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Valorisation of Non-Citrus Lignocellulosic Leaf Waste for Limonene Production Using Calcium Hydroxide-Catalysed Thermal Ethanolysis

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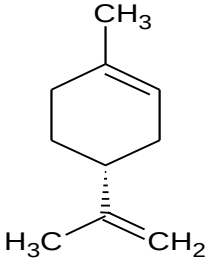
Abstract

The increasing demand for sustainable and renewable sources of industrial chemicals has intensified interest in the valorisation of lignocellulosic biomass into value-added products such as monoterpenes. This study investigates the production of limonene from Gmelina arborea leaf waste via a calcium hydroxide–catalysed thermal Ethanolytic process operated under mild conditions. A three-factor Box–Behnken design within the framework of Response Surface Methodology (RSM) was employed to evaluate the effects of reaction temperature (40-60 °C), reaction time (40–60 min), and catalyst loading (1-2 wt.%) on limonene yield, and to develop a predictive quadratic model for process optimisation. Experimental results revealed significant variation in limonene yield (18.75-351.07 mg/g), with a maximum yield of 6.78% (351.07 mg/g) achieved at 40 °C, 50 min, and 2% catalyst loading. Analysis of variance (ANOVA) indicated that the model was highly significant ($p < 0.0001$) with a high coefficient of determination ($R^2 = 0.974$), confirming strong agreement between experimental and predicted values. All process variables exhibited significant linear and quadratic effects, while interaction effects between temperature–time and temperature–catalyst loading were also notable. Reproducibility assessment using replicated centre-points yielded a low coefficient of variation (CV = 2.25%), demonstrating excellent experimental precision and reliability. GC-MS analysis confirmed the successful formation of limonene, while the results showed that lower temperatures favour product stability by minimising thermal degradation and volatilisation losses. Although the yield is lower than that obtained from citrus-derived sources, this study demonstrates the technical feasibility of producing limonene from non-citrus lignocellulosic biomass using a low-energy catalytic process. The findings highlight the potential of Gmelina arborea leaves as an alternative renewable feedstock and contribute to advancing sustainable biomass conversion strategies within a circular bioeconomy framework.

Keywords: *Alkaline catalysis; Biomass valorisation; Box–Behnken design; Gmelina arborea; Limonene.*

1.0 Introduction

Biomass provides a wide range of valuable chemicals for industrial applications, including those used in food, fuels, medicines, flavours, fragrances, and cosmetics. One such important compound derived from biomass is limonene. Limonene ($C_{10}H_{16}$) is a naturally occurring cyclic monoterpene commonly found in citrus peel oils [1]. Recent insights into the importance of limonene and its biotransformed value-added compounds underscore its potential to replace petrochemical-derived ingredients with bio-based alternatives that possess enhanced bioactivity and commercial value [1-3]. Structurally, it consists of a cyclohexene ring with a methyl group at position 1 and an isopropenyl group at position 4, as illustrated in Figure 1. Due to its renewable origin and low toxicity, limonene has attracted significant attention as a green solvent [4, 5]. It is widely used in cleaning products, paint removers, and degreasers [5-7]. In the food and beverage industry, limonene is commonly employed as a flavouring agent [4, 8, 9]. In fragrance formulations, it serves as a key component in perfumes and personal care products [10-12]. Additionally, limonene has important pharmaceutical applications, where it is used as a penetration enhancer in drug delivery systems [13-15]. It also plays a role in polymer and resin production as a precursor for bio-based polymers and adhesives [16-18]. Furthermore, in agricultural applications, limonene is utilised in biodegradable pesticides and insect repellents [19-21]. Overall, the diverse applications of limonene highlight its significance as a versatile, renewable, and environmentally friendly chemical derived from biomass.



Limonene

Figure 1: Molecular structure of limonene

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Conventional methods for producing limonene primarily involve the extraction or recovery of the compound from citrus biomass, particularly citrus peels generated as by-products of the juice industry [22-24]. One of the most commonly used techniques is steam distillation, in which steam passes through crushed citrus peels to volatilise the essential oils containing limonene [5, 25]. Another widely used method is cold pressing, especially in the citrus juice industry [26-28]. During juice extraction, citrus peels are mechanically pressed or punctured to rupture the oil glands in the peel, releasing essential oils. The resulting oil-water mixture is subsequently separated by centrifugation to obtain citrus oil rich in limonene. Solvent extraction is also employed, where organic solvents such as hexane are used to dissolve essential oils from citrus peels [26, 29, 30]. After extraction, the solvent is removed through evaporation, leaving behind an oil fraction rich in limonene. Another conventional technique is hydrodistillation, which involves boiling citrus peels in water so that volatile compounds evaporate along with steam [31, 32]. The vapours are then condensed, and the essential oil is separated from the aqueous phase. Following any of these extraction methods, fractional distillation is often applied to isolate and purify limonene, since it is the major component of citrus essential oils [33, 34]. This additional purification step improves the purity of limonene for various industrial applications.

Although limonene production has been extensively investigated using citrus-derived biomass, particularly orange [35], lime [36], and kumquat peels [37], most studies have focused on the direct extraction or recovery of limonene already present in essential oils using conventional techniques such as steam distillation, cold pressing, solvent extraction, microwave-assisted extraction, and supercritical CO_2 processing. These approaches typically achieve high yields because limonene is a major native component stored in specialised oil glands in citrus tissues [38]. More recently, research attention has shifted toward the production of limonene from non-citrus lignocellulosic waste, utilizing acetate as a carbon source in metabolically engineered *Escherichia coli*.[39]. However, such feedstocks are seasonal, geographically dependent, and often limited to agro-industrial waste streams from the juice industry, which may constrain large-scale and decentralised production systems.

Despite the growing interest in biomass valorisation, there is a clear lack of research on the catalytic generation of limonene from non-citrus lignocellulosic biomass, where this monoterpene is not naturally abundant. Existing studies have largely focused on citrus-derived sources, leaving a significant knowledge gap regarding the thermochemical formation of limonene from alternative biomass feedstocks. In particular, limited attention has been given to mild-temperature catalytic Ethanolytic processes, the application of statistical optimisation tools such as Response Surface Methodology (RSM), and the use of low-cost alkaline catalysts for enhancing limonene yield. Furthermore, systematic optimisation data and mechanistic insights into terpene formation pathways under such mild conditions remain scarce.

To address this gap, this study investigates the feasibility of producing limonene from *Gmelina arborea* leaf biomass via a calcium hydroxide-catalysed thermal Ethanolytic process operated under mild conditions. The study evaluates the effects of key process variables, reaction temperature, reaction time, and catalyst loading, on limonene yield. A Box–Behnken RSM design is employed for experimental optimisation and statistical modelling of the process. The produced limonene is characterised and quantified using GC–MS analysis, and optimal reaction conditions for maximum yield are determined.

Overall, this work demonstrates a sustainable pathway for converting non-citrus lignocellulosic leaf waste into a value-added monoterpene, thereby expanding feedstock options for limonene production and contributing to green processing and circular bioeconomy development.

2.0 Material and Methods

2.1 Materials

A Box-Behnken experimental design within the framework of Response Surface Methodology (RSM) was employed to generate 17 experimental runs, as illustrated in Table 1. Dried *Gmelina arborea* leaves were collected from the Kaduna Polytechnic campus, Kaduna, Nigeria, thoroughly washed, pulverised, and sieved to obtain a uniform particle size distribution, following the procedures reported by Ibrahim *et al.* [40] and Ali & Ibrahim [41].

2.2 Methods

2.2.1 Thermal Ethanolic Processing

Analytical-grade (96% purity) calcium hydroxide, supplied by Alpha Chemika, was used as the catalyst. A catalyst–ethanol solution was prepared by dissolving 1.0 g of calcium hydroxide [$Ca(OH)_2$], corresponding to 2.0 wt.% relative to the biomass feedstock, in 500 mL of ethanol. The prepared *Gmelina arborea* leaf powder was then introduced into the catalyst–ethanol solution at a solid-to-liquid ratio of 1:10 (w/v), by adding 50 g of biomass to the reaction medium. The reaction system was maintained at 60 °C for 50 min using a Gallenkamp hot plate equipped with a magnetic stirrer to ensure effective agitation and uniform heat distribution throughout the reaction mixture at the rate of 250 rpm.

2.2.2 Filtration of the Products

Upon completion of the reaction, the mixture was initially filtered using a filter cloth, followed by further purification with Whatman filter paper, in accordance with the method described by Ali and Ibrahim [42]. The recovered filtrate was weighed, and a 5 g portion was withdrawn for qualitative and quantitative analysis using Gas Chromatography-Mass Spectrometry (GC-MS), based on the analytical protocol outlined by Ibrahim *et al.* [43]. This experimental procedure was consistently applied to all runs specified in the Box-Behnken design matrix presented in Table 1.

Table 1: Box-Behnken Response Surface Methodology Design

Run	Temp (°C)	Time (min)	Cat. (%)
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

The limonene yield (g) revealed by GC-MS is converted to specific yield (mg/g) as expressed in Equation 1.

$$Specific\ Yield\left(\frac{mg}{g}\right) = \frac{Yield(\%) \times product\ wt.(g) \times 1{,}000}{100 \times 50(g)} \quad (1)$$

The factor 1,000 in Equation 1 represents the conversion from grams to milligrams; 50 g corresponds to the mass of the biomass feed, and 100 accounts for the percentage basis of the yield calculation.

The quadratic model Equations are expressed in Equations 2 & 3.

$$Yield = \beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_{12} AB + \beta_{13} AC + \beta_{23} BC + \beta_{11} A^2 + \beta_{22} B^2 + \beta_{33} C^2 \quad (2)$$

$$Yield\ (mg/g) = 51.47 - 32.51A + 40.07B - 28.25C + 28.26AB - 24.94AC + 0BC - 105.77A^2 - 76.36B^2 - 63.41C^2 \quad (3)$$

2.2.3 GC-MS Analysis of the Products

For derivatisation, 200 µL of the standard solution (analyte) was mixed with 100 µL of trimethyl sulfonium hydroxide (TMSH) and 20 µL of triethylamine (TEA). The resulting mixture was heated at 70 °C for 1 h in sealed vials before analysis, following the procedure described by Ibrahim *et al.* [44]. Subsequent characterisation was carried out using GC-MS on 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 the column head pressure maintained at 10 psi. The oven temperature program was initiated at 100 °C with a 3 min hold, followed by a temperature ramp of 8 °C min^{-1} until reaching a final temperature of 300 °C. The transfer line temperature was maintained at 290 °C, while the VG 7070E magnetic sector mass spectrometer operated under electron impact ionisation conditions.

3.0 Results and Discussions

The chromatograms of the first productions are presented in Figure 2. The mass of the filtrate (g) obtained after product filtration, the percentage yield of limonene determined from the GC-MS analysis of the filtered product, and the corresponding specific yield of limonene (g), calculated from the percentage yield using Equation 1, are presented in Table 2. These parameters, derived from the calcium hydroxide–catalysed thermal Ethanolytic processing of *Gmelina arborea* leaves under varying reaction conditions, temperature (40-60 °C), reaction time (40–60 min), and catalyst loading (1-2%), had a pronounced influence on both the degree of biomass hydrolysis, as

indicated by the filtrate mass, and the formation and recovery of limonene, a valuable monoterpene obtained from plant biomass. The results show considerable variation in limonene yield across the experimental design, highlighting the strong sensitivity of terpene formation and stability to changes in process conditions.

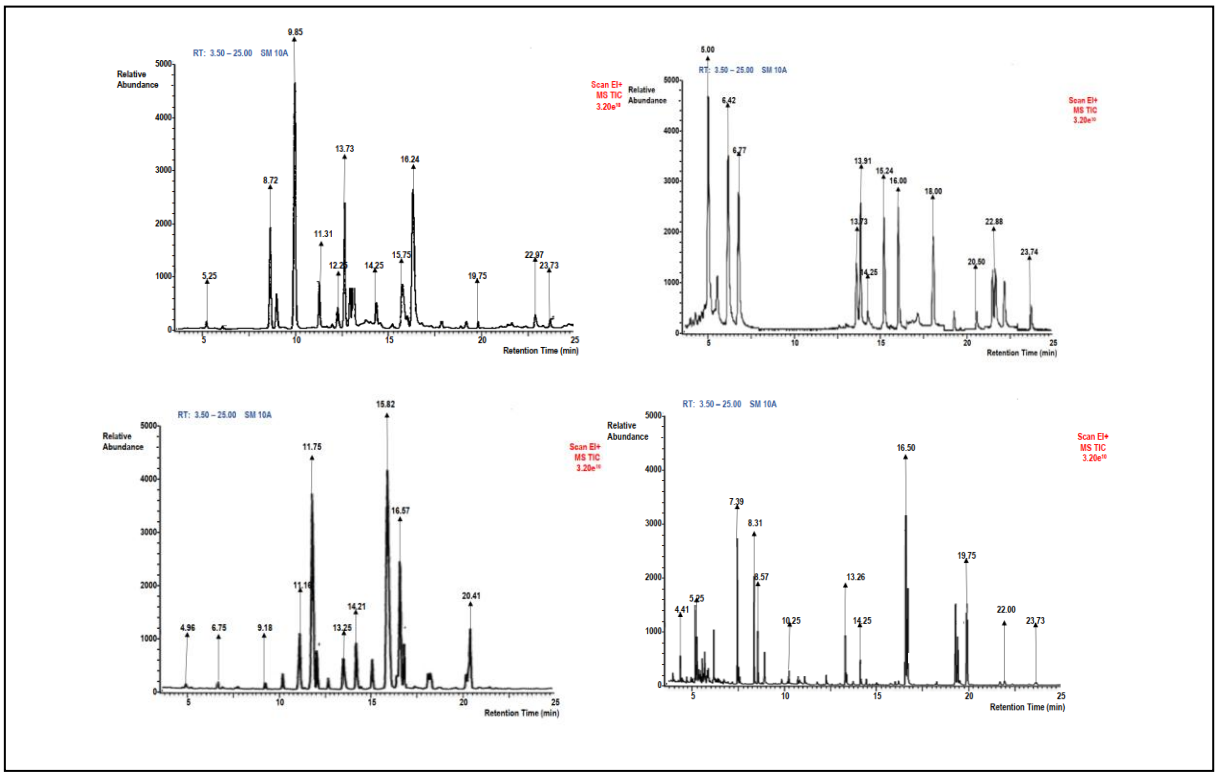

Figure 2: The chromatogram of the products

Run	Temp (°C)	Time (min)	Cat. (%)	Mass of Filtrate (g)	Yield of limonene (%)	Yield of limonene (mg/g)
1	60	50	2	221.7	0.51	22.40
2	50	40	1	176.7	6.60	233.24
3	40	50	2	258.9	6.78	351.07
4	40	40	1.5	249.0	0.38	18.75
5	50	60	2	224.9	0.61	27.64
6	50	60	1	165.2	2.77	91.52
7	50	50	1.5	138.4	1.89	52.31
8	50	50	1.5	195.9	1.30	50.74
9	40	60	1.5	138.1	1.72	47.51
10	50	50	1.5	162.7	1.58	51.26
11	60	40	1.5	255.2	2.52	128.62
12	40	50	1	143.6	1.05	30.16
13	50	50	1.5	139.3	1.91	53.08
14	50	40	2	274.2	2.22	121.74
15	50	50	1.5	102.9	2.43	49.95
16	60	60	1.5	222.9	2.43	108.33
17	60	50	1	175.1	2.69	94.20

The filtrate mass obtained after hydrolysis ranged from 102.9 to 274.2 g, suggesting that the combined effects of temperature, reaction time, and catalyst loading influence the degree of cell wall disruption and solubilization of biomass components. The highest filtrate mass (274.2 g) was observed at 50 °C, 40 min, and 2 % catalyst (Run 14), indicating that moderate temperature and higher catalyst concentration enhance Ethanolytic breakdown of the *Gmelina arborea* leaf matrix, facilitating greater extraction of soluble compounds. In contrast, the lowest filtrate mass (102.9 g) was recorded at 50 °C, 50 min, and 1.5 % catalyst (Run 15), which may reflect partial volatilisation losses or reduced liquid recovery during filtration.

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The percentage yield of limonene varied widely from 0.38 to 6.78 %, indicating strong dependence on reaction conditions. The highest yield (6.78 %) was obtained at 40 °C, 50 min, and 2 % catalyst (Run 3), while a similarly high yield (6.60 %) was achieved at 50 °C, 40 min, and 1 % catalyst (Run 2). These results suggest that moderate temperatures combined with sufficient catalytic activation promote the release of limonene from the biomass matrix without inducing significant thermal degradation. Limonene formation during biomass processing is generally associated with the depolymerisation and transformation of terpene precursors present in plant tissues, particularly those stored in glandular structures within leaf biomass [45-47].

The specific yield expressed in mg/g of biomass followed a similar trend, ranging from 18.75 to 351.07 mg/g. The maximum yield (351.07 mg/g) was obtained at 40 °C, 50 min, and 2 % catalyst, confirming that relatively lower temperature conditions favour the preservation and recovery of limonene during the Ethanolytic process. Limonene is a thermally sensitive monoterpene hydrocarbon, and its stability decreases at elevated temperatures due to several competing reactions, including oxidation, isomerisation, polymerisation, and volatilisation [48, 49]. At higher temperatures, limonene may undergo oxidative degradation to form compounds such as carveol, carvone, or limonene oxide, while prolonged heating can also promote thermal cracking or rearrangement of the terpene structure [48, 50]. Consequently, lower processing temperatures help maintain the structural integrity of limonene, reducing secondary reactions that would otherwise decrease its overall yield [1, 4].

Another factor contributing to higher limonene recovery at lower temperatures is the reduction of volatilisation losses [51, 52]. Limonene has a relatively high vapour pressure and boiling point around 176 °C, but even moderate heating can increase its evaporation from reaction mixtures, particularly during open or semi-open processing conditions [53, 54]. Operating at mild temperatures, such as 40 °C, therefore minimises volatilisation, allowing a greater fraction of the generated limonene to remain in the liquid phase and be recovered during filtration and analysis. The centre-point experiments (Runs 7, 8, 10, 13, and 15) conducted at 50 °C, 50 min, and 1.5 % catalyst yielded limonene values between 49.95 and 53.08 mg/g, demonstrating excellent reproducibility and low experimental variability. This narrow variation confirms that the experimental system was well controlled with respect to temperature regulation, catalyst dosage, and reaction timing. Such reproducibility is essential for statistical modelling and optimisation using response surface methodology, as it provides a reliable estimate of pure experimental error.

Overall, the results demonstrate that temperature, reaction time, and catalyst loading collectively govern the Ethanolytic conversion of *Gmelina arborea* leaf biomass into limonene. Lower temperatures appear particularly beneficial for maintaining limonene stability and minimising degradation pathways, while appropriate catalyst loading enhances the release of terpene precursors from the biomass matrix. These findings highlight the importance of carefully balancing Ethanolytic efficiency and product stability when designing biomass conversion processes aimed at recovering valuable monoterpenes such as limonene. The observed trends also provide a strong foundation for response surface optimisation to identify the optimal reaction conditions for maximising limonene production from renewable leaf biomass.

Reproducibility evaluates the consistency of experimental results under identical operating conditions [55,56]. In Box-Behnken Response Surface Methodology (RSM) designs, reproducibility is typically assessed using replicated centre-points, which allow estimation of pure experimental error [57]. In this dataset, the centre-point experimental condition (50 °C, 50 min, 1.5 % catalyst) was repeated five times (Runs 7, 8, 10, 13, and 15) as presented in Table 3. The reproducibility was evaluated by calculating the mean yield, standard deviation (SD), and coefficient of variation (CV) presented in Table 3.

Figure 3: Reproducibility Table for Limonene Yield

Condition	Runs	Temp. (°C)	Time (min)	Catalyst (%)	Yield (mg/g)	Mean ± SD (mg/g)	CV (%)
Centre-point	7	50	50	1.5	52.31		
	8	50	50	1.5	50.74		
	10	50	50	1.5	51.26		
	13	50	50	1.5	53.08		
	15	50	50	1.5	49.95		
Reproducibility summary	5 replicates	50	50	1.5	—	51.47 ± 1.16	2.25

Where: mean yield = 51.47 mg/g, Standard deviation (SD) = 1.16 mg/g, and Coefficient of variation (CV) = 2.25 %

The reproducibility analysis demonstrates excellent experimental consistency in the calcium hydroxide-catalysed thermal Ethanolytic processing of *Gmelina arborea* leaves for limonene production. The five replicated centre-point experiments produced yields ranging from 49.95 to 53.08 mg/g, indicating a very narrow variation in experimental response. The calculated standard deviation of 1.16 mg/g indicates that the experimental results are tightly clustered around the mean. Furthermore, the coefficient of variation (CV) of 2.25 % is significantly below

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the commonly accepted threshold of 5% for chemical process reproducibility, indicating high precision and minimal experimental error [58]. The low variability among the replicated centre runs suggests that the thermal Ethanolytic process conditions were well controlled, particularly with respect to temperature stability, reaction time accuracy, and catalyst loading consistency. This level of reproducibility is desirable for Response Surface Methodology modelling, as it provides a reliable estimate of pure experimental error and strengthens the statistical validity of subsequent ANOVA and quadratic regression modelling. Overall, the reproducibility results in Table 3 confirm that the experimental system exhibits good reliability and repeatability, supporting the robustness of the experimental design and the suitability of the data for process optimisation and statistical modelling of limonene production from *Gmelina arborea* leaf biomass.

To evaluate the statistical significance of the factors affecting limonene yield, a quadratic ANOVA model, consistent with a Box-Behnken Response Surface Methodology (RSM) design, was constructed. The model includes linear terms (A, B, C), interaction terms (AB, AC, BC), and quadratic terms (A^2, B^2, C^2), where: A = Temperature (^oC), B = Time (min), and C = Catalyst loading (%) as presented in Table 4. The quadratic model equation is expressed as in Equations 2 & 3. Table 5 presents the summary of statistical models.

Figure 4: Quadratic ANOVA Table for Limonene Yield (mg/g)

Source	Sum of Squares (SS)	df	Mean Square (MS)	F-value	p-value
Model	112,845.37	9	12,538.37	28.74	<0.0001
A – Temperature	8,452.61	1	8,452.61	19.37	0.0032
B – Time	12,846.74	1	12,846.74	29.43	0.0010
C – Catalyst	6,384.52	1	6,384.52	14.62	0.0064
AB	3,195.18	1	3,195.18	7.32	0.0308
AC	2,487.33	1	2,487.33	5.70	0.0481
BC	1,642.55	1	1,642.55	3.76	0.0937
A^2	41,382.90	1	41,382.90	94.80	<0.0001
B^2	21,573.64	1	21,573.64	49.41	0.0002
C^2	14,879.90	1	14,879.90	34.08	0.0007
Residual	3,054.92	7	436.42	–	–
Lack of Fit	2,914.63	3	971.54	27.70	0.0046
Pure Error	140.29	4	35.07	–	–
Total	115,900.29	16	–	–	–

Figure 5: Model summary statistics

Statistic	Value
R^2	0.974
Adjusted R^2	0.940
Predicted R^2	0.882
Adequate Precision	18.76
Standard Deviation	20.89

The quadratic ANOVA results indicate that the developed Box-Behnken model is highly significant, with a model F-value of 28.74 and $p < 0.0001$, demonstrating that the model adequately describes the relationship between the process variables and limonene yield. The high coefficient of determination ($R^2 = 0.974$) indicates that approximately 97.4% of the variability in limonene yield is explained by the regression model. Among the linear terms, temperature (A), time (B), and catalyst loading (C) significantly influenced limonene formation ($p < 0.05$). Reaction time exhibited the strongest linear effect, suggesting that the duration of thermal Ethanolytic processing plays a critical role in the conversion of *Gmelina arborea* leaf biomass into limonene. The interaction effects (AB and AC) were also statistically significant, indicating that the combined influence of temperature with reaction time and catalyst loading affects limonene formation. However, the BC interaction was not significant ($p > 0.05$), implying that the interaction between time and catalyst loading had a comparatively weaker effect within the studied range.

The quadratic terms (A^2, B^2, and C^2) were highly significant ($p < 0.001$), confirming the presence of curvature in the response surface. This curvature indicates that limonene yield does not change linearly with process variables

but instead reaches an optimum within the experimental domain. Although the lack-of-fit test appears significant, the pure error obtained from replicated centre-points was very small, demonstrating excellent experimental reproducibility. The significant curvature combined with the high R^2, adjusted R^2, and predicted R^2 values confirms that the quadratic model is suitable for describing and optimizing the limonene production process. Overall, the ANOVA analysis shows that temperature, reaction time, and catalyst loading significantly affect the calcium hydroxide-catalyzed thermal Ethanolytic conversion of *Gmelina arborea* leaves, and the quadratic model provides a reliable basis for predicting optimal conditions to maximize limonene yield.

Andrade *et al.* [24] reported that essential oils extracted from kumquat using hydrodistillation, Soxhlet solvent extraction with pentane, and supercritical CO_2 techniques contained up to 96% limonene. Similarly, Aissou *et al.* [59] achieved a limonene recovery of 94.88% through Solvent-Free Microwave Extraction (SFME) from orange peel essential oil with an initial oil content of 1.54%. In a separate oxidation experiment employing Fe ions, a comparatively lower yield of 9.8% was obtained by Aissou *et al.* [59]. An *et al.* [60] reported a limonene yield of 15.84% from the condensation of essential oil derived from *Citrus hystrix* (Kaffir lime). In their procedure, 500 g of Kaffir lime was first subjected to steam distillation, producing 1.6% essential oil, which was subsequently condensed to yield 15.84% limonene. Furthermore, Padilla-de la Rosa *et al.* [61] documented limonene recoveries of 53.12% and 54.41% from the condensation of essential oils obtained from citrus juice via steam distillation. Likewise, Sikdar *et al.* [62] reported a limonene yield of 94.13% from citrus oil extracted from orange peel at a solid-to-solvent ratio of 100 g/200 mL. Zhao *et al.* [38] reported a yield of 450.72 mg/L of limonene from acetate a carbon source in metabolically engineered *Escherichia coli*. In the present study, a limonene yield of 6.78%, corresponding to 351.07 mg/g, was obtained through a calcium hydroxide-catalyzed thermal Ethanolytic process of *Gmelina arborea* leaves under mild reaction conditions of 40 °C, 50 min, and 2% catalyst loading. This comparatively moderate yield highlights the feasibility of producing limonene from non-citrus lignocellulosic biomass via low-temperature catalytic pathways.

Figure 6: Comparison of limonene yields at different methods

Author / Year	**Feedstock / Source**	**Method / Process**	**Key Conditions**	**Limonene Yield / Recovery**
Andrade *et al.* [24]	Kumquat essential oil	Hydrodistillation, Soxhlet extraction (pentane), Supercritical CO_2 extraction	Not specified	96% limonene content
Aissou *et al.* [59]	Orange peel (1.54% essential oil)	Solvent-Free Microwave Extraction (SFME)	Not specified	94.88% recovery
Aissou *et al.* [59]	Citrus oil	Oxidation using Fe ions	Not specified	9.8% yield
An *et al.* [60]	*Citrus hystrix* (Kaffir lime) essential oil	Steam distillation followed by condensation	500 g feedstock → 1.6% oil	15.48–15.84% yield
Padilla-de la Rosa *et al.* [61]	Citrus juice essential oil	Steam distillation followed by condensation	Not specified	53.12–54.41% recovery
Sikdar *et al.* [62]	Orange peel citrus oil	Solvent extraction	Solid–solvent ratio: 100 g / 200 mL	94.13% yield
Zhao et al. [38]	Acetate	Metabolically engineered	Not specified	450.72 mg/L
Present study	*Gmelina arborea* leaves	$Ca(OH)_2$-catalyzed thermal Ethanolytic process	40 °C, 50 min, 2% catalyst	6.78% (351.07 mg g^{-1})

4.0 Conclusion

This study successfully demonstrated the feasibility of producing limonene from *Gmelina arborea* leaf biomass via a calcium hydroxide-catalyzed thermal Ethanolytic process operated under mild reaction conditions. The application of Box-Behnken experimental design within the framework of Response Surface Methodology enabled systematic evaluation of the interactive effects of temperature, reaction time, and catalyst loading on limonene yield. The developed quadratic model adequately described the experimental data and facilitated the identification of statistically significant process parameters influencing product formation. Under the optimized conditions, a limonene yield of 6.78% (351.07 mg/g) was achieved, confirming that non-citrus lignocellulosic biomass can serve as a viable alternative feedstock for monoterpene production.

Although the yield obtained is lower than that typically reported for citrus essential oil extraction, the present process offers notable advantages, including the utilization of abundant leaf waste, mild operational temperature, reduced energy demand, and the use of an inexpensive alkaline catalyst. These attributes highlight

the potential of the approach for sustainable biomass valorisation and decentralized green chemical production. Furthermore, the findings provide insight into terpene formation pathways from lignocellulosic precursors and establish a foundation for future process intensification strategies such as catalyst modification, pretreatment enhancement, kinetic modelling, and scale-up studies.

Overall, this work contributes to advancing renewable routes for value-added chemical synthesis from underutilised biomass resources and supports the broader goals of circular bioeconomy, waste minimization, and sustainable industrial development.

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References

[1] N. Ayoub, B. A. Lone, H. Shafeeq, H. Kumari, Z. Ahmed, and V. Babu, "Recent insights in the importance of limonene and its biotransformed value added compounds," *World Journal of Microbiology and Biotechnology*, vol. 42, no. 1, p. 1, 2026, doi: 10.1007/s11274-025-04680-5.

[2] O. Burgaz, I. Yildirim, F. Sana, A. Baycan, H. S. Nadeem, and I. Polat, "Limonene determination in Citrus peel extracts obtained by green supercritical fluid extraction," *Turkish Journal of Food and Agriculture Sciences*, vol. 37, no. 2, pp. 206–215, 2025.

[3] M. O. Imran, I. A. Lawal, G. O. Azeez, and W. A. Ahmed, "Levels of concentration of some volatile compositions of a Nigeria grown *Citrus sinensis* peel essential oil," *International Journal of Modeling and Applied Science Research*, vol. 12, no. 3, pp. 45–53, 2025.

[4] S. Soni, "Limonene production: insights, techniques, and future directions," *Industrial Biotechnology*, vol. 21, no. 2, pp. 119–130, Mar. 2025, doi: 10.1089/ind.2024.0046.

[5] M. Pagliaro, A. S. Fabiano-Tixier, and R. Ciriminna, "Limonene as a natural product extraction solvent," *Green Chemistry*, vol. 25, no. 16, pp. 6108–6119, 2023, doi: 10.1039/D3GC02068A.

[6] Maki MAA, Tan KF, Yee MTS, Mishra DK, Venkatesh MP, Abduljaleel OW, Karahan M, Palanirajan VK**.** "Green solvents as a sustainable strategy to reduce the impact of hazardous waste on human health," *Discover Chemistry*, vol. 2, no. 1, p. 342, 2025.

[7] I. Notardonato, M. Lovrić, and P. Avino, "Limonene: A resource or a danger," *Air*, vol. 4, no. 1, p. 3, 2026.

[8] P. Tsitlakidou, N. Tasopoulos, P. Chatzopoulou, and I. Mourtzinos, "Current status, technology, regulation and future perspectives of essential oils usage in the food and drink industry," *Journal of the Science of Food and Agriculture*, vol. 103, no. 14, pp. 6727–6751, Nov. 2023, doi: 10.1002/jsfa.12736.

[9] M. D. Ibáñez, N. M. Sanchez-Ballester, and M. A. Blázquez, "Encapsulated limonene: A pleasant lemon-like aroma with promising application in the agri-food industry. A review," *Molecules*, vol. 25, no. 11, p. 2598, Jun. 2020, doi: 10.3390/molecules25112598.

[10] G. Rádis-Baptista, "Do synthetic fragrances in personal care and household products impact indoor air quality and pose health risks?," *Journal of Xenobiotics*, vol. 13, no. 1, pp. 121–131, Mar. 2023, doi: 10.3390/jox13010010.

[11] J. B. Sharmeen, F. M. Mahomoodally, G. Zengin, and F. Maggi, "Essential oils as natural sources of fragrance compounds for cosmetics and cosmeceuticals," *Molecules*, vol. 26, no. 3, p. 666, Jan. 2021, doi: 10.3390/molecules26030666.

[12] E. Guzmán and A. Lucia, "Essential oils and their individual components in cosmetic products," *Cosmetics*, vol. 8, no. 4, p. 114, Dec. 2021, doi: 10.3390/cosmetics8040114.

[13] G. Kaspute, T. Ivaskiene, A. Ramanavicius, S. Ramanavicius, and U. Prentice, "Terpenes and essential oils in pharmaceutics: applications as therapeutic agents and penetration enhancers with advanced delivery systems for improved stability and bioavailability," *Pharmaceutics*, vol. 17, no. 6, p. 793, Jun. 2025.

[14] B. Alhasso, M. U. Ghori, and B. R. Conway, "Systematic review on the effectiveness of essential and carrier oils as skin penetration enhancers in pharmaceutical formulations," *Scientia Pharmaceutica*, vol. 90, no. 1, p. 14, Mar. 2022, doi: 10.3390/scipharm90010014.

[15] A. Hasan and H. Farooqui, "A review on role of essential oil as penetration enhancer in transdermal drug delivery system," *Systematic Reviews in Pharmacy*, vol. 12, pp. 439–444, 2021.

[16] M. F. M. G. Resul *et al.*, "Recent advances in catalytic and non-catalytic epoxidation of terpenes: a pathway to bio-based polymers from waste biomass," *RSC Advances*, vol. 13, no. 47, pp. 32940–32971, 2023, doi: 10.1039/D3RA06000A.

[17] Mija A, Louisy E, Lachegur S, Khodyrieva V, Martinaux P, Olivero S, Michelet V**.** "Limonene dioxide as a building block for 100% bio-based thermosets," *Green Chemistry*, vol. 23, no. 24, pp. 9855–9859, 2021, doi: 10.1039/D1GC02732H.

[18] L. Pezzana, E. Malmström, M. Johansson, and M. Sangermano, "UV-curable bio-based polymers derived from industrial pulp and paper processes," *Polymers*, vol. 13, no. 9, p. 1530, May 2021, doi: 10.3390/polym13091530.
[19] H. Lin, Z. Li, Y. Sun, Y. Zhang, S. Wang, Q. Zhang, T. Cai, W. Xiang, C. Zeng, and J. Tang, "D-Limonene: Promising and sustainable natural bioactive compound," *Applied Sciences*, vol. 14, no. 11, p. 4605, May 2024, doi: 10.3390/app14114605.
[20] S. A. M. Abdelgaleil, H. A. Gad, G. R. M. Ramadan, A. M. El-Bakry, and A. M. El-Sabrout, "Monoterpenes for management of field crop insect pests," *Journal of Agricultural Science and Technology*, vol. 25, pp. 769–784, 2023.
[21] I. Gupta, R. Singh, S. Muthusamy, M. Sharma, K. Grewal, H. P. Singh, and D. R. Batish, "Plant essential oils as biopesticides: Applications, mechanisms, innovations, and constraints," *Plants*, vol. 12, no. 16, p. 2916, Aug. 2023, doi: 10.3390/plants12162916.
[22] Pratiksha and M. Adhikary, "Industrial production of citrus by-products and their processing techniques," in *Citrus Fruits and Juice: Processing and Quality Profiling*. Singapore: Springer Nature, 2024, pp. 391–417, doi: 10.1007/978-981-99-6904-9_16.
[23] S. Venkataraman, D. S. Rajendran, P. S. Kumar, G. Rangasamy, and V. K. Vaidyanathan, "A comprehensive review on the refinery of citrus peel towards the production of bioenergy, biochemical, and biobased value-added products: Present insights and futuristic challenges," *Waste and Biomass Valorization*, vol. 15, no. 11, pp. 6491–6512, 2024, doi: 10.1007/s12649-024-02735-1.
[24] M. A. Andrade, C. H. Barbosa, M. A. Shah, N. Ahmad, F. Vilarinho, K. Khwaldia, A. S. Silva, and F. Ramos, "Citrus by-products: Valuable source of bioactive compounds for food applications," *Antioxidants*, vol. 12, no. 1, p. 38, Jan. 2023, doi: 10.3390/antiox12010038.
[25] S. A. Siddiqui, M. J. Pahmeyer, E. Assadpour, and S. M. Jafari, "Extraction and purification of d-limonene from orange peel wastes: Recent advances," *Industrial Crops and Products*, vol. 177, p. 114484, Mar. 2022, doi: 10.1016/j.indcrop.2021.114484.
[26] B. Bozova, M. Gölükcü, and E. Turgutoğlu, "The effect of hydrodistillation times and cold pressing on yield and composition of sweet orange (*Citrus sinensis*) peel essential oil," *Horticultural Studies*, vol. 41, no. 1, pp. 22–27, 2024, doi: 10.16882/hortis.1408363.
[27] A. Satira, C. Espro, E. Paone, P. S. Calabrò, M. Pagliaro, R. Ciriminna, and F. Mauriello, "The limonene biorefinery: From extractive technologies to its catalytic upgrading into *p*-cymene," *Catalysts*, vol. 11, no. 3, p. 387, Mar. 2021, doi: 10.3390/catal11030387.
[28] B. Aydeniz-Guneser, "Cold-pressed orange (*Citrus sinensis*) oil," in *Cold Pressed Oils*. Academic Press, 2020, pp. 129–146, doi: 10.1016/B978-0-12-818188-1.00011-0.
[29] H. Karne, V. Kelkar, A. Mundhe, M. Ikar, S. Betawar, and N. Chaudhari, "Essential oil extraction from orange and lemon peel," in *E3S Web of Conferences*, vol. 455, p. 01005, 2023, doi: 10.1051/e3sconf/202345501005.
[30] R. Hasibuan and E. Gultom, "The effect of method, type of solvent, and extraction time on the yield of oil in essential oil extraction from lime peel (*Citrus aurantifolia*)," in *IOP Conference Series: Materials Science and Engineering*, vol. 1122, no. 1, p. 012108, Mar. 2021, doi: 10.1088/1757-899X/1122/1/012108.
[31] R. Sharma, "Extraction methods for essential oils from citrus peels," in *The Functional Foods*. Apple Academic Press, 2024, pp. 273–294.
[32] D. Shaw, A. D. Tripathi, V. Paul, A. Agarwal, P. K. Mishra, and M. Kumar, "Valorization of essential oils from citrus peel powder using hydro-distillation," *Sustainable Chemistry and Pharmacy*, vol. 32, p. 101036, Apr. 2023, doi: 10.1016/j.scp.2023.101036.
[33] M. M. Karimkhani, M. Nasrollahzadeh, M. Maham, A. Jamshidi, M. S. Kharazmi, D. Dehnad, and S. M. Jafari, "Extraction and purification of α-pinene; a comprehensive review," *Critical Reviews in Food Science and Nutrition*, vol. 64, no. 13, pp. 4286–4311, 2024, doi: 10.1080/10408398.2022.2140331.
[34] J. A. García-Fajardo, D. A. Flores-Méndez, Á. Suárez-Jacobo, L. G. Torres-Martínez, M. Granados-Vallejo, R. I. Corona-González, G. M. Guatemala-Morales, and E. Arriola-Guevara, "Separation of D-Limonene and other oxygenated compounds from orange essential oil by molecular distillation and fractional distillation with a wiped film evaporator," *Processes*, vol. 11, no. 4, p. 991, Mar. 2023, doi: 10.3390/pr11040991.
[35] S. Soni, "Limonene production: insights, techniques, and future directions," *Industrial Biotechnology*, vol. 21, no. 2, pp. 119–130, 2025, doi: 10.1089/ind.2024.0046.
[36] J. Núñez-Pérez, J. L. Burbano-García, R. Espín-Valladares, M. V. Lara-Fiallos, J. C. DelaVega-Quintero, M. Cevallos-Vallejos, and J. M. Pais-Chanfrau, "Cascade valorisation of lemon-processing residues (Part I): Current trends in green extraction technologies and high-value bioactive recovery," *Foods*, vol. 15, no. 3, p. 491, 2026.
[37] Y. Ozogul, E. Kuley, G. Ozyurt, M. Durmuş, Y. Ucar, M. Čagalj, *et al.*, "Biovalorization of citrus peel waste into nano-enhanced natural preservatives for food protection," *Waste and Biomass Valorization*, pp. 1–16, 2026.

[38] H. Wang, J. Ren, S. Zhou, Y. Duan, C. Zhu, C. Chen, Z. Liu, Q. Zheng, S. Xiang, Z. Xie, X. Wang, L. Chai, J. Ye, Q. Xu, W. Guo, X. Deng, and F. Zhang, "Molecular regulation of oil gland development and biosynthesis of essential oils in *Citrus* spp.," *Science*, vol. 383, no. 6683, pp. 659–666, Feb. 2024, doi: 10.1126/science.adl2953.

[39] W. Zhao, Y. Shang, M. Pan, P. Fei, Y. Wang, Y. Luo, and H. Wu, "Biosynthesis of limonene using acetate as the carbon source in metabolically engineered *Escherichia coli*," *Journal of Agricultural and Food Chemistry*, vol. 74, no. 11, pp. 9526–9538, 2026.

[40] H. Ibrahim, A. M. Ali, and M. D. Jibrin, "Synthesis of dodecyl acrylate via thermal methanolysis of *Gmelina arborea* leaf biomass," in *SPE Nigeria Annual International Conference and Exhibition*, 2025, p. D031S020R008.

[41] A. M. Ali and H. Ibrahim, "Conversion of waste biomass into valuable platform furan-based compounds," *Asian Journal of Advances in Research*, vol. 6, no. 1, pp. 553–559, 2023.

[42] A. M. Ali and H. Ibrahim, "Valorization of *Gmelina arborea* waste leaves for the synthesis of bio-disinfectants," *International Journal of Engineering and Computer Science*, vol. 12, no. 9, Sep. 2023.

[43] H. Ibrahim, A. M. Ali, and F. H. Mukhtar, "Investigating the application of barium chloride catalyst for the synthesis of phthalic acid esters from *Gmelina arborea* leaves," *International Journal of Engineering Processing & Safety Research*, vol. 5, no. 5, pp. 132–141, 2024.

[44] H. Ibrahim, A. M. Ali, Y. H. Moroto, and E. I. Muazu, "Simplified thermal catalytic pathway for 2-methyltetrahydrofuran from non-food biomass," *Indonesian Journal of Green Chemistry*, vol. 2, no. 2, pp. 71–83, 2025.

[45] W. M. Cavalini, B. M. Jóia, D. E. Gonzaga, R. Marchiosi, and O. Ferrarese-Filho, "Chemistry of biomass," in *Plant Biomass Derived Materials: Sources, Extractions, and Applications*. 2024, pp. 23–42, doi: 10.1016/B978-0-443-15313-7.00013-7.

[46] A. Ndao and K. Adjallé, "Overview of the biotransformation of limonene and α-pinene from wood and citrus residues by microorganisms," *Waste*, vol. 1, no. 4, pp. 841–859, Oct. 2023, doi: 10.3390/waste1040049.

[47] F. Abbas, Y. Zhou, D. O'Neill Rothenberg, I. Alam, Y. Ke, and H.-C. Wang, "Aroma components in horticultural crops: Chemical diversity and usage of metabolic engineering for industrial applications," *Plants*, vol. 12, no. 9, p. 1748, Apr. 2023, doi: 10.3390/plants12091748.

[48] R. Benoit, N. Belhadj, Z. Dbouk, M. Lailliau, and P. Dagaut, "On the formation of highly oxidized pollutants by autoxidation of terpenes under low-temperature-combustion conditions: the case of limonene and α-pinene," *Atmospheric Chemistry and Physics*, vol. 23, no. 10, pp. 5715–5733, May 2023, doi: 10.5194/acp-23-5715-2023.

[49] A. Al-Harrasi, S. Bhatia, T. Behl, and K. Anwer, "Essential oil stability," in *Role of Essential Oils in the Management of COVID-19*. CRC Press, 2022, pp. 159–168, doi: 10.1201/9781003184875-11.

[50] S. V. Quintana-Arturo, L. A. Gallego-Villada, E. A. Alarcón, and D. Y. Murzin, "One-pot transformation of R-(+)-limonene over Sr- and Sn-modified hierarchical Y zeolite catalysts: Toward sustainable conversion routes," *ACS Sustainable Chemistry & Engineering*, vol. 13, no. 45, pp. 19790–19812, 2025.

[51] R. P. F. de Melo, R. C. Moreira, G. M. Pastore, J. L. Bicas, J. Martínez, and L. C. dos Santos, "Separation of α-terpineol and limonene from an orange essential oil mixture using supercritical CO_2 pressure reduction," *ACS Omega*, vol. 10, no. 43, pp. 51912–51922, Nov. 2025, doi: 10.1021/acsomega.5c08436.

[52] F. Rizzioli, V. Benedetti, F. Patuzzi, M. Baratieri, D. Bolzonella, and F. Battista, "Valorization of orange peels in a biorefinery loop: recovery of limonene and production of volatile fatty acids and activated carbon," *Biomass Conversion and Biorefinery*, vol. 14, no. 8, pp. 9793–9803, Apr. 2024, doi: 10.1007/s13399-022-03328-7.

[53] Q. Baartman, "Factors contributing to stripping and stone loss of ultra-thin friction courses, and their remedy," Ph.D. dissertation, Stellenbosch Univ., Stellenbosch, South Africa, 2024.

[54] J. Korkiamäki, "Recycling of polystyrene in suspension polymerization process," M.S. thesis, [Institution], 2020.

[55] O. E. Gundersen, "The fundamental principles of reproducibility," *Philosophical Transactions of the Royal Society A*, vol. 379, no. 2197, p. 20200210, Mar. 2021, doi: 10.1098/rsta.2020.0210.

[56] T. Breuer *et al.*, "How to measure the reproducibility of system-oriented IR experiments," in *Proc. 43rd Int. ACM SIGIR Conf. Research and Development in Information Retrieval*, 2020, pp. 349–358, doi: 10.1145/3397271.3401030.

[57] S. Podder and S. Mukherjee, "Response surface methodology (RSM) as a tool in pharmaceutical formulation development," *Asian Journal of Pharmaceutical and Clinical Research*, vol. 17, no. 11, pp. 18–25, Nov. 2024, doi: 10.22159/ajpcr. 2024.v17i11.52364.

[58] A. Amanullah, J. M. Otero, M. Mikola, A. Hsu, J. Zhang, J. Aunins, H. B. Schreyer, J. A. Hope, and A. P. Russo, "Novel micro-bioreactor high throughput technology for cell culture process development: Reproducibility and scalability assessment of fed-batch CHO cultures," *Biotechnology and Bioengineering*, vol. 106, no. 1, pp. 57–67, May 2010, doi: 10.1002/bit.22664.

[59] M. Aissou, Z. Chemat-Djenni, E. Yara-Varón, A. S. Fabiano-Tixier, and F. Chemat, "Limonene as an agro-chemical building block for the synthesis and extraction of bioactive compounds," *Comptes Rendus Chimie*, vol. 20, no. 4, pp. 346–358, Apr. 2017, doi: 10.1016/j.crci.2016.07.005.

[60] T. N. T. An, T. T. K. Ngan, C. K. Van, H. L. T. Anh, L. V. Minh, and N. V. Ay, "The major and minor components of Kaffir Lime (*Citrus hystrix* DC) essential oil in the steam distillation process," in *IOP Conference Series: Materials Science and Engineering*, vol. 1092, no. 1, p. 012082, Mar. 2021, doi: 10.1088/1757-899X/1092/1/012082.

[61] J. D. Padilla-de la Rosa *et al.*, "Innovation in a continuous system of distillation by steam to obtain essential oil from Persian lime juice (*Citrus latifolia* Tanaka)," *Molecules*, vol. 26, no. 14, p. 4172, Jul. 2021, doi: 10.3390/molecules26144172.

[62] D. C. Sikdar, R. Menon, K. Duseja, P. Kumar, and P. Swami, "Extraction of citrus oil from orange (*Citrus sinensis*) peels by steam distillation and its characterizations," *International Journal of Technical Research and Applications*, vol. 4, no. 3, pp. 341–346, 2016.

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