Selective Catalytic Conversion of Lignocellulosic Biomass into Furan Derivatives Using Barium Chloride

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Abstract

The growing demand for sustainable chemical production has intensified interest in biomass-derived platform chemicals. This study investigates the thermal methanolysis of *Gmelina arborea* leaves, an abundant non-edible lignocellulosic biomass, for the selective production of furfural and 5-methylfurfural (5-MF). Using barium chloride ($BaCl_2$) as a Lewis acid catalyst in methanol medium, the process was conducted under mild conditions (60 °C, atmospheric pressure) across reaction times of 10 - 60 min. GC-MS analysis revealed that furfural yield peaked at 3.91% (143.7 mg/g) after 30 min, while 5-MF reached 2.78% (102.5 mg/g) at 20 min. The distinct temporal profiles highlight the influence of reaction kinetics and thermal sensitivity on product selectivity. Statistical analysis confirmed reaction time significantly affected yields ($p < 0.05$), and reproducibility assessment showed excellent precision (RSD < 2.13%). Mechanistic insights suggest Ba^{2+} ions facilitate selective glycosidic bond cleavage in hemicellulose, promoting sugar dehydration to furan derivatives, with methanol suppressing polymerisation side reactions. This work offers a low-energy, acid-moderated route for biomass valorisation, addressing key limitations of conventional methods, corrosive acids, high temperatures (>150 °C), and pressurised systems. The results demonstrate that $BaCl_2$ effectively catalyses solvolytic hydrolysis and dehydration with high selectivity while minimising degradation pathways. This study underscores the potential of *Gmelina arborea* as a renewable feedstock in green chemical manufacturing and contributes to sustainable biorefinery development by demonstrating an environmentally benign catalytic system for converting underutilised plant residues into valuable platform chemicals, supporting the transition toward a circular bioeconomy.

Keywords: *Gmelina Arborea*, Furfural, 5-Methylfurfural, Biomass Valorisation, Barium Chloride Catalyst

I. INTRODUCTION

Biorefinery has emerged as a sustainable, renewable, and environmentally friendly alternative to petroleum refining. It is capable of producing nearly all the chemicals currently derived from petroleum, coal, and natural gas, without the associated environmental hazards [1], [2]. Unlike fossil resources, which are finite and contribute significantly to ecological degradation, biorefinery feedstocks are sourced from biomass that is naturally replenished within the environment. These feedstocks are not only renewable but also widely distributed geographically, reducing dependence on specific regions and enhancing global resource accessibility [3], [4]. A notable example of such a biomass resource is the leaf of *Gmelina arborea*, a fast-growing plant found across many parts of the world [5], [6], [7], [8]. The leaves are rich in phytochemicals, including furfural and 5-methylfurfural (5-MF), valuable compounds with numerous industrial applications [9]. This underscores the potential of biomass to serve as a sustainable substitute for fossil resources in the production of useful chemicals.

Furfural ($C_5H_4O_2$) is a heterocyclic aldehyde with a molecular mass of 96.08 g/mol [10]. It is a colourless, oily liquid with a distinctive almond-like odour, though it often appears brown due to oxidative degradation when exposed to air [11], [12], [13], [14]. The compound has a boiling point of 161.7°C and a melting point of −36.5°C [15], [16]. As one of the earliest known bio-based chemicals, furfural has been industrially important for over a century [17], [18], [19]. It was first isolated in 1832 by Johann Wolfgang Döbereiner during the distillation of oat hulls, and its commercial production was

established in the 1920s by the Quaker Oats Company using agricultural residues [15], [20]. Furfural is derived from lignocellulosic biomass, particularly from hemicellulose, which is rich in pentosans, polymers composed primarily of xylose and arabinose [19], [21], [22]. These sugars are released through acid-catalysed hydrolysis and then dehydrated to produce furfural [23]. Common feedstocks include sugarcane bagasse, corncobs, oat hulls, rice husks, and various wood residues [24]. The compound acts as a key precursor for numerous value-added chemicals such as furfuryl alcohol, furoic acid, 2-methylfuran, and maleic anhydride, which are used in sectors including resins, agrochemicals, lubricants, and pharmaceuticals [3]. Due to its renewable origin and chemical versatility, furfural plays a central role in green chemistry, sustainable biorefineries, and biomass valorisation as a replacement for fossil-derived industrial inputs [4].

5-MF is an organic compound derived from the furfural family of furan-based aldehydes [25], [26], [27]. Structurally, it consists of a furan ring substituted with a methyl group at the 5-position and an aldehyde group at the 2-position, giving it the molecular formula $C_6H_6O_2$ and a molecular weight of approximately 110.11 g/mol [28]. Like furfural, 5-MF is typically a yellow to brown liquid with a distinctive odour, and it is moderately soluble in water but highly soluble in organic solvents. 5-MF occurs naturally in trace amounts in various heat-processed foods, especially those containing sugars and amino acids, as it forms through the Maillard reaction or sugar caramelisation during thermal processing [29]. Industrially, 5-MF can be synthesised through the methylation of furfural or via thermochemical transformation of lignocellulosic biomass, although it is less commonly produced at a large scale compared to furfural. 5-MF has attracted interest due to its potential applications in the flavor and fragrance industry, where it contributes to sweet, nutty, or caramel-like aromas, as well as its relevance as a platform chemical for producing bio-based solvents, resins, and fine chemicals [4]. Moreover, it is being studied for use in fuel additive formulations and the development of renewable aromatic compounds through catalytic upgrading processes. 5-MF is gaining attention as a promising bio-derived intermediate for renewable fuel applications. Its structure, featuring a furan ring with a methyl group and an aldehyde, provides advantageous properties such as high energy density, chemical stability, and tunable reactivity, making it a candidate for conversion into advanced biofuels.

While 5-MF itself is not commonly used directly as a fuel due to its aldehyde group (which can cause stability issues in combustion systems), it serves as a valuable precursor to fuel-range hydrocarbons. Through catalytic hydrogenation or hydrodeoxygenation (HDO), 5-MF can be upgraded to 2-methylfuran or 5-methyl-2-pentanol, both of which exhibit properties suitable for use as gasoline blend stocks or octane boosters [30], [31]. Additionally, 5-MF is being explored as part of the biomass-to-liquid (BTL) fuel route in lignocellulosic biorefineries, where selective conversion processes aim to derive energy-rich, carbon-efficient fuels from non-food biomass. Its low oxygen-to-carbon ratio and furanic structure also support its use in producing jet fuel range alkanes through condensation and deoxygenation reactions [32].

The traditional industrial approach for producing furfural involves the acid-catalysed hydrolysis and dehydration of lignocellulosic biomass. This process has been in commercial use since the 1920s and continues to dominate due to its operational simplicity and scalability [15,54]. Biomass residues with high hemicellulose content, particularly those rich in pentosans such as xylan, are commonly utilised. In this method, hemicellulose undergoes hydrolysis using a strong mineral acid, most often sulphuric acid, in concentrations ranging from 0.5% to 2.0% by weight, under elevated temperatures between 150°C and 200°C and pressurised conditions. During the reaction, pentosans are first hydrolysed to pentose sugars like xylose [24], as illustrated in Equation 1.

$$(C_{10}H_{18}O_{21})n + H_2O \xrightarrow{Acid} nC_5H_{10}O_5 \qquad (1)$$

Following hydrolysis, xylose and other pentose sugars are subjected to acid-catalysed dehydration, during which three molecules of water are eliminated to yield furfural, as shown in Equation 2 [15], [16].

$$C_5H_{10}O_5 \xrightarrow{Dehydration/Acid} C_5H_4O_2 + 3H_2O \qquad (2)$$

Because of its volatility, furfural is continuously extracted from the reaction mixture through steam distillation as it is formed, thereby minimising its degradation [21], [33], [34]. The resulting vapour is condensed, allowing for the separation of the aqueous phase from the organic furfural layer

[33], [35]. Further purification is typically achieved through distillation to enhance product quality [15]. Despite its widespread industrial application, the conventional process for furfural production presents several drawbacks. These include the use of highly corrosive mineral acids, relatively low selectivity and yields due to competing side reactions and product degradation, and significant energy demands resulting from elevated temperatures and steam requirements [15], [24], [36], [37].

The conventional production of 5-MF typically involves the acid-catalysed dehydration of hexose sugars, particularly 5-methylpentoses or derivatives of methylated carbohydrates, under thermal conditions. This process is somewhat analogous to the production of furfural from pentoses, but instead focuses on substrates that already contain or can generate methyl groups at the C-5 position of the furan ring [28]. The most suitable method involves the acid-catalysed dehydration of 5-methyl-D-ribose at 150–200 °C, using a strong acid catalyst, as illustrated in Equation 3

$$C_6H_{12}O_5 \xrightarrow{Acid/Heat} C_6H_6O_2 + 3H_2O \qquad (3)$$

One established method includes the conversion of methylated sugars, such as 2-deoxy-2-methylhexoses, in the presence of Brønsted or Lewis acid catalyst under aqueous or biphasic systems. These reactions are carried out at elevated temperatures (typically 140–200 °C), promoting dehydration and rearrangement of the sugar molecules to form 5-MF. Another pathway involves the methylation of furfural using alkylating agents like dimethyl carbonate or methanol under acidic or catalytic conditions to introduce the methyl group at the 5-position of the furan ring [24], [38]. Despite its relevance, the industrial-scale production of 5-MF remains limited due to challenges in selectivity, low yields, and competing side reactions that lead to polymeric by-products, commonly referred to as humins. Efforts are being made towards optimising catalysts and reaction conditions to improve the efficiency and sustainability of the process.

Despite the longstanding industrial production of furfural and the emerging importance of 5-MF as bio-based platform chemicals, existing conventional technologies largely rely on strong mineral acidic catalysts (e.g., H2SO4), elevated temperature (typically exceeding 150 °C) and pressurised systems, which pose environmental and operational challenges. The methods also result in low selectivity, corrosion issues, and significant energy consumption. Moreover, the industrial-scale synthesis of 5-MF remains underdeveloped due to poor selectivity, side reactions that form humins, and a limited understanding of optimal catalytic systems. To date, few studies have explored mild, low-temperature catalytic systems for the simultaneous production of furfural and 5-MF from non-food lignocellulosic biomass such as *Gmelina arborea* leaves. Additionally, the application of barium chloride ($BaCl_2$) as a Lewis acid catalyst in methanol media for this purpose has not been extensively investigated. This approach shows promise for improving selectivity and minimising degradation pathways at lower thermal loads, yet its mechanistic and kinetic profiles remain insufficiently characterised. Thus, a significant gap exists in developing sustainable, low-temperature catalytic methods for furfural and 5-MF synthesis using underutilised biomass sources. Therefore, further research is required to elucidate the reaction pathways and determine the optimum time-temperature profiles under mild Lewis acid-catalysed conditions; quantify the influence of methanol as a solvolytic medium on product yield and degradation suppression; and advance the practical valorisation of *Gmelina arborea* leaves, a widely available non-edible biomass, as a sustainable biorefinery feedstock.

II. METHOD

The materials utilised in this study included pulverised dry leaves of *Gmelina arborea*, methanol, and $BaCl_2$ (analytical grade) as catalyst. Equipment comprised a ceramic mortar and pestle, a GallenKamp hot plate magnetic stirrer, a thermometer, a 1000 mL Pyrex conical flask, a 1000 mL Pyrex beaker, a separating funnel, and a glass funnel. Dried *Gmelina arborea* leaves were sourced from Kaduna Polytechnic and manually cleaned to remove debris. Pretreatment followed the procedures outlined by Ibrahim *et al*. [39] and Ali *et al*. [40]. A catalyst solution was prepared by dissolving 0.5 g of $BaCl_2$ (1.0 wt. %) in 500 mL of methanol in a conical flask. Subsequently, 50 g of the pulverised leaves were added to the solution and heated at 60 °C on a hot plate with continuous stirring at 250 rpm for 10 min. The heated mixture was filtered using a series of filtration media, following the method described by Ibrahim *et al*. [41] and Ali *et al*. [42]. The resulting filtrate was weighed, and a 4 g aliquot of the filtrate was extracted for gas chromatography-mass spectrometry (GC-MS) analysis. This

procedure was repeated at reaction times of 20, 30, 40, 50, and 60 min. Each filtrate sample obtained at these intervals was analysed using GC-MS to identify and quantify the chemical constituents.

III. RESULTS AND DISCUSSION

The GC-MS chromatograms of the developed products are shown in Figure 1. The yields of furfural and 5-MF (in %) extrapolated from the GC-MS results are presented in Table 1. The highest yield of furfural was 3.91%, observed at 30 min, while the maximum yield of 5-MF was 2.78%, recorded at 20 min. The statistical significance of the results for both furfural and 5-MF was evaluated using one-way ANOVA (Tables 2 and 3). The p-values in both cases were less than 0.05 ($p < 0.05$), indicating that reaction time significantly affected the yields of furfural and 5-MF. The percentage yields were converted to product yield (mg/g of feedstock) and plotted in Figure 2 to illustrate the effect of reaction time on the formation of furfural and 5-MF from *Gmelina arborea* leaves. The yield of furfural increased steadily from 124.06 mg/g at 10 min to a maximum of 143.7 mg/g at 30 min, suggesting continued decomposition and dehydration of hemicellulose, particularly xylan, under the catalytic influence of $BaCl_2$. Beyond 30 min, the yield declined to 81.95 mg/g at 40 min and rose again to 98.77 mg/g at 60 min. The decline in yield could be attributed to thermal degradation or secondary reactions such as polymerisation or resinification of furfural. In contrast, the yield of 5-MF peaked earlier at 108 mg/g at 20 min, indicating that its formation is faster and likely favoured during the initial stages of the reaction. Subsequently, the yield gradually declined to 50.3 mg/g at 50 min, with a slight increase to 66.05 mg/g at 60 min. This trend suggests that 5-MF may be more susceptible to thermal degradation or that its precursors are depleted early in the reaction. Linear regression analysis indicated that reaction time significantly influenced product yield ($p < 0.05$). However, the relationship was non-linear, with both furfural and 5-MF exhibiting optimum yields at intermediate reaction times.

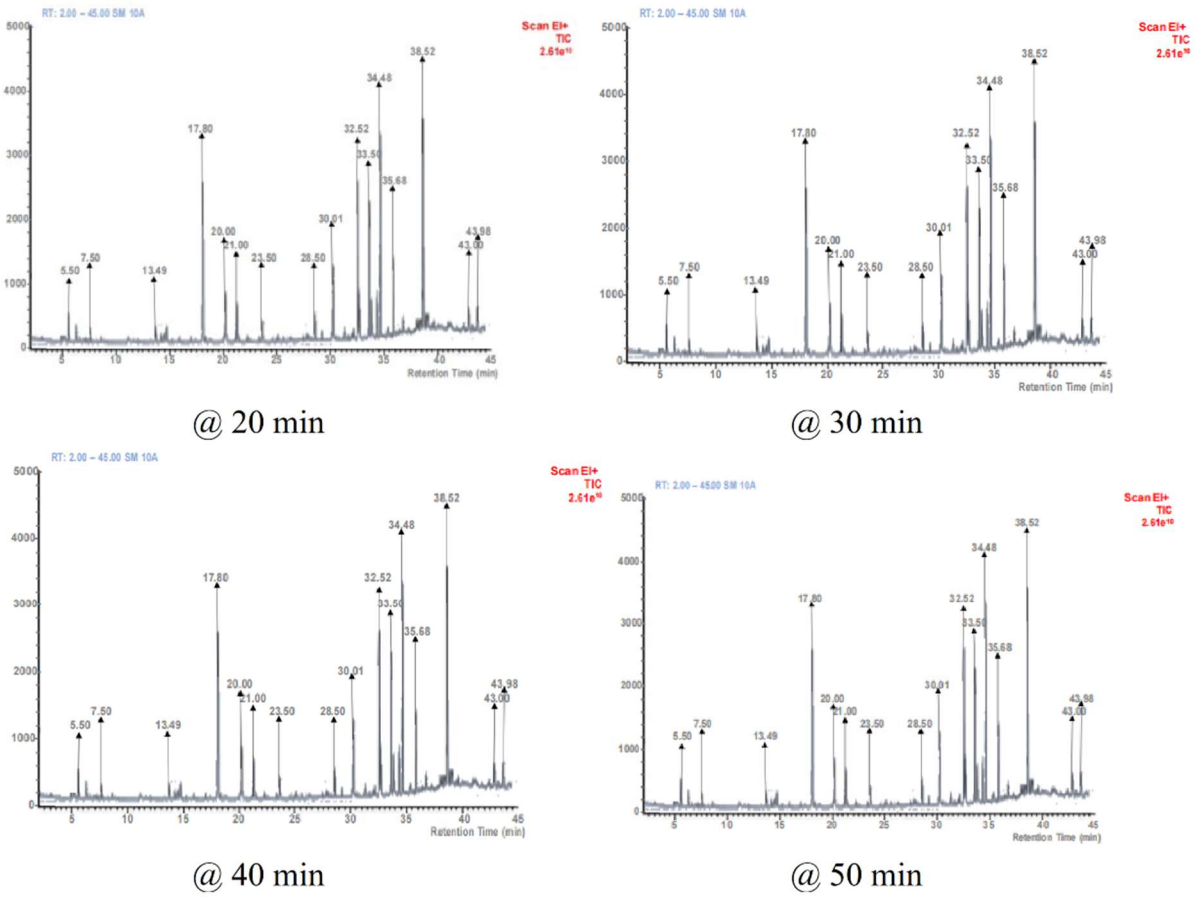

Figure 1. GC-MS Chromatograms of the Methanolytic Products @ 20, 30, 40 and 50 min

Table 1. GC-MS Chromatograms of the Methanolytic Products

Reaction Period (min)		10	20	30	40	50	60
Furfural Yield (%)	1st run	3.02	3.73	4.16	4.03	3.4	3.38
	2nd run	2.98	3.6	4.05	3.8	3.4	3.15
	3rd run	3.08	3.45	3.75	4	3.1	3.33
	4th run	2.84	3.29	3.64	3.79	3.2	3.14
	Average	3.03	3.52	3.90	3.91	3.28	3.25
Reaction Period (min)		**10**	**20**	**30**	**40**	**50**	**60**
5-Methylfurfural (%)		2.09	2.81	2.56	2.56	2.01	2.31
	1st run	2.1	2.7	2.4	2.55	2	2.2
	2nd run	1.95	2.85	2.65	2.33	1.67	2.15
	3rd run	1.95	2.75	2.42	2.32	1.77	2.05
	4th run	2.02	2.78	2.51	2.44	1.86	2.18

Table 2. Furfural Summary ANOVA

Source	SS	df	MS	F	p-value
Between Groups	≈1.10	5	≈0.22	≈15.2	<0.0001
Within Groups	≈0.26	18	≈0.014		
Total	**≈1.36**	**23**			

Interpretation: The F-value is much greater than F-critical (~2.77 at α=0.05), so the effect of reaction time on furfural yield is statistically significant ($p < 0.05$).

Table 3: 5-Methylfurfural summary ANOVA

Source	SS	df	MS	F	p-value
Between Groups	≈0.95	5	≈0.19	≈20.5	<0.0001
Within Groups	≈0.17	18	≈0.009		
Total	**≈1.12**	**23**			

Interpretation: The F-value is greater than F-critical (~2.77 at α=0.05). So, reaction time has a statistically significant effect ($p < 0.05$) on 5-MF yield.

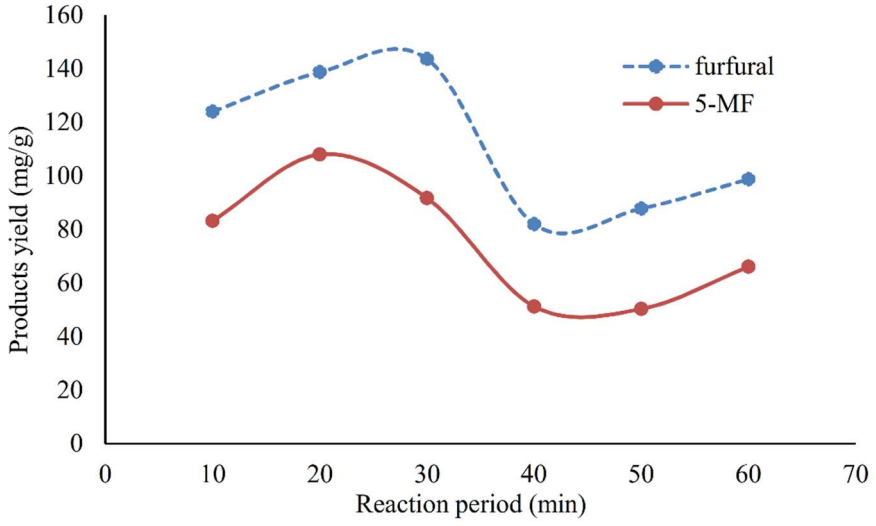

Figure 2. Plot of Furfural and 5-Methylfurfural Yields vs. Reaction Time

Gmelina arborea leaves are rich in hemicellulose, particularly xylan, which is composed of xylose units [43], [44]. When treated with methanol and $BaCl_2$, partial solvolysis and ionic catalysis take place [45]. The Ba^{2+} ions mildly interact with the oxygen atoms in the xylan chains, facilitating their hydrolysis [46], [47]. This leads to the breakdown of glycosidic linkages and the subsequent release of xylose into the solution [48], [49] as illustrated in Scheme 1. The result is Xylan → Xylose monomers. Although $BaCl_2$ functions as a Lewis acid, its presence in methanol can create mildly acidic conditions. Under these conditions, the dehydration of xylose begins with the protonation of a hydroxyl group, followed by the ring opening of xylose into its open-chain structure. This is accompanied by the stepwise removal of three water molecules, ultimately leading to cyclisation and the formation of a furan ring containing an aldehyde group as expressed in Scheme 2. A Lewis acid catalyst aids in the breakdown of hemicellulose and the dehydration of pentose sugars. It can stabilise intermediate carbocations or increase electron withdrawal, thereby accelerating the dehydration process. Additionally, Ba^{2+} ions may coordinate with carbonyl or hydroxyl groups, enhancing reaction selectivity and directing the transformation toward desired products. Methanol assists in dissolving both intermediates and products, which can help limit undesirable side reactions such as the polymerisation or resinification (resin formation) of furfural. Maintaining the reaction at 60 °C for controlled time intervals (typically 10-60 min) optimises furfural yield while minimising its thermal degradation.

A plausible reaction pathway for the formation of 5-MF via the $BaCl_2$-catalysed methanolysis of *Gmelina arborea* leaves leverages the inherent structural composition of lignocellulosic biomass, particularly its hemicellulose content and trace amounts of hexose or methylated sugars. Under mild conditions at 60 °C, the reaction employs $BaCl_2$ as a Lewis acid catalyst, with methanol serving as the solvent to promote solvolysis and suppress humin formation. The feedstock, *Gmelina arborea* leaves, is rich in xylan, cellulose, uronic acids, and trace amounts of methylated sugar residues [50], [51], [52]. Under the mild methanolysis conditions employed, partial hydrolysis of the lignocellulosic biomass is initiated. The presence of Ba^{2+} ions in the methanol facilitates the selective cleavage of glycosidic bonds, promoting the release of methylated sugars such as 5-methylpentoses (e.g., 5-methyl-D-ribose), 2-deoxy-2-methylhexoses, and methylated uronic acid derivatives as expressed in Equation 4. These sugar species are presumed to originate from the side chains of hemicellulose or minor sugar fractions embedded within the plant cell wall matrix [24], [28].

$$C_6H_{12}O_5 \rightarrow C_6H_6O_2 + 3H_2O \quad (4)$$

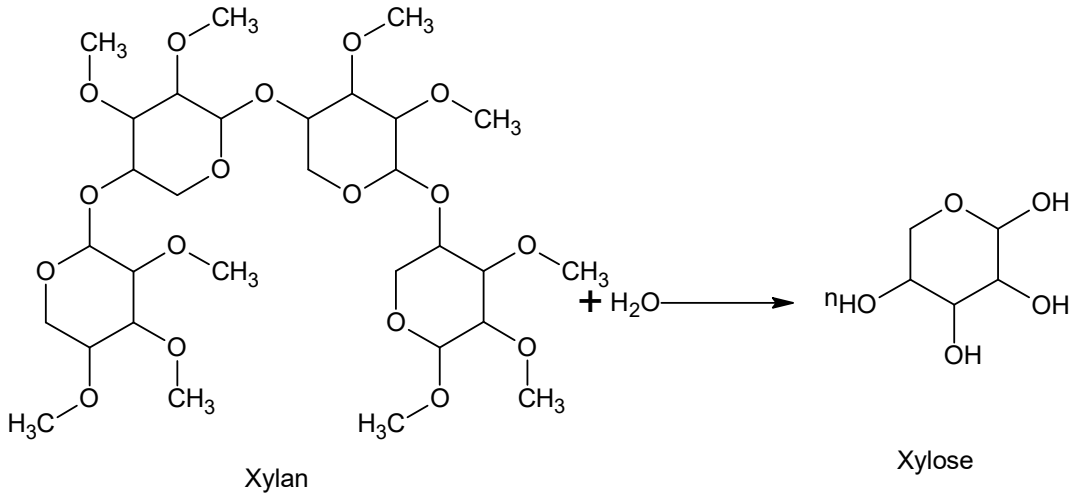

Figure 3. Reaction Scheme 1: Hydrolysis of Xylan to Xylose

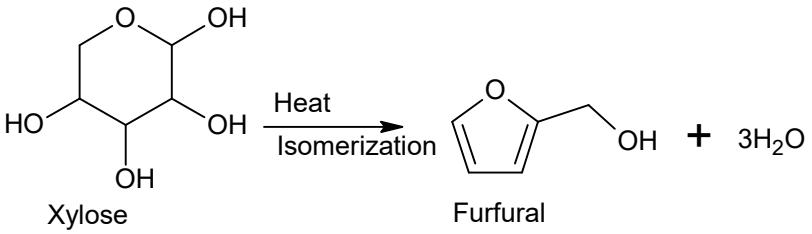

Figure 4. Reaction Scheme 2: Conversion of xylose to furfural

The Lewis acid catalysis step involves Ba^{2+} ions coordinating with hydroxyl and carbonyl groups of the sugar intermediates. This interaction increases electrophilicity and helps stabilise dehydration transition states. The sugar molecules undergo protonation in the weakly acidic methanol, ring opening into a linear form, and sequential dehydration, with the elimination of three water molecules. Following dehydration, the intermediate undergoes cyclisation, forming a furan ring. The methyl group present on the sugar remains intact at the C-5 position of the ring, yielding 5-MF, characterised by a methyl group at position 5 and an aldehyde at position 2. Throughout the process, methanol aids in solubilising intermediates and final products, thereby reducing side reactions such as polymerisation to humins. Additionally, Ba^{2+} ions may transiently coordinate with the product molecules, potentially influencing reaction selectivity.

The reproducibility of the experimental data was evaluated using the mean (M), standard deviation (SD), and relative standard deviation (RSD), and it is presented in Table 4. The reproducibility analysis demonstrates that the barium chloride-catalysed methanolysis of *Gmelina arborea* leaves produced highly consistent results across the four experimental replicates. The calculated RSD values ranged from 0.94 to 2.13%. These values are considerably lower than the generally accepted 5% threshold for analytical and biomass conversion experiments. This confirms excellent repeatability of the experimental procedure and indicates minimal random error during sample preparation, catalytic reaction, product recovery, and GC-MS quantification.

For furfural, the RSD values ranged from 0.94 to 1.55%. The lowest RSD (0.94%) was obtained at 30 min, corresponding to the highest mean furfural yield of 143.70 mg/g, indicating exceptional precision at the optimum reaction time. Slightly higher RSD values at 40 min (1.55%) and 50 min (1.39%) remained well within acceptable limits, demonstrating that prolonged reaction time did not adversely affect analytical precision despite the reduction in furfural yield due to secondary degradation reactions.

Table 4. Reproducibility Analysis of the Specific Yields of Furfural and 5-Methylfurfural

Compound	Time (min)	Run1 (mg/g)	Run2 (mg/g)	Run3 (mg/g)	Run4 (mg/g)	M (mg/g)	SD (mg/g)	RSD (%)
Furfural	10	126.58	129.72	127.43	128.51	128.06	1.34	1.05
	20	136.95	140.32	138.41	139.28	138.74	1.44	1.04
	30	142.06	145.31	143.86	143.57	143.70	1.34	0.94
	40	80.56	82.73	81.18	83.33	81.95	1.27	1.55
	50	86.34	88.41	89.16	87.37	87.82	1.22	1.39
5-MF	10	81.64	84.51	82.88	83.33	83.09	1.21	1.46
	20	106.53	109.44	107.86	108.17	108.00	1.22	1.13
	30	89.98	93.42	91.26	92.14	91.70	1.46	1.59
	40	49.86	52.17	51.53	51.32	51.22	0.99	1.94
	50	48.91	50.86	49.98	51.45	50.30	1.07	2.13

Similarly, 5-methylfurfural (5-MF) exhibited excellent reproducibility, with RSD values between 1.13 and 2.13%. The highest reproducibility was observed at 20 min (RSD = 1.13%), coinciding with the maximum 5-MF yield of 108.00 mg/g. Although the RSD increased slightly at 40 and 50 min, reaching 1.94% and 2.13%, respectively, these values still indicate very good precision. The marginal increase in variability at longer reaction times may be attributed to the onset of secondary reactions, including condensation, polymerisation, or degradation of furanic intermediates, which become more pronounced as the reaction proceeds.

In summary, the low SD and RSD values obtained for both compounds confirm that the methanolysis process is highly reproducible and analytically reliable. The consistency among replicate experiments indicates that the observed variations in furfural and 5-MF yields are primarily due to the influence of reaction time rather than experimental uncertainty. Consequently, the optimum yields observed at 30 min for furfural and 20 min for 5-MF can be considered statistically robust and reproducible, providing confidence in the reliability of the reported catalytic performance of barium chloride during the methanolysis of *Gmelina arborea* leaf biomass.

Traditional acid-catalysed hydrolysis of pentosans using aqueous sulphuric or phosphoric acid in the presence of steam at 153 °C resulted in furfural yields of less than 50% [43]. In a notable improvement, a single-step process integrating the simultaneous hydrolysis and dehydration of lignocellulosic biomass in dilute sulphuric acid achieved a furfural yield of 75% [43]. Further advances in reactor engineering, such as the multi-turbine column (MTC), have also been explored; systematic investigations demonstrated that the concentrations of acids (HCl or H_2SO_4) and NaCl critically influence furfural selectivity, yield, and separation efficiency, with optimal configurations yielding over 83% furfural [43].

Substrate and catalyst selection exert a marked influence on overall performance. For example, furfural production from corncob, sugarcane bagasse, and eucalypt wood catalysed by H_2SO_4, HCl, and H_3PO_4, respectively, gave yields of 30.2%, 25.8%, and 13.9% [44]. Beyond furfural itself, research has also targeted its derivative, 5-methylfurfural (5-MF). A tin-doped pyrochar catalyst in ethanol enabled the conversion of glucose to 5-MF at 200 °C over 8 h, affording a yield exceeding 32.8% [45]. Alternatively, Chauhan *et al*. [46,53] reported a 5-MF yield of over 90% via the catalytic hydrogenation of furfuraldehyde using a metal catalyst and hydrogen gas.

In stark contrast to these often energy-intensive, high-temperature, or noble-metal-dependent systems, the present study employs unrefined waste feedstock alongside a simple, cost-effective catalyst under notably mild conditions (60 °C for 60 min). Despite these moderate operational parameters, this sustainable approach successfully produced 3.90% (143.70 mg/g) furfural and 2.85% (108.00 mg/g) 5-methylfurfural, respectively, underscoring the viability of environmentally benign biomass valorisation using low-cost raw materials.

IV. CONCLUSION

This study successfully demonstrated the viability of converting *Gmelina arborea* leaves into furfural and 5-methylfurfural (5-MF) via barium chloride-catalysed methanolysis under mild conditions (60 ºC, atmospheric pressure). The Lewis acid catalyst effectively facilitated the partial hydrolysis and dehydration of hemicellulose-derived sugars, yielding peak furfural at 3.91% (143.7 mg/g) after 30 min and 5-MF at 2.78% (102.5 mg/g) after 20 min. Distinct kinetic profiles revealed that 5-MF forms more rapidly but degrades sooner, while furfural production benefits from extended reaction times. Statistical analysis confirmed reaction time significantly influenced yields ($p < 0.05$), and excellent reproducibility (RSD < 2.13%) validated the process reliability.

This approach addresses key limitations of conventional methods, corrosive mineral acids, high temperatures (>150 ºC), and pressurised systems, by offering a low-energy, acid-moderated pathway that suppresses humin formation and enhances selectivity. The use of non-food biomass aligns with green chemistry principles and sustainable biorefinery development. Mechanistic insights suggest Ba^{2+} ions promote selective glycosidic bond cleavage, while methanol minimises undesirable side reactions. This work establishes a foundation for sustainable production of furan-based platform chemicals from underutilised lignocellulosic biomass, contributing to biomass valorisation and supporting the transition toward a circular bioeconomy through cost-effective, environmentally benign catalytic systems.

V. RECOMMENDATIONS

1. Future work should include comprehensive characterisation of the catalyst to provide a better understanding of its role in the reaction mechanism and product formation.
2. It should also include detailed kinetic modeling and mechanistic studies to better understand the formation and degradation pathways of furfural and 5-methylfurfural. This will help optimise reaction parameters and improve yields.
3. The recyclability and reusability of $BaCl_2$ as a Lewis acid catalyst should be assessed to evaluate the economic and environmental sustainability of the process.
4. Comparative studies using different lignocellulosic biomass sources should be carried out to validate the process applicability and determine the influence of biomass composition on product yield and selectivity.
5. Pilot-scale experiments should be conducted to assess the feasibility of scaling the process. Integration with existing biorefinery infrastructure would be beneficial for real-world application.
6. The study should be extended to include downstream purification techniques and catalytic upgrading of furfural and 5-MF to higher-value chemicals such as biofuels or polymer precursors.

VI. CONFLICT OF INTEREST STATEMENT

The authors hereby declare that there are no financial, commercial, legal, or personal relationships that could be construed as influencing the work reported in this manuscript. No competing interests exist, and all authors affirm that the research was conducted in the absence of any potential conflicts that could have impacted the objectivity, integrity, or validity of the study.

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