

Valorization of Biogenic Calcium-Rich Wastes as a Composite CaO Catalyst for Optimized Palm Kernel Oil Biodiesel Synthesis

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Abstract

Biodiesel is a sustainable alternative to petroleum diesel, but developing efficient, low-cost, and environmentally friendly heterogeneous catalysts remains challenging. This study investigated biodiesel production from crude palm kernel oil using a composite calcium oxide catalyst derived from waste eggshells and snail shells. The catalyst was calcined at 900 °C for 3 h and characterized by XRD and FTIR, confirming predominantly crystalline CaO with minor Ca(OH)₂ and carbonate species. Response Surface Methodology using a Central Composite Design optimized reaction time, temperature, catalyst loading, and methanol-to-oil ratio. The quadratic model was significant ($F = 60.25$, $p < 0.0001$) and demonstrated high predictive capability ($R^2 = 0.9825$, Adjusted $R^2 = 0.9662$, Predicted $R^2 = 0.9099$). Optimum conditions of 82.5 min, 60 °C, 5.5 wt% catalyst, and 6:1 methanol-to-oil ratio yielded 91.273 wt% biodiesel. The composite catalyst outperformed calcined eggshell (87.0 wt%) and snail shell (85.5 wt%) catalysts under identical conditions. Biodiesel properties complied with ASTM specifications, with acid value of 0.431 mg KOH.g⁻¹, flash point of 129 °C, and dynamic viscosity of 4.53 mPa.s. The findings demonstrate the catalyst's potential for sustainable and low-cost biodiesel production while promoting agricultural waste valorization without the need for further catalyst modification.

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1. Introduction

The increasing global energy demand, declining fossil fuel reserves, and growing concerns over greenhouse gas emissions have intensified the search for sustainable alternative fuels. Biodiesel is among the most promising renewable alternatives to petroleum diesel due to its renewability, biodegradability, low toxicity, and ability to reduce emissions of particulate matter, sulfur oxides, carbon monoxide, and unburned hydrocarbons [1,2].

Biodiesel is commonly produced through the transesterification of vegetable oils or animal fats with short-chain alcohols, particularly methanol, in the presence of a catalyst [3]. The process efficiency largely depends on catalyst reactivity, making catalyst development crucial. Catalysts are broadly classified as homogeneous or heterogeneous. Although NaOH and KOH offer high reaction rates and biodiesel yields, they can cause soap formation, difficult catalyst recovery, and substantial wastewater generation during purification [4,5]. These drawbacks have driven research into heterogeneous catalysts, which provide easier separation, better recyclability,

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lower environmental impact, and reduced processing costs [6,7]. Among heterogeneous catalysts, CaO is widely used for biodiesel production due to its strong basicity, low cost, abundance, and high catalytic activity [8]. Eggshells and snail shells offer inexpensive biomass sources for CaO production while promoting waste valorization and sustainability [9,10]. However, single-source CaO catalysts can undergo deactivation through moisture and CO₂ exposure, leaching, pore blockage, limited surface area, and loss of active basic sites, reducing catalytic efficiency and reusability [11-15].

Recent research has explored composite biomass-derived catalysts combining two or more calcium-rich wastes to overcome the limitations of single-source catalysts. These composites can enhance surface area, pore volume, basicity, thermal stability, and active-site accessibility, improving transesterification efficiency and biodiesel conversion [16-18]. They may also improve resistance to deactivation, mechanical strength, and reusability, while reducing catalyst costs and supporting sustainable waste management [19,20]. Although eggshell- and snail-shell-derived catalysts have been widely studied individually, their combination as composite catalysts for biodiesel production remains limited [21-25]. Thus, combining these calcium-rich wastes may improve biodiesel yield, catalyst stability, and reusability, particularly for palm kernel oil transesterification under optimized conditions, representing an important research gap.

Therefore, this study investigates the synthesis of biodiesel from palm kernel oil using a

composite heterogeneous catalyst prepared from calcined eggshell and snail shell wastes. The research evaluates the effectiveness of the composite catalyst in enhancing biodiesel production while promoting the valorization of agricultural wastes into value-added catalytic materials.

2. Materials and Methods

2.1. Materials

Crude palm kernel oil (PKO), which served as the feedstock for biodiesel production, was purchased from a local market in Benin City, Edo State, Nigeria. Waste eggshells and snail shells were collected from local restaurants and utilized as precursor materials for the preparation of the heterogeneous catalyst. Analytical-grade methanol, sulphuric acid, sodium hydroxide, potassium hydroxide, benzene, ethanol, chloroform, acetic acid, and phenolphthalein indicator were obtained from LUCO Laboratory, Benin City, Nigeria.

2.2. Preparation and Characterization of Composite Catalyst

Figure 1 illustrates the catalyst preparation process. Waste eggshells and snail shells were thoroughly washed, sun-dried, and oven-dried at 105 °C for 3 h to remove moisture. The dried shells were crushed, pulverized, and sieved to 250 µm before being separately calcined in a muffle furnace at 900 °C for 3 h at a heating rate of 10 °C min⁻¹. The calcination temperature influences CaO formation and catalytic activity, with

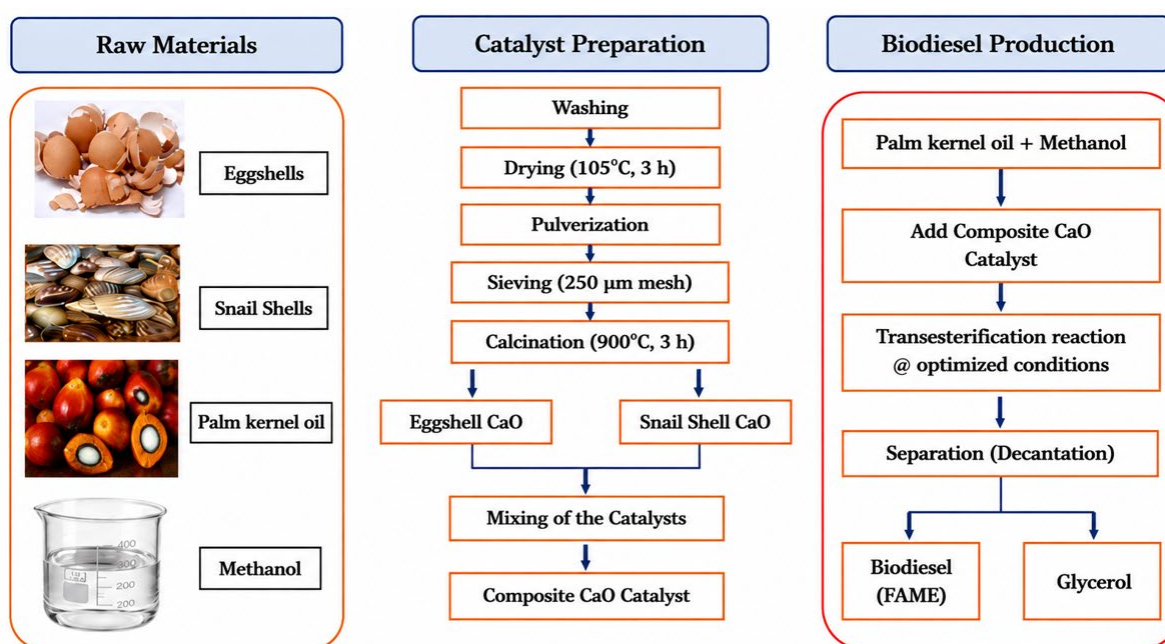


Figure 1. Flowchart for biodiesel synthesis from kernel oil using composite biomass-derived catalyst.

insufficient or excessive temperatures potentially reducing catalyst performance, therefore, 900 °C was selected in the present study based on recent evidence of effective CaCO_3 -to- CaO conversion and favourable catalytic performance of shell-derived catalysts at this temperature [26]. Calcination decomposed calcium carbonate (CaCO_3) into calcium oxide (CaO), the active catalytic phase. The resulting CaO powders were cooled in a desiccator to minimize moisture absorption and carbonation. The calcined eggshell and snail shell-derived CaO catalysts were combined at a constant weight ratio 1:1 to obtain the equal masses of the two catalysts, which were thoroughly mixed to ensure uniform distribution before use in the transesterification reaction.

The synthesized catalysts were characterized using Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Diffraction (XRD). FTIR analysis was conducted over $4000\text{--}400\text{ cm}^{-1}$ to identify functional groups, while XRD using radiation of over a 2θ range of $4\text{--}75^\circ$ was employed to determine crystalline phases and confirm CaO formation after calcination.

2.3. Biodiesel Production

2.3.1. Esterification of palm kernel oil

To reduce the free fatty acid (FFA) content of the crude palm kernel oil, 500 g of PKO was esterified using 25 wt % methanol in the presence of 1 wt % sulphuric acid catalyst. The reaction mixture was maintained at 60 °C under continuous stirring for 90 min. The esterification process was repeated until the FFA content was reduced to approximately 1 %, thereby minimizing soap formation during the subsequent transesterification process.

2.3.2. Transesterification and biodiesel purification

As depicted in Figure 1, transesterification reactions were carried out in a 1000 mL three-neck round-bottom flask equipped with a reflux condenser, thermometer, magnetic stirrer, and heating mantle. 500 g of the esterified palm kernel oil was preheated to the desired reaction temperature before the methanol-composite catalyst mixture was introduced into the reactor. The reaction was conducted at atmospheric pressure with continuous stirring at 700 rpm for the reaction time specified by the experimental design. Following completion of the reaction, the product mixture was transferred into a separating funnel and allowed to settle until biodiesel and glycerol formed two distinct layers. The biodiesel phase was separated and purified by repeated washing with warm distilled water to remove residual methanol, glycerol, catalyst

particles, and soap. Washing continued until the wash water became clear, after which the biodiesel was dried prior to characterization.

2.4. Experimental Design and Process Optimization

The optimization of biodiesel production was carried out using Response Surface Methodology (RSM) based on a Central Composite Design (CCD) in Design-Expert® Version 13.0.6 (Stat-Ease Inc., Minneapolis, USA). Four key process variables were investigated: reaction time (15-150 min), reaction temperature (40-80 °C), catalyst loading (1.0-10.0 wt %), and methanol-to-oil molar ratio (3:1-9:1), with center points of 82.5 min, 60 °C, 5.5 wt %, and 6:1, respectively. These variables were selected because of their significant influence on the transesterification reaction and biodiesel yield.

A total of 30 experimental runs were generated by the CCD to systematically evaluate the individual, interaction, and quadratic effects of the selected variables. The experimental results were analyzed using regression analysis and analysis of variance (ANOVA) to develop predictive quadratic models, assess the statistical significance of the process parameters, and identify the optimum operating conditions for maximizing biodiesel yield while minimizing the number of experimental trials.

2.5 Characterization of Palm Kernel Oil and Biodiesel

The physicochemical properties of both crude palm kernel oil and the produced biodiesel were evaluated in accordance with relevant American Society of Testing Materials (ASTM) standard methods. The properties determined included acid value, peroxide value, moisture content, density, specific gravity, flash point, and kinematic viscosity. Standard analytical procedures were followed for each determination to assess the quality of the feedstock and the produced biodiesel and to compare the results with ASTM biodiesel specifications.

3. Results and Discussion

3.1. Structural and surface characterization of the calcined eggshell-snail shell blend catalyst (XRD and FTIR)

The crystalline phases and surface functional groups of the calcined eggshell-snail shell blend catalyst were investigated using X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy, and the corresponding spectra are presented in Figures 2 and 3, respectively. The combined characterization techniques provide

complementary information on the catalyst's crystalline structure and surface chemistry, thereby confirming the successful synthesis of a calcium oxide-based heterogeneous catalyst.

The XRD pattern (Figure 2) revealed that the calcined eggshell-snail shell blend catalyst was predominantly crystalline CaO, with characteristic diffraction peaks at $2\theta = 32.5^\circ$, 37.5° , 54.0° , 65.0° , and 67.5° . The intense peak at 37.5° and sharp reflections indicate high crystallinity and confirm the effective conversion of CaCO_3 in the biogenic precursors to catalytically active CaO during calcination. Minor peaks at 18.0° , 34.0° , 51.0° , and 65.0° were

assigned to portlandite (Ca(OH)_2), suggesting slight hydration following atmospheric exposure. The calculated crystallographic densities of CaO and Ca(OH)_2 were 3.34 and 2.20 g.cm^{-3} , respectively, with unit cell volumes of 111.35×10^6 and $54.46 \times 10^6 \text{ pm}^3$.

The FTIR spectrum (Figure 3) further supported the XRD findings, with major bands at 3641 , 1416 , and 872 cm^{-1} . The 3641 cm^{-1} band corresponded to O-H stretching associated with Ca(OH)_2 , while the bands at 1416 and 872 cm^{-1} were attributed to carbonate (CO_3^{2-}) stretching and bending vibrations, respectively. These features indicate slight hydration and surface

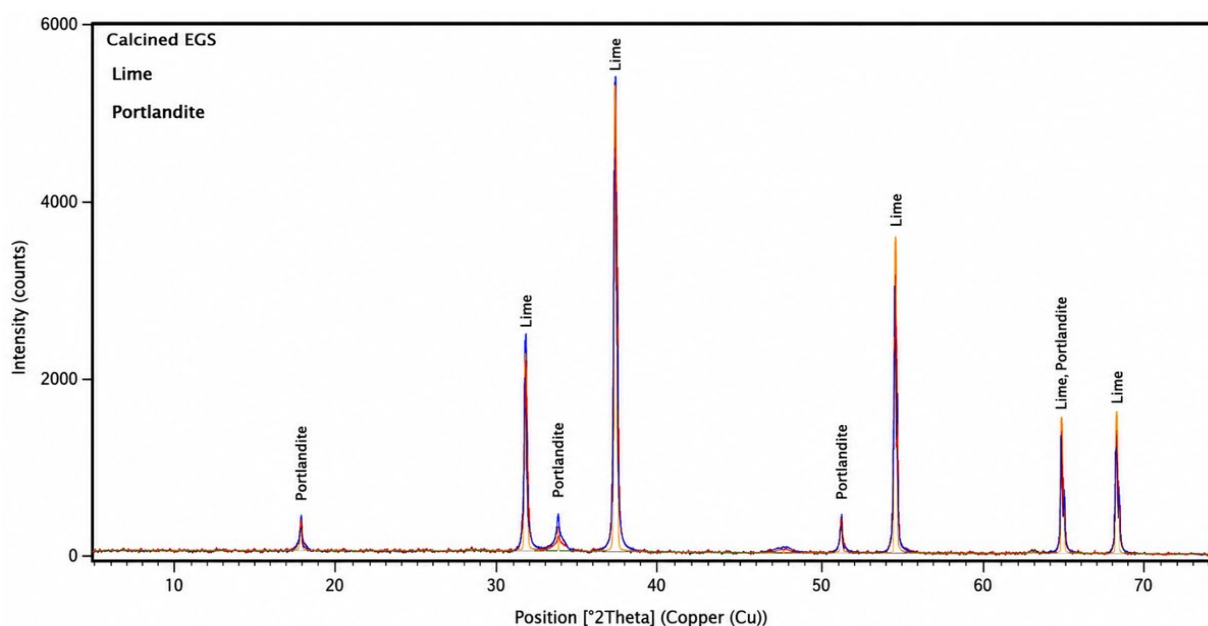


Figure 2. XRD Pattern of the calcined eggshell-snail shell composite catalyst.

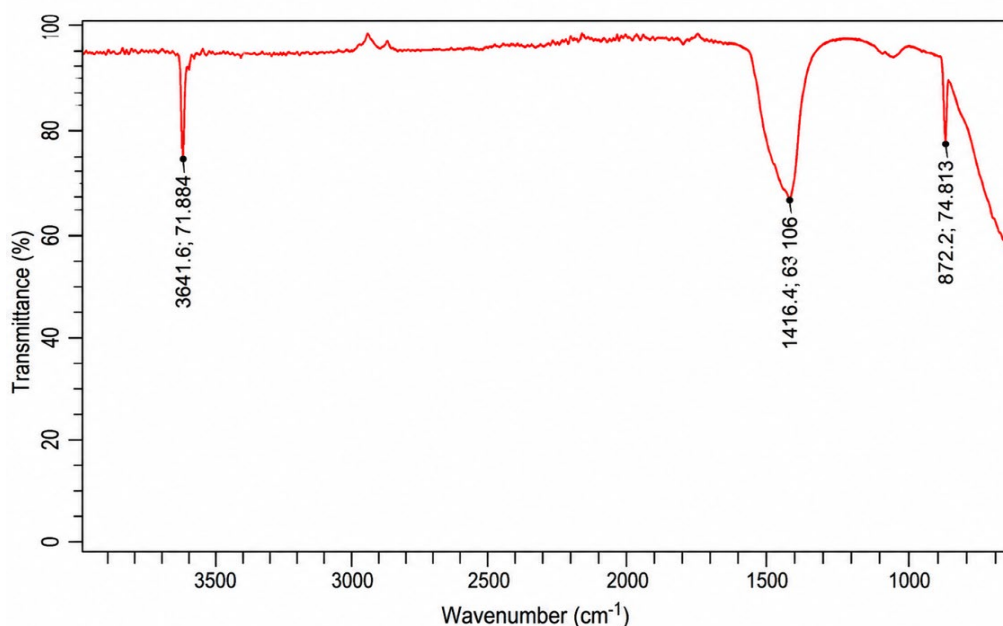


Figure 3. FTIR Spectrum of the calcined eggshell-snail shell composite catalyst.

carbonation caused by atmospheric moisture and CO₂ after calcination. Overall, the XRD, FTIR, and EDXRF results confirmed CaO as the dominant crystalline phase and calcium as the major elemental constituent, demonstrating successful formation of a highly crystalline, calcium-rich catalyst with strong basic sites suitable for biodiesel transesterification.

3.2. Results of Physicochemical Characterization of Crude Palm Kernel Oil (PKO)

The results of the physicochemical properties of the crude palm kernel oil (PKO) used in this study indicate that the oil possesses suitable characteristics for biodiesel production. The density (0.8967 g/cm³) and moisture content (0.21 wt%) fall within the recommended limits, suggesting good fuel quality and minimizing the likelihood of soap formation during base-catalyzed transesterification. The acid value (2 mg KOH/g) and free fatty acid (FFA) content (1%) are also within acceptable limits, indicating that the oil is suitable for direct alkali-catalyzed transesterification without the need for acid pretreatment. Furthermore, the flash point (186 °C) demonstrates safe handling and storage characteristics, while the saponification value (208.65 mg KOH/g) indicates the presence of fatty acids suitable for biodiesel production. Although the iodine value (108.42 g I₂/100 g) is slightly higher than the ideal value, it remains within the acceptable range and is not expected to adversely affect biodiesel quality. In addition, the peroxide value (9.4 meq/kg) indicates minimal oxidative

deterioration of the oil. Overall, these results confirm that the crude palm kernel oil is a suitable feedstock for the production of high-quality biodiesel using the synthesized heterogeneous catalyst.

3.3. Optimization of Biodiesel Yield

3.3.1. Analysis of variance (ANOVA)

The analysis of variance (ANOVA) results in Table 3 indicates that the developed quadratic model is statistically significant, with a Model F-value of 60.25. This high F-value suggests that the model adequately describes the relationship between the process variables and biodiesel yield. The probability of obtaining such an F-value due to random noise is only 0.01% ($p < 0.0001$), confirming the significance of the model. The significant model terms ($p < 0.05$) are A, B, C, D, AB, AC, AD, BC, CD, A², B², C², and D², indicating that both the individual process variables and their interaction and quadratic effects significantly influence biodiesel yield.

Furthermore, the Lack-of-Fit F-value of 3.07 is statistically insignificant ($p = 0.1139$), indicating that the lack of fit is not significantly different from the pure experimental error. The 11.39% probability that the lack-of-fit could arise from random noise further confirms that the model adequately fits the experimental data. A non-significant lack of fit is desirable because it demonstrates that the developed regression model provides a reliable representation of the experimental observations and is suitable for

Table 3. Analysis of variance (ANOVA) for the quadratic model of biodiesel yield.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	11595.52	14	828.25	60.25	<0.0001	Significant
A-Reaction Time	922.66	1	922.66	67.12	<0.0001	
B-Temperature	431.22	1	431.22	31.37	<0.0001	
C-Catalyst Loading	183.62	1	183.62	13.36	0.0023	
D-Meth:Oil Ratio	2021.29	1	2021.29	147.04	<0.0001	
AB	93.41	1	93.41	6.8	0.0198	
AC	373.2	1	373.2	27.15	0.0001	
AD	380.25	1	380.25	27.66	<0.0001	
BC	98.74	1	98.74	7.18	0.0171	
BD	33.88	1	33.88	2.46	0.1373	
CD	83.1	1	83.1	6.05	0.0266	
A ²	3957.22	1	3957.22	287.87	<0.0001	
B ²	2027.09	1	2027.09	147.46	<0.0001	
C ²	976.24	1	976.24	71.02	<0.0001	
D ²	2653.37	1	2653.37	193.02	<0.0001	
Residual	206.2	15	13.75			
Lack of Fit	177.29	10	17.73	3.07	0.1139	not significant
Pure Error	28.9	5	5.78			
Cor Total	11801.71	29				

predicting biodiesel yield within the investigated experimental range.

3.3.2. Model adequacy and regression equation for biodiesel yield

The fit statistics presented in Table 4 demonstrate that the developed quadratic model adequately describes the relationship between the process variables and biodiesel yield. The high coefficient of determination ($R^2 = 0.9825$) indicates that 98.25% of the variability in biodiesel yield is explained by the model. The close agreement between the Adjusted R^2 (0.9662) and Predicted R^2 (0.9099), with a difference of less than 0.20, confirms the model's good predictive ability. In addition, the Adequate Precision value of 23.5804, which is well above the minimum acceptable value of 4, indicates an excellent signal-to-noise ratio, while the low coefficient of variation (CV = 6.06%) reflects good precision and reproducibility. Overall, these statistical parameters confirm that the model is robust and suitable for predicting biodiesel yield within the experimental design space.

The developed quadratic regression equation model for biodiesel yield, expressed in terms of the coded process variables, is given by Equation 1. The positive coefficients of the linear terms (A, B, C, and D) indicate that increasing these variables

generally enhances biodiesel yield, whereas the negative quadratic coefficients (A^2 , B^2 , C^2 , and D^2) confirm the existence of optimum operating conditions. The interaction terms further reveal synergistic and antagonistic effects among the variables, demonstrating the suitability of Response Surface Methodology (RSM) for optimizing the transesterification process. This regression model can therefore be used to predict biodiesel yield and determine the optimum process conditions.

$$\text{Biodiesel Yield} = 90.29 + 6.20A + 4.24B + 2.77C + 9.18D + 2.24B^2 + 4.83AC + 4.88AD - 2.48BC + 1.46BD - 2.27CD - 12.01A^2 - 8.59B^2 - 5.96C^2 - 9.84D^2 \quad (1)$$

Figure 4 presents the predicted versus actual biodiesel yield values for the developed RSM model. The data points are distributed closely around the 45° reference line, indicating good agreement between the experimentally determined and model-predicted biodiesel yields. The close correspondence between the predicted and actual values further demonstrates the adequacy and reliability of the developed regression model for describing and predicting biodiesel yield within the investigated experimental range.

Table 4. Statistical fit indices of the quadratic model for biodiesel yield.

R^2	0.9825
Adjusted R^2	0.9662
Predicted R^2	0.9099
Adeq Precision	23.5804
Std. Dev.	3.71
Mean	61.16
C.V. %	6.06

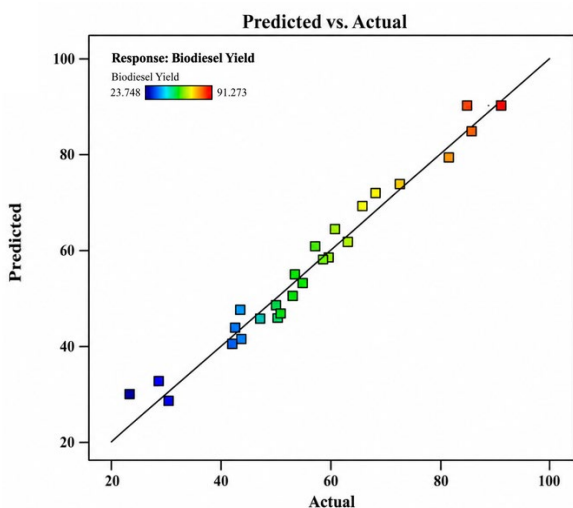


Figure 4. Predicted versus actual biodiesel yield for the developed RSM model.

3.4. Response Surface Analysis of The Effects of Process Variables on Biodiesel Yield

3.4.1. The effect of catalyst loading and temperature on biodiesel yield

Figure 5 demonstrates that biodiesel yield increased from approximately 72 wt% at 50 °C and 3.25 wt% catalyst loading to a maximum of 91.27 wt% at the optimum conditions of 60 °C and

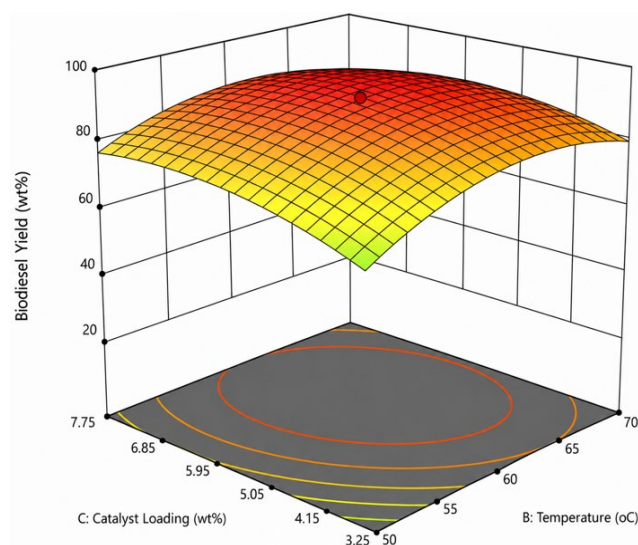


Figure 5. The response surface plot of catalyst loading and temperature on biodiesel yield.

5.5 wt% composite catalyst loading. The enhanced yield resulted from improved reaction kinetics at moderate temperatures and the increased availability of active basic CaO sites on the composite catalyst, which accelerated the transesterification reaction and promoted efficient conversion of palm kernel oil to biodiesel. The synergistic combination of eggshell- and snail shell-derived CaO contributed to higher catalytic activity and conversion efficiency than lower catalyst loadings. However, increasing the temperature to 65–70 °C or the catalyst loading beyond 6.5 wt% caused the yield to decrease slightly to approximately 82–86 wt%, mainly due to methanol evaporation, soap formation, increased slurry viscosity, and mass transfer limitations. Overall, the results confirm that the 5.5 wt% composite biomass-derived catalyst, combined with a reaction temperature of 60 °C, provided the optimum conditions for achieving the highest biodiesel yield.

3.4.2. The effect of catalyst loading and reaction time on biodiesel yield

The response surface depicted in Figure 6 demonstrates that biodiesel yield increased from approximately 60–70 wt% at low reaction time (48.75 min) and low catalyst loading (3.25 wt%) to a maximum of approximately 95–98 wt% at an intermediate reaction time of 85–90 min and a catalyst loading of 5.0–5.5 wt%. This trend indicates that the composite biomass-derived catalyst provided sufficient active basic sites at moderate loading to effectively promote the transesterification reaction, resulting in high biodiesel conversion. However, increasing the catalyst loading beyond the optimum (towards 7.75 wt%) caused the yield to decline to about 70–80 wt%, likely due to increased mixture viscosity, mass transfer limitations, and soap formation.

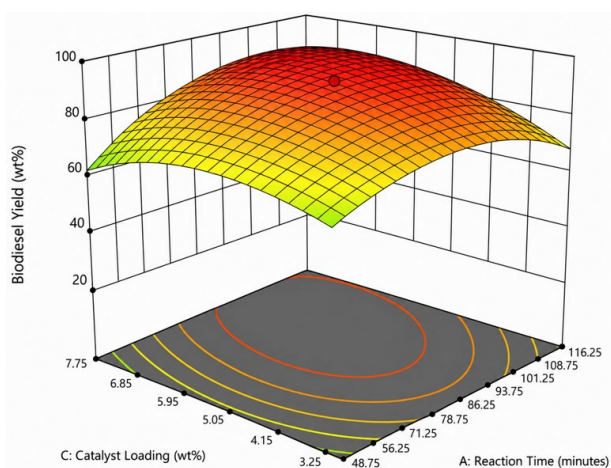


Figure 6. The response surface plot of catalyst loading and reaction time on biodiesel yield.

Similarly, extending the reaction time to 116.25 min reduced the yield to approximately 82–88 wt%, suggesting that prolonged reaction durations offered no additional catalytic benefit. The elliptical contour plot further confirms a significant quadratic interaction between reaction time and catalyst loading, highlighting that the composite catalyst achieved optimum performance at approximately 5 wt% catalyst loading, where its catalytic activity was maximized to produce biodiesel yields approaching 91.27 wt%.

3.4.3. The effect of methanol-to-oil and catalyst loading on biodiesel yield

The response surface plot (Figure 7) shows that biodiesel yield increased as catalyst loading increased from 3.25 to approximately 5.5 wt% and the methanol-to-oil ratio increased from 4.5:1 to 6:1, reaching a maximum yield of approximately 91.3 wt%. As shown in Figure 7, this improvement can be attributed to the increased availability of active catalytic sites and sufficient methanol to drive the transesterification reaction toward biodiesel formation. However, further increases in catalyst loading (above 5.5 wt%) and methanol-to-oil ratio (above 6:1) resulted in a slight reduction in yield to about 85–88 wt%, likely due to mass transfer limitations, catalyst agglomeration, and excess methanol interfering with glycerol separation.

3.4.4. The effect of methanol-to-oil and reaction time on biodiesel yield

Figure 8 illustrates the combined effect of reaction time and methanol-to-oil ratio on biodiesel yield while maintaining the composite catalyst loading at its optimum value of 5.5 wt%. The response surface exhibits a dome-shaped

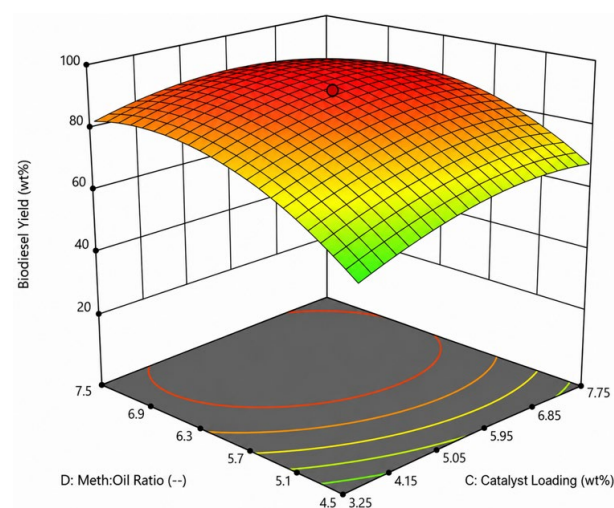


Figure 7. The response surface plot of methanol-to-oil and catalyst loading on biodiesel yield.

profile with elliptical contour lines, indicating a significant interaction between the two process variables. Biodiesel yield increased from approximately 60 wt% at 48.75 min and a 4.5:1 methanol-to-oil ratio to a maximum of 91.27 wt% at the optimum conditions of 82.5 min, 6:1 methanol-to-oil ratio, and 5.5 wt% catalyst loading.

This improvement is attributed to sufficient reaction time and adequate methanol concentration, which enhanced triglyceride conversion by providing enough active sites on the catalyst for efficient transesterification. However, further increases in reaction time (above 100 min) or methanol-to-oil ratio (above 6.5:1) caused the yield to decrease to approximately 75-82 wt%, likely due to the attainment of reaction equilibrium and increased glycerol solubility, which hinders phase separation. The plot demonstrates that the composite biomass-derived catalyst exhibited excellent catalytic activity, with the synergistic interaction of the optimized reaction conditions resulting in the highest biodiesel.

3.4.5. The effect of methanol-to-oil and temperature on biodiesel yield

Figure 9 illustrates the combined effects of reaction temperature and methanol-to-oil ratio on biodiesel yield. The yield increased from approximately 70 wt% at 50 °C and a 4.5:1 methanol-to-oil ratio to a maximum of 91.27 wt% at 60 °C and 6:1, indicating that moderate temperature and adequate methanol concentration favored ester formation. The improvement can be associated with enhanced molecular interactions and faster conversion of triglycerides, while the 5.5 wt% composite CaO catalyst provided active basic sites that promoted methanol activation and transesterification. Beyond the optimum conditions, increasing the

temperature to 65-70 °C or the methanol-to-oil ratio above 6.5:1 caused the yield to decrease to approximately 78-84 wt%. Excessive temperature may increase methanol volatilization, whereas excess methanol can increase glycerol solubility and complicate phase separation, ultimately limiting product recovery. The optimum combination of 60 °C, 6:1 methanol-to-oil ratio, 82.5 min reaction time, and 5.5 wt% catalyst loading produced the highest yield of 91.27 wt%, demonstrating that appropriate control of operating conditions is essential for maximizing biodiesel production with the biomass-derived composite catalyst.

3.4.6. The effect of temperature and reaction time on biodiesel yield

The interactive effects of reaction time (48.75-116.25 min) and temperature (50-70 °C) on biodiesel yield are presented in Figure 10. At low conditions (48.75-60 min and 50-55 °C), the yield was approximately 60-70 wt%, indicating incomplete transesterification. Increasing the reaction time to 75-95 min and temperature to 58-65 °C improved the yield to 85-92.7 wt%, due to enhanced reaction kinetics and the availability of basic CaO active sites in the snail shell-eggshell composite catalyst. The highest yield region of approximately 91.27 wt% was observed at 82-90 min and 60-63 °C, indicating favorable conditions for efficient conversion of palm kernel oil to FAME. However, further increases beyond 100 min and 65 °C resulted in a slight decline in yield to 88 wt%, likely due to methanol loss, equilibrium limitations, and side reactions. The response surface demonstrates that optimized reaction time and temperature, together with the synergistic basicity of the composite catalyst, enhanced biodiesel production under relatively mild conditions.

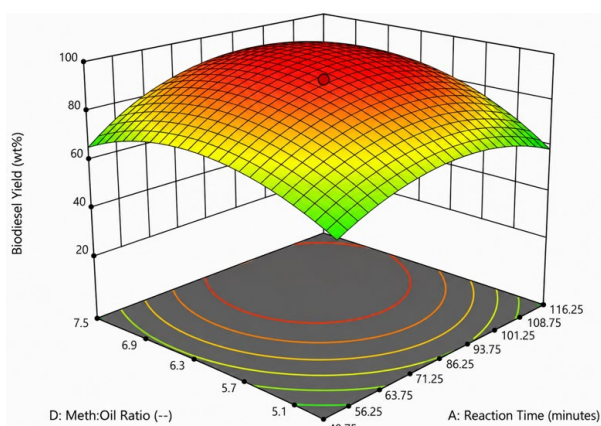


Figure 8. The response surface plot of methanol-to-oil and reaction time on biodiesel yield.

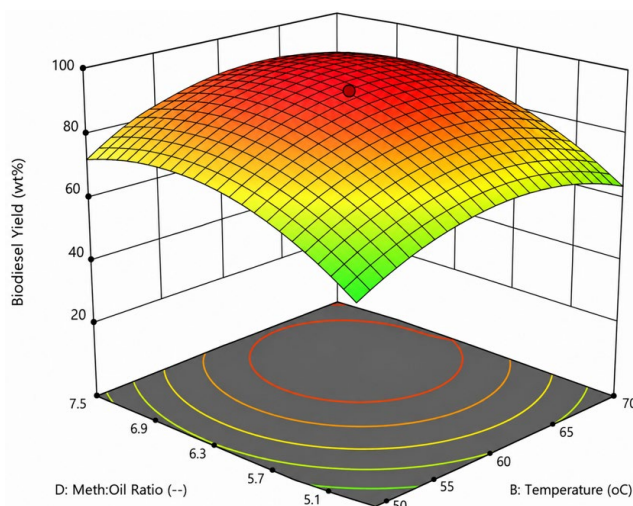


Figure 9. The response surface plot of methanol-to-oil ratio and temperature on biodiesel yield.

3.5. Comparative Evaluation of Eggshell, Snail Shell, and Composite Catalysts for Biodiesel Production

Figure 11 shows the identical reaction conditions (82.5 min, 60 °C, 5.5 wt% catalyst loading, and 6:1 methanol-to-oil ratio), the composite catalyst achieved the highest biodiesel yield of 91.273 wt%, outperforming calcined eggshell (87.0 wt%) and calcined snail shell (85.5 wt%). The higher yield is attributed to the synergistic effect of combining the two biomass-derived catalysts, which increased the availability of basic active sites (CaO), improved surface area and pore structure, and enhanced reactant adsorption and mass transfer. These improved catalytic properties promoted more efficient transesterification, resulting in superior biodiesel production compared to the individual catalysts.

Recent studies have reported biodiesel yields between 89% and 98% using modified biomass-derived CaO catalysts. For instance, previous researcher [12] reported that K-Sr-modified eggshell-derived CaO achieved a biodiesel yield of 92.5%, demonstrating that metal modification significantly enhanced catalyst basicity and transesterification efficiency. Similarly, other researcher [27] reported that calcined snail shell-derived CaO exhibited excellent catalytic activity for biodiesel production owing to its high CaO purity. Also, [28] synthesized CaO/SiO₂ composite catalysts from rice husk-derived silica and limestone at varying ratios, with the 1:3 CaO/SiO₂ ratio achieving the highest oil conversion of 60%. Furthermore, other researcher [29] demonstrated that TiO₂-modified waste eggshell-derived CaO produced 89.7% biodiesel with improved catalyst stability and reusability. Compared with these studies, the present eggshell-snail shell composite

catalyst produced a competitive biodiesel yield of 91.273 wt% under relatively mild operating conditions (82.5 min, 60 °C, 5.5 wt% catalyst loading, and a 6:1 methanol-to-oil ratio) without the need for metal impregnation or synthetic catalyst supports. These findings demonstrate that the developed composite catalyst offers a simple, low-cost, and sustainable approach for high-yield biodiesel production while simultaneously promoting the valorization of agricultural waste.

3.6. Physicochemical Properties of The Produced Biodiesel

The produced PKO biodiesel exhibited fuel properties that largely complied with the American Society for Testing Materials (ASTM) standards, indicating good fuel quality as represented in Table 6. It had a density of 0.8537 g/mL and specific gravity of 0.8474, close to the standard value (0.88). The dynamic viscosity (4.53 mPa.s) was within the ASTM limit (1.0-6.0 mPa.s), ensuring suitable flow and atomization. The flash point of 129 °C met the ASTM range (100-170 °C), indicating safe handling and storage. The biodiesel also exhibited a low moisture content (0.113%), acid value of 0.431 mg, and FFA (%) of 0.215.

Table 6. The physicochemical properties of biodiesel.

Properties Measured (Unit)	PKO Biodiesel	Standard ASTM
Density (g/mL)	0.8537	NA
Sp. Gravity	0.8474	0.88
Dyn. Viscosity (mPa.s)	4.53	1.0 – 6.0
Flash Point (°C)	129	100 – 170
Moisture Content (%)	0.113	NA
Acid value (mg KOH/g)	0.431	<0.5
FFA (%)	0.215	NA

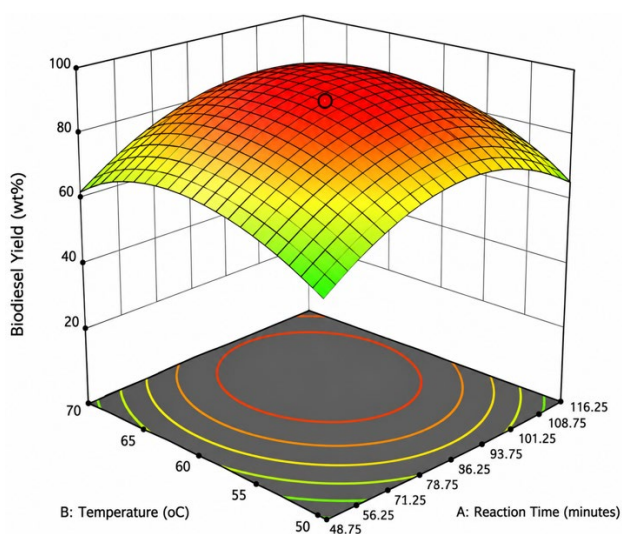


Figure 10. The response surface plot of temperature and reaction time on biodiesel yield.

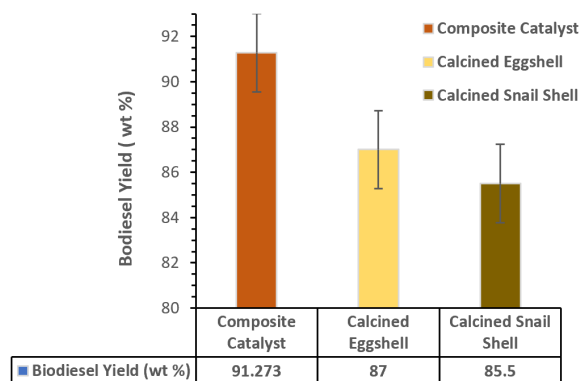


Figure 11. Comparison of biodiesel yield obtained using individual and composite catalysts at optimum conditions.

KOH/g (below the ASTM limit of 0.50 mg KOH/g), and FFA content of 0.215%, confirming efficient transesterification, good oxidative stability, and suitability for diesel engine applications.

4. Conclusion

This study established that eggshell and snail shell wastes can be effectively valorized into a composite CaO heterogeneous catalyst for the production of biodiesel from crude palm kernel oil. The combined catalyst demonstrated greater catalytic effectiveness than the individual eggshell- and snail shell-derived catalysts, confirming the advantage of their synergistic combination. Process optimization using Response Surface Methodology identified 82.5 min reaction time, 60 °C temperature, 5.5 wt% catalyst loading, and a 6:1 methanol-to-oil ratio as the most favourable conditions, resulting in a biodiesel yield of 91.273 wt%. The satisfactory fuel properties of the produced biodiesel further demonstrate the suitability of the optimized process for obtaining quality biodiesel. Beyond biodiesel production, the study provides a practical route for converting underutilized eggshell and snail shell wastes into a value-added catalyst, thereby integrating waste management with renewable fuel production. The findings highlight the potential of this approach as a simple and sustainable strategy for palm kernel oil biodiesel production, although further studies on long-term stability and process scale-up are recommended before industrial application.

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CRedit Authors Statement

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Nomenclature

A	Reaction time
ANOVA	Analysis of variance
ASTM	American society for testing and materials
B	Reaction temperature
C	Catalyst loading
CaO	Calcium oxide
CCD	Central composite design
°C	Degree celcius
D	Methanol-to-oil ratio
FAME	Fatty acid methyl ester
FFA	Free fatty acid
FTIR	Fourier transform infrared spectroscopy
Min	Minutes
NaOH	Sodium hydroxide
mPa.s	Millipascal-second
PKO	Palm kernel oil
RSM	Response surface methodology
wt %	Weight percent

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