

Integration Of CaO/K₂O Heterogeneous Catalysts with Response Surface Methodology for Efficient Biodiesel Production From Waste Cooking Oil

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Abstrak

Minyak jelantah merupakan bahan baku yang menjanjikan untuk produksi biodiesel sekaligus memberikan solusi terhadap permasalahan lingkungan. Dalam penelitian ini, katalis heterogen CaO/K₂O disiapkan dari limbah cangkang telur ayam melalui proses kalsinasi dan impregnasi KOH. Katalis tersebut digunakan dalam reaksi transesterifikasi minyak jelantah menjadi biodiesel, dengan kondisi proses yang dioptimalkan menggunakan *Response Surface Methodology* (RSM) melalui desain *Central Composite Design* (CCD). Parameter utama yang dikaji adalah jumlah katalis dan waktu reaksi. Kondisi optimum diperoleh pada penggunaan katalis sebanyak 4,5 g dan waktu reaksi 4,5 jam yang menghasilkan biodiesel sebesar 69,6%, yang mendekati nilai prediksi model sehingga menunjukkan keandalan model yang digunakan. Analisis sifat bahan bakar menunjukkan bahwa densitas, viskositas, dan kadar air telah memenuhi standar biodiesel, meskipun nilai angka asam sedikit lebih tinggi akibat adanya sisa asam lemak bebas. Hasil penelitian ini menunjukkan potensi katalis yang berasal dari limbah biomaterial untuk produksi biodiesel yang berkelanjutan serta menegaskan bahwa optimasi proses merupakan pendekatan yang efektif untuk meningkatkan rendemen dan kualitas biodiesel.

Kata kunci: biodiesel, katalis CaO/K₂O, katalis berbasis cangkang telur, minyak jelantah, response surface methodology (RSM)

Abstrak

Waste cooking oil (WCO) is a promising low-cost feedstock for biodiesel production; however, its high impurity content and variable composition often limit conversion efficiency, particularly in single-step heterogeneous catalysis. This study addresses this challenge by developing a CaO/K₂O heterogeneous catalyst derived from waste chicken eggshells and optimizing the transesterification process using Response Surface Methodology (RSM). Unlike previous studies primarily focused on yield enhancement, this work integrates statistical optimization with GC-MS-based analysis to elucidate catalyst-dependent selectivity in fatty acid methyl ester (FAME) distribution. The results show that reaction time is the dominant factor influencing biodiesel yield, while catalyst loading has a comparatively minor effect within the investigated range. Under optimal conditions (4.5 g catalyst, 4.5 h), a biodiesel yield of 69.6% was achieved, which is moderate compared to reported values (>85%) but acceptable considering the use of untreated WCO and a low-cost waste-derived catalyst. Fuel properties generally met international standards, although the acid value slightly exceeded the limit due to residual free fatty acids. This study highlights the trade-off between process simplicity and conversion efficiency and provides new insights into structure-activity-selectivity relationships in CaO/K₂O-based systems, offering a practical pathway for sustainable biodiesel production from low-quality feedstocks.

Kata kunci: waste cooking oil, biodiesel, CaO/K₂O catalyst, eggshell-derived catalyst, response surface methodology

1. PENDAHULUAN

The accelerating global energy transition is fundamentally reshaping fuel production and consumption dynamics. Increasing concerns about fossil fuel depletion, climate change, and environmental degradation have catalyzed an

urgent emphasis on developing renewable and sustainable fuel alternatives. Among these, biodiesel, especially when derived from renewable lipid-based feedstocks like waste cooking oil, stands out as a promising substitute for conventional diesel. This is due to its notable

advantages, including biodegradability, carbon neutrality, compatibility with existing diesel engines, and potential reductions in greenhouse gas emissions (Susvira et al., 2022; Lamichhane et al., 2020, Al-Mawaali et al., 2023). As countries worldwide announce net-zero emission goals and enforce sustainable energy policies, biodiesel is increasingly recognized as a pivotal element of the global clean energy portfolio (Lamichhane et al., 2020; Pattiasina et al., 2023).

The quest for alternative biodiesel feedstocks highlights waste cooking oil's substantial potential. Global consumption of vegetable oils reaches hundreds of millions of tons annually, with a significant proportion converted into waste oil (Neupane, 2022). Improper disposal practices, such as discarding this waste into sewage systems or landfills, pose severe environmental challenges, while repeated use in food preparation raises public health risks (Andalia et al., 2019). By converting this abundant waste into biodiesel, these ecological challenges are addressed, exemplifying a circular economy—transforming a problematic waste stream into a valuable renewable fuel source (Aboelazayem et al., 2018). Notably, Indonesia's situation exemplifies the global issue, where it represents one of the largest markets for cooking oil, resulting in substantial quantities of waste cooking oil annually, indicating both significant disposal challenges and significant potential for utilizing this waste as biodiesel feedstock (Shannan Al-Khalasi et al., 2024).

The efficiency of biodiesel production is heavily influenced by the choice of catalyst and reaction conditions. Traditional homogeneous alkaline catalysts have proven effective; however, they offer challenges such as soap formation and equipment corrosion, complicating product separation and limiting scalability (Susvira et al., 2022). In contrast, heterogeneous catalysts, exemplified by calcium oxide derived from waste sources like eggshells, provide advantages including reusability and reduced environmental impact (Rahman and Rodiah, 2020). Although unmodified calcium oxide suffers from deactivation due to moisture and carbon dioxide exposure, its catalytic activity and durability can be significantly improved by modifying it with potassium-based promoters (Rahman and Rodiah, 2020, Hsiao et al., 2018).

Despite the extensive use of CaO/K₂O-based catalysts, eggshell-derived materials, and Response Surface Methodology (RSM) in biodiesel research, this study offers several distinct contributions that go beyond incremental development. First, it proposes an integrated dual-waste valorization approach by simultaneously utilizing waste cooking oil as the feedstock and chicken eggshells as the catalyst precursor, thereby strengthening the circular economy framework. Second, this work provides a detailed correlation between catalyst loading and fatty acid methyl ester (FAME) distribution through GC–MS analysis, revealing catalyst-dependent selectivity shifts that are rarely discussed in previous studies.

Third, the integration of statistical optimization with mechanistic interpretation enables the identification of reaction time as the dominant factor controlling biodiesel yield, while catalyst loading plays a comparatively minor role within the studied range. Furthermore, the study highlights the functional role of a multiphase CaO–K₂O–K₂CO₃ catalytic system in enhancing basicity and improving tolerance toward free fatty acids. These combined aspects provide a more comprehensive understanding of structure–activity–selectivity relationships and offer new insights for the efficient utilization of low-quality feedstocks in biodiesel production.

Optimizing various process variables is critical for maximizing biodiesel yield while minimizing energy inputs and resource consumption (Al-Mawaali et al., 2023). Conventional experimental designs often fall short when addressing multiple interacting parameters, highlighting the utility of statistical and computational methods. Response Surface Methodology (RSM) presents a robust framework for modeling complex reaction systems, enabling the identification of key interactions and optimum processing conditions, ultimately enhancing biodiesel production efficiency and industrial viability (Maqsood and Alsaady, 2022, Abdel-Hamid et al., 2023).

The present study introduces an innovative dual-waste valorization approach, integrating waste cooking oil as the lipid feedstock and eggshells as a precursor for a potassium-modified calcium oxide catalyst. This strategy addresses two global waste management challenges while simultaneously generating a renewable fuel that aligns with sustainable energy goals (Kanjiya et al., 2019, Reşitoğlu and

Keskin, 2018). Furthermore, process optimization via RSM with Central Composite Design facilitates the efficient determination of optimal catalyst loading and reaction durations, ensuring high biodiesel yield and fuel quality with minimal experimental trials (Maqsood and Alsaady, 2022). This approach, focusing on the dual challenges of waste-to-energy conversion and catalyst modification, represents a significant intersection of renewable energy innovation, circular economy applications, and sustainable global practices.

2. MATERIAL AND METHODS

2.1. Materials

Waste cooking oil (WCO) was collected from local food vendors. Chicken eggshells were used as the precursor for calcium oxide (CaO) catalyst. Analytical-grade potassium hydroxide (KOH, 11% v/v), methanol (99%), ethanol (95%), potassium hydroxide solution (0.1 N), and distilled water were used for all experiments.

2.2 Catalyst Preparation

Eggshells were thoroughly washed, oven-dried at 110 °C for 4 h, ground, and sieved to 100 mesh. The powder was calcined at 900 °C for 3 h to obtain CaO. To enhance activity, CaO was impregnated with KOH (11% v/v) by stirring at 85 °C for 3 h, followed by drying at 110 °C for 12 h and calcination at 300 °C for 3 h. The resulting catalyst was denoted as KOH-impregnated CaO (CaO/K₂O).

2.3 Transesterification Process

Biodiesel was synthesized via transesterification of WCO with methanol at 65 °C, using a methanol-to-oil molar ratio of 12:1. Catalyst loading (1.5, 3.0, and 4.5 wt% relative to oil mass) and reaction time (1.5, 3.0, and 4.5 h) were investigated as the main independent variables. After reaction, the mixture was allowed to settle in a separating funnel to remove glycerol. Excess methanol and water were removed by evaporation at 105 °C under vacuum. All transesterification reactions were conducted under controlled conditions to ensure reproducibility. The reaction temperature was maintained at 65 ± 2 °C using a thermostatically controlled hot plate equipped with a magnetic stirrer. The stirring speed was kept constant at 600 rpm to minimize mass transfer limitations and ensure uniform mixing of reactants. A reflux condenser was employed to prevent methanol loss during the reaction. After completion, the

reaction mixture was allowed to settle for 12 h to ensure complete phase separation between biodiesel and glycerol. All experiments were performed in duplicate, and the average values are reported.

2.4 Experimental Design

Response Surface Methodology (RSM) with Central Composite Design (CCD) was applied to optimize biodiesel yield and quality parameters. The independent variables were catalyst loading and reaction time, while the response variables included biodiesel yield and physicochemical properties. The selection of catalyst loading and reaction time as the primary independent variables was based on their fundamental roles in heterogeneous transesterification systems.

Catalyst loading directly determines the availability of active sites for methanol activation and triglyceride conversion, while reaction time governs the extent to which the reaction approaches equilibrium. These parameters are widely recognized as critical factors influencing biodiesel yield and process efficiency. The selected ranges (1.5–4.5 g for catalyst loading and 1.5–4.5 h for reaction time) were determined based on preliminary experiments and literature reports, ensuring sufficient variation to capture both low and high conversion regimes while maintaining practical feasibility for laboratory-scale operation.

2.5 Biodiesel Characterization

The biodiesel produced in this study was evaluated for both yield and physicochemical properties in accordance with internationally recognized fuel standards (ASTM D6751 and EN 14214). The yield was calculated as the mass ratio of biodiesel to the initial oil used in the reaction. The density of the biodiesel was determined using a pycnometer, while its kinematic viscosity was measured with an Ostwald viscometer. The acid value was obtained through titration against a standardized potassium hydroxide solution (0.1 N), and the moisture content was determined by oven-drying at 105 °C until a constant weight was achieved. Furthermore, the chemical composition of the fatty acid methyl esters (FAMES) in the biodiesel was analyzed using gas chromatography–mass spectrometry (GC–MS) to verify the conversion efficiency of triglycerides and to identify the dominant methyl esters present. In addition to fuel property evaluation, the crystalline structure

of the catalyst before and after modification was characterized by X-ray diffraction (XRD) to confirm phase composition and structural stability.

Catalyst characterization in this study was primarily conducted using X-ray diffraction (XRD) to identify the crystalline phases present after synthesis and modification. While XRD provides valuable information on phase composition, it does not fully capture surface properties such as surface area, pore structure, and basicity, which are critical for catalytic performance. The absence of complementary techniques such as Brunauer–Emmett–Teller (BET) surface area analysis and CO₂ temperature-programmed desorption (CO₂-TPD) represents a limitation of this study. Future work will focus on incorporating these analyses to establish a more comprehensive correlation between catalyst physicochemical properties and catalytic activity.

Table 1. Central Composite Design (CCD) matrix for biodiesel yield optimization

Run	Coded Level A (Catalyst, g)	Coded Level B (Time, h)	Actual Catalyst (g)	Actual Time (h)	Biodiesel Yield (%)
1	0	0	3.0	3.0	66.1
2	+1	+1	4.5	4.5	69.4
3	0	+1	3.0	4.5	70.4
4	0	0	3.0	3.0	66.9
5	+1	-1	4.5	1.5	64.8
6	-1	+1	1.5	4.5	71.2
7	0	0	3.0	3.0	65.8
8	-1	-1	1.5	1.5	63.6
9	0	0	3.0	3.0	66.6
10	0	-1	3.0	1.5	64.2
11	0	0	3.0	3.0	65.5
12	0	0	3.0	3.0	67.3
13	+1	0	4.5	3.0	68.1

3. RESULT AND DISCUSSION

3.1 Synthesis of CaO/K₂O Catalyst

The synthesis of the CaO/K₂O catalyst was initiated using chicken eggshells, a waste material primarily composed of calcium carbonate (CaCO₃), which offers a sustainable and cost-effective precursor for catalyst production. Eggshells were first washed thoroughly to remove organic residues and then oven-dried to eliminate surface moisture. Subsequently, they were subjected to calcination in a muffle furnace at 900 °C for 3 h. This high-temperature treatment induced the

decomposition of CaCO₃ into calcium oxide (CaO) while releasing carbon dioxide (CO₂). The process not only transforms the crystalline structure but also generates a porous morphology that enhances the accessibility of active sites. The overall reaction is represented as:



The use of calcined calcium oxide (CaO) as a catalyst presents certain inherent limitations, particularly its tendency towards hygroscopicity and susceptibility to carbonation when exposed to ambient conditions. These characteristics can hinder the catalytic effectiveness of CaO in various applications, particularly in biodiesel production via transesterification processes. To mitigate these issues and simultaneously improve the catalytic performance of CaO, impregnation with potassium hydroxide (KOH) has been employed. This technique introduces potassium ions (K⁺) into the porous structure of the CaO matrix, thereby enhancing the catalytic properties of CaO through an increase in surface

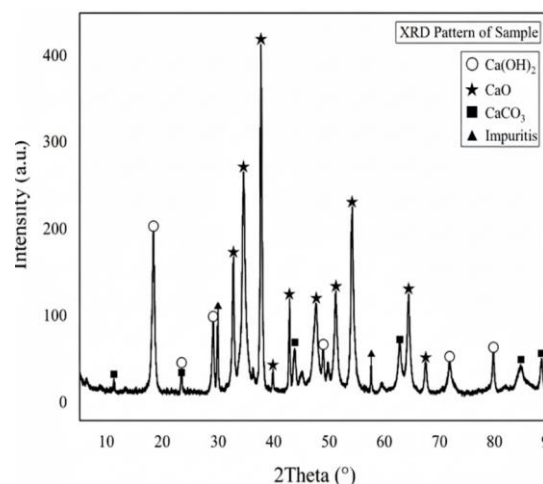


Figure 1. X-ray diffraction (XRD) pattern of CaO/K₂O catalyst after calcination. The diffraction peaks correspond to Ca(OH)₂ (○), CaO (★), CaCO₃ (■), and impurity phases (▲).

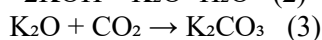
basicity and the creation of additional active sites.

The KOH treatment notably improves the surface characteristics of CaO, allowing it to maintain higher catalytic activity by minimizing the likelihood of deactivation during transesterification reactions. Research indicates that the addition of KOH can significantly

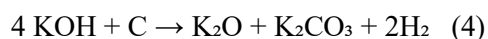
increase the surface area and basicity of the catalyst, which are critical parameters influencing the efficacy of transesterification reactions (Kusmiyati et al., 2019, Hossain et al., 2021). For instance, KOH-impregnated catalysts have shown substantial enhancements in biodiesel yield due to a more effective interaction with triglycerides, which is essential for the conversion process. Furthermore, the modification with KOH also plays a crucial role in reducing the formation of carbonates that may otherwise lead to catalyst blocking and performance decline (Praikaew et al., 2022, Papargyriou et al., 2019).

Synthesis methods for KOH-impregnated CaO have demonstrated that various concentrations of KOH can impact the catalytic performance, with optimized ratios leading to better surface characteristics and catalytic efficiency. Treatment with KOH aids in overcoming the shortcomings associated with pure CaO, enabling catalysts that can withstand the rigors of biodiesel production processes (Kusmiyati et al., 2019, Hossain et al., 2021, Maroa and Inambao, 2021). Therefore, the impregnation of CaO with KOH presents a promising approach to elevate the catalytic efficiency and longevity of this material in biodiesel production applications.

Following impregnation, the composite material was subjected to a secondary calcination step at 500 °C for 5 h. This treatment facilitated the decomposition of KOH into potassium oxide (K₂O), water vapor, and potassium carbonate (K₂CO₃) according to the following reactions:



At higher temperatures (around 427 °C), molten KOH can also react with residual carbonaceous species, producing additional K₂O and K₂CO₃ along with hydrogen gas:



The investigation of catalysts for biodiesel production from waste cooking oil (WCO) has demonstrated the efficacy of a multiphase catalyst system primarily composed of CaO, K₂O, and K₂CO₃. This synergistic combination plays a crucial role in enhancing catalytic activity and stability. The presence of CaO in the catalyst framework provides robust Lewis basic

sites that facilitate the activation of methanol molecules during the transesterification reaction (Meka and Asere, 2022). Concurrently, K₂O contributes substantive electron-donating properties, which further improve the catalytic efficiency (Kanjiya et al., 2019). The K₂CO₃ component aids in maintaining catalytic stability by acting as a buffer against carbon dioxide and moisture, ultimately leading to prolonged durability of the catalyst under operational conditions (Aboelazayem et al., 2018).

Moreover, the integration of potassium into the CaO framework appears to modify the surface architecture and pore distribution, optimizing the dispersion of active sites while enhancing resistance to leaching (Susvira et al., 2022). These attributes are particularly advantageous for processing low-quality feedstocks like waste cooking oil, which typically presents elevated levels of free fatty acids (FFA) and water content that can interfere with biodiesel yield by forming soaps through reactions with CaO (Nnamani et al., 2020).

However, the CaO/K₂O composite catalyst exhibits superior tolerance to these impurities, resulting in a more efficient transesterification process that converts triglycerides into methyl esters whilst retaining product selectivity (Abdel-Hamid et al., 2023). The production of biodiesel from WCO employing the CaO/K₂O composite catalyst not only illustrates an innovative approach to resource utilization but also emphasizes sustainability through the use of waste materials such as eggshells (Rahman and Rodiah, 2020). As such, the creation of this multiphase catalyst adeptly addresses the limitations presented by single-component CaO catalysts, offering a feasible and effective solution for enhancing biodiesel production efficiency while ensuring environmental benefits through improved reusability and stability (Al Doorri et al., 2021).

Table 2. Physicochemical properties of waste cooking oil (WCO) feedstock.

Parameter	Unit
Kinematic viscosity (40 °C)	15.59 cSt
Density (40 °C)	884.6 kg/m ³
Average molecular weight	833.8 g/mol
Color	Light brown
Free fatty acid (FFA) content	1.02 %

3.2 XRD Analysis of CaO Catalyst

The crystalline structure of the synthesized CaO/K₂O catalyst was thoroughly investigated using X-ray diffraction (XRD), affirming that calcium hydroxide Ca(OH)₂ was a significant crystalline phase, constituting approximately 64.1% of the total composition. This observation is indicative of incomplete decomposition of CaCO₃ during calcination, suggesting that rehydration occurred upon exposure to atmospheric moisture. Such behavior is typical for CaO-based catalysts, which are known for their hygroscopic nature, leading to the regeneration of Ca(OH)₂ or even back to CaCO₃ in ambient conditions, thus diminishing the density of strong basic sites that are critical for effective catalytic activity (Halilović et al., 2024).

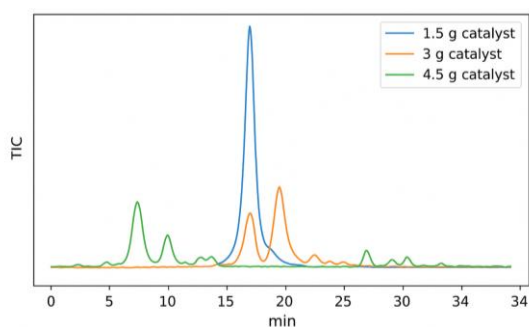


Figure 2. Total Ion Chromatograms (TIC) of FAMEs Obtained at Different Catalyst Loadings (1.5 g, 3 g, and 4.5 g)

The formation of CaO from eggshell-derived CaCO₃ was confirmed by the presence of characteristic CaO peaks in the XRD pattern, with a dominant reflection at $2\theta \approx 37.47^\circ$,

purity (>80%), the lower CaO fraction in this work may contribute to the moderate biodiesel yield obtained.

Nevertheless, the coexistence of CaO and Ca(OH)₂ may provide a balance between catalytic activity and tolerance toward free fatty acids, which is advantageous for processing waste cooking oil. This highlights that catalyst performance in this study is governed not only by phase composition but also by its adaptability to low-quality feedstocks (Elfina et al., 2024). The simultaneous existence of CaO and Ca(OH)₂ implies a multiphase system, wherein CaO can facilitate high catalytic conversion through its strong basicity, while the presence of Ca(OH)₂ may also extend the catalyst's tolerance to free fatty acids, which traditionally catalyze catalyst deactivation (Widiarti et al., 2018).

In addition, the XRD diffractogram revealed minor peaks linked to unidentified impurities, potentially originating from incomplete decomposition, secondary reactions during KOH impregnation, or carbonation occurring during the cooling and handling process. While these impurities accounted for relatively low concentrations, they may still influence catalytic performance by altering surface morphology or obstructing active sites (Moradi et al., 2015).

The dominance of Ca(OH)₂ observed in the XRD pattern clearly indicates that partial rehydration of CaO occurred during post-calcination handling and exposure to ambient moisture. This transformation has important implications for catalytic performance. While

Table 3. Comparison of biodiesel properties with international

Parameter	Unit	Produced Biodiesel	ASTM D6751 Specification	EN 14214 Specification
Yield	%	71.2	–	–
Kinematic viscosity (40 °C)	cSt	5.98	1.9 – 6.0	3.5 – 5.0
Density (40 °C)	kg/m ³	860.45	– (not specified)	860 – 900
Moisture content	%	0.039	Max. 0.05	Max. 0.05
Acid value	mg KOH/g	1.122	Max. 0.50	Max. 0.50

indicating successful calcination. However, the significant presence of Ca(OH)₂ (~64.1%) suggests partial rehydration of CaO during post-calcination handling. This phase transformation is critical, as it reduces the density of strong basic sites typically associated with CaO. Compared to previous studies reporting higher CaO phase

CaO provides strong Lewis basic sites that are highly active for transesterification, the formation of Ca(OH)₂ may reduce the overall basic strength and consequently lower catalytic efficiency. However, this effect is not entirely detrimental. The presence of Ca(OH)₂ can

enhance the catalyst’s tolerance toward free fatty acids by moderating excessive basicity, which may help suppress soap formation under certain conditions. Therefore, the coexistence of CaO and Ca(OH)₂ results in a trade-off between catalytic activity and stability, forming a multiphase system that may still perform effectively for low-quality feedstocks such as waste cooking oil.

Table 4. Relative Composition of Major Fatty Acid Methyl Esters (FAMEs) Identified in GC–MS Analysis of Samples with Different Catalyst Loadings

Compound	Composition (%Area)		
	1.5 g catalyst	3 g catalyst	4.5 g catalyst
Methyl laurate	0.10	0.44	0.33
Methyl myristate	0.83	2.00	1.71
Methyl pentadecanoate	—	0.17	0.08
Methyl palmitoleate	0.72	1.29	0.34
Methyl palmitate	33.18	34.60	33.73
Methyl oleate	48.19	33.47	33.78
Methyl oleate isomers	—	12.98	13.72
Methyl stearate	5.91	9.92	10.65
Ethyl oleate	1.03	—	—
Others (minor peaks)	~10.04	~5.13	~5.66

Nevertheless, it is important to note that a more comprehensive understanding of catalyst performance requires additional characterization, particularly in terms of surface area, pore structure, and basicity. Techniques such as Brunauer–Emmett–Teller (BET) analysis and CO₂ temperature-programmed desorption (CO₂-TPD) would provide valuable insights into the distribution and strength of active sites. The absence of these analyses represents a limitation of the present study and should be addressed in future work to establish a more direct structure–activity relationship.

Table 5. Sequential model sum of squares for biodiesel yield optimization using RSM.

Source	Sum of Squares	df	Mean Square	F-value	p-value	Remarks
Mean vs Total	58,209.69	1	58,209.69	—	—	—
Linear vs Mean	57.09	2	28.55	35.76	< 0.0001	Suggested
2FI vs Linear	2.25	1	2.25	3.53	0.0929	—

Source	Sum of Squares	df	Mean Square	F-value	p-value	Remarks
Quadratic vs 2FI	1.41	2	0.7043	1.14	0.3728	—
Cubic vs Quadratic	2.81	2	1.40	4.62	0.0730	Aliased
Residual	1.52	5	0.3037	—	—	—
Total	58,274.77	13	4,482.67	—	—	—

From a catalytic perspective, the presence of Ca(OH)₂ in CaO/K₂O systems presents both challenges and opportunities. While excessive hydroxide formation can hinder the availability of active CaO sites, reducing catalyst efficiency, strategic incorporation of K₂O species through KOH impregnation can mitigate this limitation. K₂O and K₂CO₃, formed from KOH thermal decomposition, interact synergistically with CaO, potentially leading to an increase in available basic sites, which enhances overall catalytic robustness. As stated in the literature, alkaline earth metal oxides are shown to promote better phase interactions, therefore increasing active sites for chemical reactions (Lakhani et al., 2024).

This multiphase catalyst combines the strong basicity of CaO with enhanced catalytic activity from K₂O, offering stabilizing effects through carbonate or hydroxide species. This hybrid system is particularly well-suited for transesterification processes essential for converting feedstocks like waste cooking oil into biodiesel (Luo et al., 2021). Furthermore, characterization techniques, such as X-ray diffraction (XRD), confirm that these catalysts consist of Ca(OH)₂ along with active phases of CaO, which are critical for ensuring desired catalytic effectiveness (Taylor et al., 2020). Despite limitations from incomplete calcination and subsequent hydroxylation, the presence of potassium species can help counterbalance these issues by providing additional active sites, thereby improving catalyst stability (Xiao et al., 2023).

The careful balance of these catalytic phases underscores the potential of CaO/K₂O catalysts as efficient, low-cost, and sustainable alternatives for biodiesel production. This potential relies on the optimization of synthesis parameters to achieve controlled phase composition while minimizing excessive hydroxylation during catalyst preparation (Zhang et al., 2022). Such optimizations could significantly enhance the stability and longevity of these catalysts in practical applications,

reaffirming their viability for large-scale biodiesel production (Yu et al., 2023).

Table 6. Sequential model sum of squares for biodiesel yield response

Source	Sum of Squares	df	Mean Square	F-value	p-value	Remarks
Linear	6.53	6	1.09	3.00	0.1536	Suggested
2FI	4.28	5	0.8563	2.36	0.2130	–
Quadratic	2.87	3	0.9576	2.64	0.1860	–
Cubic	0.0663	1	0.0663	0.1826	0.6912	Aliased
Pure Error	1.45	4	0.3630	–	–	–

3.3 Physicochemical Properties of Waste Cooking Oil and Its Biodiesel Product

Waste cooking oil was subjected to preliminary pretreatment by filtration to remove suspended particulates and ensure a cleaner feedstock for subsequent catalytic conversion. Comprehensive characterization was then carried out to assess its suitability as a biodiesel precursor and to establish a baseline for process optimization. The characterization focused on kinematic viscosity, density, molecular weight, color, and free fatty acid (FFA) content, which collectively determine both the reactivity of the oil during transesterification and the quality of the final biodiesel product.

The kinematic viscosity of the feedstock at 40 °C was 15.59 cSt, substantially higher than the standard limits for biodiesel fuels. Such elevated viscosity is a direct consequence of thermal and oxidative polymerization of triglycerides and the accumulation of degradation products from repeated frying. High viscosity not only hinders efficient atomization in combustion engines but also signals the necessity of chemical modification through transesterification to break down larger triglyceride molecules into lower-molecular-weight methyl esters. This reinforces the critical role of catalytic transformation in improving the physicochemical properties of degraded oils. The waste cooking oil exhibited a kinematic viscosity of 15.59 cSt and an FFA content of 1.02%, values comparable to those reported for used frying oils (typically 10–20 cSt and 0.5–2.5% FFA).

Table 7. Model summary statistics for biodiesel yield response

Source	Std. Dev.	R ²	Adjusted R ²	Predicted R ²	PRESS	Remarks
Linear	7.68	0.1375	-0.0350	-0.8573	1270.68	–
2FI	7.80	0.1995	-0.0674	-3.0627	2779.57	–
Quadratic	6.92	0.5097	0.1594	-7.0767	5525.80	Suggested

Source	Std. Dev.	R ²	Adjusted R ²	Predicted R ²	PRESS	Remarks
Cubic	4.03	0.8811	0.7146	-2.3292	2277.69	Aliased

Following transesterification, the viscosity decreased to 5.98 cSt, falling within ASTM limits but slightly exceeding the stricter EN 14214 range. The density (860.45 kg/m³) and moisture content (0.039%) met international standards, indicating effective conversion and purification. However, the acid value (1.122 mg KOH/g) exceeded the standard limit (0.5 mg KOH/g), suggesting incomplete FFA conversion. Compared to studies using pretreated WCO or homogeneous catalysts, which often report acid values below 0.5 mg KOH/g, the higher value observed here reflects the limitations of single-step heterogeneous catalysis. Despite this, the overall fuel properties remain within an acceptable range for practical applications. The relatively narrow variation in replicate runs (<2%) indicates good experimental consistency, although further statistical analysis would strengthen the reliability of the results.

Table 8. Analysis of variance (ANOVA) for biodiesel yield model

Source	Sum of Squares	df	Mean Square	F-value	p-value	Remarks
Model	57.09	2	28.55	35.76	< 0.0001	Significant
A – Catalyst loading (g)	0.667	1	0.667	0.835	0.3823	Not significant
B – Reaction time (h)	56.43	1	56.43	70.68	< 0.0001	Significant
Residual	7.98	10	0.798			
Lack of Fit	6.53	6	1.09	3.00	0.1536	Not significant
Pure Error	1.45	4	0.363			
Cor Total	65.08	12				

The most significant parameter for process feasibility, however, was the FFA content, measured at 1.02%. This level is well below the critical 2% threshold above which a pre-esterification step is typically required. Consequently, the waste cooking oil in this study can be directly processed via a single-step base-catalyzed transesterification, simplifying the reaction pathway, reducing energy input, and lowering overall production costs.

From a process engineering perspective, this represents a major advantage for scaling up biodiesel production, particularly in decentralized or resource-limited settings where

multi-step pretreatments may be impractical. Taken together, these findings confirm that although waste cooking oil exhibits signs of significant chemical degradation during its prior use, its fundamental properties remain within a range that supports efficient conversion into biodiesel. This underscores the dual benefit of utilizing waste oils: mitigating environmental challenges associated with improper disposal and providing a low-cost, sustainable, and globally abundant feedstock for renewable fuel production.

The acid value of the produced biodiesel slightly exceeded the standard limits specified by ASTM D6751 and EN 14214, indicating the presence of residual free fatty acids (FFA) that were not fully converted during the transesterification process. This limitation is primarily attributed to the use of untreated waste cooking oil and the application of a single-step base-catalyzed reaction, which is less effective in handling feedstocks with appreciable FFA content.

To improve biodiesel quality, several strategies can be considered. One of the most widely adopted approaches is the implementation of an acid-catalyzed pre-esterification step prior to transesterification, which can effectively reduce FFA levels and prevent soap formation. Alternatively, the use of bifunctional catalysts possessing both acidic and basic active sites offers a promising route for simultaneous esterification and transesterification in a single process. In addition, further optimization of process parameters, such as increasing the methanol-to-oil ratio or improving catalyst dispersion, may enhance FFA conversion and reduce the final acid value.

3.4 GC–MS Elucidation of Catalyst-Dependent FAME Distribution in Transesterification Reactions

The influence of catalyst loading on the transesterification process was systematically evaluated by combining GC–MS compositional analysis with comparative chromatographic profiles. The results demonstrate a clear relationship between catalyst dosage and the distribution of fatty acid methyl esters (FAMES), with notable implications for reaction

selectivity, pathway competition, and biodiesel quality.

GC–MS analysis revealed that methyl oleate and methyl palmitate were the dominant FAMES across all catalyst loadings, together accounting for more than 65% of the total composition. At low catalyst loading (1.5 g), methyl oleate reached 48.19%, indicating high selectivity toward unsaturated esters. Increasing catalyst loading led to a reduction in methyl oleate content and an increase in saturated FAMES such as methyl stearate, suggesting the occurrence of secondary reactions including isomerization and partial hydrogenation. These compositional changes have direct implications for fuel properties. Higher unsaturated FAME content (e.g., methyl oleate) is generally associated with improved cold-flow properties but reduced oxidative stability, whereas increased saturated FAMES enhance oxidation resistance at the expense of flow behavior. The observed shift toward a more saturated profile at higher catalyst loadings may therefore contribute to improved stability but could negatively affect low-temperature performance. This highlights the importance of optimizing catalyst dosage not only for yield but also for fuel quality.

Collectively, these findings underscore the critical importance of optimizing catalyst dosage. While increasing catalyst concentration improves conversion efficiency, it also shifts the selectivity away from unsaturated esters toward a more heterogeneous mixture enriched in saturated and isomerized products. Such compositional changes may adversely affect biodiesel properties, particularly oxidative stability and low-temperature performance. Thus, maintaining a moderate catalyst loading (1.5–3 g in this system) appears optimal, achieving both high conversion and selectivity toward desirable FAMES. These results align with prior literature emphasizing that excessive catalyst not only fails to improve overall yield but also promotes unwanted reactions, ultimately compromising biodiesel quality and stability.

3.5 Optimization of Reaction Time and Catalyst Loading Using RSM

The optimization of biodiesel production parameters was carried out using Response Surface Methodology (RSM) with a Central Composite Design (CCD) framework. In this study, catalyst loading and reaction time were

selected as the independent variables, while biodiesel yield was considered the response variable. The primary objective was to systematically investigate the individual and interactive effects of these parameters on biodiesel yield and to determine the optimal operating conditions that maximize production efficiency.

The RSM analysis indicates that the linear model is the most appropriate representation of the system, as supported by its statistical significance ($p < 0.05$) and insignificant lack-of-fit. Although higher-order models (quadratic and cubic) showed improved R^2 values, they were either statistically insignificant or aliased, indicating overfitting and lack of reliability. Therefore, the linear model was selected based on the principle of parsimony. It is important to note that while the model is statistically significant, the relatively moderate R^2 value suggests that only part of the variability in biodiesel yield is explained by the selected variables. This indicates the potential influence of additional factors such as mass transfer limitations, catalyst heterogeneity, or feedstock variability. Consequently, the model is suitable for identifying general trends and dominant factors—particularly the strong influence of reaction time—but its predictive capability should be interpreted with caution.

The lack-of-fit test was employed to evaluate the adequacy of the regression model in describing the experimental data. This statistical tool essentially measures the deviation between the fitted model and the actual experimental observations that cannot be explained by random error. In other words, it determines whether the selected model sufficiently captures the underlying relationship between the independent variables and the response, or whether a higher-order model may be required. As summarized in Table 6, the analysis revealed that the linear model demonstrated an insignificant lack of fit, indicating that the model provides an appropriate representation of the data. A larger F-value corresponds to a smaller p-value, both of which are used as decision criteria in this test. In this context, the insignificant lack of fit confirms that the discrepancy between the predicted and experimental values is within the range of experimental error, rather than arising from model inadequacy. The model recommended by the Design Expert software was the linear model, which yielded the smallest lack-of-fit value with statistical insignificance. This finding validates

the suitability of the linear regression equation for describing the effect of catalyst loading and reaction time on biodiesel yield. The insignificance of the lack-of-fit test also implies that introducing more complex polynomial terms would not substantially improve the model's predictive power, thereby confirming the efficiency and simplicity of the linear approach.

From a methodological standpoint, the acceptance of the linear model is advantageous because it minimizes overfitting, ensures ease of interpretation, and provides reliable predictive capability within the studied experimental range. This result reinforces the earlier conclusion from the Sequential Model Sum of Squares analysis, where the linear model was also identified as the most appropriate. Collectively, these statistical validations strengthen the confidence in using the linear model for further response optimization and process prediction.

The model summary statistics provide further validation of the most appropriate regression model by evaluating prediction accuracy and the potential for overfitting. One of the key parameters considered in this analysis is the Predicted Residual Error Sum of Squares (PRESS), which quantifies the predictive capability of the model. In general, a smaller PRESS value indicates that the model is able to predict experimental responses with higher accuracy, whereas larger PRESS values suggest weaker predictive reliability. As shown in Table 7, the cubic model exhibited the lowest PRESS value of 9.82, suggesting high predictive accuracy. However, despite its numerical advantage, the cubic model was marked as *aliased*. Aliasing occurs when higher-order terms cannot be uniquely distinguished from one another due to the limitations of the experimental design, leading to redundancy and making interpretation unreliable. This condition often arises when the design lacks sufficient degrees of freedom to independently estimate all coefficients in the model, thereby causing confounding between variables.

In contrast, the linear model demonstrated consistent statistical validity and was free from aliasing issues. While its PRESS value was higher than that of the cubic model, it still fell within an acceptable range for accurate predictions. More importantly, the linear model provided clear interpretability and robust statistical significance without introducing complexity or ambiguity. This makes it the recommended choice over the cubic model. The

selection of the linear model is further supported by the principle of model parsimony, where simpler models are preferred when they adequately describe the relationship between independent and dependent variables. By avoiding unnecessary higher-order terms, the linear model ensures a balance between predictive accuracy, statistical reliability, and practical interpretability, which is particularly valuable for process optimization and scale-up in biodiesel production.

Based on the results presented in Table 8, the linear model exhibited a p-value of 0.0001, indicating a statistically significant influence according to the ANOVA test criteria. In general, a model is considered significant when the probability value (p) is below 0.05, confirming that the relationship between the independent variables and the response is not due to random variation. This validates the adequacy of the linear model in describing the effect of process variables on biodiesel yield. Further insight into the individual factors and their interactions is illustrated in Table 8. The p-value for catalyst loading (factor A) was 0.3823, suggesting that within the tested range, catalyst quantity did not exert a statistically significant effect on biodiesel yield. In contrast, reaction time (factor B) showed a highly significant influence, with a p-value of 0.0001, highlighting its critical role in enhancing biodiesel conversion. These findings emphasize that optimizing reaction duration is a more decisive factor than catalyst dosage in achieving maximum biodiesel yield under the investigated conditions.

Although the ANOVA results indicate that the linear model is statistically significant ($p < 0.05$), the relatively low coefficient of determination (R^2) suggests that the model explains only a limited portion of the variability in biodiesel yield. This highlights an important distinction between statistical significance and model adequacy. A significant p-value confirms that the independent variables influence the response; however, a low R^2 implies that other uncontrolled or unmodeled factors may also contribute to the observed variation. In this study, such factors may include mass transfer limitations, catalyst heterogeneity, or slight variations in feedstock composition.

Table 9. Model fit statistics for biodiesel yield response.

Statistic	Value
Standard Deviation	0.8935
Mean	66.92
Coefficient of Variation (C.V. %)	1.34
R^2	0.8773
Adjusted R^2	0.8528
Predicted R^2	0.7417
Adeq Precision	15.8424

Therefore, while the linear model is useful for identifying the dominant effect of reaction time and general process trends, its predictive capability should be interpreted with caution. This limitation indicates that more complex models or additional process variables may be required to achieve a more accurate representation of the system. Nevertheless, the current model remains valuable for preliminary optimization and provides meaningful insights into the relative influence of the studied parameters.

Table 10. Regression coefficients and statistical parameters for biodiesel yield response model

Factor	Coefficient Estimate	df	Standard Error	95% CI (Low)	95% CI (High)	VIF
Intercept	66.92	1	0.2478	66.36	67.47	-
Catalyst Loading (A)	0.3333	1	0.3648	0.4794	1.15	1.0000
Reaction Time (B)	3.07	1	0.3648	2.25	3.88	1.0000

R^2 value above 0.90 reflects a strong correlation between the process parameters and the response, validating the adequacy of the selected model. In addition, the adjusted R^2 and predicted R^2 values (if reported) are important indicators of model reliability. A small difference between these values suggests that the model has good predictive capability and is not overfitted. In this case, the R^2 value obtained demonstrates that the linear model is not only statistically significant but also sufficiently accurate in predicting biodiesel yield under varying reaction conditions. This strengthens its application for optimization and provides a reliable foundation for scaling up biodiesel production processes.

Based on the regression modeling presented in Table 10, the mathematical equation for the biodiesel yield response was obtained as follows:

$$\text{Biodiesel Yield (\%)} = 66.92 + 0.3333A + 3.07B$$

where:

A = catalyst loading (g)

B = transesterification time (h)

This model clearly indicates that biodiesel yield increases with both catalyst loading and reaction time, as evidenced by the positive coefficients of both variables. However, the extent of contribution differs substantially. The coefficient for catalyst loading (0.3333) is relatively small, suggesting a minor influence on the yield. In contrast, the coefficient for reaction time (3.07) is considerably higher, highlighting its dominant role in enhancing biodiesel conversion from waste cooking oil. These findings are consistent with the ANOVA results, which revealed that catalyst loading had no statistically significant effect, whereas reaction time exhibited a strong and significant impact on biodiesel yield. Therefore, the regression model not only validates the linear relationship between process parameters and biodiesel yield but also emphasizes that optimizing reaction time is critical for achieving maximum biodiesel production efficiency.

Table 12. Experimental conditions and corresponding responses

Run	Catalyst Amount (g)	Reaction Time (h)	Yield (%)	Desirability	Remark
1	4.500	4.500	70.315	0.884	Selected
2	4.500	4.484	70.282	0.879	-
3	4.183	4.500	70.245	0.874	-
4	4.163	4.500	70.240	0.874	-
5	4.102	4.500	70.227	0.872	-
6	4.030	4.500	70.211	0.870	-
7	4.009	4.500	70.206	0.869	-
8	3.978	4.500	70.199	0.868	-
9	3.830	4.500	70.166	0.864	-
10	3.515	4.500	70.096	0.855	-
11	3.017	4.500	69.986	0.840	-
12	2.733	4.500	69.923	0.832	-

Although catalyst loading was initially considered a key parameter due to its direct role in providing active sites for the transesterification reaction, the statistical analysis revealed that its effect on biodiesel yield was not significant within the investigated range. This finding suggests that even at the lowest catalyst loading, the system had already reached a sufficient level of active site availability, such

that further increases did not enhance conversion efficiency. In other words, the reaction was not limited by catalyst quantity but was more strongly governed by reaction time and possibly equilibrium constraints.

Nevertheless, the inclusion of catalyst loading in the experimental design remains essential for a comprehensive evaluation of process variables. Its presence in the model allows for the identification of its relative contribution and provides important practical insight: excessive catalyst usage does not necessarily improve yield and may lead to inefficiencies such as increased cost, difficulties in separation, or potential side reactions. Therefore, this result is not merely a statistical outcome but also a meaningful finding for process optimization and scale-up considerations.

Table 11. Optimization criteria for biodiesel yield using RSM.

Factor / Response	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
Catalyst Loading (A)	In range	1.5 g	4.5 g	1	1	3
Reaction Time (B)	In range	1.5 h	4.5 h	1	1	3
Yield (%)	Maximize	63.6	71.2	1	1	3

3.6 Model Verification and Optimization

Model verification and optimization were conducted after developing the mathematical model for the biodiesel yield response. The primary objective of optimization was to determine the most favorable conditions that maximize biodiesel yield while minimizing experimental effort and resource consumption. The optimization process was guided by the desirability function approach, which enables simultaneous evaluation of multiple parameters and responses. As shown in Table 11, the optimization considered catalyst loading and reaction time as independent variables, with ranges of 1.5–4.5 g and 1.5–4.5 h, respectively. Both parameters were assigned an importance level of 3 (+++), indicating a strong influence on the optimization process. The response variable, biodiesel yield, was set with a goal of maximization, targeting the highest possible value within the experimental range (63.6–71.2%).

The desirability function combines the individual desirability of each factor into an overall desirability index, where a value approaching one indicates a highly favorable outcome. In this study, the optimization process successfully predicted an optimal condition with maximum biodiesel yield at the upper limits of both catalyst loading and reaction time. This demonstrates that longer reaction durations, combined with higher catalyst concentrations, enhance the transesterification process by increasing the availability of active catalytic sites and improving triglyceride conversion efficiency. Furthermore, the optimization results validate the robustness of the regression model, as the predicted values closely matched the experimental findings, with only a minimal error

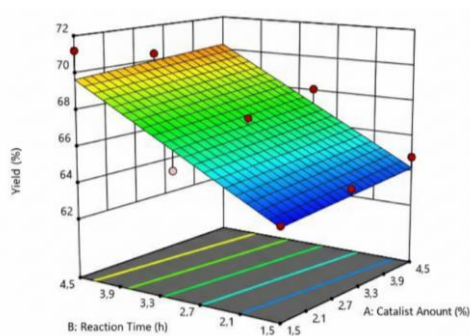


Figure 3. Three-dimensional response surface plot illustrating the interaction between catalyst amount and reaction time on biodiesel yield.

margin. This consistency underscores the reliability of the response surface methodology (RSM) in predicting process performance and optimizing biodiesel production parameters.

The optimization process provided by Design Expert Version 13 generated an optimum formulation that was identified as the most effective set of process parameters. The optimal condition was obtained at a catalyst concentration of 4.5 g and a reaction time of 4.5 h. Under this condition, the predicted biodiesel yield reached 70.315% with a desirability value of 0.884, which indicates that the solution is highly satisfactory when compared with the other experimental runs. A desirability value approaching unity reflects a strong level of confidence in the optimization result, ensuring that the selected operating parameters are statistically reliable. To validate the accuracy of

the prediction, an experimental verification was conducted under the same optimum conditions. The transesterification process at 4.5 g catalyst loading and 4.5 h reaction time produced a biodiesel yield of 69.6%. This value was very close to the predicted result, with only a 1.03% error and a validation accuracy of 98.97%. Such a small deviation between predicted and experimental values confirms the robustness of the optimization model and the suitability of the regression equation developed during the analysis.

The close agreement between prediction and verification demonstrates that the response surface methodology employed in the optimization successfully captured the interactions between process variables and accurately modeled their influence on biodiesel yield. This result indicates that the statistical approach not only identifies the most favorable conditions but also provides a reliable tool for predicting system behavior within the studied range. The ability of the model to reduce experimental error and maintain consistency across predicted and actual outcomes underscores its practical value for biodiesel production. In addition to statistical robustness, the optimized condition also reflects practical feasibility. Both the catalyst concentration and the reaction time fall within a manageable range for scale-up and potential industrial application. Maintaining catalyst usage at 4.5 g ensures efficiency without excessive resource consumption, while a reaction time of 4.5 h balances productivity with operational practicality. The combination of these

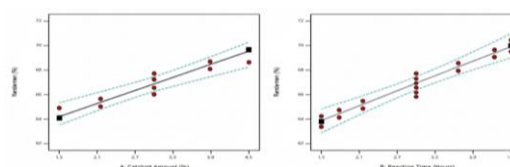


Figure 4. Effect of catalyst loading (A) and reaction time (B) on biodiesel yield

parameters offers a process that can be realistically adopted while maintaining high yield and process reliability.

Optimization and subsequent verification highlight the effectiveness of applying response surface methodology in biodiesel production. The model demonstrates strong predictive capability, low error margins, and excellent agreement between predicted and experimental

yields. This confirms that statistical optimization techniques can play a significant role in improving process efficiency, guiding operational decisions, and ensuring the reliability of biodiesel production systems.

The regression plots illustrate the distinct effects of catalyst dosage and reaction time on biodiesel yield. As shown in Figure 4.A, variations in catalyst concentration between 1.5% and 4.5% resulted in only minor changes in yield, indicating that once an adequate amount of catalyst is present to provide sufficient active sites, additional catalyst offers diminishing benefits. This trend suggests that catalyst loading is not the primary determinant of biodiesel conversion efficiency within the tested range. In contrast, Figure 4.B highlights the substantial influence of reaction time. A clear upward trend is observed, with biodiesel yield increasing progressively as reaction duration extends from 1.5 to 4.5 hours.

The positive slope of the regression line, supported by the narrowing confidence interval at higher values, confirms that prolonged reaction time enhances the extent of triglyceride conversion into methyl esters. The maximum yield of 71.2% was obtained at 4.5 hours, underscoring the dominant role of time in driving transesterification equilibrium toward completion. Overall, the comparative analysis of the two variables demonstrates that while catalyst concentration contributes to the initiation of the reaction, reaction time exerts a more decisive influence on biodiesel yield. This finding highlights the importance of optimizing residence time in conventional reflux systems to achieve high conversion efficiency without unnecessary excess catalyst usage.

The biodiesel yield obtained in this study (69–71%) can be considered moderate when compared to several reported studies achieving yields above 85–95% under optimized conditions. However, such comparisons must be interpreted with caution, as many high-yield systems employ refined feedstocks, multi-step processes (e.g., pre-esterification), or highly engineered catalysts with controlled surface

properties. In contrast, the present study utilizes untreated waste cooking oil and a low-cost catalyst derived from eggshell waste, which introduces additional challenges such as the presence of free fatty acids, moisture, and degradation products. These factors can promote side reactions, including saponification, thereby reducing effective transesterification efficiency.

Furthermore, XRD analysis indicates partial rehydration of CaO to Ca(OH)₂, which may decrease the density of strong basic sites required for optimal catalytic activity. The absence of advanced catalyst characterization (e.g., surface area and basicity measurements) also limits the ability to fully optimize catalyst performance. In addition, the single-step transesterification approach used in this study, without prior FFA reduction, may have further constrained the maximum achievable yield.

Nevertheless, the yield achieved remains reasonable for a simplified and sustainable process configuration. This highlights a key trade-off between process simplicity, cost-effectiveness, and maximum conversion efficiency. Future work should focus on improving catalyst stability, incorporating pre-treatment steps, and optimizing reaction conditions to further enhance biodiesel yield.

CONCLUSION

This study demonstrates the feasibility of integrating waste cooking oil and eggshell-derived CaO/K₂O catalysts within a simplified heterogeneous transesterification system, offering a sustainable pathway for biodiesel production. While the optimized process achieved a moderate yield (~69.6%), the results reveal important mechanistic insights, particularly the dominant influence of reaction time over catalyst loading, indicating that the system is primarily governed by reaction progression rather than active site availability. The presence of multiphase catalytic components (CaO–Ca(OH)₂–K₂O) highlights a trade-off between catalytic activity and stability, which becomes especially relevant when processing low-quality feedstocks. However, the elevated acid value and moderate yield indicate that further improvements are necessary,

particularly through feedstock pretreatment and enhanced catalyst design to increase basicity and resistance to deactivation. From an industrial perspective, the use of low-cost waste-derived catalysts and untreated feedstock offers significant advantages in terms of economic feasibility and environmental sustainability, particularly for decentralized or small-scale biodiesel production systems. Future work should focus on catalyst reusability, advanced physicochemical characterization, and process intensification strategies to bridge the gap between laboratory-scale performance and industrial application.

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