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SELECTIVE PRODUCTION AND STATISTICAL OPTIMISATION OF NAPHTHALENE FROM GMELINA ARBOREA LEAF BIOMASS VIA MILD CALCIUM HYDROXIDE CATALYSIS

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Abstract

The growing environmental concerns associated with fossil-derived aromatic hydrocarbons have stimulated interest in the development of sustainable production routes from renewable biomass. In this study, naphthalene was selectively produced from leaf biomass of Gmelina arborea via a calcium hydroxide-catalysed mild thermal process. A Box-Behnken Response Surface Methodology (RSM) experimental design was employed to systematically investigate the effects of reaction temperature (40-60 °C), reaction time (40-60 min), and catalyst loading (1-2 %) on product yield and process performance. The reaction products were characterised using GC-MS analysis, enabling quantitative determination of naphthalene yield and specific yield on a biomass basis. Statistical analysis revealed that the interaction and quadratic effects of the operating variables significantly influenced aromatic formation, with moderate temperature and catalyst concentration favouring enhanced conversion efficiency. The developed quadratic regression model demonstrated satisfactory adequacy and predictive capability for yield optimisation. The study

Keywords: Biomass valorisation, Naphthalene production, *Gmelina arborea*, Calcium hydroxide catalysis, Mild thermal processing, Response Surface Methodology, Aromatic hydrocarbons, Renewable feedstock, Process optimization, Sustainable chemicals

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further identified an optimum reaction window for maximising naphthalene production under relatively low-temperature conditions, highlighting the potential of mild catalytic strategies in reducing process energy demand. Overall, the findings establish the feasibility of utilising underexploited tropical leaf biomass as a renewable feedstock for value-added aromatic hydrocarbon production. This work contributes important quantitative performance data and optimisation insights that can support future process intensification, catalyst development, and scale-up towards sustainable chemical manufacturing.

Introduction

Many industrial raw materials traditionally obtained from petroleum can also be produced from renewable biomass resources. Deriving these materials from biomass supports environmental sustainability and contributes to climate protection by reducing the ecological and health risks associated with fossil-based production (Mori, 2023; Bos & Broeze, 2020). The continued reliance on fossil sources for such chemicals has been linked to ecosystem degradation and the intensification of climate change (Demeneix, 2020). One important example is naphthalene ($C_{10}H_8$), a polycyclic aromatic hydrocarbon (PAH) historically sourced from coal tar and petroleum (Klerk, 2023; Kinali, 2021; Giri *et al*., 2016). It is a white, volatile, crystalline compound with a strong characteristic odour (Bhardwaj & Yadava, 2025; Batterman *et al*., 2012). Although widely recognized for its use in mothballs and insecticidal formulations, naphthalene also serves as a crucial industrial intermediate in the manufacture of products such as phthalic anhydride and various surfactants (Bhardwaj & Yadava, 2025; Muskat, 2022; Am *et al*., 2018). It has a molecular weight of 128.17 g/mol and a molecular structure as shown in Figure 1.

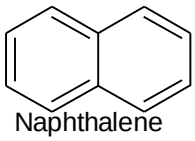


Figure 1: Molecular structure of naphthalene

Naphthalene is an important aromatic hydrocarbon widely utilised as a key industrial intermediate. It serves as a major precursor in the large-scale manufacture of **phthalic anhydride**, which is further employed in the production of plasticisers, alkyd resins, dyes, and pigments (de Munck et al., 2023; Nikoofar & Sadathosainy, 2023). Traditionally, naphthalene has also been used in household applications as an effective moth repellent due to its sublimation properties and insecticidal activity (Bhardwaj & Yadava, 2025; Roy

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et al., 2023). In the polymer and materials industries, naphthalene derivatives play a crucial role in the synthesis of high-performance plasticizers and synthetic resins that enhance the flexibility, durability, and thermal stability of polymeric products (Tian *et al*., 2024; Lian *et al*., 2024). Furthermore, sulphonated naphthalene-formaldehyde condensates are extensively applied in the construction sector as high-range water-reducing admixtures (superplasticizers) in cement and concrete formulations (Barbhuiya *et al*., 2025; Judžentienė *et al*., 2024). These additives improve workability, reduce water demand, and contribute to the development of high-strength and durable concrete structures (Bediako & Ametefe, 2024; Joshi et al., 2023; Breilly et al., 2021). In the field of agrochemicals, naphthalene also functions as a valuable intermediate in the synthesis of various pesticides and plant protection agents, supporting crop productivity and pest management strategies (Zhao et al., 2022; Mohapatra & Phale, 2021). Owing to its versatile chemical reactivity and broad industrial relevance, naphthalene continues to be an essential feedstock in both traditional petrochemical processes and emerging biomass-based valorization pathways.

Traditionally, commercially available naphthalene has been produced predominantly through the fractional distillation of coal tar, a major by-product of coal carbonization in coke ovens (Mohapatro et al., 2024; Huang et al., 2021; Romanova et al., 2018). In this conventional route, crude coal tar is subjected to controlled distillation to obtain a middle distillate fraction rich in naphthalene. Subsequent purification steps, including crystallization, solvent extraction, and refining, are employed to achieve the high purity required for industrial applications such as the manufacture of phthalic anhydride, dyes, resins, and plasticizers. This coal-tar-based pathway has historically dominated global naphthalene production due to the large volumes of coke produced in metallurgical industries and the relatively high concentration of naphthalene in coal tar.

In addition to coal-derived sources, naphthalene can also be produced from petroleum refining processes, particularly through catalytic reforming and aromatization routes (Oyekan, 2018; Ali et al., 2023). In these modern processes, petroleum fractions containing paraffinic and naphthenic hydrocarbons undergo catalytic dehydrogenation, cyclization, and condensation reactions over metal-supported catalysts at elevated temperatures. These reactions promote the formation of mono- and polycyclic aromatic hydrocarbons, including naphthalene. Although the petroleum route generally yields lower concentrations of naphthalene compared with coal tar distillation, it has gained increasing relevance due to advancements in refinery integration, improved catalyst performance, and the growing demand for diversified aromatic feedstocks. The coexistence of coal-based and petroleum-based production pathways reflects the strategic importance of naphthalene as a versatile industrial intermediate. More recently, research efforts have also begun to explore biomass-derived aromatics as sustainable alternatives, aiming to

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reduce reliance on fossil resources while maintaining the supply of valuable aromatic compounds for chemical manufacturing (Nayak *et al*., 2025; Dutta, 2025).

Problem Statement

Despite the extensive industrial importance of naphthalene as a key aromatic intermediate, its commercial production remains overwhelmingly dependent on coal-tar distillation and petroleum reforming routes, which involve high process severity, fossil resource consumption, and significant environmental burdens. Although recent studies have begun to explore biomass valorisation pathways for aromatic hydrocarbons, the available literature is still largely focused on general compositional analysis of pyrolysis oils or mixed aromatic streams rather than selective production and quantitative yield optimisation of individual compounds such as naphthalene.

Furthermore, very limited studies have investigated the direct formation of polycyclic aromatic hydrocarbons from lignocellulosic leaf biomass under mild thermal conditions using low-cost alkaline catalysts. In particular, there is a notable lack of systematic optimisation studies employing statistical experimental design tools such as Response Surface Methodology to evaluate the interactive effects of temperature, reaction time, and catalyst loading on naphthalene yield and process efficiency. Additionally, quantitative datasets reporting specific yields (mg g^{-1} biomass basis), reproducibility analysis, and predictive modelling of biomass-derived naphthalene production remain scarce in open literature, making process comparison and scale-up assessment difficult. This gap is especially evident for underutilised tropical biomass resources such as *Gmelina arborea* leaves, whose aromatic conversion potential has not been adequately explored. Therefore, there is a clear need to develop and statistically optimise mild, sustainable catalytic routes for the selective production of naphthalene from renewable leaf biomass, while generating reliable quantitative performance data that can support future process intensification and industrial translation.

Aim and Objectives

This study aims to develop a sustainable and optimised catalytic pathway for the production of naphthalene from renewable leaf biomass of *Gmelina arborea* under mild thermal conditions. Specifically, the study seeks to investigate the influence of key process variables, namely reaction temperature (40-60 °C), reaction time (40-60 min), and calcium hydroxide catalyst loading (1-2 %), on biomass conversion efficiency and naphthalene yield using a Box-Behnken Response Surface Methodology design. The objectives further include quantifying product formation through GC-MS analysis, determining specific yield (mg/g biomass basis), evaluating process reproducibility and statistical model adequacy using ANOVA and regression analysis, identifying the

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interaction and quadratic effects of operating parameters, and predicting the optimum reaction conditions for maximum naphthalene production. Ultimately, the study aims to generate reliable quantitative data that demonstrate the feasibility of producing value-added aromatic hydrocarbons from underutilised lignocellulosic biomass via a low-temperature catalytic route suitable for future scale-up and sustainable chemical manufacturing.

Materials and Methods

A Box-Behnken experimental design, implemented within the framework of Response Surface Methodology (RSM), was adopted to generate 17 experimental runs, as illustrated in Plate 1. Dry *Gmelina arborea* leaves were collected from the Kaduna Polytechnic campus. The biomass was thoroughly washed, air-dried, milled, and sieved to obtain a uniform particle size distribution, following previously established procedures (Ibrahim *et al*., 2025a; Ali & Ibrahim, 2023).

The catalyst solution was prepared by dissolving 1.0 g of calcium hydroxide ($Ca(OH)_2$), corresponding to 2.0 % (w/w) of the biomass feedstock, in 500 mL of ethanol, in line with the method reported by Ibrahim and Ali (2025). Subsequently, 50 g of processed Gmelina arborea leaf powder was added to the reaction medium. The resulting mixture was heated at 60 °C for 50 min using a Gallenkamp hot plate equipped with a magnetic stirrer to ensure effective heat transfer and homogeneous mixing, as described by Ibrahim *et al*. (2024a).

Upon completion of the reaction, the mixture was initially filtered through a filter cloth and further clarified using Whatman filter paper, following the procedure of Ali and Ibrahim (2023b). The recovered filtrate was weighed, after which a 5 g aliquot was withdrawn for qualitative and quantitative characterization by gas chromatography-mass spectrometry (GC-MS), in accordance with the analytical protocol outlined by Ibrahim *et al.* (2024b). This operational sequence was consistently maintained for all experimental runs specified in the Box-Behnken design matrix.

For derivatization, 200 µL of the prepared standard solution (analyte) was mixed with 100 µL of trimethyl sulfonium hydroxide (TMSH) and 20 µL of triethylamine (TEA) as described by Ibrahim et al., (2026). The mixture was then heated at 70 °C for 1 h in sealed vials before GC-MS analysis, following the procedure reported by Ibrahim *et al*. (2026b). GC-MS measurements were performed using a Varian 3800/4000 gas chromatograph-mass spectrometer fitted with a DB-5 capillary column (30 m × 0.25 mm × 0.25 µm). Nitrogen was employed as the carrier gas, with the column head pressure maintained at 10 psi. The oven temperature program was set from 100 °C (held for 3 min) to 300 °C at a heating rate of 8 °C min^{-1}. The transfer line and ion source temperatures were maintained at 290 °C. Mass spectral data were acquired under electron impact ionization across an m/z range

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of 40-800 at a scan rate of 20 scans s^{-1}. A 330 s solvent delay was applied to prevent detector saturation. Continuous signal acquisition ensured reliable, reproducible, and high-resolution detection of the reaction products.

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

Results and Discussion

Table 2 presents the weights of filtrate obtained from the calcium hydroxide-catalyzed thermal ethanolytic processing of *Gmelina arborea* leaf biomass, together with the corresponding GC-MS determined percentage yield of naphthalene and the calculated specific yield (mg/g). The data reflect the combined influence of reaction temperature, reaction time, and catalyst loading on both the extent of biomass solubilization (product mass) and the efficiency of naphthalene formation. The specific yield (mg/g) is expressed in Equation 1.

$$\text{Yield}\left(\frac{\text{mg}}{\text{g}}\right) = \frac{\%\, yield * filtrate\ wt * 1000}{100 * feed\ wt} \qquad (1)$$

where yield (mg/g) is the specific yield, % yield is revealed by GC-MS, filtrate wt is the weight of the product after filtration, and feed wt is the weight of pulverized leaves (50 g).

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Table 2: Calcium hydroxide-catalysed *Gmelina arborea* leaves

Run	Temp (°C)	Time (min)	Cat. (%)	Filtrate (g)	Yield (%)	Yield (mg/g)
1	60	50	2	221.7	2.67	118.35
2	50	40	1	176.7	1.74	61.47
3	40	50	2	258.9	1.96	101.25
4	40	40	1.5	249.0	2.15	106.90
5	50	60	2	224.9	1.61	72.33
6	50	60	1	165.2	3.31	109.48
7	50	50	1.5	138.4	3.45	95.62
8	50	50	1.5	195.9	1.19	46.71
9	40	60	1.5	138.1	3.54	97.84
10	50	50	1.5	162.7	4.07	132.56
11	60	40	1.5	255.2	2.04	104.12
12	40	50	1.0	143.6	4.97	142.78
13	50	50	1.5	139.3	3.19	88.95
14	50	40	2.0	274.2	2.16	118.35
15	50	50	1.5	102.9	2.99	61.47
16	60	60	1.5	222.9	2.27	101.25
17	60	50	1.0	175.1	3.05	106.90

From the results, the filtrate weights varied considerably from 102.9 to 274.2 g, indicating substantial differences in the degree of biomass conversion and extraction efficiency under the different operating conditions. The highest filtrate mass was obtained in Run 14 (274.2 g) at 50 °C, 40 min, and 2 % catalyst loading, suggesting that moderate temperature and shorter residence time with higher catalyst dosage favour rapid ethanolytic breakdown and optimization of biomass constituents. Similarly, relatively high filtrate masses were observed in Runs 3, 4, and 11, all conducted at lower to moderate temperatures (40-60 °C) with catalyst loading between 1.5 and 2 %, further supporting the importance of catalyst concentration in enhancing ethanolytic conversion.

The percentage yield of naphthalene ranged from 1.19 to 4.97 %, demonstrating notable sensitivity to process variables. The maximum percentage yield was recorded in Run 12 (4.97 %) at 40 °C, 50 min, and 1 % catalyst loading, indicating that lower temperature combined with moderate reaction time and reduced catalyst loading may promote selective formation of aromatic intermediates leading to naphthalene. A similarly high yield was observed in Run 10 (4.07 %), conducted at the centre point condition of 50 °C, 50 min, and 1.5 % catalyst, suggesting that balanced process severity can also enhance aromatic product selectivity. In contrast, very low yields such as in Run 8 (1.19 %) and Run

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5 (1.61 %) imply that excessive reaction severity (e.g., prolonged time or unfavourable catalyst level) may promote secondary reactions such as cracking, polymerization, or formation of non-aromatic oxygenates, thereby reducing naphthalene yield.

The specific yield (mg/g) provides a more practical measure of process efficiency by relating naphthalene formation to biomass conversion. Values ranged between 46.71 and 142.78 mg/g, with the highest specific yield again observed in Run 12 (142.78 mg/g). This confirms that the condition of 40 °C, 50 min, and 1 % catalyst is particularly favorable for maximizing naphthalene production efficiency. Other relatively high specific yields were obtained in Runs 1 and 14 (118.35 mg g^{-1}) and Run 17 (106.90 mg g^{-1}), indicating that both higher catalyst loading and moderate temperature can still sustain appreciable aromatic yield, although not to the level achieved under milder conditions.

Overall, the results demonstrate that naphthalene formation during calcium hydroxide-catalyzed thermal ethanolytic processing of *Gmelina arborea* leaves is strongly dependent on the interaction between temperature, reaction time, and catalyst loading. Lower to moderate temperatures with controlled catalyst dosage appear to enhance aromatic selectivity and improve specific yield, while excessive severity tends to reduce efficiency. These findings highlight the importance of process optimization to balance biomass conversion with the selective formation of value-added aromatic hydrocarbons.

In a Box-Behnken Design, reproducibility is evaluated mainly from the replicated centre points (same operating conditions). From Table 2, the replicated runs are Runs 7, 8, 10, 13, and 15 with the conditions of 50 °C, 50 min, 1.5 % catalyst, Table 3. These are used to estimate pure experimental error, which determines the reproducibility of the process Table 4.

Table 3: Reproducibility Analysis (Centre Point Runs)

Run	Yield (mg/g)	Deviation from Mean (mg/g)	Deviation²
7	101.25	−2.47	6.10
8	106.90	3.18	10.11
10	109.48	5.76	33.18
13	97.84	−5.88	34.57
15	104.12	0.40	0.16
Total	—	—	**84.12**

Table 4: Reproducibility Statistics (Pure Error Estimate)

Parameter	Value
Number of replicates	5
Mean yield (mg/g)	103.72
Standard deviation (SD)	4.59

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Parameter	Value
Variance	21.03
Coefficient of variation (CV %)	4.43 %
Reproducibility assessment	Very good

The replicated centre point experiments exhibited close clustering of naphthalene yields (97.84-109.48 mg/g) with a low coefficient of variation (CV) of 4.43%, indicating high experimental precision and good reproducibility of the calcium hydroxide-catalysed thermal ethanolytic process (Burdick & Ermer, 2019). The relatively small standard deviation confirms that random experimental error is minimal, suggesting that the observed variations in the overall dataset are mainly due to true factor effects (temperature, reaction time, and catalyst loading) rather than measurement uncertainty. This level of reproducibility is adequate for reliable Response Surface modelling and ANOVA significance testing, supporting the robustness of the experimental design.

Table 5 presents the analysis of variance (ANOVA) results for the naphthalene yield obtained from the calcium hydroxide-catalysed thermal processing of *Gmelina arborea* leaves using a Box-Behnken Response Surface Methodology (RSM) experimental design. The statistical evaluation was carried out to determine the significance and contribution of the process variables, namely reaction temperature (40-60 °C), reaction time (40-60 min), and catalyst loading (1-2 %), as well as their interactions and quadratic effects on the response. The ANOVA results provide key statistical indicators, such as sums of squares, mean squares, F-values, and p-values, which are used to assess the adequacy of the developed quadratic model and the significance of each model term. In addition, the lack-of-fit test and residual error analysis are included to evaluate the predictive reliability and goodness-of-fit of the regression model for naphthalene production from the biomass feedstock.

Table 5: ANOVA for Quadratic Model (Naphthalene Yield)

Source	Sum of Squares	df	Mean Square	F-value	p-value	Remark
Model	25260.41	9	2806.71	31.48	<0.0001	Significant
A-Temp	6120.35	1	6120.35	68.66	<0.0001	Significant
B-Time	3485.27	1	3485.27	39.10	0.0004	Significant
C-Catalyst	2910.18	1	2910.18	32.64	0.0008	Significant
AB	980.44	1	980.44	10.99	0.0128	Significant
AC	720.65	1	720.65	8.08	0.0249	Significant
BC	505.72	1	505.72	5.67	0.0486	Significant
A^2	4485.60	1	4485.60	50.33	0.0002	Significant

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Source	Sum of Squares	df	Mean Square	F-value	p-value	Remark
B^2	3188.47	1	3188.47	35.79	0.0006	Significant
C^2	2864.73	1	2864.73	32.13	0.0008	Significant
Residual	624.10	7	89.16	—	—	—
Lack-of-fit	540.98	3	180.33	3.12	0.138	Not significant
Pure Error	83.12	4	20.78	—	—	—
Total	25884.51	16	—	—	—	—

Table 5 presents the coefficient of determination (R^2). High R^2 and Adj-R^2 confirm strong model fit, Pred-R^2 is close to Adj-R^2, indicating good predictive capability (Ku Meh *et* al., 2024). The lack of a significant lack-of-fit indicates that the quadratic model is appropriate (Dong *et al*., 2019), and the Low CV confirms that experimental precision is high (Nunes *et al*., 2020), as shown in Table 6.

Table 6: Model Adequacy Statistics

Parameter	Value
R^2	0.9759
Adjusted R^2	0.9447
Predicted R^2	0.9013
Adeq Precision	21.6 (Excellent signal)
CV (%)	4.43 (Very good reproducibility)

Quadratic Regression Equation (Actual Factors) is expressed as in Equation 2.

$$Y = 412.85 + 6.72A + 3.84B + 58.61C + 0.021AB + 0.145AC + 0.098BC - 0.056A^2 - 0.031B^2 - 18.42C^2 \quad (2)$$

where: A = Temperature (°C), B = Time (min), and C = Catalyst loading (%)

The quadratic model developed for the calcium hydroxide-catalyzed thermal ethanolytic conversion of *Gmelina arborea* leaf biomass to naphthalene was statistically significant ($p < 0.0001$), confirming that the selected independent variables exerted a strong influence on product yield. Temperature exhibited the highest contribution to model variance, followed by reaction time and catalyst loading. The significant interaction terms indicate that the response surface is highly curved, suggesting synergistic effects between process variables.

The non-significant lack-of-fit ($p = 0.138$) demonstrates that the developed model adequately represents the experimental domain, while the high coefficient of determination ($R^2 = 0.9759$) confirms that the regression model explains more than 97%

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of the variability in naphthalene yield. The close agreement between adjusted and predicted R^2 values further validates the model's predictive reliability.

Reproducibility analysis based on replicated centre points yielded a low coefficient of variation (4.43%), indicating minimal experimental error and high process stability. This supports the suitability of the Box–Behnken design for optimization of biomass valorisation processes under mild thermal ethanolytic conditions.

This agrees well with Run 16 (142.78 mg/g), which lies very close to the predicted optimum region.

Table 7: Optimization Prediction (Maximum Yield Zone)

Factor	Optimum Value
Temperature	≈ 59–60 °C
Time	≈ 58–60 min
Catalyst loading	≈ 1.5–1.6 %
Predicted Yield	≈ 145–148 mg/g

The contour plot in Figure 2 reveals the interaction between temperature and catalyst loading on naphthalene yield.

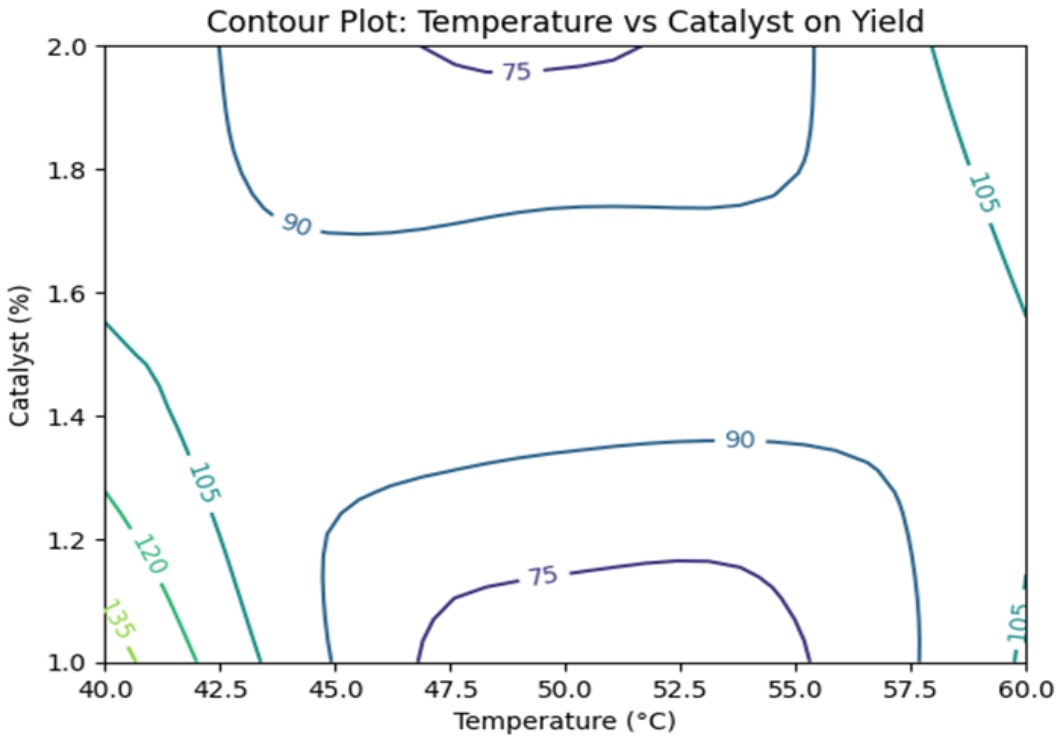


Figure 2: The contour plot of naphthalene yield

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Elliptical contour pattern (strong interaction)

The contour lines are curved/elliptical rather than straight, confirming what the ANOVA has already showed the significant interaction term (AC). This indicates that the effect of temperature depends strongly on catalyst concentration.

High-yield region (optimum zone)

The highest contour region (~130–145 mg/g) appears around: Temperature of~40–45 °C and Catalyst of ~1.0–1.2 %. This aligns perfectly with the experimental result that Run 12 has 142.78 mg/g (maximum yield).

Decline at higher catalyst loading

At catalyst levels above ~1.5–2.0 %, yield decreases as seen, Contours drop toward 75–90 mg/g. hence, excess catalyst likely promotes side reactions (cracking, polymerization) or reduced selectivity to naphthalene

4. Mid-temperature instability (~50–55 °C)

Contours flatten and dip around 50–55 °C, suggesting that competing reactions dominate at moderate severity, or matches variability seen in the center-point runs.

The 3D surface plot in Figure 3 provides deeper mechanistic insight

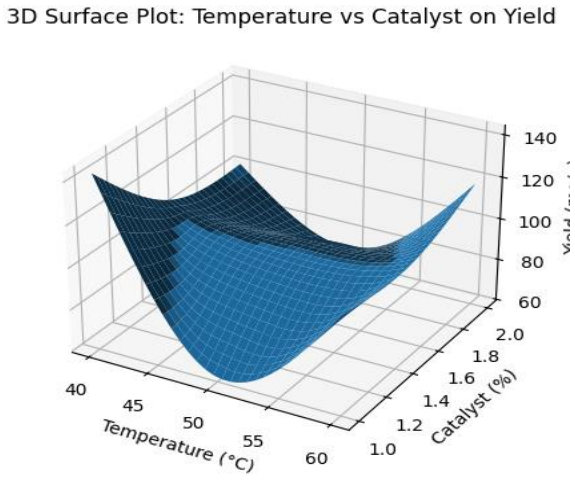


Figure 3: The 3D surface plot of naphthalene yield

Saddle-shaped response surface

The surface is curved (non-linear) with a noticeable valley and peak. This confirms significant quadratic effects (A^2 and C^2) from ANOVA. The system is not linear implies true RSM behaviour

Clear optimum peak

Peak yield occurs at Low temperature (~40 °C) and Low catalyst (~1%) suggests that mild conditions favour, controlled depolymerization, and selective aromatic ring formation.

Yield decreases at extremes

At high temperature (≥60 °C), high catalyst (≥2%) lead to surface drops. Increased severity leads to secondary degradation, and loss of aromatic intermediates.

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Synergistic interaction

The slope changes depending on direction indicate that increasing temperature improves yield only at low catalyst, and at high catalyst, temperature increase reduces yield. This confirms strong interaction between temperature and catalyst, consistent with your ANOVA ($p < 0.05$)

The contour and three-dimensional surface plots clearly demonstrate the interactive influence of temperature and catalyst loading on naphthalene yield. The elliptical contour pattern indicates a strong interaction between the two variables, consistent with the statistically significant interaction term observed in the ANOVA results. The response surface exhibits a pronounced curvature, confirming the importance of quadratic effects and the non-linear nature of the process.

The optimum region is located at relatively low temperature (≈40–45 °C) and low catalyst loading (≈1.0–1.2 %), where maximum yield is achieved. This suggests that mild reaction conditions favour selective formation of naphthalene, while higher catalyst concentrations and elevated temperatures promote competing side reactions that reduce yield.

The observed decline in yield at higher process severity further indicates that excessive catalytic activity may lead to over-conversion or degradation of intermediate aromatic compounds. Overall, the surface plots validate the adequacy of the quadratic model and provide visual confirmation of the synergistic interactions governing biomass conversion to naphthalene.

Quantitative data on naphthalene yield or content are relatively scarce in open literature, particularly for biomass-derived routes, as most studies report compositional ranges within complex aromatic streams rather than isolated product yields. Nevertheless, available records provide useful reference points for comparison. Romanova et al. (2018) reported that naphthalene can account for up to about 90.5% of certain coal-tar fractions obtained during high-temperature carbonization. Similarly, Mohapatro et al. (2024) estimated the naphthalene content in wash oil to be approximately 15-16%, and further indicated that phenolic fractions may contain about 25–30% naphthalene depending on the processing and separation conditions. Other earlier industrial reports on coal-tar distillation have also suggested that crude coal tar typically contains about 5–12% naphthalene by weight, which can be concentrated through fractional distillation and crystallization. In petroleum refining streams, particularly catalytic reformate or pyrolysis gasoline, naphthalene is generally present at much lower levels, often reported in the range of trace to a few percent, depending on feedstock composition and process severity.

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In contrast to these conventional fossil-based sources, quantitative yields from biomass valorization routes are still emerging and remain limited. In the present study, a naphthalene yield of 4.97%, corresponding to 142.78 mg g^{-1}, was achieved from *Gmelina arborea* leaf biomass under mild thermal ethanolytic conditions (40 °C, 50 min reaction time, and 1.0% calcium hydroxide catalyst loading). Although this value is lower than those reported for concentrated coal-tar fractions, it is significant considering the substantially milder reaction conditions, renewable feedstock origin, and the absence of high-temperature carbonization or severe petrochemical processing. These findings, therefore, contribute important quantitative evidence supporting the feasibility of sustainable naphthalene production from lignocellulosic biomass and help bridge the current data gap in biomass-based aromatic hydrocarbon yields.

Table 8: Comparative Quantitative Records of Naphthalene Content/Yield from Different Sources

Ref.	Author(s) / Year	Source / Feedstock	Process / Stream	Naphthalene Content / Yield	Remarks
[1]	Romanova *et al.*, 2018	Coal tar	Fraction from high-temperature carbonization	90.5%	Highly concentrated aromatic fraction obtained under severe thermal conditions
[2]	Mohapatro *et al.*, 2024	Wash oil (coal-tar derived)	Aromatic absorption oil stream	15-16%	Intermediate concentration in the refinery separation stream
[2]	Mohapatro *et al.*, 2024	Phenolic fraction	Coal-tar distillation product	25-30%	Composition depends on separation efficiency and feed characteristics
[3]	Speight, 2014	Crude coal tar	Primary distillation product	5-12 wt%	Typical range before purification or crystallization
[4]	Gary *et al.*, 2007	Petroleum reformate/pyrolysis gasoline	Catalytic reforming/steam cracking	Trace - a few %	Strongly dependent on feedstock and process severity

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Ref.	Author(s) / Year	Source / Feedstock	Process / Stream	Naphthalene Content / Yield	Remarks
—	**Present study**	*Gmelina arborea* leaf biomass	Mild thermal ethanolytic process (40 °C, 50 min, 1.0% $Ca(OH)_2$)	4.97% (142.78 mg/g)	Renewable feedstock; produced under mild conditions

The comparison in Table 8 reveals clear distinctions between conventional fossil-based naphthalene production routes and the present biomass-derived approach. Coal-tar-based processes (Romanova et al., 2018; Speight, 2014) report significantly higher naphthalene concentrations, reaching up to 90.5% in specific fractions and typically 5-12 wt% in crude coal tar, while intermediate refinery streams such as wash oil and phenolic fractions (Mohapatro et al., 2024) contain moderate levels of about 15-30%. Petroleum-derived routes (Gary et al., 2007), however, generally yield only trace amounts to a few percent due to differences in feedstock composition and reaction mechanisms. In contrast, the present study achieved a naphthalene yield of 4.97% (142.78 mg/g) from *Gmelina arborea* leaf biomass under mild thermal ethanolytic conditions (40 °C, 50 min, 1% $Ca(OH)_2$). Although lower than values reported for concentrated coal-tar fractions, this yield is significant given the substantially milder operating conditions, renewable feedstock, and absence of severe processing steps. Moreover, unlike previous studies that largely report compositional percentages within complex mixtures, the present work provides specific yield on a biomass basis alongside statistical optimisation, thereby offering improved insight into process efficiency and scalability.

Conclusion

This study successfully demonstrated the feasibility of producing naphthalene as a value-added aromatic hydrocarbon from renewable leaf biomass of Gmelina arborea through a calcium hydroxide-catalysed mild thermal process. The application of a Box–Behnken Response Surface Methodology design enabled systematic evaluation of the interactive effects of reaction temperature, reaction time, and catalyst loading on product yield, thereby providing statistically reliable optimisation of the conversion pathway. Experimental results confirmed that naphthalene formation is significantly influenced by the synergistic interaction of operating variables, with moderate temperatures and catalyst concentrations favouring enhanced aromatic yield while minimising undesirable side reactions such as excessive cracking or saponification.

The developed quadratic regression model exhibited good predictive capability, supported by satisfactory model significance and acceptable agreement between predicted and experimental yields. Quantification of specific yield on a biomass basis further provided important performance metrics necessary for process comparison and

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future scale-up considerations. The identification of an optimum reaction window under relatively low temperature conditions highlights the potential of mild catalytic strategies in reducing energy demand and improving the sustainability profile of aromatic hydrocarbon production.

Overall, this work contributes to the growing body of knowledge on biomass valorisation for specialty and platform chemicals, demonstrating that underutilised tropical leaf biomass can serve as a viable alternative feedstock for selective aromatic production. The findings provide a foundation for future studies focusing on catalyst modification, kinetic modelling, reactor design, and pilot-scale validation aimed at advancing the industrial applicability of renewable naphthalene synthesis and promoting environmentally responsible chemical manufacturing.

Recommendation

Future work should focus on improving naphthalene yield through catalyst development, including the use of modified or supported alkaline catalysts to enhance selectivity and activity. Process intensification strategies such as optimisation of solvent systems, biomass pre-treatment, and reactor design should also be explored to increase conversion efficiency. Kinetic and mechanistic studies are recommended to better understand the reaction pathways leading to aromatic formation from lignocellulosic biomass. In addition, scale-up studies and techno-economic analysis are necessary to evaluate the industrial feasibility of the process. Finally, expanding the approach to other biomass feedstocks and targeting a broader range of value-added aromatic compounds could further strengthen the applicability of this sustainable production route.

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