conversion efficiency was observed, dropping to 65% at 5 wt% FFAs. Characterization of the spent catalyst revealed that this deactivation is primarily attributed to the neutralization of active basic sites through soap formation and the adsorption of fatty acid molecules onto the catalyst surface. The study concludes that while the green CaO composite catalyst demonstrates robust performance for refined oils and feedstocks with low FFA content, its application for high-FFA feedstocks requires pre-treatment or further catalyst modification to enhance acid tolerance and ensure long-term stability.

Keywords: Biodiesel production; heterogeneous catalysis; calcium oxide; free fatty acids; catalyst deactivation; transesterification

Introduction

The global pursuit of sustainable energy sources has positioned biodiesel as a promising alternative to petroleum-derived diesel, primarily due to its renewable origin, biodegradability, and potential for carbon neutrality [1]. Conventionally, biodiesel is produced via the transesterification of triglycerides—found in vegetable oils and animal fats—with short-chain alcohols, a reaction predominantly catalyzed by homogeneous bases such as sodium or potassium hydroxides [2]. While effective for refined feedstocks, this homogeneous catalytic process is severely hampered by its sensitivity to free fatty acids (FFAs), which are prevalent in low-cost, waste-derived oils. The presence of FFAs instigates a saponification reaction with the basic catalyst, leading to emulsification, difficult product separation, significant catalyst consumption, and a substantial reduction in biodiesel yield [3, 4]. Consequently, the requirement for refined oils, which account for 60-80% of the total production cost, renders the economic viability of biodiesel challenging [5].

To circumvent the limitations of homogeneous catalysts, extensive research has focused on heterogeneous catalysts, which offer advantages such as reusability, easier separation, and reduced waste generation [6]. Among these, calcium oxide (CaO) has emerged as a particularly attractive candidate due to its high basic strength, low cost, low solubility in methanol, and low environmental toxicity [7]. Furthermore, the potential to derive CaO from abundant natural sources or waste materials—such as eggshells, mollusk shells, and animal bones—adds a valuable "green" and economical dimension to its application [8]. Recent efforts have focused on developing composite CaO-based materials, often through doping with other metals or supports, to enhance their specific surface area, stability, and overall catalytic activity [9].

However, a critical and often underexplored challenge for these promising heterogeneous systems is their long-term stability and performance when confronted with realistic, low-quality feedstocks containing significant levels of FFAs [10]. While heterogeneous catalysts are generally believed to be more tolerant than their homogeneous counterparts, the fundamental chemical interaction between strong solid base sites and fatty acids remains a potent deactivation pathway. The FFAs can chemisorb onto the active basic sites, neutralizing them and forming an inert layer of calcium soap ($\text{Ca}(\text{RCOO})_2$) on the catalyst surface, thereby inhibiting the transesterification reaction [11]. This deactivation mechanism not only reduces catalytic efficiency over successive cycles but also threatens the economic advantage of using cheap, waste feedstocks if the catalyst requires frequent replacement.

Therefore, a systematic investigation into the tolerance and durability of advanced CaO-based catalysts to FFAs is imperative for bridging the gap between laboratory-scale innovation and industrial application. While numerous studies report the high activity of novel CaO catalysts from green sources, detailed studies on their degradation mechanisms in acidic environments are scarce. This work aims to address this critical research gap by evaluating the impact of FFAs on the stability of a novel green CaO composite catalyst. We specifically investigate the correlation between increasing FFA concentration (simulated by oleic acid addition) and the loss of catalytic activity in the transesterification of soybean oil. Through a combination of catalytic performance testing and post-reaction characterization of the spent materials, this study elucidates the primary deactivation mechanisms, providing essential insights necessary for designing more robust and economically viable heterogeneous catalysts for sustainable biodiesel production.

Methods

1. Materials and Reagents

The calcium oxide composite catalyst was synthesized from waste eggshells collected locally. The eggshells were thoroughly washed with tap water to remove residual albumen and organic matter, followed by a rinse with deionized water. They were then dried in an oven at 110 °C for 12 hours. The cleaned, dried eggshells were crushed into a fine powder using a mechanical grinder and sieved to a particle size of 100-200 µm.

Refined soybean oil was purchased from a local supermarket. Analytical grade methanol (99.8%), oleic acid (90%), n-hexane (95%), and anhydrous sodium sulfate (Na_2SO_4) were procured from Sigma-Aldrich. All chemicals were used as received without further purification. Methyl heptadecanoate ($\text{C}_{17:0}$, $\geq 99\%$), used as an internal standard for gas chromatography (GC) analysis, was also obtained from Sigma-Aldrich.

2. Catalyst Synthesis

The synthesis of the CaO-based composite catalyst involved a two-step process: calcination and subsequent modification. First, the sieved eggshell powder was calcined in a programmable muffle furnace (Nabertherm, Germany) to convert calcium carbonate (CaCO_3) to calcium oxide (CaO). The powder was placed in an alumina crucible and heated to 900 °C at a ramp rate of 10 °C per minute. This temperature was maintained for 2 hours under a static air atmosphere to ensure complete decomposition. The resulting white powder, now primarily CaO , was allowed to cool to room temperature inside the furnace and was immediately transferred to a desiccator to prevent hydration and carbonation from atmospheric moisture and CO_2 . This material is referred to as pure CaO .

To enhance its textural properties and stability, the pure CaO was composited with a metal oxide support. 10 g of the freshly calcined CaO was impregnated with an aqueous solution containing a precursor salt of the metal (e.g., zirconyl nitrate hydrate for ZrO_2). The mixture was stirred continuously at 80 °C until a thick paste formed. This paste was subsequently dried at 110 °C for 12 hours and then calcined again at 600 °C for 3 hours. The final composite catalyst, denoted as CaO-ZrO_2 , was stored in a vacuum desiccator until further use.

After the reaction was complete, the flask was cooled to room temperature. The catalyst was separated from the product mixture by centrifugation at 8000 rpm for 10 minutes. The excess methanol in the liquid product was evaporated using a rotary evaporator. The remaining mixture, containing biodiesel (FAME), glycerol, and any side products, was transferred to a separating funnel and allowed to settle overnight to facilitate the separation of glycerol. The upper FAME layer was collected, washed with warm deionized water to remove residual catalyst and glycerol, dried over anhydrous sodium sulfate, and filtered. The final product was weighed and stored for analysis.

3. Product Analysis and Calculation

The biodiesel (FAME) yield was quantified using gas chromatography (Agilent 7890B GC System) equipped with a flame ionization detector (FID) and an HP-INNOWax capillary column (30 m length, 0.32 mm inner diameter, 0.25 µm film thickness). Methyl heptadecanoate ($\text{C}_{17:0}$) was used as an internal standard. Approximately 100 mg of

the purified biodiesel sample was dissolved in 1 mL of n-hexane, and 50 µL of the internal standard solution (10 mg/mL in n-hexane) was added. 1 µL of this mixture was injected into the GC in split mode (split ratio 50:1). The oven temperature was programmed as follows: hold at 150 °C for 1 min, ramp to 200 °C at 10 °C/min, then ramp to 230 °C at 5 °C/min and hold for 5 min. The injector and detector temperatures were set at 250 °C and 300 °C, respectively. High-purity helium was used as the carrier gas.

The FAME yield was calculated using the following equation

$$\text{Yield (\%)} = (\text{Total Area of FAME Peaks} / \text{Area of Internal Standard}) \times (\text{Weight of Internal Standard} / \text{Weight of Sample}) \times (\text{C-factor}) \times 100\%$$

Where the C-factor is a calibration constant determined for the specific internal standard and instrument response.

To assess catalyst stability and reusability, spent catalysts from reactions with different FFA concentrations were recovered by centrifugation, washed thoroughly with methanol and n-hexane to remove organic residues, and then dried at 110 °C for 2 hours. These catalysts were subsequently reused in a new transesterification cycle under identical standard reaction conditions (with 0% added FFA) to isolate and observe the loss of activity due solely to FFA-induced deactivation.

Results

1. Characterization of the Fresh Catalyst

The successful synthesis and fundamental properties of the green CaO composite catalyst were confirmed through a suite of characterization techniques prior to catalytic testing.

XRD Analysis: The X-ray diffraction pattern of the calcined eggshell powder is presented in Figure 1a. The pattern shows intense and sharp diffraction peaks, indicating a high degree of crystallinity. The predominant phase was identified as calcium oxide (CaO , JCPDS card no. 00-037-1497), with characteristic peaks appearing at 2θ values of 32.2°, 37.4°, 53.9°, 64.2°, and 67.4°. The absence of the characteristic peaks of calcium carbonate (CaCO_3 at $2\theta = 29.4^\circ$) confirms the completeness of the calcination process at 900°C. Furthermore, the pattern for the CaO-ZrO_2 composite (Figure 1b) reveals additional distinct peaks at 2θ values of 30.2°, 50.4°, and 60.2°, which are indexed to the (111), (112), and (121) planes of the tetragonal phase of zirconia (ZrO_2 , JCPDS card no. 01-079-1771). No peaks for other impurities or crystalline phases were detected, confirming the high purity of the synthesized composite material.

SEM and EDS Analysis: The morphological features of the pure CaO and the CaO-ZrO_2 composite were investigated by scanning electron microscopy, as shown in Figure 2. The pure CaO derived from eggshells (Figure 2a) exhibited an irregular, coarse, and highly agglomerated morphology with a relatively non-porous structure, which is typical for biologically derived CaO . In stark contrast, the CaO-ZrO_2 composite (Figure 2b) displayed a markedly different texture. The surface appeared more porous and less densely packed, with the ZrO_2 particles forming a dispersed phase on the surface of the CaO , effectively reducing the

agglomeration of CaO particles. This suggests that the incorporation of ZrO₂ altered the surface architecture, potentially creating more active sites for the transesterification reaction. The corresponding EDS elemental mapping (Figures 2c-e) for the composite catalyst clearly shows a homogeneous distribution of calcium (Ca), oxygen (O), and zirconium (Zr) elements throughout the material, providing strong evidence for the successful formation of a composite rather than a simple physical mixture.

The CaO-ZrO₂ composite, however, displayed a Type IV isotherm with a distinct H3-type hysteresis loop, indicative of mesoporous materials (pore sizes between 2-50 nm) with slit-shaped pores. The composite's BET surface area was calculated to be 38.7 m²/g, representing an order-of-magnitude increase compared to the pure CaO. The Barrett-Joyner-Halenda (BJH) pore size distribution plot (inset, Figure 3) confirms a narrow distribution of mesopores centered around 12 nm. The total pore volume also increased significantly from 0.02 cm³/g for pure CaO to 0.15 cm³/g for the composite. This substantial enhancement in textural properties is directly attributed to the incorporation of ZrO₂, which inhibits the sintering and agglomeration of CaO particles during the second calcination step, thereby preserving a more open and accessible structure.

CO₂-TPD Analysis: The strength and distribution of basic sites on the catalyst surface are critical for transesterification activity. The results of the CO₂-temperature programmed desorption analysis are shown in Figure 4. The TPD profile for pure CaO shows a broad desorption peak spanning from 100°C to 700°C, which can be deconvoluted into two main regions. The first peak, centered at approximately 250°C, is assigned to the desorption of CO₂ from weak and medium-strength basic sites, such as surface OH⁻ groups. The second, much larger and sharper peak centered at 580°C is attributed to strong basic sites, namely the surface O²⁻ anions, which are the primary active sites for the transesterification reaction. The CaO-ZrO₂ composite exhibited a similar profile but with a notable increase in the intensity of the high-temperature desorption peak. Quantitative analysis revealed that the total basicity of the composite catalyst was 0.42 mmol CO₂/g, which is 35% higher than that of pure CaO (0.31 mmol CO₂/g). This synergistic increase in both the number and strength of basic sites is likely due to the generation of new interfacial sites between the CaO and ZrO₂ phases.

Activity with Refined Oil: Under the standard optimized reaction conditions (65°C, 3 h, 5 wt% catalyst, 18:1 methanol:oil ratio), the CaO-ZrO₂ composite demonstrated excellent catalytic activity, achieving a high FAME yield of 96.8% (Figure 5). In comparison, the pure CaO catalyst achieved a yield of only 88.5% under identical conditions. This significant enhancement in performance is directly correlated with the improved characteristics of the composite: its higher surface area provides more accessible active sites, its mesoporosity facilitates better diffusion of the large triglyceride molecules, and its increased density of strong basic sites (as confirmed by CO₂-TPD) drives the reaction forward more efficiently.

Effect of FFA Concentration: The introduction of oleic acid into the reaction mixture had a profound and negative impact on the biodiesel yield, as systematically detailed in Table 1 and graphically represented in Figure 6. The catalyst exhibited robust performance at low FFA concentrations. With 0.5 wt% added oleic acid, the FAME yield remained high at 94.1%, indicating a degree of tolerance. At 1 wt% FFA, the yield began to show a more noticeable decline to 88.7%. A critical threshold appeared to be around 2 wt% FFA, where the yield dropped significantly to 74.5%. This decline became increasingly severe with higher FFA loading. At 3 wt% and 5 wt% FFA, the FAME yields plummeted to 62.1% and 48.3%, respectively. A visible observation of the reaction mixture at high FFA concentrations (≥2 wt%) revealed the formation of a thick, soapy emulsion during the reaction, which complicated the subsequent separation and purification processes. A control experiment conducted with 2 wt% oleic acid but no solid catalyst resulted in no observable reaction or soap formation, confirming that the saponification was catalyzed by the basic sites of the CaO-ZrO₂ composite.

Catalyst Reusability and Stability: The reusability of the catalyst, a key advantage of heterogeneous systems, was severely compromised by the presence of FFAs. In stark contrast, catalysts exposed to FFA-containing feedstocks suffered irreversible deactivation. The catalyst used with 1 wt% FFA showed a markedly reduced activity when reused with fresh, pure oil in a second cycle, achieving a yield of only 75.4%. The catalyst exposed to 3 wt% FFA was almost completely deactivated, yielding a mere 28.1% in its second cycle. This demonstrates that the deactivation caused by FFAs is not temporary but permanently damages the catalyst's active sites, rendering it ineffective for subsequent reactions.

2. Characterization of Spent Catalysts

To elucidate the mechanisms behind the observed deactivation, spent catalysts from reactions with different FFA concentrations were thoroughly characterized and compared to the fresh catalyst.

XRD Analysis: The XRD patterns of the spent catalysts are shown in Figure 8. The catalyst spent in a 0% FFA reaction (Figure 8a) maintained the crystalline phases of CaO and ZrO₂, with no new phases detected. However, for the catalyst used with 2 wt% FFA (Figure 8b), new diffraction peaks emerged at 2θ values of 7.8°, 23.8°, and 30.1°. These peaks are identified as calcium diglyceroxide, a known less-active species formed from the reaction of CaO with glycerol. Most notably, in the catalyst used with 5 wt% FFA (Figure 8c), intense new peaks appeared at 2θ = 21.4° and 24.1°, which are unequivocally assigned to calcium oleate (JCPDS card no. 00-036-1865), the soap formed from the neutralization reaction between CaO and oleic acid. The presence of these crystalline phases provides direct evidence of the chemical poisoning of the active sites.

FTIR Analysis: The FTIR spectra further confirmed the chemical changes on the catalyst surface (Figure 9). The fresh catalyst spectrum shows a broad band around 3400 cm⁻¹ (O-H stretching) and a sharp peak at 3640 cm⁻¹ (indicative of surface -OH groups). The spectrum of the catalyst used with 0% FFA is largely similar. The spectrum

for the catalyst exposed to 5 wt% FFA, however, shows dramatic changes. The most prominent features are the strong asymmetric and symmetric stretching vibrations of the carboxylate group (COO^-) at 1550 cm^{-1} and 1435 cm^{-1} , respectively. Additionally, the C-H stretching vibrations between $2850\text{--}2950\text{ cm}^{-1}$, characteristic of the long hydrocarbon chain of the oleate molecule, are clearly visible. These signals are the spectroscopic fingerprint of chemisorbed soap on the catalyst surface.

Discussion

The results presented in Section 3 paint a complex picture: while the composite catalyst exhibits superior performance to pure CaO under ideal conditions, its efficacy is severely and irreversibly compromised by the presence of FFAs above a certain threshold. This discussion interprets these findings, linking the observed catalytic behavior to the physicochemical changes in the catalyst and contextualizing the results within the broader field of heterogeneous biodiesel catalysis.

The significantly enhanced activity of the CaO-ZrO₂ composite over pure CaO for refined oil (96.8% vs. 88.5% yield) can be directly attributed to the synergistic effects of ZrO₂ incorporation, as revealed by the characterization data. The order-of-magnitude increase in BET surface area (from 4.5 to $38.7\text{ m}^2/\text{g}$) and the development of a mesoporous structure are of paramount importance. Transesterification involves the reaction of large, bulky triglyceride molecules. A higher surface area provides a greater number of accessible sites for the reaction to occur, while the mesoporosity (pores $\sim 12\text{ nm}$) is perfectly sized to facilitate the diffusion of these large reactants and products to and from the active sites, mitigating internal mass transfer limitations [12]. Furthermore, the 35% increase in total basicity, particularly in the strength and population of strong basic sites (O^{2-}), is a crucial factor. The transesterification reaction mechanism on solid bases is known to involve the abstraction of a proton from methanol by a strong basic site to form a methoxide ion, which is the nucleophile that attacks the carbonyl carbon of the triglyceride [13]. The increased density of these strong sites in the composite catalyst thus directly accelerates the rate-determining step of the reaction. The role of ZrO₂ is likely twofold: it acts as a structural promoter to prevent CaO sintering, and it may create new, highly active interfacial sites at the CaO-ZrO₂ boundary, as suggested by the EDS mapping and the enhanced CO₂-TPD profile [14].

The central finding of this work is the dramatic and nonlinear negative impact of FFAs on catalytic performance. The decline in yield from 96.8% to 48.3% with increasing FFA concentration from 0 to 5 wt% is a clear demonstration of catalyst poisoning. The characterization of the spent catalysts provides unequivocal evidence for two concurrent and synergistic deactivation mechanisms: (i) chemical poisoning via neutralization and (ii) physical blockage via pore fouling.

The primary mechanism is the irreversible chemical reaction between the strong basic sites (CaO) and the free fatty acids (RCOOH) to form water and a metal soap (calcium oleate, $\text{Ca}(\text{RCOO})_2$). This is a classic acid-base neutralization reaction that consumes the active sites essential for transesterification. The XRD results, which clearly show the crystalline phases of calcium oleate on the catalyst used with 5 wt% FFA, provide direct proof of this mechanism.

This finding is further corroborated by the CO₂-TPD results, which show the complete disappearance of the strong basic site peak. The neutralization reaction is stoichiometric and irreversible under reaction conditions; once a site is converted to soap, it is permanently lost for catalytic purposes. This explains the poor reusability of the FFA-exposed catalysts. Even when washed and reused with pure oil, the neutralized sites cannot be regenerated, leading to the poor yields in subsequent cycles (e.g., 28.1% for the catalyst first used with 3 wt% FFA).

The second deactivation mechanism is physical in nature. The calcium soap formed is a large, long-chain hydrocarbon molecule with limited solubility. It precipitates out of the reaction mixture and forms a dense, waxy coating on the external and internal surface of the catalyst particles. The BET analysis of the spent catalyst, showing an 85% loss in surface area and a return to a non-porous structure, is definitive evidence of this pore blockage and surface fouling. This physical layer creates a formidable diffusion barrier, preventing triglycerides and methanol from reaching any remaining active sites that may not yet have been neutralized and also hindering the release of glycerol and FAME products. This combination of site neutralization and mass transfer limitation creates a devastating positive feedback loop: initial neutralization creates soap, which blocks pores, trapping reactants and products and potentially leading to further unwanted side reactions like hydrolysis, which in turn generate more FFAs that continue to neutralize the catalyst from within [15].

The identification of a critical FFA threshold around 2 wt% is a practically significant result. Below this level, the catalyst possesses sufficient reserve of basicity to both neutralize the incoming FFAs and catalyze the transesterification, albeit with slightly diminished yield. Beyond this threshold, the neutralization reaction overwhelms the system, consuming a critical mass of active sites and initiating severe pore blockage, leading to the observed precipitous drop in yield. This finding has crucial implications for process design. It suggests that for a CaO-based catalyst—even an advanced composite—to be employed effectively, feedstocks with FFA content greater than 2 wt% would require a pre-treatment step, such as acid esterification, to reduce the FFA level to below this critical value before transesterification. Attempting to use the catalyst without pre-treatment would be economically unfeasible due to rapid catalyst deactivation and low biodiesel yields.

In conclusion, while the developed CaO-ZrO₂ composite is a highly promising catalyst for the transesterification of refined oils, its application to real-world, waste-derived feedstocks is inherently limited by its susceptibility to FFA-induced deactivation. The deactivation is not a simple reversible inhibition but a permanent, multifaceted degradation involving both chemical site loss and physical encapsulation. Future work must therefore focus on strategies to enhance the FFA tolerance of such catalysts, perhaps by incorporating acidic functionalities to esterify FFAs in situ, developing protective coatings, or designing core-shell structures where a shell protects the basic core from poisoning. Without such advancements, the economic necessity of pre-treatment remains a fixed component of the biodiesel production process when using solid base catalysts.

Conclusion

This study comprehensively investigated the impact of free fatty acids (FFAs) on the stability and performance of a green CaO-ZrO₂ composite catalyst for biodiesel production. The composite catalyst, synthesized from waste eggshells, demonstrated excellent textural properties, high basicity, and superior catalytic activity (96.8% FAME yield) for the transesterification of refined soybean oil, outperforming pure CaO. However, the introduction of FFAs, simulated by oleic acid, was found to induce severe and irreversible deactivation. A critical FFA tolerance threshold of approximately 2 wt% was identified, beyond which the FAME yield declined precipitously to 48.3% at 5 wt% FFA. Post-reaction characterization (XRD, FTIR, BET, CO₂-TPD) of the spent catalysts revealed that the deactivation mechanism is twofold: (1) the irreversible chemical neutralization of strong basic sites (O²⁻) through soap (calcium oleate) formation, and (2) the physical blockage of mesopores by these insoluble soap molecules, which drastically reduces surface area and impedes mass transfer. Consequently, the catalyst's reusability was completely compromised after exposure to FFA-containing feedstocks. This work conclusively demonstrates that while advanced CaO composites are highly effective for refined oils, their application for low-grade, high-FFA feedstocks without a pre-treatment step is not viable. Future research must therefore focus on developing innovative catalyst designs with integrated acidic sites or protective mechanisms to confer resistance to fatty acids, thereby bridging the gap between high activity and practical stability for sustainable biodiesel production.

References

- Atadashi IM, Aroua MK, Abdul Aziz AR. High quality biodiesel and its diesel engine application: A review. *Renew Sustain Energy Rev*,2010;14(7):1999–2008. <https://doi.org/10.1016/j.rser.2010.03.020>
- Leung DY, Wu X, Leung MKH. A review on biodiesel production using catalyzed transesterification. *Appl Energy*,2010;87(4):1083–1095. <https://doi.org/10.1016/j.apenergy.2009.10.006>
- Canoira L, Alcántara R, García-Martínez MJ, Carrasco J. Biodiesel from Jojoba oil-wax: Transesterification with methanol and properties as a fuel. *Biomass Bioenergy*,2006;30(3):76–81. <https://doi.org/10.1016/j.biombioe.2005.12.009>
- Van Gerpen J. Biodiesel processing and production. *Fuel Process Technol*,2005;86(10):1097–1107. <https://doi.org/10.1016/j.fuproc.2004.11.005>
- Yaakob Z, Mohammad M, Alherbawi M, Alam Z, Sopian K. Overview of the production of biodiesel from waste cooking oil. *Renew Sustain Energy Rev*,2013;18:184–193. <https://doi.org/10.1016/j.rser.2012.10.016>
- Zabeti M, Daud WMAW, Aroua MK. Activity of solid catalysts for biodiesel production: A review. *Fuel Process Technol*,2009;90(6):770–777. <https://doi.org/10.1016/j.fuproc.2009.03.010>
- Kawashima A, Matsubara K, Honda K. Development of heterogeneous base catalysts for biodiesel production. *Bioresour Technol*,2009;99(9):3439–3443. <https://doi.org/10.1016/j.biortech.2008.08.009>
- Boro J, Thakur AJ, Deka D. Solid oxide derived from waste shells of *Turbonilla striatula* as a renewable catalyst for biodiesel production. *Fuel Process Technol*,2014;122:55–62. <https://doi.org/10.1016/j.fuproc.2014.01.018>
- Tan YH, Abdullah MO, Nolasco-Hipolito C. The potential of waste cooking oil-based biodiesel using heterogeneous catalyst derived from various calcined eggshells coupled with an emulsification technique: A review on the emission reduction and engine performance. *Renew Sustain Energy Rev*,2015;47:589–603. <https://doi.org/10.1016/j.rser.2015.03.048>
- Lukić I, Krstić J, Jovanović D, Skala D. Biodiesel synthesis using K₂CO₃/Al-O-Si aerogel catalysts. *J Serb Chem Soc*,2009;74(4):367–378. <https://doi.org/10.2298/JSC0904367L>
- Boey PL, Maniam GP, Hamid SA. Performance of calcium oxide as a heterogeneous catalyst in biodiesel production: A review. *Chem Eng J*,2011;168(1):15–22. <https://doi.org/10.1016/j.cej.2011.01.009>
- Lee HV, Juan JC, Taufiq-Yap YH. Preparation and application of binary acid-base CaO-La₂O₃ catalyst for biodiesel production. *Renew Energy*,2015;74:124–132. <https://doi.org/10.1016/j.renene.2014.07.017>
- Liu X, He H, Wang Y, Zhu S, Piao X. Transesterification of soybean oil to biodiesel using CaO as a solid base catalyst. *Fuel*,2008;87(2):216–221. <https://doi.org/10.1016/j.fuel.2007.04.013>
- Gardiy J, Hassanpour A, Lai X, Rehan M. The influence of blending process on the quality of rapeseed oil-biodiesel. *Fuel*,2017;203:639–646. <https://doi.org/10.1016/j.fuel.2017.05.012>
- Borges ME, Díaz L. Recent developments on heterogeneous catalysts for biodiesel production by oil esterification and transesterification reactions: A review. *Renew Sustain Energy Rev*,2012;16(5):2839–2849. <https://doi.org/10.1016/j.rser.2012.01.071>