



LONG-CHAIN HYDROCARBON PRODUCTION FROM LIGNOCELLULOSIC LEAVES USING MILD CALCIUM HYDROXIDE CATALYSIS

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Abstract

The conversion of renewable biomass into long-chain hydrocarbons offers a sustainable alternative to fossil-derived fuels and petrochemicals. This study reports a low-severity catalytic route for the selective synthesis of (C₂₀-C₂₉) hydrocarbons from *Gmelina arborea* leaf biomass via calcium hydroxide-catalyzed ethanolysis under atmospheric pressure. A Box-Behnken Response Surface Methodology was applied to evaluate and optimise the effects of reaction temperature (40-60 °C), reaction time (40-60 min), and catalyst loading (1-2 wt%) on hydrocarbon yield. The GC-MS analysis confirmed the formation of fifteen long-chain saturated hydrocarbons within the C₂₀-C₂₉ range, alongside other industrially relevant phytochemicals. The hydrocarbon yield ranged from 5.40 to 11.76%, corresponding to 17.3-521.3 mg/g of biomass. The analysis of variance indicated that

temperature was the most influential parameter, followed by catalyst loading, with all linear and interaction terms being statistically significant ($p < 0.0001$). The maximum yield of 11.76%

Keywords:

Gmelina arborea leaves, lignocellulosic biomass, calcium hydroxide catalysis, thermal ethanolytic process, long-chain hydrocarbons, renewable biofuels

(521.3 mg/g) was achieved at 60 °C, 50 min, and 2 wt% Ca(OH)₂/wt of feed. These results demonstrate that mild alkaline catalysis combined with statistical optimisation provides an efficient, low-energy pathway for producing fuel-range long-chain hydrocarbons from leaf-derived lignocellulosic biomass.

Introduction

In response to the escalating global energy demands and intensifying environmental concerns, the development of sustainable and environmentally benign alternatives to fossil-derived fuels has become a critical focus of contemporary scientific research. Bio-based hydrocarbons derived from renewable biomass resources have attracted significant attention as viable substitutes for conventional petrochemical feedstocks, owing to their potential to reduce greenhouse gas emissions and dependence on finite fossil reserves (Lecinena, 2020; Van Maldegem, 2017). Among these renewable hydrocarbons, the production of long-chain alkanes in the $C_{20}H_{42}$ - $C_{29}H_{60}$ range has garnered particular interest due to their wide-ranging industrial relevance. This fraction encompasses long-chain saturated hydrocarbons, commonly referred to as paraffins, extending to eicosane ($C_{20}H_{42}$) (Bays et al., 2023; Salgado-Brito et al., 2007). These compounds constitute the heavy alkane fraction and exhibit distinctive physicochemical properties, including high thermal stability, low reactivity, and favourable lubricity, which make them suitable for applications as biofuels, lubricants, waxes, and specialty chemicals (Dhar et al., 2018; Nieto-Draghi et al., 2015).

Conventional sources of C_{20} alkanes, such as petroleum-derived waxes and Fischer-Tropsch synthesis, are increasingly constrained by sustainability concerns, high energy requirements, and economic limitations (Kumbhakar et al., 2016; Misuraca et al., 2023). As a result, lignocellulosic biomass has emerged as a promising renewable feedstock for the production of long-chain hydrocarbons, particularly due to its intrinsic content of waxy lipids, long-chain fatty acids, alcohols, and other oxygenated precursors embedded within plant tissues and surface layers (Mitra et al., 2020). Within this framework, *Gmelina arborea* represents an attractive yet underutilized biomass resource. As a fast-growing tropical species with abundant leaf biomass, *Gmelina arborea* leaves are enriched with surface waxes and long-chain oxygenated compounds that can serve as direct precursors for heavy alkanes (Ameh et al., 2025; Jose et al., 2024; Adenaiya, 2021). However, the effective conversion of these oxygen-rich components into stable C_{20} hydrocarbons requires catalytic systems capable of promoting selective dehydration, decarboxylation, and deoxygenation while suppressing excessive cracking and aromatization.

Previous studies have demonstrated that aromatic hydrocarbons such as benzene, toluene, and xylene, as well as light alkanes, can be generated through deoxygenation of lignocellulosic biomass vapours over HZSM-5 zeolite catalysts (Pagano et al., 2025; Artillo et al., 2023; Yan et al., 2023; Yan & Li, 2020). During catalytic upgrading, cellulose-derived vapours undergo sequential dehydration, decarbonylation, and aromatisation reactions, resulting in the formation of fuel-range hydrocarbons (He et al., 2025; Lin et al., 2020). Hydrothermal liquefaction has also been widely reported as an effective route for converting wet lignocellulosic biomass into biocrude, which can subsequently be

upgraded into hydrocarbon fuels (Batalha *et al.*, 2023; Venkatachalam *et al.*, 2022; Hao *et al.*, 2021). Similarly, reductive depolymerization of lignin using metal-based or alkaline catalysts facilitates its transformation into alkylated aromatic compounds and paraffinic hydrocarbons (Zhang *et al.*, 2023; Mankar *et al.*, 2022; Lu *et al.*, 2021).

Notably, investigations involving leaf and agricultural biomass extracts have reported the occurrence of long-chain hydrocarbons in the C₂₀-C₃₀ range, largely attributed to waxes, cuticular lipids, and lignin-derived intermediates (Özdemir, 2025; Sarmah *et al.*, 2025). In biological conversion pathways, lignocellulosic biomass is first transformed into oxygenated intermediates, which are subsequently upgraded into hydrocarbons through catalytic or thermochemical processes (Yan *et al.*, 2025a; Han *et al.*, 2019; Davis *et al.*, 2018). Furthermore, fermentation-derived intermediates such as ethanol and fatty acids obtained from lignocellulosic sugars have been successfully catalytically upgraded into drop-in hydrocarbons, including alkanes and alkenes, suitable for fuel applications (Redda *et al.*, 2024; Shanmugam *et al.*, 2023; James & Maity, 2022).

Current biomass-to-hydrocarbon conversion strategies predominantly target the production of light alkanes and aromatic hydrocarbons via catalytic pyrolysis, hydrothermal liquefaction, or metal-assisted upgrading processes (Imran-Shaukat *et al.*, 2025; Kella *et al.*, 2025). While effective, these methods often operate under severe reaction conditions and rely on costly catalysts, limiting their selectivity toward long-chain saturated hydrocarbons (Yan *et al.*, 2025b; Li *et al.*, 2024). As a result, C₂₀-C₃₀ alkanes, despite their industrial importance as diesel-range fuels, lubricants, and waxes, are typically obtained only as minor fractions rather than as targeted products. Moreover, the majority of reported studies focus on woody biomass or agricultural residues, whereas leaf biomass, which is inherently rich in epicuticular waxes and long-chain oxygenated compounds, remains underexplored. The potential of mild alkaline catalysts, particularly calcium hydroxide, to selectively promote ethanolysis and long-chain hydrocarbon formation under low-temperature and atmospheric-pressure conditions has not been systematically investigated. Additionally, there is limited application of statistical optimisation techniques, such as Response Surface Methodology, for elucidating the combined and interactive effects of key process variables on long-chain hydrocarbon yield from leaf biomass. Accordingly, this work fills an important research gap by developing and optimising a calcium hydroxide-catalysed ethanolysis process for the selective production of eicosane hydrocarbons from *Gmelina arborea* leaves, offering a low-energy and sustainable alternative to conventional biomass upgrading routes.

This study aims to develop and optimise a low-severity route for the selective production of eicosane hydrocarbons from *Gmelina arborea* leaf biomass via calcium hydroxide-catalysed ethanolysis. Using a Box-Behnken Response Surface Methodology design, the effects and interactions of temperature, reaction time, and catalyst loading on

hydrocarbon yield are systematically evaluated, statistically validated by ANOVA, and optimised to identify conditions that maximise C₂₀-C₃₀ hydrocarbon formation under mild reaction conditions.

Experimental Design

A Box-Behnken experimental design based on Response Surface Methodology (RSM) was employed to generate 17 experimental runs, as presented in Table 1. The design was used to evaluate the effects of temperature, reaction time, and catalyst loading on the yield of long-chain hydrocarbons.

Biomass Preparation

Dry leaves of *Gmelina arborea* were collected from the Kaduna Polytechnic premises. The samples were thoroughly cleaned, milled, and sieved to obtain a uniform particle size, following the procedures reported by Ibrahim et al. (2025a) and Ali and Ibrahim (2023a).

Preparation of Catalytic Reaction System

The catalytic solution was prepared by dissolving 1.0 g of calcium hydroxide (Ca(OH)₂), corresponding to 2.0% (w/w) of the biomass feed, in 500 mL of ethanol. Subsequently, 50 g of the processed *Gmelina arborea* leaf powder was introduced into the solution.

Thermal Ethanolysis Procedure

The reaction mixture was heated at 60 °C for 50 minutes using a Gallenkamp hot plate equipped with a magnetic stirrer to ensure homogeneous mixing. After completion of the reaction, the mixture was initially filtered through a filter cloth and further clarified using Whatman filter paper, following the method described by Ali and Ibrahim (2023b). The recovered filtrate was weighed, and a 5 g portion was withdrawn for subsequent analysis. This experimental procedure was consistently applied to all runs specified in the Box-Behnken design matrix (Table 1).

Experimental Design Matrix

Table 1: Box Behnken Response Surface Methodology experimental design

Run	Temp (°C)	Time (min)	Catalyst (%)
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

Run	Temp (°C)	Time (min)	Catalyst (%)
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

Derivatisation Procedure

For derivatisation, 200 µL of the analyte was mixed with 100 µL of trimethyl sulphonium 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 the method reported by Ibrahim et al. (2025b) and Ibrahim et al., (2024).

GC-MS Analysis

The GC-MS analyses were carried out using a Varian 3800/4000 gas chromatograph-mass spectrometer equipped with a DB-5 capillary column (30 m × 0.25 mm × 0.25 µm). Nitrogen was used as the carrier gas with a column head pressure maintained at 10 psi. The oven temperature program was set to an initial temperature of 100 °C (held for 3 minutes), followed by a ramp of 8 °C min⁻¹ to a final temperature of 300 °C. The transfer line temperature was maintained at 290 °C. The VG 7070E magnetic sector mass spectrometer operated under electron impact ionisation conditions.

Results and Discussion

Some few samples of the GC-MS chromatograms are presented in Figure 1. The GC-MS analysis revealed the presence of fifteen long-chain hydrocarbons spanning the eicosane (C₂₀H₄₂) to 2-methyloctacosane (C₂₉H₄₀) range, as summarized in Table 2. In addition to these hydrocarbons, several other phytochemicals of notable industrial relevance were detected, underscoring the chemical diversity of the product mixture and its potential applicability in fuel, lubricant, and specialty chemical industries.

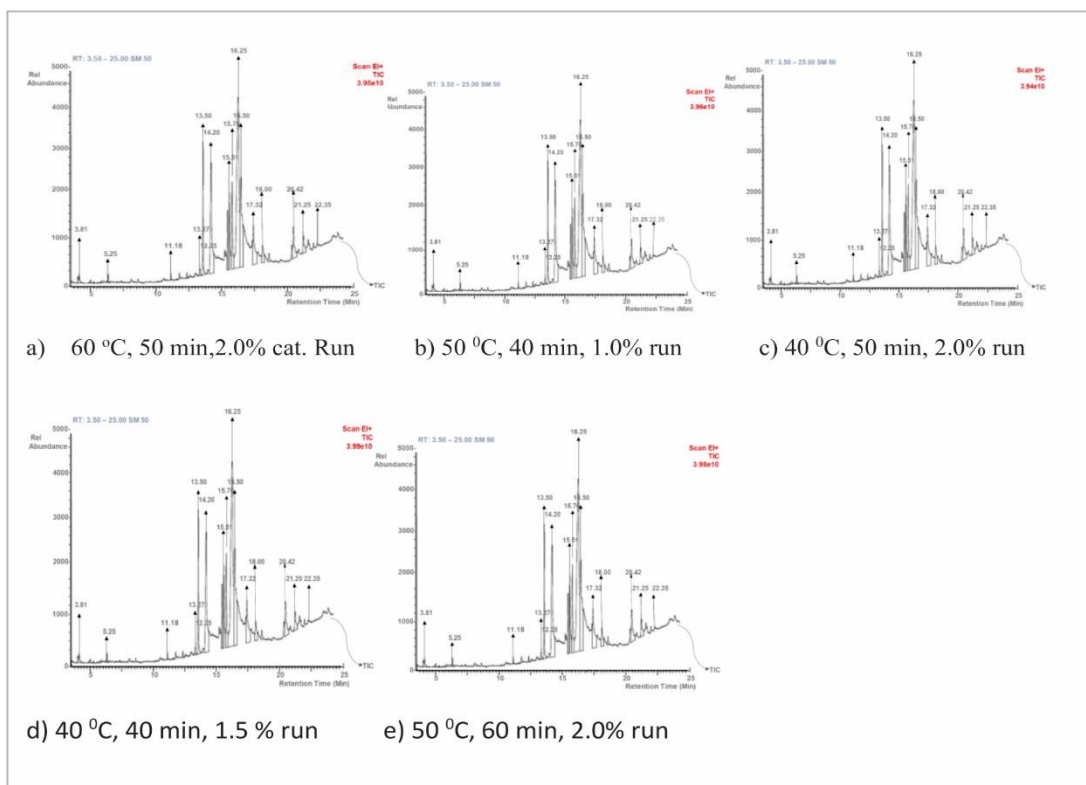


Figure 1: products chromatograms

Table 2: Eicosane hydrocarbons obtained from the *Gmelina arborea* leaf

S/N	Compounds	Molecular Formula
1.	Eicosane	C ₂₀ H ₄₂
2.	Heneicosane	C ₂₁ H ₄₄
3.	Docosane	C ₂₂ H ₄₆
4.	Tricosane	C ₂₃ H ₄₈
5.	11-Methyltricosane	C ₂₄ H ₅₀
6.	Pentacosane	C ₂₅ H ₅₂
7.	2-Methyltetracosane	C ₂₅ H ₅₂
8.	Heneicosane, 11-(1-ethylpropyl)	C ₂₆ H ₅₄
9.	Hexacosane	C ₂₆ H ₅₄
10.	11-Methylpentacosane	C ₂₆ H ₅₄
11.	Heptacosane	C ₂₇ H ₅₆
12.	13-Methylheptacosane	C ₂₈ H ₅₈
13.	9-Octyl eicosane,	C ₂₈ H ₅₈
14.	Octacosane	C ₂₈ H ₅₈
15.	2-methyloctacosane	C ₂₉ H ₆₀

The Box-Behnken response surface design was employed to evaluate the combined effects of reaction temperature (40-60 °C), reaction time (40-60 min), and calcium hydroxide catalyst loading (1-2 %) on the yield of long-chain hydrocarbons (eicosane to 2-methyloctacosane) obtained from the calcium hydroxide-catalyzed ethanolysis of *Gmelina arborea* leaves. The results reveal a strong dependence of hydrocarbon yield on both individual factors and their interactions. The weight of the products (filtrates), the percentage yields of the eicosane to 2-methyloctacosane as revealed by GC-MS, and the specific yield (mg/g) are presented in Table 3.

The specific yield in (mg/g) is expressed as in Equation 1.

$$\text{Yield} \left(\frac{\text{mg}}{\text{g}} \right) = \frac{\text{Yield} (\%)}{100 \times \text{mass of the feed (50g)}} \times \text{mass of filtrate (product)} (C20 - C29) \times 1000 \quad (1)$$

The product yield (%) varied from 1.25 to 11.76 %, while the specific yield expressed in mg/g ranged from 17.3 to 521.3 mg/g, (Table 3) indicating a wide response window and good experimental sensitivity for model development. Generally, higher yields were observed at moderate to high temperatures (50-60 °C) combined with intermediate to higher catalyst loadings (1.5-2 %), suggesting that calcium hydroxide effectively promotes ethanolysis and subsequent formation of long-chain hydrocarbons under mild thermal conditions. The maximum yield of 11.76 % and a corresponding 521.3 mg/g were obtained at 60 °C, 50 min, and 2 % catalyst loading (run 1). This condition reflects an optimal balance between sufficient catalytic activity and controlled reaction severity, minimising secondary degradation or volatilisation of the formed hydrocarbons. Similarly, high yields were recorded at 60 °C and 1.5-2 % catalyst loading (runs 11 and 16), confirming the positive influence of elevated temperature on reaction kinetics and mass transfer.

Table 3: The yield of C20-C29 hydrocarbons from *Gmelina arborea* leaf

Run	Temp (°C)	Time (min)	Catalyst (%)	Product (g)	Yield (%)	Yield (mg/g)
1	60	50	2.0	221.7	11.76	521.44
2	50	40	1.0	176.7	5.63	198.96
3	40	50	2.0	258.9	1.93	99.94
4	40	40	1.5	249.0	2.72	135.46
5	50	60	2.0	224.9	6.40	287.87
6	50	60	1.0	165.2	1.25	41.30
7	50	50	1.5	138.4	7.78	215.35
8	50	50	1.5	195.9	5.50	215.49
9	40	60	1.5	138.1	0.66	18.23

Run	Temp (°C)	Time (min)	Catalyst (%)	Product (g)	Yield (%)	Yield (mg/g)
10	50	50	1.5	162.7	6.62	215.42
11	60	40	1.5	255.2	7.78	397.09
12	40	50	1.0	143.6	0.60	17.23
13	50	50	1.5	139.3	7.73	215.36
14	50	40	2.0	274.2	6.08	333.43
15	50	50	1.5	102.9	10.46	215.27
16	60	60	1.5	222.9	7.79	347.28
17	60	50	1.0	175.1	6.37	223.08

In contrast, experiments conducted at low catalyst loading (1 %) and lower temperatures (40-50 °C) generally resulted in reduced yields, as seen in Runs 6, 9, and 12. The notably low mg/g values (17.3-41.3 mg/g) under these conditions indicate insufficient catalytic sites to effectively drive ethanolysis and subsequent hydrocarbon chain formation. This highlights the critical role of catalyst concentration in facilitating bond cleavage and rearrangement reactions leading to C₂₀-C₂₉ hydrocarbons. The centre point runs (Runs 7, 8, 10, 13, and 15), all conducted at 50 °C, 50 min, and 1.5 % catalyst, exhibited moderate and reproducible yields, particularly evident from the consistent 215.3 mg/g values. This reproducibility confirms good experimental control and supports the adequacy of the Box-Behnken design for modeling the system. The observed variability in percentage yield among these centre points reflects natural experimental error rather than systematic bias, further validating the robustness of the dataset.

Overall, the results demonstrate that calcium hydroxide is an effective, low-cost catalyst for promoting the conversion of *Gmelina arborea* leaf biomass into long-chain hydrocarbons via ethanolysis. The response trends indicate that temperature-catalyst interactions play a more dominant role than reaction time alone, with excessive or insufficient conditions leading to sub-optimal yields. These findings underscore the potential of mild alkaline catalysis combined with statistical optimisation as a viable pathway for producing fuel-range hydrocarbons from renewable leaf biomass.

Reproducibility

The reproducibility of the experimental design was assessed using replicated centre-point runs under identical operating conditions of 50 °C reaction temperature, 50 min reaction time, and 1.5% catalyst loading. Five independent experiments conducted at these conditions yielded almost the same results, as summarized in Table 4. The individual yields were identical (215.3 mg/g), resulting in a mean of 215.27-215.49 mg/g, a standard deviation of 0.082 mg/g, and a coefficient of variation of 0.038 %. This confirms excellent

reproducibility, high experimental precision, and the reliability of the applied Box-Behnken Response Surface Methodology for modeling the production of long-chain hydrocarbons (C₂₀–C₂₉) from *Gmelina arborea* leaf biomass.

Table 4: Parameter Value

Parameter	Value
Temperature (°C)	50
Time (min)	50
Catalyst (%)	1.5
Number of replicates	5
Individual yields (mg/g)	215.35, 215.49, 215.42, 215.36, 215.27
Mean yield (mg/g)	215.38
Standard deviation (mg/g)	0.082
Coefficient of variation (%)	0.038

ANOVA analysis for the two-factor interaction (2FI) model

The analysis of variance (ANOVA) for the two-factor interaction (2FI) model demonstrates that the developed model is highly significant for describing the yield of the long-chain hydrocarbons obtained from the calcium hydroxide-catalyzed ethanolysis of *Gmelina arborea* leaves. The overall model exhibits an extremely large F-value (9.95×10^7) with a corresponding p-value < 0.0001 (Table 5), confirming that the model adequately explains the variability in the experimental response and is statistically reliable. The developed quadratic model for predicting the yield of long-chain hydrocarbons (C₂₀–C₂₉) in terms of coded factors is expressed in Equation 2:

$$Y = 215.3 + 96.8A + 45.4B + 67.2C + 25.8AB + 54.0AC + 28.1BC \quad (2)$$

The positive coefficients of temperature, time, and catalyst loading indicate their synergistic contribution to hydrocarbon yield, while the interaction terms further confirm the combined influence of process variables, consistent with the highly significant ANOVA results ($p < 0.0001$).

Table 5: ANOVA of two-factor Interaction

Source	Sum of Squares	DF	Mean Squares	F-value	p-value	Remark
Model	3.073×10^5	6	51220.12	9.951×10^7	< 0.0001	significant
A-Temperature	1.968×10^5	1	1.968×10^5	3.823×10^8	< 0.0001	
B-Time	20614.65	1	20614.65	4.005×10^7	< 0.0001	
C-Catalyst loading	72485.28	1	72485.28	1.408×10^8	< 0.0001	

Source	Sum of Squares	DF	Mean Squares	F-value	p-value	Remark
AB	2667.72	1	2667.72	5.183×10^6	<0.0001	
AC	11653.20	1	11653.20	2.264×10^7	<0.0001	
BC	3147.21	1	3147.21	6.115×10^6	<0.0001	
Residual	0.0051	10	-	-	-	
Lack of Fit	0.0051	6	-	-	-	
Pure Error	0.0000	4	-	-	-	
Cor. Total	3.073×10^{16}	16	-	-	-	

Significance of main (linear) effects

All three linear factors, temperature (A), reaction time (B), and catalyst loading (C), are statistically significant, each with p-values < 0.0001. Among these, temperature (A) shows the highest F-value (3.82×10^8), indicating that it is the most influential parameter governing hydrocarbon yield. This result confirms that thermal energy plays a dominant role in enhancing reaction kinetics, ethanolysis efficiency, and long-chain hydrocarbon formation. Catalyst loading (C) also exerts a strong effect, as reflected by its high F-value (1.41×10^8), highlighting the importance of calcium hydroxide in providing active alkaline sites for bond cleavage and rearrangement reactions. Reaction time (B), although comparatively less dominant, remains highly significant ($F = 4.01 \times 10^7$), indicating that sufficient residence time is required to achieve effective conversion.

Interaction effects

The interaction terms AB (temperature-time), AC (temperature-catalyst loading), and BC (time-catalyst loading) are all statistically significant at $p < 0.0001$, confirming that the factors do not act independently. Among the interaction terms, AC shows the highest F-value (2.26×10^7), indicating a strong synergistic interaction between temperature and catalyst loading. This suggests that temperature increases significantly enhance the catalytic effectiveness of calcium hydroxide, leading to higher yields when both variables are simultaneously optimized. The AB and BC interactions, though less pronounced, are still significant, implying that the effect of reaction time depends on temperature and catalyst concentration, respectively.

Model adequacy and error analysis

The residual sum of squares is extremely low (0.0051), indicating minimal unexplained variation between experimental and predicted values. Furthermore, the lack-of-fit is insignificant relative to the pure error, demonstrating that the model fits the experimental data well and that no major systematic deviation exists. This confirms the suitability of the 2FI model for navigating the design space and predicting hydrocarbon yield within the studied ranges.

Overall interpretation

Overall, the ANOVA results confirm that the yield of eicosane hydrocarbons is strongly influenced by both individual process variables and their interactions, with temperature being the most dominant factor. The statistical significance of all model terms, combined with negligible residual error, validates the robustness and predictive capability of the developed response surface model. This strong model performance supports its application for process *optimisation* and scale-up considerations in the sustainable production of fuel-range hydrocarbons from *Gmelina arborea* leaf biomass.

There is relatively limited literature on the direct production of hydrocarbons from biomass, with most reported routes relying on severe thermal conditions. French and Czernik (2010) investigated the pyrolysis of cellulose, lignin, and wood in quartz reactors with direct catalyst contact at 400-600 °C, achieving a maximum hydrocarbon yield of 16%. Notable exceptions include the carbonisation of corn straw and wood chips by Fei-fei et al. (2011) at 500-600 °C and 600-700 °C, respectively, which produced 48.42% and 52.36% carbon-rich products, with corn straw containing 17.15% alkanes. Similarly, Mortimer et al. (2012) reported the formation of 6.3% long-chain (C₂₉-C₃₃) saturated hydrocarbons from *Nicotiana glauca* leaves. In contrast, the present study achieved 11.76 % (521.30 mg/g) long-chain hydrocarbons from *Gmelina arborea* leaves via calcium hydroxide-catalysed ethanolysis under markedly milder conditions (60 °C, 50 min, and 2.0 % catalyst loading), highlighting the energy efficiency and sustainability of the proposed approach.

Table 6: Comparison of Hydrocarbon Production from Biomass

S/N	Biomass Source	Process Catalyst	Operating Conditions	Hydrocarbon Yield	Remarks	References
1	Cellulose, lignin, wood	Catalytic pyrolysis	400-600 °C	16%	Severe thermal conditions	French & Czernik (2010)
2	Corn straw	Carbonization	500-600 °C	48.42% (17.15% alkanes)	High carbon-rich fraction	Fei-fei et al. (2011)
3	Wood chips	Carbonization	600-700 °C	52.36%	High temperature required	Fei-fei et al. (2011)
4	<i>Nicotiana glauca</i> leaves	Thermal conversion	Not specified	6.3% (C ₂₉ -C ₃₃ hydrocarbons)	Long-chain hydrocarbons	Drapal et al. (2022)
5	<i>Gmelina arborea</i> leaves	Ca(OH) ₂ -catalysed ethanolysis	60 °C, 50 min, 2.0 % catalyst	3.65% (101.56 mg/g)	Mild, energy-efficient process	In this study

A critical comparison of the present study with previously reported biomass-to-hydrocarbon conversion processes (Table 6) reveals several important advancements in

terms of reaction severity, selectivity, and sustainability. Conventional approaches, such as the catalytic pyrolysis of cellulose, lignin, and wood reported by French and Czernik (2010), typically operate at high temperatures (400-600 °C) and yield approximately 16% hydrocarbons. While the yield is relatively moderate, these processes are energy-intensive and often favour the formation of aromatic hydrocarbons and lighter fractions, rather than selectively producing long-chain alkanes.

Similarly, carbonisation processes investigated by Fei-fei et al. (2011) for corn straw and wood chips require even more severe conditions (500-700 °C), producing high overall carbon yields (48–52%). However, only a fraction ($\approx 17.15\%$) corresponds to alkanes, indicating limited selectivity toward fuel-range long-chain hydrocarbons. These processes are therefore less efficient when targeting specific hydrocarbon fractions such as C_{20} - C_{29} . In comparison, the work of Mortimer et al. (2012) on *Nicotiana glauca* leaves reported 6.3% long-chain hydrocarbons, demonstrating the feasibility of obtaining higher molecular weight hydrocarbons from leaf biomass. However, the process conditions were not clearly defined, and the yield remains lower than that achieved in the present study.

In contrast, the present work demonstrates a significant advancement by achieving a maximum yield of 11.76% (521.3 mg/g) of C_{20} - C_{29} hydrocarbons under remarkably mild conditions (60 °C, 50 min, 2% $Ca(OH)_2$). This represents a substantial reduction in energy demand compared to conventional thermochemical routes. Furthermore, unlike pyrolysis and carbonisation, which often produce complex mixtures, the present method shows enhanced selectivity toward long-chain saturated hydrocarbons, attributable to the controlled ethanolysis and mild alkaline catalytic environment. Another key distinction is the application of Response Surface Methodology (RSM), which enabled systematic optimisation of process variables and identification of significant interaction effects. This level of statistical optimisation is largely absent in earlier studies, making the present work more robust and scalable.

Overall, the comparison highlights that the present study offers: lower energy consumption (mild temperature and atmospheric pressure), improved selectivity toward C_{20} - C_{29} hydrocarbons, comparable or superior yields relative to some prior works, and better process control and optimisation through RSM

Conclusion

This study demonstrates a viable low-severity pathway for the selective production of long-chain hydrocarbons (C_{20} - C_{29}) from *Gmelina arborea* leaf biomass using calcium hydroxide-catalyzed ethanolysis under atmospheric pressure. The GC-MS analysis confirmed the formation of fifteen saturated hydrocarbons within the eicosane range, highlighting the intrinsic suitability of leaf biomass as a precursor for fuel- and lubricant-range hydrocarbons. The statistical optimisation using a Box-Behnken Response Surface

Methodology revealed that reaction temperature and catalyst loading exert the most significant influence on hydrocarbon yield, with strong synergistic interactions among process variables. The highest yield of 11.76 %, corresponding to 521.3 mg/g of biomass, was achieved at 60 °C, 50 min, and 2 wt% Ca(OH)₂, reflecting an optimal balance between catalytic activity and reaction severity. The high model significance, negligible residual error, and excellent reproducibility confirm the robustness and predictive capability of the developed process. Overall, the results establish calcium hydroxide as an effective, low-cost catalyst for upgrading leaf-derived lignocellulosic biomass into fuel-range hydrocarbons under mild conditions, offering a sustainable and energy-efficient alternative to conventional high-severity biomass conversion routes.

Recommendations for Future Work

To further advance this research and enhance its industrial applicability, the following recommendations are proposed:

Catalyst Optimization and Modification

Future studies should explore modified or supported alkaline catalysts (e.g., Ca(OH)₂ on porous supports or mixed metal oxides) to improve catalytic activity, selectivity, and reusability.

Mechanistic Studies

Detailed investigation into the reaction pathways (ethanolysis, decarboxylation, and deoxygenation mechanisms) using advanced analytical tools (e.g., GC-MS kinetics, FTIR, isotopic labeling) would provide deeper insight into hydrocarbon formation.

Catalyst Reusability and Stability

The recyclability and long-term stability of calcium hydroxide should be evaluated to assess economic feasibility and process sustainability.

Scale-Up Studies

Transition from laboratory-scale to pilot-scale reactors is necessary to evaluate heat and mass transfer limitations and confirm industrial viability.

Process Integration

Integration of this process into a biorefinery framework, combining upstream biomass pretreatment and downstream product upgrading, should be explored.

Feedstock Diversification

Investigation of other leaf-based and agricultural biomass with high wax content could validate the general applicability of the process.

Product Upgrading and Fuel Testing

Further upgrading of the produced hydrocarbons and evaluation of their fuel properties (cetane number, viscosity, cold flow properties) will be essential for real-world applications.

Life Cycle and Techno-Economic Analysis

Comprehensive life cycle assessment (LCA) and techno-economic analysis (TEA) should be conducted to quantify environmental benefits and economic competitiveness relative to fossil-based processes.

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