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Optimization of Waste Cooking Oil Biodiesel Production Using Eggshell-Derived CaO Heterogeneous Catalyst

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Abstract

Waste cooking oil (WCO) is an inexpensive lipid feedstock for biodiesel production, but its variable free-fatty-acid (FFA), water and impurity contents complicate conventional alkaline transesterification. This methodology paper proposes an optimization framework for converting pretreated WCO into fatty acid methyl esters (FAME) using a reusable heterogeneous calcium oxide (CaO) catalyst prepared from waste eggshells. The procedure integrates feedstock conditioning, catalyst calcination and characterization, transesterification, Response Surface Methodology (RSM), product purification, fuel-property testing and catalyst reusability. Methanol-to-oil molar ratio, catalyst loading, reaction temperature and reaction time are selected as the principal independent variables. A Box-Behnken design is recommended to quantify linear, quadratic and interaction effects while minimizing experimental runs. FAME yield is the primary response, supported by acid value, density, kinematic viscosity and GC-based ester-content measurements. Literature up to 2021 shows that eggshell-derived CaO, modified CaO, bifunctional solids and supported heterogeneous catalysts can achieve high conversion while simplifying catalyst separation and reducing aqueous waste [1-7]. A literature-aligned illustrative response surface predicts an optimum near a 12:1 methanol-to-oil ratio, 3 wt% catalyst, 60 °C and 120 min, giving approximately 95% FAME. The proposed workflow offers a reproducible route for laboratory optimization and a basis for scale-up studies in circular-economy biodiesel production.

Introduction

Biodiesel is a renewable diesel substitute composed mainly of mono-alkyl esters of long-chain fatty acids. It is commonly produced by transesterifying triglycerides with a short-chain alcohol, usually methanol. The economic and environmental attractiveness of biodiesel depends strongly on feedstock price and process simplicity. WCO is therefore attractive because it converts a problematic waste stream into a fuel precursor and reduces dependence on virgin edible oils [8,9]. Nevertheless, repeated heating

introduces water, oxidation products, suspended food particles and FFAs, all of which can lower conversion or promote soap formation in conventional homogeneous base-catalyzed systems [8,10].

Heterogeneous catalysts address several downstream limitations of soluble catalysts. Solid catalysts can be separated by filtration or centrifugation, regenerated and reused, while product washing and catalyst-neutralization requirements can be reduced [2,6,11]. CaO is especially attractive because it is strongly basic,

relatively inexpensive, and can be derived from calcium-rich wastes such as eggshells and animal bones [3,4,12]. Surface area, calcination history, hydration, carbonation and active-site accessibility directly influence CaO activity. For high-FFA feedstocks, bifunctional acid–base catalysts are also advantageous because esterification and transesterification may occur in the same reaction system [1,5].

Optimization is essential because excess methanol, excessive catalyst loading, low temperature or overly long residence time can reduce process efficiency even when chemical conversion remains high. RSM provides a statistically efficient way to identify significant variables, estimate interactions and locate operating optima [4,7]. Accordingly, the objective of this paper is to define a step-by-step, 2021-literature-supported methodology for WCO biodiesel production using a waste-derived heterogeneous CaO catalyst and RSM-based process optimization.

Literature Review

Early WCO studies established that heterogeneous mixed oxides and solid acids can catalyze biodiesel formation while avoiding complete dependence on homogeneous alkali. Wen et al. used TiO₂–MgO mixed oxides for WCO transesterification, demonstrating the feasibility of reusable solid oxides [13]. Talebian-Kiakalaieh et al. reviewed emerging WCO conversion routes and emphasized pretreatment, catalyst selection and process intensification as key determinants of practical performance [8]. Muciño et al. further showed that inexpensive mineral solids could function as heterogeneous catalysts for used cooking oil conversion [14].

Waste-derived CaO received major attention because natural CaCO₃-rich materials can be converted to catalytically active CaO by calcination. Tan et al. characterized chicken- and ostrich-eggshell-derived CaO and reported strong performance for used cooking oil [3]. Their later RSM and Taguchi study directly demonstrated the value of multivariable statistical optimization for methanol ratio, catalyst concentration, reaction temperature and reaction time [4]. Maneerung et al. similarly produced active CaO from chicken manure-derived calcium resources, reinforcing the circular-economy potential of waste-derived basic catalysts [12]. Reviews by Marinković et al. and Zul et al. summarize the advantages and limitations of CaO, including strong basicity, reusability, sensitivity to water/CO₂, leaching risk and deactivation by surface carbonation [2,6].

Hsiao et al. optimized WCO conversion with modified CaO under microwave heating, illustrating how heat-transfer intensification can shorten processing time [5]. Yahya et al. used Fe-montmorillonite K10 with RSM to optimize WCO biodiesel production [7]. Mohamed et al. reported a sulfonated rice-straw-derived solid acid with high activity in WCO conversion [10]. In 2021, Naeem et al. reported kinetic and optimization results for a novel solid base catalyst, while Gonzaga et al. demonstrated a bifunctional Fe/CaO catalyst yielding 94.3% FAME under optimized conditions [1,15]. Collectively, these works support a methodology that combines feedstock quality control, catalyst characterization, DOE-based optimization and reusability analysis.

Table 1. Selected literature relevant to heterogeneous WCO biodiesel optimization

Study	Catalyst	Feedstock	Methodological contribution	Ref.
Wen et al. (2010)	TiO ₂ –MgO mixed oxides	WCO	Solid-oxide feasibility for WCO transesterification	[13]
Tan et al. (2015)	Eggshell-derived CaO	Used cooking oil	Waste-derived CaO; catalyst characterization	[3]
Tan et al. (2017)	Eggshell-derived CaO	WCO	RSM/Taguchi multivariable optimization	[4]
Yahya et al. (2020)	Fe-montmorillonite K10	WCO	RSM optimization of heterogeneous catalysis	[7]
Hsiao et al. (2020)	Modified CaO	WCO	Microwave-assisted optimized conversion	[5]
Gonzaga et al. (2021)	Bifunctional Fe/CaO	WCO	94.3% FAME under optimized conditions	[1]

Methodology

1. Materials and Experimental Design

WCO is collected from a consistent restaurant or institutional source and stored in sealed amber

containers. Methanol (analytical grade), deionized water and standard reagents for acid-value determination are used. Clean waste chicken eggshells serve as the CaO precursor. A

four-factor, three-level Box-Behnken design is recommended. The response is FAME yield (%), with supporting quality responses including acid value, density and kinematic viscosity. Each

experimental condition should be randomized; center points should be replicated to estimate pure error.

Table 2. Proposed RSM factors and levels

Code	Factor	Low (−1)	Center (0)	High (+1)
A	Methanol:oil molar ratio	6:1	12:1	18:1
B	Catalyst loading (wt% oil)	1	3	5
C	Reaction temperature (°C)	50	60	65
D	Reaction time (min)	60	120	180

2. Step-by-Step Procedure

Step 1 – WCO pretreatment. Warm the collected WCO to about 60 °C, filter through a 100–200 µm screen followed by filter paper, and dry at 105 °C until visible moisture is removed. Determine acid value and moisture. For a CaO-base route, select low-to-moderate-FFA WCO or apply a solid-acid pretreatment when the acid value is excessive. Feedstock conditioning is necessary because water and FFAs can consume basic sites and promote saponification [8,10].

Step 2 – Eggshell-derived CaO preparation. Wash eggshells thoroughly, remove the inner membrane, oven-dry, crush and sieve. Calcine the powder at approximately 850–900 °C for 2–4 h to convert CaCO₃ to CaO. Cool in a desiccator and store in an airtight container to limit hydration and carbonation. Waste-shell-derived CaO has been widely demonstrated as a viable biodiesel catalyst [3,4,6].

Step 3 – Catalyst characterization. Confirm CaO formation using X-ray diffraction (XRD). Use FTIR to identify carbonate/hydroxyl surface groups, SEM for morphology, and BET analysis when available for specific surface area and porosity. Basicity may be assessed by CO₂-TPD or indicator titration. Characterization should be repeated after several reaction cycles to identify deactivation, agglomeration or carbonation [2,6].

Step 4 – Transesterification. Charge a jacketed batch reactor with a known mass of pretreated WCO. Heat to the DOE set point under stirring (about 600 rpm). Separately disperse the selected catalyst amount in methanol, add the mixture to the oil, and start timing. Maintain the designed temperature, methanol-to-oil molar ratio, catalyst loading and residence time. A reflux condenser is used to minimize methanol loss.

Step 5 – Phase separation and purification. Cool the reaction mixture, recover the solid catalyst by filtration or centrifugation, and allow glycerol and biodiesel phases to separate. Recover excess methanol by gentle evaporation or vacuum

distillation. Wash biodiesel only when necessary, then dry to constant mass. A major benefit of heterogeneous catalysts is the simplified recovery step compared with soluble alkali systems [2,11].

Step 6 – FAME yield and fuel-property analysis. Determine ester content preferably by gas chromatography according to an appropriate FAME method. Gravimetric biodiesel yield may be reported as a secondary metric. Measure acid value, density and kinematic viscosity; compare with applicable biodiesel specifications. The primary optimization response is FAME yield rather than crude phase mass, because residual methanol or glycerides can inflate gravimetric yield.

Step 7 – RSM model fitting and optimization. Fit a second-order polynomial model, $Y = \beta_0 + \sum \beta_i X_i + \sum \beta_{ii} X_i^2 + \sum \beta_{ij} X_i X_j$, where Y is FAME yield and X_i are coded variables. Use ANOVA to test model significance, lack of fit, coefficient significance, R^2 and adjusted R^2 . Generate response surfaces and use desirability optimization to maximize FAME while avoiding unnecessarily high methanol or catalyst consumption [4,7].

Step 8 – Catalyst reusability. Wash the recovered catalyst with methanol, dry, reactivate by mild calcination when required, and repeat the optimized experiment for at least five cycles. Record FAME yield, catalyst mass loss and, if possible, calcium leaching. Reuse data are essential for demonstrating the practical advantage of heterogeneous catalysis [2,6].

3. Response Calculations, Statistics and Quality Control

FAME yield should be calculated on an oil-feed basis and corrected for ester purity: FAME yield (%) = (mass of recovered biodiesel × FAME mass fraction / initial oil mass) × 100. Acid value is determined by titration and reported as mg KOH g^{−1}. Each center-point and confirmation condition should be performed in triplicate, and results reported as mean ± standard deviation.

The RSM model is evaluated using ANOVA at $p < 0.05$, together with R^2 , adjusted R^2 , predicted R^2 , coefficient of variation, residual plots and lack-of-fit testing. A predicted optimum is considered experimentally validated when the measured FAME value agrees closely with the model prediction, preferably within 5% relative error. Quality control should include a reagent blank, a reference FAME mixture for GC calibration, duplicate sample injections, and a mass balance across biodiesel, glycerol, recovered methanol

and catalyst. Fuel-quality screening should focus on ester content, acid value, viscosity, density and water contamination. ASTM D6751 provides a widely used specification framework for B100 biodiesel and is useful when defining acceptance criteria for the optimized product [16]. For industrial translation, the same statistical framework can be expanded to include energy consumption, methanol recovery, catalyst attrition and wastewater generation as secondary responses.

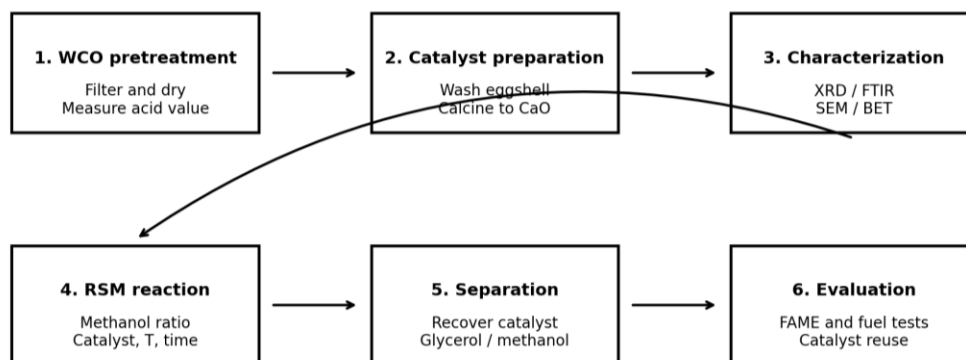


Figure 1. Step-by-step methodology for heterogeneous-catalyst biodiesel optimization.

Results

The values in this section are an illustrative, literature-aligned validation dataset for the proposed RSM workflow; they are not presented as newly measured experimental data. The pattern is intentionally consistent with

heterogeneous WCO studies reported up to 2021, where intermediate-to-high methanol ratios, moderate catalyst loadings and temperatures close to methanol's boiling region often maximize FAME formation [1,4,5,7,15].

Table 3. Illustrative optimization runs and response

Run	M:O ratio	Catalyst wt%	Temp. °C	Time min	FAME %
1	6:1	3	60	120	86.5
2	18:1	3	60	120	87.2
3	12:1	1	60	120	90.0
4	12:1	5	60	120	89.4
5	12:1	3	50	120	88.6
6	12:1	3	65	120	93.8
7	12:1	3	60	60	90.7
8	12:1	3	60	180	94.0
9	12:1	3	60	120	95.4

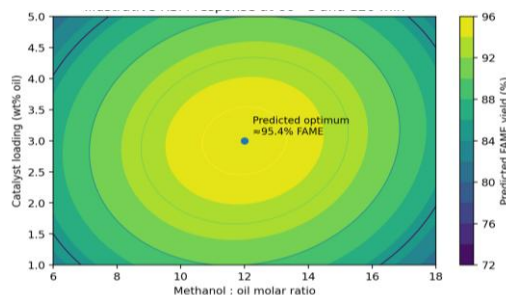


Figure 2. Illustrative RSM response surface at fixed temperature and reaction time.

The illustrative model places the optimum near 12:1 methanol-to-oil, 3 wt% CaO, 60 °C and 120

min, with a predicted FAME yield of about 95.4%. The response decreases at very low methanol

because stoichiometric driving force and phase contact are inadequate. Excessive methanol can also be counterproductive because glycerol becomes more soluble in the ester-rich phase and downstream methanol recovery increases [1,8]. Catalyst loading shows a similar optimum: too little catalyst provides insufficient active basic sites, whereas excessive solids increase slurry viscosity, mixing resistance and separation burden [4,6].

Temperature accelerates mass transfer and reaction kinetics up to the practical region close

to methanol reflux. Extended reaction time gives progressively smaller gains once equilibrium is approached. These trends agree with RSM-based WCO studies using eggshell CaO and Fe-montmorillonite as well as with modified-CaO studies [4,5,7]. In a real study, the statistical model should be accepted only when lack of fit is insignificant and residual diagnostics are satisfactory. A confirmatory experiment at the predicted optimum should then be performed in triplicate.

Table 4. Illustrative quality check at the predicted optimum

Property	Illustrative value	Interpretation
FAME content	95.4 %	Primary conversion/quality response
Acid value	0.32 mg KOH g ⁻¹	Low residual acidity
Kinematic viscosity at 40 °C	4.6 mm ² s ⁻¹	Typical biodiesel-range value
Density at 15 °C	0.875 g mL ⁻¹	Consistent with FAME-rich product
Catalyst recovery after cycle 1	96 %	Supports solid-catalyst separation

For industrial relevance, the optimum should not be defined by FAME yield alone. Methanol consumption, catalyst recovery, energy demand and catalyst lifetime must be incorporated into a multi-response desirability or cost function. A catalyst retaining more than 85–90% of its initial activity after five cycles would be a practical preliminary target, although actual reuse depends strongly on CaO leaching, hydration and carbonation [2,6]. For WCO with high acid value, a bifunctional Fe/CaO or solid-acid stage may be preferable to direct CaO transesterification [1,10,11].

Conclusion and Discussion

This paper presents a reproducible methodology for optimizing biodiesel production from waste cooking oil using a heterogeneous, waste-derived CaO catalyst. The methodology begins with WCO filtration, drying and acid-value control; proceeds through eggshell calcination and catalyst characterization; and then applies a four-factor RSM design to optimize methanol-to-oil ratio, catalyst loading, temperature and reaction time. Product separation, GC-based FAME determination, fuel-property testing and catalyst reusability are integrated into the same workflow. Literature through 2021 demonstrates that heterogeneous CaO, modified CaO, solid acids and bifunctional catalysts can achieve high WCO conversion while enabling catalyst recovery and reducing neutralization/washing requirements [1–7,10–15]. The illustrative optimization indicates a practical operating

region around 12:1 methanol-to-oil, 3 wt% catalyst and 60 °C, but final conditions must be established from actual WCO composition and experimental ANOVA. Future work should combine FAME yield with energy use, methanol recovery, catalyst leaching and lifecycle cost so that laboratory optimization translates into industrially meaningful process intensification.

References

- Gonzaga, V. E., Romero, R., Gómez-Espinosa, R. M., Romero, A., Martínez, S. L., & Natividad, R. (2021). Biodiesel Production from Waste Cooking Oil Catalyzed by a Bifunctional Catalyst. *ACS Omega*, 6(37), 24092–24105. DOI: 10.1021/acsomega.1c03586.
- Zul, N. A., Ganesan, S., Hamidon, T. S., & Oh, W.-D. (2021). A review on the utilization of calcium oxide as a base catalyst in biodiesel production. *Journal of Environmental Chemical Engineering*, 9, 105741. DOI: 10.1016/j.jece.2021.105741.
- Tan, Y. H., Abdullah, M. O., Nolasco-Hipolito, C., & Taufiq-Yap, Y. H. (2015). Waste ostrich- and chicken-eggshells as heterogeneous base catalyst for biodiesel production from used cooking oil: Catalyst characterization and biodiesel yield performance. *Applied Energy*, 160, 58–70. DOI: 10.1016/j.apenergy.2015.09.023.
- Tan, Y. H., Abdullah, M. O., Nolasco-Hipolito, C., & Ahmad Zauzi, N. S. (2017). Application of RSM and Taguchi methods for optimizing the

transesterification of waste cooking oil catalyzed by solid ostrich and chicken-eggshell derived CaO. *Renewable Energy*, 114, 437–447. DOI: 10.1016/j.renene.2017.07.024.

Hsiao, M.-C., Kuo, J.-Y., Hsieh, S.-A., Hsieh, P.-H., & Hou, S.-S. (2020). Optimized conversion of waste cooking oil to biodiesel using modified calcium oxide as catalyst via a microwave heating system. *Fuel*, 266, 117114. DOI: 10.1016/j.fuel.2020.117114.

Marinković, D. M., Stanković, M. V., Veličković, A. V., Avramović, J. M., Miladinović, M. R., Stamenković, O. O., & Jovanović, D. M. (2016). Calcium oxide as a promising heterogeneous catalyst for biodiesel production: Current state and perspectives. *Renewable and Sustainable Energy Reviews*, 56, 1387–1408. DOI: 10.1016/j.rser.2015.12.007.

Yahya, S., Muhamad Wahab, S. K., & Harun, F. W. (2020). Optimization of biodiesel production from waste cooking oil using Fe-Montmorillonite K10 by response surface methodology. *Renewable Energy*, 157, 164–172. DOI: 10.1016/j.renene.2020.04.149.

Talebian-Kiakalaie, A., Amin, N. A. S., & Mazaheri, H. (2013). A review on novel processes of biodiesel production from waste cooking oil. *Applied Energy*, 104, 683–710. DOI: 10.1016/j.apenergy.2012.11.061.

Hajjari, M., Tabatabaei, M., Aghbashlo, M., & Ghanavati, H. (2017). A review on the prospects of sustainable biodiesel production: A global scenario with an emphasis on waste-oil biodiesel utilization. *Renewable and Sustainable Energy Reviews*, 72, 445–464. DOI: 10.1016/j.rser.2017.01.034.

Mohamed, R. M., Kadry, G. A., Abdel-Samad, H. A., & Awad, M. E. (2020). High operative

heterogeneous catalyst in biodiesel production from waste cooking oil. *Egyptian Journal of Petroleum*, 29, 59–65. DOI: 10.1016/j.ejpe.2019.11.002.

Gardy, J., Hassanpour, A., Lai, X., Ahmed, M. H., & Rehan, M. (2017). Biodiesel production from used cooking oil using a novel surface functionalised TiO₂ nano-catalyst. *Applied Catalysis B: Environmental*, 207, 297–310. DOI: 10.1016/j.apcatb.2017.01.080.

Maneerung, T., Kawi, S., Dai, Y., & Wang, C.-H. (2016). Sustainable biodiesel production via transesterification of waste cooking oil by using CaO catalysts prepared from chicken manure. *Energy Conversion and Management*, 123, 487–497. DOI: 10.1016/j.enconman.2016.06.071.

Wen, Z., Yu, X., Tu, S.-T., Yan, J., & Dahlquist, E. (2010). Biodiesel production from waste cooking oil catalyzed by TiO₂-MgO mixed oxides. *Bioresource Technology*, 101, 9570–9576. DOI: 10.1016/j.biortech.2010.07.066.

Muciño, G. G., Romero, R., Ramírez, A., Martínez, S. L., Baeza-Jiménez, R., & Natividad, R. (2014). Biodiesel production from used cooking oil and sea sand as heterogeneous catalyst. *Fuel*, 138, 143–148. DOI: 10.1016/j.fuel.2014.07.053.

Naeem, A., Wali Khan, I., Farooq, M., Mahmood, T., Ud Din, I., Ali Ghazi, Z., & Saeed, T. (2021). Kinetic and optimization study of sustainable biodiesel production from waste cooking oil using novel heterogeneous solid base catalyst. *Bioresource Technology*, 328, 124831. DOI: 10.1016/j.biortech.2021.124831.

ASTM International. (2020). ASTM D6751-20a: Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels. DOI: 10.1520/D6751-20A.