FUDMA Journal of Sciences (FJS)
ISSN online: 2616-1370
ISSN print: 2645 - 2944
Vol. 10 No. 5, March, 2026, pp 347 – 354
DOI: https://doi.org/10.33003/fjs-2026-1005-4896

RENEWABLE ROUTE TO CYMENE FROM NON-FOOD LEAF BIOMASS USING CALCIUM HYDROXIDE CATALYSIS

***Haruna Ibrahim, Abubakar M. Ali & Fatima Mukthar Hussaini**

Department of Chemical Engineering, Kaduna Polytechnic, Kaduna State, Nigeria.

*Corresponding authors’ email: ibrahimhauna@gmail.com

ABSTRACT

The growing demand for sustainable aromatic platform chemicals has intensified research into biomass-derived production pathways. This study investigates the mild thermal ethanolytic catalytic conversion of lignocellulosic *Gmelina arborea* leaf biomass into cymene using calcium hydroxide as an inexpensive alkaline catalyst under near-ambient pressure conditions. A Box-Behnken experimental design based on Response Surface Methodology was employed to evaluate the effects of temperature (40-60 °C), reaction time (40-60 min), and catalyst loading (1-2 %) on biomass depolymerisation, cymene selectivity, and process reproducibility. Gas chromatography-mass spectrometry analysis revealed cymene yields ranging from 1.30 % to 7.72 % (of the filtrate) corresponding to specific yields of 64.55-198.40 mg/g biomass. Moderate reaction conditions (50 °C, 50 min, 1.5 % catalyst) provided the most stable and reproducible performance, with a mean yield of 159.73 mg/g and an excellent coefficient of variation of 0.61 %. Analysis of variance confirmed that temperature, reaction time, and catalyst loading significantly influence cymene formation, with temperature exerting the strongest effect. The results demonstrate that selective aromatisation of hydrolysis intermediates, rather than total biomass liquefaction, governs cymene yield. Compared with conventional petrochemical and high-severity terpene-upgrading routes, the proposed process offers a simple, energy-efficient pathway to produce valuable aromatic hydrocarbons from non-food biomass residues. This work advances sustainable biomass valorisation strategies and supports the development of green catalytic processes for the production of renewable chemicals.

Keywords: Cymene production, *Gmelina arborea* biomass, Mild thermal catalysis

INTRODUCTION

One of the most versatile biomass-derived compounds for industrial applications is cymene. Cymene ($C_{10}H_{14}$) is a naturally occurring, colourless aromatic hydrocarbon belonging to the monoterpene family and is commonly found in essential oils of plants such as thyme, cumin, and citrus (Mohammed *et al*., 2025; Baginska *et al*., 2023; Marchese *et al*., 2017). It is an aromatic organic compound with a molecular weight of 134.22 g/mol, consisting of a benzene ring substituted with a methyl group and an isopropyl group, as shown in Figure 1 (Alsharif, 2023).

It has attracted considerable scientific and industrial interest due to its antimicrobial, anti-inflammatory, and antioxidant properties, which underpin its growing relevance in pharmaceutical and therapeutic research (Pyo & Jung, 2024; Vassiliou *et al*., 2023). Beyond its biological activities, cymene serves important roles as a green solvent and chemical intermediate in the synthesis of fine chemicals, pesticides, and aroma compounds, and it is also employed as a flavouring agent in regulated applications (Satira *et al*., 2021; Ibáñez *et al*., 2020). Furthermore, its favourable physicochemical and combustion characteristics have stimulated investigations into its use as a bio-based fuel additive (Fitri *et al*., 2022; Saha *et al*., 2020). Owing to this broad spectrum of applications in pharmaceuticals, fragrances, chemical manufacturing, fuel formulation, and agrochemicals**,** cymene represents a valuable platform molecule in biomass valorisation and sustainable chemistry research (Sánchez-Velandia *et al*., 2025; Satira *et al*., 2021)**.**

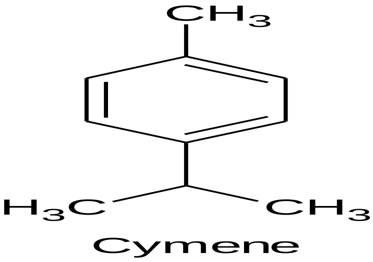


Figure 1: Cymene Molecular Structure

Cymene exhibits notable anti-inflammatory, antimicrobial, analgesic, and antioxidant activities, supporting its use in treating skin inflammation, inhibiting microbes, relieving mild pain, and scavenging free radicals (Li et al., 2022; Marques et al., 2019; Abd Rashed et al., 2021; Chouhan et al., 2017; Aly et al., 2026; Yousofvand & Moloodi, 2023; Chen et al., 2023; Diniz do Nascimento et al., 2020). These properties underpin its relevance in drug formulation and natural product–based therapeutics, aligning with biomass valorisation research. Industrially, cymene is used as a fragrance and flavouring agent in cosmetics, detergents, and food products (Rana et al., 2025; Rocha et al., 2023; Tsitlakidou et al., 2023), and as an intermediate in producing aroma chemicals such as thymol, carvacrol, p-cresol, and cuminaldehyde (Sell, 2020; Bad et al., 2017; El Hadi et al., 2013). It also serves as a green solvent in organic synthesis, particularly in metathesis reactions (Quadros et al., 2025; Makarouni et al., 2022; Granato et al., 2017). Additionally, cymene finds applications in polymer and resin production, bio-based fuel additives, biopesticides, and eco-friendly agrochemical formulations, highlighting its versatility in green chemistry and sustainable chemical processes (Satira et al., 2021; Lapuerta et al., 2023; Assadpour et al., 2024; Gupta et al., 2023; Bratovcic, 2025; Sánchez-Velandia et al., 2025; Correa et al., 2015).

Gmelina arborea is a fast-growing deciduous tree widely distributed in tropical regions and commonly used in timber, paper, and biomass-based applications (Kumar *et al*., 2021; Lal & Bhandari, 2020). Its leaves, like most lignocellulosic biomass, are composed primarily of cellulose, hemicellulose, and lignin. Cellulose, the dominant structural polysaccharide, typically constitutes about 30-40% of the leaf biomass and provides mechanical strength (Adenaiya, 2021; Yaya Lancheros *et al*, 2021). Hemicellulose, a heterogeneous branched polymer, accounts for roughly 20-30% and contributes to flexibility and structural support (Adenaiya, 2021). Lignin, an aromatic polymer responsible for rigidity and resistance to degradation, is generally present in lower amounts in leaves, ranging from about 10-20% (Majekobaje, 2018). These components make *Gmelina arborea* leaves a promising feedstock for biomass valorisation, as cellulose and hemicellulose can be converted into fermentable sugars and platform chemicals, while lignin serves as a source of aromatic compounds.

One of the most common routes to cymene is the acid-catalyzed alkylation of toluene with propylene using solid acid catalysts such as zeolites, silica–alumina, or $AlCl_3$, typically at 200–350 °C and moderate pressures (Gajbhiye et al., 2019; Malkar & Yadav, 2020; Ma et al., 2016; Al-Kinany et al., 2012). Cymene can also be produced via catalytic dehydrogenation or isomerization of monoterpenes such as limonene, α-pinene, and γ-terpinene using metal or acid catalysts (e.g., Pd/C, Pt/Al_2O_3, zeolites) at 250-400 °C, a pathway relevant to biomass-derived feedstocks (Sánchez-Velandia et al., 2025; Baginska et al., 223; Lapuerta et al., 2023; Alsharif, 2023). Hydrodistillation of terpene-rich essential oils followed by thermal cracking, reforming, or hydrodeoxygenation can also yield cymene, though product distribution depends on feedstock and conditions (Yingngam, 2022; Satira et al., 2021; Kumar, 2024). Laboratory synthesis includes Friedel–Crafts alkylation of aromatics with alkyl halides or alcohols using Lewis acids (e.g., $AlCl_3$, $FeCl_3$), though this is less favored industrially due to corrosion and environmental concerns (Santoso et al., 2013). Cymene may also form as a by-product during catalytic reforming or aromatization of light hydrocarbons in refineries, from which it is recovered by distillation (Hattori & Ono, 2015).

Despite the growing importance of cymene as a platform aromatic, conventional production relies on petrochemical feedstocks or high-severity terpene upgrading, requiring high temperatures, pressures, costly catalysts, and energy-intensive conditions. Although high yields have been reported from citrus oils and purified terpenes, such methods often involve pretreatment, solvent-intensive extraction, or supercritical processes, limiting scalability and sustainability. Research on direct mild-thermal catalytic conversion of lignocellulosic leaf biomass into cymene remains scarce, particularly using low-cost catalysts under near-ambient conditions. Most biomass valorisation studies focus on fuels or furans rather than selective aromatic production, with limited work on optimization and reproducibility. Thus, a clear gap exists in developing simple, energy-efficient, and reproducible routes for cymene production from abundant residues like *Gmelina arborea* leaves within a green chemistry and circular bioeconomy framework.

This study aims to develop an energy-efficient and sustainable catalytic pathway for the production of cymene from lignocellulosic *Gmelina arborea* leaf biomass through mild thermal ethanolytic processing. To achieve this, the study seeks to investigate the influence of key reaction variables, namely temperature, reaction time, and calcium hydroxide catalyst loading, on biomass depolymerization, cymene selectivity, and overall process efficiency. It further aims to apply Response Surface Methodology based on a Box-Behnken experimental design to optimize operating conditions for maximum cymene yield and to evaluate process reproducibility using statistical indicators such as standard deviation and coefficient of variation.

MATERIALS AND METHODS

A Box-Behnken design based on Response Surface Methodology (RSM) was employed to generate 17 experimental runs, as presented in Table 1. Dried *Gmelina arborea* leaves were sourced from the Kaduna Polytechnic campus. The leaves were thoroughly washed, pulverized, and sieved to obtain a uniform particle size distribution, following the procedures previously reported by Ibrahim *et al*. (2025a) and Ali & Ibrahim (2023a).

The catalytic reaction medium was prepared by dissolving 1.0 g of calcium hydroxide ($Ca(OH)_2$), corresponding to 2.0 % (w/w) relative to the biomass feedstock, in 500 mL of ethanol. Subsequently, 50 g of the prepared *Gmelina arborea* leaf powder was introduced into the solution. The reaction mixture was maintained at 60 °C for 50 min using a Gallenkamp hot plate fitted with a magnetic stirrer to ensure effective and uniform mixing throughout the process.

Upon completion of the reaction, the mixture was sequentially filtered first through filter cloth and then through Whatman filter paper, in line with the method described by Ali et al. (2026). The filtrate obtained was weighed, and a 5 g aliquot was withdrawn for both qualitative and quantitative characterisation using Gas Chromatography-Mass Spectrometry (GC-MS), following the analytical protocol reported by Ibrahim *et al*. (2024). This same experimental procedure was consistently applied to all runs defined in the Box-Behnken design matrix (Table 1).

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 mixture was heated at 70 °C for 1 h in sealed vials before analysis, according to the procedure described by Ibrahim *et al*. (2025b). GC-MS analysis was subsequently performed 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 the column head pressure maintained at 10 psi. The oven temperature program was initiated at 100 °C (held for 3 min) and then ramped at 8 °C min^{-1} to a final temperature of 300 °C. The transfer line temperature was set at 290 °C, while the VG 7070E magnetic sector mass spectrometer operated under electron impact ionization conditions.

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

RESULTS AND DISCUSSION

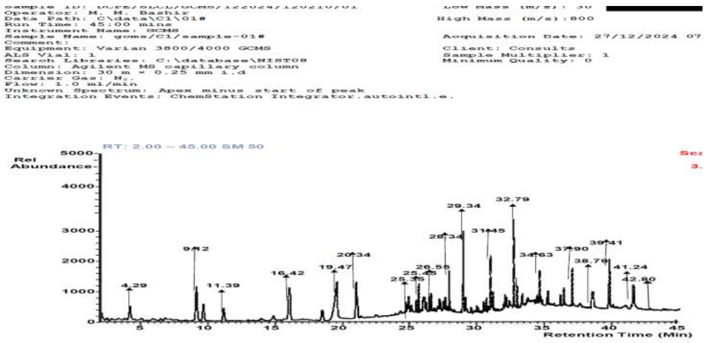
Table 2 presents the mass of filtrate (product), percentage yield of cymene (o-cymene and p-cymene) obtained from GC-MS analysis, and the corresponding specific yield (mg/g) obtained during the calcium hydroxide-catalyzed thermal ethanolytic processing of *Gmelina arborea* leaves under varying reaction temperatures, residence times, and catalyst loadings. The GC-MS chromatograms of a few of the runs are presented in Figure 2. This dataset enables evaluation of the influence of reaction severity on filtrate generation, selectivity toward cymene formation, and the efficiency of biomass conversion expressed as specific yield. The conversion of percentage (%) yield cymene to its specific yields (mg/g) is expressed is in Equation 1.

$$SY\left(\frac{mg}{g}\right) = \frac{\%yield \times Ft_m \times 1000}{100 \times F_m} \qquad (1)$$

where, SY (mg/g) is specific yield, F_m is mass of feed (50 g), Ft_m is mass of filtrate, 1000 is conversion factor (g to mg)

Table 2: The Yields of Cymene from *Gmelina Arborea* Leaves

Run	Temp (°C)	Time (min)	Cat. (%)	Filtrate (g)	Yield (%)	Yield (mg/g)
1	60	50	2.0	221.7	4.47	198.40
2	50	40	1.0	176.7	2.34	82.65
3	40	50	2.0	258.9	2.34	121.30
4	40	40	1.5	249.0	1.30	64.55
5	50	60	2.0	224.9	3.92	176.20
6	50	60	1.0	165.2	3.16	104.35
7	50	50	1.5	138.4	5.74	158.75
8	50	50	1.5	195.9	4.09	160.22
9	40	60	1.5	138.1	3.44	95.10
10	50	50	1.5	162.7	4.91	159.64
11	60	40	1.5	255.2	2.80	142.80
12	40	50	1.0	143.6	2.55	73.25
13	50	50	1.5	139.3	5.78	161.05
14	50	40	2.0	274.2	2.47	135.70
15	50	50	1.5	102.9	7.72	158.98
16	60	60	1.5	222.9	3.78	168.45
17	60	50	1.0	175.1	3.39	118.60



```
[redacted]
Operator: M. M. Bashir                                  High Mass (m/z):800
Data Path: C:\data\C1\01#
Run Time: 45:00 mins
Instrument Name: GCMS
Sample Name: gcms/C1/sample-01#                          Acquisition Date: 27/12/2024 07
Comment:
Equipment: Varian 3800/4000 GCMS                         Client: Consults
ALS Vial: 1                                              Sample Multiplier: 1
Search Libraries: C:\database\NIST08                     Minimum Quality: 0
Column: Agilent MS capillary column
Dimension: 30 m × 0.25 mm i.d
Carrier Gas: N₂.
Flow: 1.0 ml/min
Unknown Spectrum: Apex minus start of peak
Integration Events: ChemStation Integrator.autointl.e.
```

Figure 2: Products Chromatograms

The results obtained from the calcium hydroxide-catalysed thermal ethanolic processing of *Gmelina arborea* leaves under the Box-Behnken design reveal important relationships between operating variables (temperature, time, and catalyst loading) and the response variables (filtrate weight, % cymene yield, and specific yield).

Overall, the filtrate weight varies widely from 102.9 to 274.2 g, indicating that the severity of reaction conditions significantly affects the extent of biomass solubilisation. However, a higher filtrate weight does not directly translate to higher cymene yield. For instance, Run 14 produced the highest filtrate (274.2 g) but only 2.47% yield (135.70 mg/g), whereas Run 15, with the lowest filtrate (102.9 g), gave the highest % yield (7.72%) and a high specific yield (158.98 mg/g). This suggests that cymene formation depends more on selective conversion pathways than on total extractable material.

The % yield of cymene ranges from 1.30 to 7.72%, showing strong sensitivity to process conditions. The highest yields are consistently observed at the centre point conditions (50°C, 50 min, 1.5% catalyst), as seen in Runs 7, 10, 13, and 15 (4.91-7.72%). This indicates that moderate conditions favour the formation of cymene, likely due to optimal balance between reaction kinetics and prevention of secondary degradation.

The specific yield (64.55-198.40 mg/g) follows a similar but not identical trend. The highest specific yield (198.40 mg/g) occurs at 60°C, 50 min, 2.0% catalyst (Run 1), suggesting that higher temperature and catalyst loading enhance conversion efficiency per unit mass, even if selectivity (% yield) is not maximal. Conversely, the lowest specific yield (64.55 mg/g) at low temperature and moderate catalyst (Run 4) indicates insufficient energy for effective transformation.

Temperature effects show that moderate temperature (≈50°C) favours higher % yield, while higher temperature (60°C) improves specific yield but may reduce selectivity due to possible side reactions. Reaction time also plays a role, with 50 min appearing optimal, as shorter or longer times tend to reduce % yield, possibly due to incomplete reaction or product degradation, respectively.

Catalyst loading demonstrates a non-linear effect: 1.5% catalyst consistently gives better % yields, while 2.0% catalyst enhances specific yield but may promote side reactions, reducing selectivity.

Reproducibility at the centre point (Runs 7, 8, 10, 13, 15) is reasonably good for specific yield (~158-161 mg/g), though % yield shows some variability (4.09-7.72%), indicating minor experimental fluctuations or sensitivity of cymene formation to subtle conditions. In summary, the results indicate that optimal cymene production is achieved under moderate conditions (50°C, 50 min, 1.5% $Ca(OH)_2$), where selectivity is maximized, while higher temperature and catalyst loading favour overall conversion but reduce selectivity.

Reproducibility

To achieve full reproducibility, we analyze yield consistency for each reaction factor level (Temperature, Time, and Catalyst loading). Reproducibility is evaluated using the mean yield ($\bar{x}$), Standard deviation (SD), Coefficient of variation (CV %), which is the main indicator for reproducibility index (Arachchige *et al*., 2022), and Number of observations (n). A lower CV (%) indicates better reproducibility (higher experimental reliability). The centre point condition is Temp = 50 °C, Time = 50 min, Catalyst = 1.5 % has runs 7, 8, 10, 13 and 15 with corresponding yields 158.75, 160.22, 159.64, 161.05, and 158.98 mg/g, respectively. Hence, the mean, SD, and CV are found to be 159.73 mg/g, 0.98 mg/g, and 0.61%, respectively, as presented in Table 3.

Table 3: Reproducibility Results

Reaction Factor	Level	N	Mean Yield (mg/g)	SD (mg/g)	CV (%)	Reproducibility Assessment
Temperature (°C)	40	4	88.55	25.96	29.33	Poor
	50	9	144.17	33.36	23.14	Moderate
	60	4	157.06	34.11	21.72	Moderate
Reaction Time (min)	40	4	106.43	36.56	34.35	Poor
	50	6	143.72	30.75	21.39	Moderate
	60	3	148.55	44.03	29.64	Poor
Catalyst (%)	1.0	4	94.71	20.20	21.33	Moderate
	1.5	9	140.39	38.71	27.58	Poor-Moderate
	2.0	4	157.90	34.62	21.93	Moderate
Centre Point (50 °C, 50 min, 1.5%)	—	5	159.73	0.98	0.61	Excellent

The centre-point condition exhibits outstanding reproducibility (CV < 1%), confirming very low experimental error and strong reliability of the thermal ethanolytic processing system (Aquinas *et al*., 2024). Higher variability at lower temperature and shorter reaction time indicates unstable cymene formation kinetics and incomplete biomass conversion. Catalyst loading shows improved yield consistency at higher loadings (2%), although interactions with temperature and time still introduce variability. Overall, reproducibility improves under moderate to high-severity reaction conditions, suggesting enhanced reaction control and stabilisation of product formation pathways. At 50 °C, reproducibility is very high (CV < 1%), indicating stable thermal ethanolytic conversion of *Gmelina arborea* biomass under moderate temperature. At 50 min, the yield variation is minimal, which suggests a reaction equilibrium region or stable kinetics. Catalyst Loading of 1.5 % $Ca(OH)_2$ gives the most consistent performance. Lower (1%) or higher (2%) catalyst levels show a wider yield spread across non-replicated runs, leading to possible mass-transfer or secondary reaction effects. The experimental design shows very strong reproducibility at the centre point, confirming good process stability and low experimental error. A CV of 0.61% is statistically excellent for biomass thermal processing studies. This supports the reliability of the Response Surface optimization results for cymene production.

ANOVA

To evaluate the ANOVA of cymene yield, the experimental data were analysed using a linear factorial model aligned with Response Surface Methodology screening, in which the primary effects of temperature (A), reaction time (B), and catalyst loading (C) were considered (Table 4). Using the experimental data in Table 4, the full fitting quadratic RSM model equation is expressed as in Equation 2.

$$Y = -1183.25 + 21.08A + 23.27B + 85.86C - 0.0122AB + 1.5875AC + 0.9400BC - 0.1942A^2 - 0.2258B^2 - 49.68C^2 \qquad (2)$$

Table 4: ANOVA Results for Cymene Yield

Source	DF	Sum of Squares (SS)	Mean Square (MS)	F-value	p-value	Significance
Temperature (A)	2	11154.82	5577.41	5.76	0.028	Significant
Time (B)	2	8426.35	4213.18	4.35	0.049	Significant
Catalyst (C)	2	9368.47	4684.24	4.83	0.039	Significant
Pure Error	4	3.85	0.96	—	—	—
Residual	6	5811.62	968.60	—	—	—
Total	16	34765.11	—	—	—	—

Effect of Variable Factors

Temperature shows the highest contribution to yield variation with an F-value of 5.76. This indicates that cymene formation during the thermal ethanolytic processing of *Gmelina arborea* leaves is thermally controlled. Increasing temperature leads to biomass depolymerisation, the formation of volatile intermediates, and aromatisation pathways that yield cymene (Nayak & Gupta, 2025; Sánchez-Velandia *et al*., 2025). However, excessive temperature variability may also introduce secondary degradation reactions, which could explain the moderate reproducibility at extreme levels. Reaction time is statistically significant ($p < 0.05$), confirming that short residence time leads to incomplete conversion and longer reaction time leads to improved yield but higher variability. This suggests the reaction approaches a pseudo-equilibrium region near the centre point (50 min). Catalyst loading also significantly influences yield. Calcium hydroxide likely enhances ethanolytic cleavage, deoxygenation, and cyclisation/aromatisation reactions. The significance indicates that catalyst concentration governs reaction pathway selectivity, not only reaction rate.

Pure Error and Model Reliability

The very low pure error (MS = 0.96) confirms high experimental precision, strong reproducibility at replicated centre conditions, and reliability of statistical conclusions. This is consistent with the earlier CV ≈ 0.61 % obtained for centre-point runs. Overall process insight, all three factors significantly affect cymene yield. Temperature exerts the dominant control, followed by catalyst loading and reaction time. The statistical results validate the use of Response Surface Optimization for identifying optimal mild-thermal processing conditions.

Reported yields of *p*-cymene from different biomass-derived or terpene feedstocks vary widely depending on the catalyst system, reaction pathway, and operating conditions. Dávila *et al*. (2015) obtained a high yield of 97 % *p*-cymene from orange peels. Similarly, Yılmazoğlu & Akgün (2018) reported yields of up to 80 % through supercritical ethanolysis and propanolysis of orange peels using Pd/Al_2O_3 and Pt/Al_2O_3 catalysts under short residence times (10-50 s), elevated temperatures (245-340 °C), and pressures of 6.5-12.5 MPa. In contrast, Mohamed (2017) observed only 3.54 % *p*-cymene during the extraction of green cumin oil. Catalytic dehydroisomerization routes have also demonstrated excellent performance. Alsharif *et al*. (2023) reported that cyclic monoterpenes such as α-pinene and β-pinene yielded 91-95 % *p*-cymene over CdO supported on silica at 325-375 °C, while limonene, α-terpinene, γ-terpinene, and terpinolene achieved complete (100 %) yield at lower temperatures of 200-250 °C. Earlier, Alsharif *et al*. (2021) showed that silica-supported ZnO enabled the conversion of α-pinene to *p*-cymene with about 90 % yield at full conversion at 370 °C, whereas limonene produced 100 % *p*-cymene at 325 °C. Furthermore, Bueno *et al*. (2008) demonstrated aerobic dehydrogenation of readily available *para*-menthenic terpenes (γ-terpinene, α-terpinene, limonene, and terpinolene) using *p*-benzoquinone with $Cu(OAc)_2$ as a co-catalyst in acetic acid solution (80-100 °C, 5-10 atm), achieving yields as high as 95 %.

In comparison, the present study achieved a o-cymene and *p*-cymene yield of 4.47%, corresponding to a specific yield of 198.40 mg/g, under significantly milder conditions (60 °C, 50 min, and 2.0 wt% catalyst loading) through calcium hydroxide-catalyzed thermal ethanolytic processing of waste *Gmelina arborea* leaves. This highlights the potential of low-temperature, low-pressure biomass valorisation routes as energy-efficient and sustainable alternatives, despite the comparatively lower conversion efficiency.

Table 5: Comparative Yields of Cymene

Author / Year	Feedstock / Reactant	Catalyst / Method	Conditions	*p*-Cymene Yield (%)
Dávila et al. (2015)	Orange peels	Not specified (biomass conversion)	Not specified	97
Yılmazoğlu & Akgün (2018)	Orange peels	Pd/Al_2O_3 and Pt/Al_2O_3 (supercritical ethanolysis/propanolysis)	245–340 °C, 6.5–12.5 MPa, 10–50 s	80
Mohamed (2017)	Green cumin oil	Extraction process	Not specified	3.54
Alsharif *et al*. (2023)	α-Pinene and β-Pinene	CdO/SiO_2 (dehydroisomerization)	325–375 °C	91–95
Alsharif *et al*. (2023)	Limonene, α-terpinene, γ-terpinene, terpinolene	CdO/SiO_2 (dehydroisomerization)	200–250 °C	100
Alsharif *et al*. (2021)	α-Pinene	ZnO/SiO_2 (dehydroisomerization)	370 °C	90
Alsharif *et al*. (2021)	Limonene	ZnO/SiO_2 (dehydroisomerization)	325 °C	100
Bueno *et al*. (2008)	*Para*-menthenic terpenes (γ-terpinene, α-terpinene, limonene, terpinolene)	*p*-Benzoquinone + $Cu(OAc)_2$ (aerobic dehydrogenation)	80–100 °C, 5–10 atm	95
Present study	Waste *Gmelina arborea* leaves	$Ca(OH)_2$ (thermal ethanolytic processing)	60 °C, 50 min, 2.0 wt% catalyst	4.47% (198.40 mg/g^1 specific yield)

CONCLUSION

This study demonstrates a proof-of-concept for the production of cymene from lignocellulosic *Gmelina arborea* leaf biomass via mild thermal ethanolytic processing using calcium hydroxide as a low-cost alkaline catalyst under near-ambient pressure conditions. The results show that cymene formation is influenced by temperature, reaction time, and catalyst loading, with statistical analysis confirming the significance of these variables in governing yield and selectivity.

Moderate operating conditions (around 50 °C, 50 min, and 1.5 % catalyst loading) provided the most consistent performance, indicating that controlled reaction severity favours selective aromatisation pathways over excessive biomass liquefaction. While higher temperatures and catalyst loadings enhanced overall conversion (specific yield), they reduced selectivity, highlighting the need to balance reaction conditions to minimise secondary reactions.

However, the overall cymene yields obtained in this study remain relatively low compared to conventional and terpene-based routes, indicating that the process is still at an early stage of development. In addition, although good reproducibility was observed at the centre point for specific yield, further validation is required to improve quantification accuracy and confirm consistency across broader operating conditions.

Overall, this work establishes the feasibility of generating aromatic hydrocarbons such as cymene directly from non-food leaf biomass under mild conditions, providing a foundation for future research. Further studies should focus on improving yield, refining analytical quantification, elucidating reaction mechanisms, and evaluating catalyst performance to advance this approach toward practical biomass valorisation applications.

REFERENCES

Abd Rashed, A., Rathi, D. N. G., Ahmad Nasir, N. A. H., & Abd Rahman, A. Z. (2021). Antifungal properties of essential oils and their compounds for application in skin fungal infections: Conventional and nonconventional approaches. *Molecules*, *26*(4), 1093.

Adenaiya, A. O. (2021). *Bioincision of Gmelina arborea Roxb. Heartwood for Permeability Improvement to Chemical Treatment* (Doctoral dissertation).

Ali, A. M., & Ibrahim, H. (2023). Conversion of Waste Biomass into Valuable Platform Furan-Based Compounds. *Asian Journal of Advances in Research*, *6*(1), 553-559.

Ali, A. M., Shuaibu, H., & Ibrahim, H. (2026). Statistical evaluation and optimisation of biodiesel production from Gmelina arborea leaf biomass using calcium hydroxide catalysis under mild conditions. *FUDMA Journal of Sciences*, *10*(3), 94-101.

Al-Kinany, M. C., Al-Megren, H. A., Al-Ghilan, E. A., Edwards, P. P., Xiao, T., Al-Shammari, A. S., & Al-Drees, S. A. (2012). Selective zeolite catalyst for alkylation of benzene with ethylene to produce ethylbenzene. *Applied Petrochemical Research*, *2*(3), 73-83.

Alsharif, A. A. (2023). *Selective dehydroisomerisation of cyclic monoterpenes to p-cymene over bifunctional metal-acid catalysts* (Doctoral dissertation, The University of Liverpool (United Kingdom)).

Alsharif, A., Kozhevnikova, E. F., & Kozhevnikov, I. V. (2023). Selective dehydroisomerization of cyclic monoterpenes to p-cymene over silica-supported CdO. *Applied Catalysis B: Environmental*, *325*, 122362.

Alsharif, A., Smith, N., Kozhevnikova, E. F., & Kozhevnikov, I. V. (2021). Dehydroisomerisation of α-pinene and limonene to p-cymene over silica-supported ZnO in the gas phase. *Catalysts*, *11*(10), 1245.

Aly, S. H., Thabet, A. A., Bahgat, D. M., Mahmoud, O. A., Elhawary, E. A., El-Nashar, H. A., & Eldahshan, O. A. (2026). Plant-Derived Compounds: A Potential Treasure for

Development of Analgesic and Antinociceptive Therapeutics. *Phytotherapy Research*, *40*(1), 35-63.

Aquinas, N., Ramananda, B. M., & Selvaraj, S. (2024). Optimization of curdlan production and ultrasound-assisted extraction processes from Priestia megaterium. *Scientific Reports*, *14*(1), 26709.

Arachchige, C. N., Prendergast, L. A., & Staudte, R. G. (2022). Robust analogs to the coefficient of variation. *Journal of Applied Statistics*, *49*(2), 268-290.

Assadpour, E., Can Karaça, A., Fasamanesh, M., Mahdavi, S. A., Shariat-Alavi, M., Feng, J., & Jafari, S. M. (2024). Application of essential oils as natural biopesticides; recent advances. *Critical Reviews in Food Science and Nutrition*, *64*(19), 6477-6497.

Badi, H. N., Abdollahi, M., Mehrafarin, A., Ghorbanpour, M., Tolyat, M., Qaderi, A., & Yekta, M. G. (2017). An overview on two valuable natural and bioactive compounds, thymol and carvacrol, in medicinal plants.

Baginska, S., Golonko, A., Swislocka, R., & Lewandowski, W. (2023). Monoterpenes as Medicinal Agents: Exploring the Pharmaceutical Potential of p-Cymene, p-Cymenene, and γ-Terpinene. *Acta Poloniae Pharmaceutica*, *80*(6).

Bratovcic, A. (2025). Eco-Friendly Weed Management: Nanoformulated Bioherbicides for Improved Crop Productivity. *Advances in Nanoparticles*, *14*(4), 101-120.

Bueno, A. C., Brandão, B. B., & Gusevskaya, E. V. (2008). Aromatization of para-menthenic terpenes by aerobic oxidative dehydrogenation catalyzed by p-benzoquinone. *Applied Catalysis A: General*, *351*(2), 226-230.

Chen, X., Shang, S., Yan, F., Jiang, H., Zhao, G., Tian, S., & Dang, Y. (2023). Antioxidant activities of essential oils and their major components in scavenging free radicals, inhibiting lipid oxidation and reducing cellular oxidative stress. *Molecules*, *28*(11), 4559.

Chouhan, S., Sharma, K., & Guleria, S. (2017). Antimicrobial activity of some essential oils—present status and future perspectives. *Medicines*, *4*(3), 58.

Dávila, J. A., Rosenberg, M., & Cardona, C. A. (2015). Techno-economic and environmental assessment of p-cymene and pectin production from orange peel. *Waste and Biomass Valorization*, *6*(2), 253-261.

Diniz do Nascimento, L., Barbosa de Moraes, A. A., Santana da Costa, K., Pereira Galúcio, J. M., Taube, P. S., Leal Costa, C. M., ... & Guerreiro de Faria, L. J. (2020). Bioactive natural compounds and antioxidant activity of essential oils from spice plants: New findings and potential applications. *Biomolecules*, *10*(7), 988.

El Hadi, M. A. M., Zhang, F. J., Wu, F. F., Zhou, C. H., & Tao, J. (2013). Advances in fruit aroma volatile research. *Molecules*, *18*(7), 8200-8229.

Fitri, N., Riza, R., Akbari, M. K., Khonitah, N., Fahmi, R. L., & Fatimah, I. (2022). Identification of citronella oil fractions as efficient bio-additive for diesel engine fuel. *Designs*, *6*(1), 15.

G. Correa, A., W. Paixao, M., & S. Schwab, R. (2015). Application of bio-based solvents in catalysis. *Current Organic Synthesis*, *12*(6), 675-695.

Gajbhiye, S. R., Deshmukh, G. P., Vinu, A., & Mannepalli, L. K. (2019). Production of p-Cymene by Alkylation of Toluene with Propan-2-Ol. *Catalysis in Green Chemistry and Engineering*, *2*(2).

Granato, A. V., Santos, A. G., & Dos Santos, E. N. (2017). p-Cymene as solvent for olefin metathesis: matching efficiency and sustainability. *ChemSusChem*, *10*(8), 1832-1837.

Gupta, I., Singh, R., Muthusamy, S., Sharma, M., Grewal, K., Singh, H. P., & Batish, D. R. (2023). Plant essential oils as biopesticides: Applications, mechanisms, innovations, and constraints. *Plants*, *12*(16), 2916.

Hattori, H., & Ono, Y. (2015). *Solid acid catalysis: from fundamentals to applications*. CRC Press.

Ibáñez, M. D., Sanchez-Ballester, N. M., & Blázquez, M. A. (2020). Encapsulated limonene: A pleasant lemon-like aroma with promising application in the agri-food industry. A review. *Molecules*, *25*(11), 2598.

Ibrahim, H., Ali, A. M., & Jibrin, M. D. (2025a). Synthesis of Dodecyl Acrylate Via Thermal Methanolysis of Gmelina Arborea Leaf Biomass. In *SPE Nigeria Annual International Conference and Exhibition* (p. D031S020R008). SPE.

Ibrahim, H., Ali, A. M., Moroto, Y. H., & Muazu, E. I. (2025b). Simplified Thermal Catalytic Pathway for 2-Methyltetrahydrofuran from Non-Food Biomass. *Indonesian Journal of Green Chemistry*, *2*(2), 71-83

Ibrahim, H., Ali, A.M., & & Mukhtar F.H. (2024). 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, Published by Cambridge Research and Publications, Vol. 5 No. 5, 132-141.

Jacob, T. N. (2025). Synthetic investigations on Azulenes.

Kumar, A., Shabnam, S., & Malik, M. S. (2021). *Doubling Farmers Income through Agroforestry*. Scientific Publishers.

Kumar, P. (2024). *Valorization of Commercially Important Essential Oils of Poaceae and Lamiaceae Families Using Heterogeneous Catalysts* (Doctoral dissertation, RMIT University).

Lal, P., & Bhandari, S. (2020). *Agroforestry with commercial clonal plantations in India*. The Energy and Resources Institute (TERI).

Lapuerta, M., Tobío-Pérez, I., Ortiz-Alvarez, M., Donoso, D., Canoira, L., & Piloto-Rodríguez, R. (2023). Heterogeneous catalytic conversion of terpenes into biofuels: an open pathway to sustainable fuels. *Energies*, *16*(6), 2526.

Li, C., Zhu, H., Zhao, K., Li, X., Tan, Z., Zhang, W., & Zhang, L. (2022). Chemical constituents, biological activities and anti-rheumatoid arthritis properties of four citrus essential oils. *Phytotherapy Research*, *36*(7), 2908-2920.

Ma, X., Su, C., & Xu, Q. (2016). N-Alkylation by hydrogen autotransfer reactions. *Hydrogen transfer reactions: reductions and beyond*, 291-364.

Majekobaje, A. R. (2018). *Potential of Chromolaena odorata Linn. Extract as wood preservative against fungal attack* (Doctoral dissertation, M. Sc Thesis. Department of Forest Production and Products, University of Ibadan, Nigeria. 94p).

Makarouni, D., Lycourghiotis, S., Kordouli, E., Bourikas, K., Kordulis, C., & Dourtoglou, V. (2018). Transformation of limonene into p-cymene over acid activated natural mordenite utilizing atmospheric oxygen as a green oxidant: A novel mechanism. *Applied Catalysis B: Environmental*, *224*, 740-750.

Malkar, R. S., & Yadav, G. D. (2020). Development of green and clean processes for perfumes and flavors using heterogeneous chemical catalysis. *Current Catalysis*, *9*(1), 32-58.

Marchese, A., Arciola, C. R., Barbieri, R., Silva, A. S., Nabavi, S. F., Tsetegho Sokeng, A. J., ... & Nabavi, S. M. (2017). Update on monoterpenes as antimicrobial agents: A particular focus on p-cymene. *Materials*, *10*(8), 947.

Marques, F. M., Figueira, M. M., Schmitt, E. F. P., Kondratyuk, T. P., Endringer, D. C., Scherer, R., & Fronza, M. (2019). In vitro anti-inflammatory activity of terpenes via suppression of superoxide and nitric oxide generation and the NF-κB signalling pathway. *Inflammopharmacology*, *27*(2), 281-289.

Mohamed, A. A. B. (2017). *Effect of Cuminum Cyminum oil on the edible oil (Sunflower oil) properties and antibacterial activities* (Doctoral dissertation, Faroug Bakheit Mohamed Ahmed Elsonni).

Mohammed, H. A., Sulaiman, G. M., Al-Saffar, A. Z., Mohsin, M. H., Khan, R. A., Hadi, N. A., ... & Abomughaid, M. M. (2025). Aromatic volatile compounds of essential oils: distribution, chemical perspective, biological activity, and clinical applications. *Food Science & Nutrition*, *13*(9), e70825.

Nayak, R. R., & Gupta, N. K. (2025). Renewable aromatic production from waste: exploring pathways, source materials, and catalysts. *Green Chemistry*, *27*(27), 8055-8111.

Pyo, Y., & Jung, Y. J. (2024). Microbial fermentation and therapeutic potential of p-Cymene: Insights into biosynthesis and antimicrobial bioactivity. *Fermentation*, *10*(9), 488

Quadros, G. T., Valente, L. C., Abenante, L., Barcellos, T., Hartwig, D., & Lenardão, E. J. (2025). Bio-based Green Solvents in Organic Synthesis. An Updated Review. *Sustainability & Circularity NOW*, *2*(continuous publication).

Rana, P., Pathania, D., Gaur, P., Patel, S. K., Bajpai, M., Singh, N. T., & Dwivedi, A. (2025). Regulatory frameworks for fragrance safety in cosmetics: a global overview. *Toxicological Research*, *41*(3), 199-220.

Rocha, F., Ratola, N., & Homem, V. (2023). Fragrances in the environment: Properties, applications, and emissions. In *Fragrances in the Environment* (pp. 1-36). Cham: Springer International Publishing.

Saha, D., Sinha, A., & Roy, B. (2020). A critical review of emission and performance characteristics of CI engine using bio-additives. *Clean Technologies and Environmental Policy*, *22*(8), 1613-1638.

Sánchez-Velandia, J. E., Gallego-Villada, L. A., Mäki-Arvela, P., Sidorenko, A., & Yu. Murzin, D. (2025). Upgrading biomass to high-added value chemicals: synthesis of monoterpenes-based compounds using catalytic green chemical pathways. *Catalysis Reviews*, *67*(2), 371-496.

Santoso, M., Triwahyono, S., & Prasetyoko, D. (2013). Activities of Heterogeneous Acid-Base Catalystsfor Fragrances Synthesis: A Review. *Bulletin of Chemical Reaction Engineering & Catalysis*, *8*(1), 14-33.

Satira, A., Espro, C., Paone, E., Calabrò, P. S., Pagliaro, M., Ciriminna, R., & Mauriello, F. (2021). The limonene biorefinery: From extractive technologies to its catalytic upgrading into p-cymene. *Catalysts*, *11*(3), 387.

Sell, C. (2020). Chemistry of essential oils. In *Handbook of essential oils* (pp. 161-189). CRC Press.

Tsitlakidou, P., Tasopoulos, N., Chatzopoulou, P., & Mourtzinos, I. (2023). 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*, *103*(14), 6727-6751.

Vassiliou, E., Awoleye, O., Davis, A., & Mishra, S. (2023). Anti-inflammatory and antimicrobial properties of thyme oil and its main constituents. *International journal of molecular sciences*, *24*(8), 6936.

Yaya Lancheros, M. L., Rai, K. M., Balasubramanian, V. K., Dampanaboina, L., Mendu, V., & Terán, W. (2021). De novo transcriptome analysis of white teak (Gmelina arborea Roxb) wood reveals critical genes involved in xylem development and secondary metabolism. *BMC genomics*, *22*(1), 494.

Yılmazoğlu, E., & Akgün, M. (2018). p-Cymene production from orange peel oil using some metal catalyst in supercritical alcohols. *The Journal of Supercritical Fluids*, *131*, 37-46.

Yingngam, B. (2022). Chemistry of essential oils. In *Flavors and Fragrances in Food Processing: Preparation and Characterization Methods* (pp. 189-223). American Chemical Society.

Yousofvand, N., & Moloodi, B. (2023). An overview of the effect of medicinal herbs on pain. *Phytotherapy research*, *37*(3), 1057-1081.