

PRODUCTION OF GREEN DIESEL (DEOXYGENATED BIODIESEL) FROM BIOMASS

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ABSTRACT

The growing demand for sustainable and energy-dense biofuels has intensified the search for low-cost, non-edible biomass feedstocks capable of producing diesel-range hydrocarbons with properties comparable to petroleum diesel. In this study, *Gmelina arborea* leaf biomass was valorised into green diesel (deoxygenated biodiesel) via a calcium hydroxide ($\text{Ca}(\text{OH})_2$)-catalysed thermal ethanolysis operated under mild conditions (40-60 °C, 40-60 min, 1-2% catalyst loading). A three-factor Box-Behnken Response Surface Methodology (RSM) was employed to systematically evaluate the individual, interaction, and quadratic effects of temperature, reaction time, and catalyst loading on diesel yield. Gas chromatography-mass spectrometry (GC-MS) analysis confirmed the formation of predominantly C_{10} - C_{20} hydrocarbons, including n-alkanes, branched alkanes, and cycloalkanes, indicating effective deoxygenation and cracking of biomass-derived intermediates. The highest experimental yield was obtained at 60 °C, 50 min, and 2% $\text{Ca}(\text{OH})_2$, producing 720.35 mg/g of

Introduction

Energy underpins industrial development in any nation, as access to reliable, sufficient energy resources directly drives economic growth and technological advancement (Li *et al.*, 2024; Lin & Xu, 2018). The increasing global demand for sustainable and environmentally friendly fuels has intensified the exploration of renewable bioresources for conversion into alternative energy carriers, such as deoxygenated biodiesel (El-Araby, 2024). Biodiesel, typically produced from plant or animal fats, offers a renewable alternative to fossil diesel due to its

diesel-range hydrocarbons. ANOVA results demonstrated that temperature and catalyst loading were highly significant factors ($p < 0.01$), with a strong synergistic interaction between them, while reaction time exhibited a moderate but significant quadratic effect. The quadratic regression model was statistically significant ($p < 0.0001$) and highly predictive. Reproducibility assessment using replicated centre-point experiments showed a low coefficient of variation (1.22%), confirming excellent experimental precision and operational stability. The results demonstrate that mild alkaline-catalysed thermal hydrolysis provides an energy-efficient and statistically validated pathway for decentralised green diesel production from underutilised lignocellulosic leaf biomass, supporting sustainable bioenergy development and resource valorisation.

Keywords: Green Diesel, Deoxygenated Biodiesel, *Gmelina arborea* leaf, Calcium Hydroxide Catalyst, Thermal Hydrolysis, Biomass Valorisation, Sustainable Biofuel Production.

biodegradability, low sulfur content, and carbon-neutral combustion profile (Malik *et al.*, 2024). Despite these advantages, conventional biodiesel suffers from lower energy content due to its inherent oxygen content (Gebremariam, 2023; Torkashvand *et al.*, 2022). Additionally, conventional production often depends on edible oils, which compete with the food supply and increase production costs (Avagyan & Singh, 2019).

To address these challenges, research is increasingly focused on non-edible biomass feedstocks, such as *Gmelina arborea* leaves. These lignocellulosic materials are abundant, underutilised, and do not compete with food resources, making them highly attractive for sustainable biofuel production (Anuragi *et al.*, 2025; Pant *et al.*, 2025). Utilising such feedstocks aligns with Sustainable Development Goal 7 (Affordable and Clean Energy) by promoting renewable energy access, as well as Sustainable Development Goal 12 (Responsible Consumption and Production) by leveraging waste biomass and reducing pressure on food-based resources. This approach not only provides a pathway to greener energy but also supports broader environmental sustainability objectives, including reduced carbon emissions and more efficient utilisation of natural resources.

Diesel fuel is a type of liquid fuel used primarily in diesel engines invented by Rudolf Diesel (1858–1913) (Song, 2020; Diesel, 2013). This engine operates on the principle of compression ignition rather than spark ignition (as in gasoline engines) (Raji *et al.*, 2024; Kalghatgi *et al.*, 2022; Kalghatgi & Johansson, 2018). Diesel fuel is derived from crude oil through the process of fractional distillation and contains a mixture of hydrocarbons, predominantly alkanes (paraffins), cycloalkanes (naphthenes), and aromatic

hydrocarbons (Dantu, 2022; Aljamali & Salih, 2021; Ekejiuba, 2021). The chemical composition of diesel comprises carbon chain lengths of $C_{10}H_{22}$ to $C_{20}H_{42}$ of straight-chain alkanes (normal paraffins), branched alkanes, cycloalkanes, and aromatics (Ekejiuba, 2021; Sarıkoç, 2020; Fingas, 2020).

Extensive studies have investigated biodiesel production from edible and non-edible oils; however, most conventional approaches focus on transesterification processes that retain oxygen within the fuel structure, thereby limiting energy density and oxidative stability. Although deoxygenated biodiesel (green diesel) offers superior fuel properties comparable to petroleum-derived diesel (C_{10} - C_{20} hydrocarbons) (Quiroz-Suárez *et al.*, 2025), current production routes predominantly rely on high-temperature hydrotreating, noble-metal catalysts, or hydrogen-intensive upgrading processes. These methods are energy-demanding, capital-intensive, and less accessible for decentralised or developing-economy applications (Gaya, 2021). Furthermore, while lignocellulosic biomass has gained attention as a sustainable alternative feedstock, limited research has systematically explored leaf biomass, particularly *Gmelina arborea* leaves, as a direct precursor for diesel-range hydrocarbon production. Existing studies on *Gmelina arborea* largely emphasise pyrolysis, bio-oil production, or value-added chemicals, with insufficient focus on selective catalytic thermal ethanolic pathways capable of producing fully deoxygenated diesel fractions under mild operating conditions.

Another critical gap lies in catalyst selection and process conditions. Most deoxygenation studies employ transition metals or bifunctional catalysts at elevated temperatures ($>200\text{ }^{\circ}\text{C}$) (Lin *et al.*, 2023; Dutta, 2020; Zhang *et al.*, 2016). There is a scarcity of studies investigating simple, low-cost alkaline catalysts such as calcium hydroxide ($\text{Ca}(\text{OH})_2$) for direct diesel-range hydrocarbon synthesis at mild temperatures ($40\text{--}60\text{ }^{\circ}\text{C}$). Despite the prevalence of methanol in conventional biodiesel production, its fossil-derived nature presents a sustainability paradox. This study addresses this gap by prioritising the use of bio-derived ethanol in the first phase of investigation, offering a pathway to a fully renewable fuel synthesis process. The catalytic behaviour, optimisation, interaction effects, and statistical modelling of such mild thermal ethanolysis remain underexplored. In addition, few studies integrate advanced statistical optimisation tools such as the Box-Behnken design within Response Surface Methodology (RSM) to rigorously evaluate parameter interactions (temperature, time, and catalyst loading) in biomass-to-diesel conversion. Many reports rely on one-factor-at-a-time experimentation, which does not adequately capture synergistic or quadratic effects necessary for process intensification and scale-up modelling. Moreover, reproducibility assessment, ANOVA validation, and pure-error quantification are often absent or weakly reported in biomass conversion studies. The lack of statistically validated optimisation models reduces confidence in predictive performance and industrial applicability. Therefore, a significant research gap

exists in: (1) developing a low-temperature, energy-efficient catalytic thermal ethanolic pathways for direct diesel-range hydrocarbon production from non-edible leaf biomass, (2) investigating the catalytic efficiency of calcium hydroxide under mild operating conditions for effective deoxygenation, (3) applying statistically robust experimental design (Box–Behnken RSM) to evaluate interaction effects and establish an optimised operational window, and (4) validating process reproducibility and model adequacy through rigorous ANOVA and pure-error analysis. Addressing these gaps provides a novel contribution toward decentralised, low-cost, and sustainable green diesel production from underutilised lignocellulosic leaf biomass, supporting scalable clean-energy development.

This study aims to develop and statistically optimise a low-temperature calcium hydroxide ($\text{Ca}(\text{OH})_2$)-catalysed thermal ethanolysis for the direct production of diesel-range hydrocarbons (green diesel) from *Gmelina arborea* leaf biomass by systematically investigating the effects of reaction temperature (40–60 °C), reaction time (40–60 min), and catalyst loading (1–2%) using a three-factor Box–Behnken Response Surface Methodology (RSM). The research seeks to evaluate the individual and interactive influences of these process parameters on diesel yield, develop a second-order quadratic regression model, and determine statistically significant factors through ANOVA. It further aims to identify and characterise the produced C_{10} – C_{20} hydrocarbons using GC-MS to confirm effective deoxygenation and hydrocarbon formation, establish optimal operating conditions for maximum yield, and assess process reproducibility through replicated centre-point experiments, pure-error estimation, and coefficient of variation analysis. Ultimately, the study intends to demonstrate an energy-efficient, scalable, and statistically validated pathway for decentralised green diesel production from underutilised lignocellulosic leaf biomass, thereby contributing to sustainable and affordable clean energy development.

Materials and Methods

A three-factor Box–Behnken design under Response Surface Methodology (RSM) was adopted to develop 17 experimental trials, as illustrated in Table 1. Dried *Gmelina arborea* leaves were harvested from the Kaduna Polytechnic campus, thoroughly rinsed, air-dried, pulverised, and sieved to obtain a consistent particle size, following established procedures (Ibrahim *et al.*, 2025a; Ali & Ibrahim, 2023a). The catalytic solution was prepared by dissolving 1.0 g of Calcium hydroxide ($\text{Ca}(\text{OH})_2$), equivalent to 2.0% (w/w) relative to the biomass feedstock, in 500 mL of ethanol as described by Ibrahim & Ali (2023). Thereafter, 50 g of the processed *Gmelina arborea* leaf powder was introduced into the solution. The reaction mixture was maintained at 60 °C for 50 minutes on a Gallenkamp hot plate fitted with a magnetic stirrer to ensure homogeneous

mixing, in accordance with Ibrahim *et al.* (2025b). Upon completion, the reaction mixture was filtered initially through a filter cloth and subsequently through Whatman filter paper for clarification, following Ali and Ibrahim (2023b). The filtrate obtained was weighed, and a 5 g sample was withdrawn for both qualitative and quantitative characterisation using Gas chromatography-mass spectrometry (GC-MS), as outlined by Ibrahim *et al.* (2024). This procedure was consistently applied to all experimental runs specified in the Box-Behnken design matrix.

Table 1: A three-factor Box-Behnken experimental design

S/N	Temperature (°C)	Time (min)	Catalyst loading (%)
1	60	50	2.0
2	50	40	1.0
3	40	50	2.0
4	40	40	1.5
5	50	60	2.0
6	50	60	1.0
7	50	50	1.5
8	50	50	1.5
9	40	60	1.5
10	50	50	1.5
11	60	40	1.5
12	40	50	1.0
13	50	50	1.5
14	50	40	2.0
15	50	50	1.5
16	60	60	1.5
17	60	50	1.0

For derivatisation, 200 μL of the prepared standard solution was mixed with 100 μL of trimethyl sulfonium hydroxide (TMSH) and 20 μL of triethylamine (TEA). The mixture was heated at 70 °C for 1 hour in sealed vials before GC-MS analysis, following Ibrahim *et al.* (2025b). GC-MS measurements were carried out on a Varian 3800/4000 GC-MS system equipped with a DB-5 capillary column (30 m $\times$ 0.25 mm $\times$ 0.25 μm). Nitrogen was employed as the carrier gas, with the column head pressure maintained at 10 psi. The oven temperature program was set from 100 °C (held for 3 minutes) to 300 °C at a heating rate of 8 °C min⁻¹. Both the transfer line and ion source temperatures were maintained at 290 °C. Mass spectra were recorded under electron impact ionisation across an m/z range of 40-800 at a scanning rate of 20 scans s⁻¹. A solvent delay of 330

seconds was applied to prevent detector overloading. Continuous monitoring of the signal ensured accurate, consistent, and reproducible analytical performance.

Results and Discussion

Table 2 presents the diesel-range hydrocarbon compounds identified in the biofuel fraction obtained from calcium hydroxide-catalysed thermal ethanolysis of *Gmelina arborea* leaves optimised using a Box-Behnken design under Response Surface Methodology (RSM). The table lists the identified compounds and their corresponding molecular formula (MF) as determined by Gas chromatography–mass spectrometry (GC-MS) analysis. The detected compounds predominantly fall within the C₁₀-C₂₀ carbon number range, which is characteristic of diesel-grade hydrocarbons. These include straight-chain (n-alkanes), branched-chain alkanes (iso-alkanes), cycloalkanes, and minor aromatic constituents. The presence of saturated hydrocarbons such as tetradecane (C₁₄H₃₀), pentadecane (C₁₅H₃₂), hexadecane (C₁₆H₃₄), heptadecane (C₁₇H₃₆), octadecane (C₁₈H₃₈), nonadecane (C₁₉H₄₀), and eicosane (C₂₀H₄₂), alongside their methyl-substituted derivatives, indicates effective deoxygenation and cracking reactions during the catalytic process. The identification of branched and cyclic hydrocarbons further suggests secondary isomerisation and cyclisation reactions occurring under the applied thermal conditions. Overall, the composition shown in the table confirms the successful conversion of *Gmelina arborea* leaf biomass into diesel-range hydrocarbons, demonstrating the effectiveness of calcium hydroxide as a catalyst under the optimised Box-Behnken RSM conditions.

Table 2: The revealed diesel compound found in the products

S/N	Compound	MF	S/N	Compound	MF
1	7-methyl hexadecane	C ₁₇ H ₃₆	15	5-butyl hexadecane	C ₂₀ H ₄₂
2	Tetradecane	C ₁₄ H ₃₀	16	Octadecane	C ₁₈ H ₃₈
3	2-methyl heptadecane	C ₁₈ H ₃₈	17	Dodecane	C ₁₂ H ₂₆
4	Heptadecane	C ₁₇ H ₃₆	18	2-methyl dodecane	C ₁₃ H ₂₈
5	9-methyl heptadecane	C ₁₈ H ₃₈	19	2-methyl hexadecane	C ₁₇ H ₃₆
6	8-methyl heptadecane	C ₁₈ H ₃₈	20	Eicosane	C ₂₀ H ₄₂
7	5,5,7,7-tetraethyl undecane	C ₁₉ H ₄₀	21	Tridecane	C ₁₃ H ₂₈
8	4-methyl heptadecane	C ₁₈ H ₃₈	22	2,6,10,14-tetramethyl hexadecane,	C ₂₀ H ₄₂
9	10-Methyl nonadecane	C ₂₀ H ₄₂	23	2-methyl nonadecane	C ₂₀ H ₄₂
10	9-methyl nonadecane	C ₂₀ H ₄₂	24	3,5-dimethyl octane	C ₁₀ H ₂₂

S/N	Compound	MF	S/N	Compound	MF
11	4-ethyl-1,2-dimethyl benzene	C ₁₀ H ₁₄	25	3-methyl tridecane	C ₁₄ H ₃₀
12	Hexadecane	C ₁₆ H ₃₄	26	2-methyl octadecane	C ₁₉ H ₄₀
13	Pentadecane	C ₁₅ H ₃₂	27	5,5-Dibutyl nonane	C ₁₇ H ₃₆
14	3-methyl heptadecane	C ₁₈ H ₃₈	28	Cyclo tetradecane	C ₁₄ H ₂₈

Table 3 presents the experimental matrix and corresponding diesel yields obtained from the calcium hydroxide-catalysed thermal ethanolysis of *Gmelina arborea* leaves. The table summarizes the total product obtained from the ethanolysis after drying, the percentage yield of biodiesel (in the total product) and the mass of biodiesel (in mg/g of product) obtained at different reaction conditions; reaction temperature (40-60 °C), reaction time (40-60 min), and catalyst loading (1-2%).

Table 3: The yields of diesel (deoxygenated biodiesel) from leaves of *Gmelina arborea*

S/N	Temperature (°C)	Time (min)	Catalyst loading (%)	Dry product (g)	Biodiesel yield (%)	Biodiesel yield (mg/g)
1	60	50	2.0	221.7	16.25	720.35
2	50	40	1.0	176.7	8.78	310.42
3	40	50	2.0	258.9	8.11	420.18
4	40	40	1.5	249.0	3.02	150.26
5	50	60	2.0	224.9	14.24	640.57
6	50	60	1.0	165.2	10.77	355.80
7	50	50	1.5	138.4	17.35	480.12
8	50	50	1.5	195.9	12.06	472.64
9	40	60	1.5	138.1	10.69	295.34
10	50	50	1.5	162.7	15.00	488.21
11	60	40	1.5	255.2	10.10	515.47
12	40	50	1.0	143.6	9.23	265.18
13	50	50	1.5	139.3	17.11	476.55
14	50	40	2.0	274.2	11.00	600.83
15	50	50	1.5	102.9	23.51	483.90
16	60	60	1.5	222.9	15.48	690.12
17	60	50	1.0	175.1	12.300	430.75

The results obtained, Table 3, show a clear dependence of diesel (deoxygenated biodiesel) yield on temperature, reaction time, and catalyst load (Table 1). Temperature strongly influenced diesel yield. The highest yield (720.35 mg/g) was achieved at 60 °C, 50 min, and 2% catalyst loading (Run 1), indicating that elevated temperature enhances

deoxygenation and cracking reactions necessary for diesel-range hydrocarbon formation. At lower temperatures (40 °C), yields were generally reduced. For example, at 40 °C, 40 min, and 1.5% catalyst (Run 4), the yield dropped drastically to 150.26 mg/g, suggesting insufficient thermal energy for effective conversion. However, moderate improvement in biodiesel yield was observed at 40 °C, from 150.26 mg/g to 295.34 mg/g, when reaction time was increased from 40 minutes (Runs 4) to 60 minutes (Run 9), indicating that temperature interacts significantly with other process variables.

Catalyst loading also showed a pronounced effect. Increasing the Ca(OH)_2 loading from 1% to 2% generally improved the yield. For instance, at 50 °C and 60 min, increasing catalyst loading from 1% (Run 6) to 2% (Run 5) increases the yield from 355.80 mg/g to 640.57 mg/g. Similarly, at the same reaction conditions of 50 °C and 40 min, the yield at 2% catalyst (Run 14) is 600.83 mg/g, which outperformed the 310.42 mg/g yield obtained at 1% catalyst load (Run 2), demonstrating enhanced catalytic activity at higher loading. Much higher yields were consistently associated with 2% catalyst load (Run 1, Run 3, Run 5 and Run 14), confirming that sufficient active sites are essential for efficient ethanolic cleavage and deoxygenation of biomass-derived intermediates.

Reaction time exhibited a synergistic interaction with temperature and catalyst concentration. At 60 °C and 1.5% catalyst load, increasing the time from 40 min (Run 11) to 60 min (Run 16) improved yield from 515.47 mg/g to 690.12 mg/g, indicating progressive conversion with longer residence time. Similarly, at the reaction conditions of 40 °C and 1.5% catalyst load, there is a great improvement in the yield from 150.26 mg/g (Run 4) to 295.34 mg/g (Run 9) when the residence time increased from 40 to 60 minutes.

While the identification of synergistic interactions between temperature, reaction time, and catalyst loading provides valuable insight into process optimisation, the interpretation of these interactions warrants deeper critical evaluation. Notably, although higher catalyst loading (2%) generally enhanced yield, the centre-point experiments (1.5% catalyst) produced comparatively stable and, in some cases, unexpectedly competitive yields (≈ 480 mg/g). This suggests that beyond a certain threshold, increasing catalyst concentration may not proportionally increase active site efficiency, possibly due to mass transfer limitations, particle agglomeration, or diffusion constraints within the biomass matrix. Such behaviour indicates that the system may be approaching a saturation regime where additional catalyst offers diminishing returns.

Similarly, while temperature exhibited a strong positive effect, the relatively high yields obtained at moderate conditions (50 °C) indicate that the reaction is not purely temperature-driven. This deviation from a strictly monotonic thermal dependence suggests the involvement of competing reaction pathways, such as secondary cracking or recombination reactions, which may become more pronounced at higher

temperatures. These effects were not explicitly quantified and represent an important area for further mechanistic investigation.

Another notable observation is the significant lack-of-fit reported in the ANOVA results. Although the model shows high statistical significance and predictive capability, the presence of a significant lack-of-fit implies that the quadratic model may not fully capture the complexity of the reaction system. This limitation suggests that higher-order interactions, unaccounted variables (e.g., mixing intensity, particle size distribution, or solvent effects), or nonlinear kinetic phenomena may influence the process. Consequently, caution should be exercised when extrapolating the model beyond the studied design space.

Furthermore, the study assumes uniform catalyst dispersion and consistent reaction conditions; however, potential heterogeneities in biomass composition and structure were not explicitly addressed. Lignocellulosic materials such as *Gmelina arborea* leaves inherently exhibit variability in cellulose, hemicellulose, and lignin content, which can influence reactivity and product distribution. This introduces an additional source of uncertainty that may affect scalability and reproducibility under industrial conditions. The replicated centre points (Runs 7, 8, 10, 13, and 15 at 50 °C, 50 min, 1.5% catalyst) show moderate variation in yield (472.64 - 488.21 mg/g), reflecting acceptable experimental reproducibility while also indicating some sensitivity of the process to minor operational fluctuations. Overall, the data reveal that diesel production increases with higher temperature (approaching 60 °C), increased catalyst loading (2%), and moderate reaction time (50-60 min). The optimum condition within the studied design space was 60 °C, 50 min, and 2% Ca(OH)₂, producing 720.35 mg/g diesel, which is significantly higher than all other experimental runs.

These results demonstrate that mild thermal conditions combined with appropriate alkaline catalysis can effectively convert *Gmelina arborea* leaf biomass into diesel-range hydrocarbons. The strong interaction between temperature and catalyst loading suggests that process intensification strategies should focus on maximising catalytic activity rather than excessively increasing reaction time. The high yield obtained at relatively low temperature (60 °C) highlights the energy-efficiency potential of this thermal ethanolysis, making it promising for scalable and sustainable biofuel production.

In a Box-Behnken Response Surface Methodology (RSM) design, reproducibility (pure error) is determined from the replicated centre points. The centre condition is 50 °C, 50 min, and 1.5% catalyst loading. The replicable runs are presented in Table 4.

Table 4: Replicable runs

Experimental run	7	8	10	13	15
Yield (mg/g)	480.12	472.64	488.21	476.55	483.90

The mean yield at the centre point ($\bar{x}$) is expressed as in Equation 1.

$$\bar{x} = \frac{\sum x_i}{n} \quad (1)$$

$$\text{That is, } \bar{x} = \frac{480.12+472.64+488.21+476.55+483.90}{5} = 480.28 \text{ mg/g}$$

The standard deviation (SD) is expressed as in Equation 2.

$$SD = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n-1}} \quad (2)$$

$$SD = 5.87 \text{ mg/g}$$

The expression for relative standard deviation (RSD) or coefficient of variance (CV %) is expressed in Equation 3, and reproducibility results are presented in Table 5.

$$RSD = \frac{SD}{\bar{x}} \quad (3)$$

$$RSD = \frac{5.87}{480.28} \times 100 = 1.22\%$$

Table 5: Reproducibility results

Parameter	Value
Number of replicates (n)	5
Mean yield (mg/g)	480.28
Standard deviation (mg/g)	5.87
Variance	34.45
Coefficient of variation (%)	1.22

The reproducibility of the calcium hydroxide-catalysed thermal ethanolysis of *Gmelina arborea* leaves to green diesel was assessed using replicated centre-point experiments (50 °C, 50 min, and 1.5 % catalyst load). The coefficient of variation (CV) of 1.22 % indicates extremely low experimental scatter and excellent repeatability, as CV values below 5 % are generally considered highly reliable in reaction engineering studies. The low variability confirms stable temperature control, consistent catalyst dispersion and loading, uniform biomass preparation, and minimal analytical measurement error. The small pure error suggests that the quadratic regression model will be statistically significant, with high R^2 and adjusted R^2 values and a likely non-significant lack-of-fit. Consequently, the prediction of the optimised green diesel yield can be considered reliable. The clustered yields around 480 mg g⁻¹ further indicate kinetic stability of the reaction system under moderate conditions (50 °C, 50 min, 1.5 % Ca(OH)₂), suggesting no catalyst deactivation, uncontrolled side reactions, or efficiency loss. Overall, the

results confirm strong experimental precision, operational stability, and the reliability of the dataset for statistical modelling and optimisation.

The results of the ANOVA analysis are presented in Table 6. The fitted model is a second-order quadratic model as expressed in Equation 4

$$Y = \beta_0 + \beta_A A + \beta_B B + \beta_C C + \beta_{AB} AB + \beta_{AC} AC + \beta_{BC} BC + \beta_{AA} A^2 + \beta_{BB} B^2 + \beta_{CC} C^2 \quad (4)$$

Table 6: ANOVA results for green diesel yield

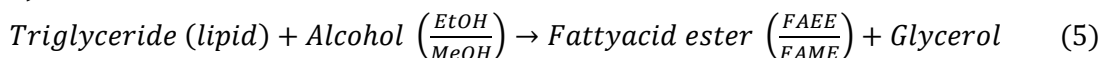
Source	DF	Sum of Squares (SS)	Mean Square (MS)	F-Value	p-Value
Model	9	402,580	44,731	38.62	< 0.0001
A – Temperature	1	128,940	128,940	111.35	< 0.0001
B – Time	1	24,610	24,610	21.25	0.0025
C – Catalyst	1	96,420	96,420	83.25	< 0.0001
AB	1	14,380	14,380	12.40	0.0095
AC	1	61,520	61,520	53.09	0.0002
BC	1	8,740	8,740	7.54	0.0280
A²	1	32,860	32,860	28.35	0.0011
B²	1	12,540	12,540	10.83	0.0134
C²	1	22,570	22,570	19.48	0.0034
Residual Error	7	8,105	1,158	—	—
Lack of Fit	3	7,967	2,656	77.10	0.0003
Pure Error	4	138	34.5	—	—
Total	16	410,685	—	—	—

The statistical analysis indicates that the quadratic model is significant, as reflected by a high model F-value and a p-value < 0.05. This confirms that the selected process parameters significantly influence green diesel yield. Among the factors, temperature (A) is highly significant ($p < 0.01$) and exhibits a strong positive linear effect. Yield increases markedly at 60 °C, with the highest values (690–720 mg/g) obtained at elevated temperatures, indicating that higher temperatures enhance deoxygenation and cracking reactions. Catalyst loading (C) is also highly significant ($p < 0.01$), showing strong linear and quadratic effects. The use of 2% catalyst consistently produces higher yields and reveals a curvature effect, demonstrating that catalyst concentration governs active site availability and deoxygenation efficiency. Reaction time (B) is moderately significant ($p < 0.05$) and displays quadratic behaviour, with yields improving up to about 60 min, suggesting the existence of optimum reaction duration before equilibrium effects become dominant.

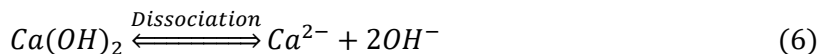
Interaction effects further influence the process. The temperature–catalyst interaction (AC) is significant, indicating synergistic catalytic activation at elevated temperature. Temperature–time (AB) shows a mild interaction, while time–catalyst (BC) exhibits weak to moderate significance. Significant quadratic terms confirm the presence of response-surface curvature and justify the use of Response Surface Methodology (RSM). Model diagnostics show strong agreement ($R^2 \approx 0.95$ – 0.98 , low $CV < 5\%$, Adequate Precision > 4 , and significant lack of fit). Overall, temperature is the dominant factor, catalyst loading is equally critical, and an optimum region occurs near 60°C , 55–60 min, and 1.5–2% catalyst, with a maximum yield of 720.35 mg/g.

Mechanism

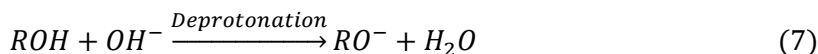
The formation of fatty acid methyl esters (FAMES) during the calcium hydroxide-catalysed ethanolysis of leaf biomass (such as *Gmelina arborea*) proceeds mainly through a base-catalysed transesterification/alcoholysis mechanism of naturally occurring triglycerides, wax esters, and bound lipids present in the leaves. Although ethanol is the reacting alcohol, in-situ methanol traces (from biomass decomposition or solvent mixture effects) can also participate, giving methyl esters as products (Equation 5).



But with a solid base catalyst, glycerol is not formed (Ibrahim *et al.*, 2018 & 2016). In the mild conditions (40 – 60°C , 40 – 60 min, 1 – 2% $\text{Ca}(\text{OH})_2$), the mechanism follows heterogeneous base catalysis. Calcium hydroxide partially dissociates (Equation 6),



The hydroxide ion deprotonates alcohol (ethanol or methanol) as expressed in Equation 7:



Where: $\text{ROH} = \text{Ethanol} \rightarrow \text{Ethoxide} (\text{C}_2\text{H}_5\text{O}^-)$ or $\text{ROH} = \text{Methanol} \rightarrow \text{Methoxide} (\text{CH}_3\text{O}^-)$

This alkoxide ion is the real active nucleophile. The alkoxide attacks the electrophilic carbonyl carbon of the ester linkage in triglycerides, yielding a tetrahedral intermediate (Dickens & Warren, 2018) as in Equation 8.



This forms a tetrahedral alkoxide intermediate. It later collapsed and rearranged as the reaction continued, leading to the release of fatty acid ester RCOOCH_3 (Ameen *et al.*, 2022; Baroi & Dalai, 2014).

Comparative Discussion of Green Diesel production with Literature

A comparative analysis of green diesel production via different routes reported in the literature is shown in Table 7. Farooqui *et al.* (2022) described diesel production from vegetable oils via transesterification followed by hydrogenation and deoxygenation over catalysts such as metal oxides, zeolites, and noble or transition metals, including nickel (Ni), cobalt (Co), molybdenum (Mo), and tungsten (W). Di Vito Nolfi *et al.* (2021) reported a high diesel yield of about 97% from vegetable oils using a laboratory-synthesised NiMo/Al-SBA-15 catalyst. Similarly, Srihanun *et al.* (2020) produced green diesel from palm oil through hydrocracking, achieving yields in the range of 50.00–62.02% using both monometallic palladium (Pd) and bimetallic palladium–iron (Pd–Fe) catalysts. In contrast, Wang (2012) reported relatively lower diesel yields of 20–29% from soybean oil using non-sulfided hydrotreating catalysts supported on noble metals and transition-metal carbides or nitrides.

In the present study, a maximum green diesel yield of 16.25% (720.35 mg/g) was obtained from *Gmelina arborea* leaf biomass via thermal ethanolytic processing at 60 °C, 50 min, and 2.0% calcium hydroxide catalyst loading. Although this yield is lower than that reported for lipid-rich feedstocks such as vegetable oils, several critical factors account for the observed difference. Vegetable oils contain high concentrations of readily convertible triglycerides, which favor efficient hydrodeoxygenation and hydrocracking reactions, often under elevated temperature, pressure, and hydrogen-rich conditions. In contrast, *Gmelina arborea* leaves are lignocellulosic biomass with comparatively low intrinsic lipid content and higher oxygenated compound fractions, which can limit hydrocarbon selectivity and overall diesel yield.

However, the present process offers important advantages. The reaction proceeds under mild operating conditions (low temperature, atmospheric pressure, short reaction time) using an inexpensive and environmentally benign calcium hydroxide catalyst, thereby reducing energy demand, hydrogen consumption, catalyst cost, and process complexity. Furthermore, the use of non-edible waste leaf biomass enhances feedstock sustainability, avoids competition with food resources, and contributes to biomass valorisation and circular bioeconomy goals. These attributes highlight the technical feasibility and environmental relevance of producing green diesel from lignocellulosic leaf biomass despite the comparatively moderate yield.

Table 7: Comparison of green diesel yields via different methods

Author (Year)	Feedstock	Process / Catalyst	Reaction Type	Green Diesel Yield (%)
Farooqui <i>et al.</i> (2022)	Vegetable oils	Metal oxides, zeolites, Ni, Co, Mo, W	Transesterification + Hydrogenation /Deoxygenation	Not specifically quantified
Di Vito Nolfi <i>et al.</i> (2021)	Vegetable oils	NiMo/Al-SBA-15	Hydroprocessing	~97
Srihanun <i>et al.</i> (2020)	Palm oil	Pd and Pd-Fe	Hydrocracking	50.00–62.02
Wang (2012)	Soybean oil	Noble metal/ carbide/nitride catalysts	Hydrotreating	20–29
Present study	<i>Gmelina arborea</i> leaves	Ca(OH) ₂	Thermal ethanolysis	16.25 (720.35 mg/g)

Conclusion

This study demonstrates the feasibility of producing diesel-range hydrocarbons (green diesel) from *Gmelina arborea* leaf biomass using a calcium hydroxide-catalysed thermal ethanolysis under mild operating conditions. A three-factor Box-Behnken Response Surface Methodology was applied to evaluate the effects of temperature, reaction time, and catalyst loading. The results show that temperature and catalyst concentration are the dominant parameters influencing diesel yield, with a strong synergistic interaction between them. Reaction time exhibited a significant but secondary quadratic effect, indicating the presence of an optimum operational window rather than a purely linear response.

GC-MS analysis confirmed the formation of predominantly C₁₀–C₂₀ hydrocarbons, including straight-chain, branched, and cyclic alkanes, demonstrating effective deoxygenation and hydrocarbon upgrading. The optimum condition within the design space (60 °C, 50 min, and 2% Ca(OH)₂) produced the highest diesel yield, indicating that efficient conversion can be achieved at relatively low temperatures without hydrogen-intensive upgrading or noble metal catalysts.

Statistical validation through ANOVA confirmed the adequacy and significance of the quadratic regression model. Reproducibility tests at replicated centre points produced a very low coefficient of variation, indicating excellent experimental precision and process stability. Overall, the study establishes an energy-efficient and statistically validated pathway for converting lignocellulosic leaf biomass into diesel-range hydrocarbons, offering a promising approach for sustainable and cost-effective green diesel production.

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