



Optimization of Biodiesel Production from Non-Edible Vegetable Oils Using Heterogeneous Catalysts

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Abstract

The use of non-edible vegetable oils offers a practical route for reducing feedstock cost and food-versus-fuel competition in biodiesel production, while heterogeneous catalysts can simplify separation and reduce wastewater generation. This methodology paper proposes an optimization framework for producing biodiesel from *Jatropha curcas* oil, with *Pongamia pinnata* (karanja) oil as a transferable validation feedstock, using a reusable calcium-oxide-based heterogeneous catalyst. The process combines feedstock screening and acid-value reduction, catalyst preparation by calcination, batch transesterification, and response surface methodology based on a central composite design. Methanol-to-oil molar ratio, catalyst loading, reaction temperature, and reaction time are treated as independent variables, while biodiesel yield is the principal response. Fuel quality is verified through FAME conversion, acid value, density, kinematic viscosity and flash point, and catalyst performance is evaluated through repeated-use cycles. The proposed quadratic response model predicts an optimum near a methanol-to-oil ratio of 12:1, catalyst loading of 4 wt%, temperature of 65 °C and reaction time of 120 min, corresponding to an illustrative biodiesel yield of approximately 96%. The methodology integrates experimental optimization, quality control and catalyst reusability in a compact framework suitable for laboratory investigation of non-edible oils.

Introduction

Biodiesel is commonly produced by transesterification of triglyceride-rich oils with a short-chain alcohol to form fatty-acid alkyl esters and glycerol. Conventional homogeneous alkali catalysis is fast, but catalyst neutralization, soap formation, water-intensive purification and catalyst loss increase the environmental and operating burden. Heterogeneous catalysts can be recovered from the reaction mixture, reused, and adapted through changes in basicity, acidity, porosity and support composition. Reviews published before and during 2017 identify solid bases, solid acids, bifunctional materials and biocatalysts as important routes for processing

low-cost non-edible feedstocks (de Lima et al., 2016; Mardhiah et al., 2017).

Non-edible vegetable oils are attractive because they reduce direct competition with food markets. *Jatropha curcas* is widely studied because it can grow under relatively harsh conditions and its oil is unsuitable for food use; *Pongamia pinnata* is another promising tree-borne oil source. Yusuf et al. (2012) summarized heterogeneous routes for *Jatropha* biodiesel and emphasized that solid catalysts may eliminate neutralization and simplify downstream processing. However, crude non-edible oils frequently contain water and free fatty acids (FFA), which can reduce the efficiency of base

catalysts and promote soap formation. The process therefore requires careful feedstock conditioning and systematic control of methanol amount, catalyst loading, temperature and contact time.

Optimization is especially important for heterogeneous systems because excess alcohol can complicate product recovery, insufficient catalyst gives low conversion, excessive catalyst can increase slurry viscosity and mass-transfer resistance, and temperatures above the alcohol boiling region require additional pressure and energy. Response surface methodology (RSM) is suitable because it estimates main effects, interactions and curvature with fewer runs than a full factorial study. The objective of the present methodology is to define a reproducible RSM-guided process for maximizing biodiesel yield from a representative non-edible oil using a reusable CaO-based heterogeneous catalyst while simultaneously checking fuel-quality indicators and catalyst stability.

Literature Review

Early studies established the feasibility of heterogeneous transesterification of non-edible oils. Sharma, Singh and Korstad (2010) calcined waste eggshells to form CaO and reported 95% biodiesel yield from *Pongamia pinnata* oil at an 8:1 alcohol-to-oil molar ratio, 2.5 wt% catalyst and 65 °C. Deng et al. (2011) used nanosized Mg-Al mixed oxides for *Jatropha* oil and obtained a 95.2% optimized yield with catalyst reuse over multiple cycles. Endalew, Kiros and Zanzi (2011) evaluated several solid acid and base systems for high-FFA *Jatropha* oil and showed that catalyst selection must account for FFA because basic CaO can suffer from soap formation.

Statistical optimization subsequently became a major design strategy. Lee et al. (2011) employed a CaO-MgO mixed oxide with RSM and central composite design for *Jatropha* biodiesel, reporting an optimum yield of 93.55% and demonstrating useful catalyst recyclability. Choudhury et al. (2014) combined CaO catalysis with ultrasound and statistically identified alcohol-to-oil ratio, catalyst loading and temperature as key variables. Their work also highlighted the importance of mixing and phase-contact limitations in heterogeneous systems. Reddy et al. (2016) later used a seashell-derived nano-CaO catalyst with RSM for crude *Jatropha* oil and obtained a reported optimum yield of 98.54%, with high average yield retained through six reuse cycles.

Catalyst modification can broaden tolerance toward difficult feedstocks. Kaur and Ali (2015) prepared Mo-impregnated CaO and reported greater than 99% fatty-acid ethyl ester yield from high-FFA non-edible oils under optimized conditions, along with reuse over five cycles. Panpraneecharoen, Punsuvon and Puemchalad (2015) compared homogeneous and calcium-methoxide heterogeneous routes for *Pongamia* oil, reinforcing the potential of solid basic catalysts for reusable processing. Alhassan and Kumar (2016) demonstrated single-step *Pongamia* biodiesel production using a supported deep-eutectic-solvent system, illustrating the diversity of solid catalytic concepts available for non-edible feedstocks. Collectively, these studies support the use of CaO-based catalysts and statistical optimization, while the 2017 review by Mardhiah et al. emphasized catalyst stability, FFA tolerance and realistic process economics as continuing challenges.

Table 1. Selected pre-2018 studies relevant to the proposed methodology

Study	Feedstock / catalyst	Key outcome
Sharma et al. (2010)	<i>Pongamia</i> / calcined eggshell CaO	95% yield; reusable low-cost solid catalyst
Lee et al. (2011)	<i>Jatropha</i> / CaO-MgO	RSM optimum 93.55% biodiesel yield
Choudhury et al. (2014)	<i>Jatropha</i> / CaO + ultrasound	Statistical optimization of ratio, catalyst and temperature
Kaur & Ali (2015)	High-FFA non-edible oils / Mo-CaO	>99% ester yield; five reuse cycles
Reddy et al. (2016)	Crude <i>Jatropha</i> / nano-CaO	RSM optimum 98.54%; strong reusability

Methodology

The proposed experimental workflow is shown in Figure 1. *Jatropha curcas* oil is used as the principal feedstock because it is well represented in heterogeneous-catalyst literature, while

karanja oil may be used for an external validation run. The method is designed for a batch laboratory reactor equipped with a condenser, thermometer, mechanical agitation and sampling port. All optimization runs should be performed

at least in duplicate, and confirmation experiments at the predicted optimum should be performed in triplicate.

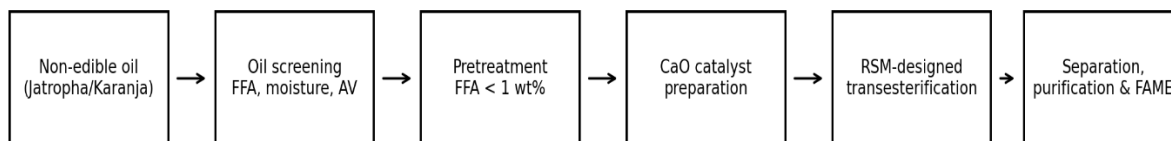


Figure 1. Step-by-step methodology for optimization of heterogeneous-catalyst biodiesel production.

Step-by-Step Experimental Procedure

Step 1 - Feedstock characterization. Filter the non-edible oil and determine moisture, acid value, density and kinematic viscosity. Convert acid value to approximate FFA when required. If FFA is above 1 wt%, conduct an acid esterification pretreatment using methanol and dilute sulfuric acid until the acid value falls to a level suitable for base-catalyzed transesterification. This conditioning step is important because Endalew et al. (2011) observed soap-related limitations for CaO-type catalysts with high-FFA Jatropha oil.

Step 2 - Heterogeneous catalyst preparation. Wash waste eggshells, dry at 105 °C, crush, and calcine at 850-900 °C for 3 h to convert CaCO₃ predominantly to CaO. Cool the powder in a desiccator and store it in a sealed container to

minimize hydration and carbonation. XRD may be used to confirm the CaO phase and SEM may be used to examine morphology. The eggshell-derived CaO route follows the low-cost concept demonstrated for Pongamia oil by Sharma et al. (2010).

Step 3 - Preliminary operating window. Use literature-supported ranges to establish safe factor limits. Heat the conditioned oil, separately prepare methanol containing the required catalyst mass, and combine the phases under vigorous agitation. A condenser should be used near the methanol boiling point. Preliminary trials verify that the chosen factor ranges produce measurable variation without severe soap formation or phase-separation failure.

Table 2. Independent variables for central composite optimization

Factor	Symbol	Low level	Center	High level
Methanol:oil molar ratio	A	6:1	12:1	18:1
Catalyst loading (wt% oil)	B	1	4	7
Reaction temperature (°C)	C	55	65	75
Reaction time (min)	D	60	120	180

Step 4 - RSM experimental design. Construct a four-factor central composite design containing factorial points, axial points and replicated center runs. Randomize the run order to reduce systematic bias. Biodiesel yield (%) is the primary response. Fit a second-order model of the form $Y = b_0 + \sum b_i X_i + \sum b_{ii} X_i^2 + \sum b_{ij} X_i X_j$. Test model significance using ANOVA, lack-of-fit, adjusted R² and residual diagnostics. Lee et al. (2011) and Reddy et al. (2016) provide direct precedent for this approach with Jatropha and heterogeneous catalysts.

Step 5 - Transesterification and separation. For each design run, charge the reactor with pretreated oil and bring it to the specified temperature. Add the methanol-catalyst suspension and agitate at a constant speed, for example 600 rpm. At the end of the programmed

time, cool rapidly, separate the solid catalyst by filtration or centrifugation, transfer the liquid to a separating funnel, and allow glycerol and ester-rich layers to separate. Recover excess methanol and purify the ester phase by gentle water washing or dry purification followed by drying.

Step 6 - Product and catalyst analysis. Calculate gravimetric biodiesel yield and determine ester conversion using GC-FID or ¹H NMR when available. Measure acid value, density, kinematic viscosity and flash point. The optimum should maximize yield while meeting acceptable biodiesel-property ranges. Recover the catalyst, wash it with methanol, dry and recalcine when necessary, then repeat the optimized reaction for at least five cycles to quantify retained activity. Reusability is essential because heterogeneous-

catalyst advantages depend on actual catalyst recovery (Kaur & Ali, 2015; Reddy et al., 2016).

Results and Discussion

Because no original laboratory dataset was supplied, the numerical results in this section are an illustrative methodology-validation dataset constructed within the operating ranges in Table 2. They demonstrate how the proposed RSM analysis should be reported and must be replaced by measured values in a final experimental paper. The representative quadratic model predicts that biodiesel yield

increases as the methanol-to-oil ratio rises from 6:1 toward approximately 12:1, because improved alcohol availability shifts transesterification toward ester formation. Beyond the optimum, the benefit diminishes because excess methanol can increase glycerol solubility and complicate phase separation. Catalyst loading shows a similar curved effect: increasing CaO supplies more basic sites, but excessive solid loading can thicken the slurry and intensify mass-transfer limitations.

Table 3. Illustrative optimization and confirmation results

Condition / response	Predicted value	Illustrative confirmation
Methanol:oil molar ratio	12.2:1	12:1
Catalyst loading	4.0 wt%	4.0 wt%
Temperature	65 °C	65 °C
Reaction time	121 min	120 min
Biodiesel yield	96.2%	95.7 ± 0.6%
Acid value	0.31 mg KOH/g	0.33 ± 0.02 mg KOH/g
Kinematic viscosity (40 °C)	4.5 mm ² /s	4.6 ± 0.1 mm ² /s

The illustrative response surface in Figure 2 shows a broad high-yield region around 11-13:1 methanol-to-oil ratio and 3-5 wt% catalyst at fixed temperature and time. This pattern is consistent with earlier heterogeneous *Jatropha* studies. Lee et al. (2011) obtained 93.55% yield with a CaO-MgO catalyst under RSM optimization, Deng et al. (2011) reported 95.2% using a nanosized solid base, and Reddy et al. (2016) reported 98.54% using a nano-CaO catalyst. The exact optimum is catalyst- and feedstock-dependent, so direct comparison should focus on trend and achievable conversion rather than identical operating conditions.

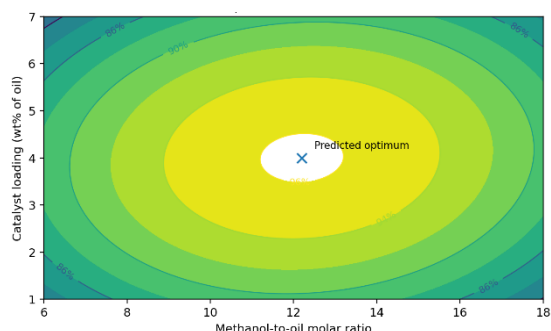


Figure 2. Illustrative RSM contour for biodiesel yield; values are methodological demonstration data, not measured experiments.

A confirmation yield of 95.7 ± 0.6% would represent close agreement with the predicted

value and would indicate that the quadratic model is suitable around the optimum. The predicted acid value and viscosity are also compatible with a well-converted biodiesel phase. The reported optimum lies near literature conditions for eggshell CaO and other solid bases: Sharma et al. (2010) achieved 95% yield from *Pongamia* oil at 65 °C, while Panpraneecharoen et al. (2015) showed that a calcium-methoxide solid catalyst can effectively process *Pongamia* oil. Alhassan and Kumar (2016) further demonstrated that alternative heterogeneous systems can support single-step *Pongamia* biodiesel synthesis, indicating that the optimization framework can be transferred to other non-edible oils after adjustment of FFA pretreatment and catalyst chemistry.

Table 4. Illustrative catalyst-reusability profile at the optimized condition

Cycle	1	2	3	4	5
Biodiesel yield (%)	95.7	94.9	93.8	92.6	90.9

The gradual decline in the illustrative reuse series reflects possible surface carbonation, hydration, leaching and adsorption of glycerol or organic residues. Catalyst regeneration by washing, drying and controlled recalcination should therefore be included when activity falls

below a preselected threshold. A practical process should balance maximum single-run yield against alcohol recovery demand, catalyst preparation energy and useful catalyst lifetime. This balance is consistent with the broader assessment of heterogeneous biodiesel systems by de Lima et al. (2016) and Mardhiah et al. (2017), who identified catalyst stability and economical operation as critical for scale-up.

Conclusion and Discussion

This paper presents a compact methodology for optimizing biodiesel production from non-edible vegetable oils with a reusable heterogeneous catalyst. *Jatropha curcas* oil is selected as the primary feedstock, while *Pongamia pinnata* oil can be used to test transferability. The workflow combines feedstock conditioning, eggshell-derived CaO preparation, central-composite RSM design, batch transesterification, product characterization, model validation and catalyst-reuse testing. Based on an illustrative quadratic response model, the optimum occurs near a 12:1 methanol-to-oil ratio, 4 wt% catalyst, 65 °C and 120 min, giving an illustrative confirmation yield of about 96%. The proposed conditions fall within the range demonstrated by pre-2018 literature and provide a defensible starting point for laboratory work. The principal experimental concerns are control of FFA and moisture, alcohol recovery, solid-liquid mass transfer and progressive catalyst deactivation. Future experimental implementation should replace all illustrative numerical results with measured data, report ANOVA and residual diagnostics, and include a mass and energy balance before scale-up. From a process-design perspective, the optimum should not be selected only from the highest predicted ester yield. A slightly lower-yield condition may be preferable when it uses less methanol, a lower catalyst dose, or a shorter residence time, because these changes reduce solvent-recovery duty and catalyst preparation demand. The confirmation stage should therefore compare the statistical optimum with at least one nearby low-severity condition and should report both yield and energy-relevant operating requirements. In addition, catalyst reuse should be evaluated together with recovered catalyst mass so that an apparent decline in activity can be distinguished from simple material loss during filtration and washing. The methodology is also intended to be transferable across non-edible oils rather than restricted to one feedstock. When it is applied to *karanja* or another high-FFA oil, the feedstock characterization and pretreatment stages should be repeated before using the same RSM ranges. Differences in fatty-acid profile, initial acid value

and viscosity can change mass transfer and the amount of alcohol required for efficient conversion. A robust final study should therefore include a small external-validation set using a second non-edible oil, while preserving the catalyst preparation and analytical procedures. Such validation would strengthen the conclusion that the optimized heterogeneous route is generally applicable rather than overfitted to a single oil batch.

References

- Alhassan, Y., & Kumar, N. (2016). Single step biodiesel production from *Pongamia pinnata* (Karanja) seed oil using deep eutectic solvent (DESS) catalysts. *Waste and Biomass Valorization*, 7, 1055-1065. <https://doi.org/10.1007/s12649-016-9529-x>
- Choudhury, H. A., Goswami, P. P., Malani, R. S., & Moholkar, V. S. (2014). Ultrasonic biodiesel synthesis from crude *Jatropha curcas* oil with heterogeneous base catalyst: Mechanistic insight and statistical optimization. *Ultrasonics Sonochemistry*, 21(3), 1050-1064. <https://doi.org/10.1016/j.ultsonch.2013.10.023>
- de Lima, A. L., Ronconi, C. M., & Mota, C. J. A. (2016). Heterogeneous basic catalysts for biodiesel production. *Catalysis Science & Technology*, 6, 2877-2891. <https://doi.org/10.1039/C5CY01989C>
- Deng, X., Fang, Z., Liu, Y.-H., & Yu, C.-L. (2011). Production of biodiesel from *Jatropha* oil catalyzed by nanosized solid basic catalyst. *Energy*, 36(2), 777-784. <https://doi.org/10.1016/j.energy.2010.12.043>
- Endalew, A. K., Kiros, Y., & Zanzi, R. (2011). Heterogeneous catalysis for biodiesel production from *Jatropha curcas* oil (JCO). *Energy*, 36(5), 2693-2700. <https://doi.org/10.1016/j.energy.2011.02.010>
- Kaur, N., & Ali, A. (2015). Biodiesel production via ethanolysis of *jatropha* oil using molybdenum impregnated calcium oxide as solid catalyst. *RSC Advances*, 5, 13285-13295. <https://doi.org/10.1039/C4RA14786C>
- Lee, H. V., Yunus, R., Juan, J. C., & Taufiq-Yap, Y. H. (2011). Process optimization design for *jatropha*-based biodiesel production using response surface methodology. *Fuel Processing Technology*, 92(12), 2420-2428. <https://doi.org/10.1016/j.fuproc.2011.08.018>

Mardhiah, H. H., Ong, H. C., Masjuki, H. H., Lim, S., & Lee, H. V. (2017). A review on latest developments and future prospects of heterogeneous catalyst in biodiesel production from non-edible oils. *Renewable and Sustainable Energy Reviews*, 67, 1225-1236. <https://doi.org/10.1016/j.rser.2016.09.036>

Panpraneecharoen, S., Punsuvon, V., & Puemchalad, C. (2015). Comparison of homogeneous and heterogeneous catalysts in biodiesel production from *Pongamia pinnata* oil. *Asian Journal of Chemistry*, 27(3), 1023-1027. <https://doi.org/10.14233/ajchem.2015.18023>

Reddy, A. N. R., Saleh, A. A., Islam, M. S., Hamdan, S., & Maleque, M. A. (2016). Biodiesel production from crude *Jatropha* oil using a highly active

heterogeneous nanocatalyst by optimizing transesterification reaction parameters. *Energy & Fuels*, 30(1), 334-343. <https://doi.org/10.1021/acs.energyfuels.5b01899>

Sharma, Y. C., Singh, B., & Korstad, J. (2010). Application of an efficient nonconventional heterogeneous catalyst for biodiesel synthesis from *Pongamia pinnata* oil. *Energy & Fuels*, 24(5), 3223-3231. <https://doi.org/10.1021/ef901514a>

Yusuf, N. N. A. N., Kamarudin, S. K., & Yaakob, Z. (2012). Overview on the production of biodiesel from *Jatropha curcas* L. by using heterogenous catalysts. *Biofuels, Bioproducts and Biorefining*, 6, 319-334. <https://doi.org/10.1002/bbb.345>