## COMMUNICATION

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# One-step conversion of hemicellulosic pentoses into furfural *via* iron(III) sulfate-catalyzed distillation

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In this study, we introduce a straightforward and effective strategy for synthesizing furfural directly from D-xylose and L-arabinose by employing hydrated iron(III) sulfate [$Fe_2(SO_4)_3 \cdot xH_2O$], under distillation at atmospheric pressure. The transformation proceeds without any organic solvent, using only pentose sugars derived from hemicellulose and 30 mol% of the catalytic agent. The process is optimized at a temperature of 170 °C. Under these conditions, after 90 minutes, D-xylose yields up to 92% furfural with 94% selectivity, while L-arabinose provides 85% yield with a selectivity of 90%. Water is the major by-product.

## Introduction

The growing urgency to transition away from fossil-based resources has made the development of renewable chemical platforms a central priority in sustainable chemistry.[1,2] In this context, biomass-derived platform molecules offer immense potential as versatile building blocks for the production of fuels, materials, and value-added chemicals.[3,4] Among them, furfural and 5-hydroxymethylfurfural (HMF) have emerged as two of the most prominent bio-based intermediates, with applications ranging from green solvents and polymer precursors to pharmaceutical agents and biofuels.[5–7] Their structural reactivity and functional diversity make them ideal cornerstones in the design of integrated biorefinery processes.[8] Historically, pentose sugars such as D-xylose and

L-arabinose, readily obtained from the hydrolysis of hemicellulose, have served as the primary feedstocks for furfural production.[9,10] Among these, D-xylose is the most abundant, typically accounting for over 70% of the hemicellulosic fraction in agricultural residues and hardwoods.[11] L-Arabinose, though less prevalent, also contributes significantly to furfural yields when isolated or enriched from biomass hydrolysates.[12] These pentoses are highly reactive under acidic or Lewis acid catalysis, undergoing dehydration *via* a well-established mechanism that leads to the formation of furfural with relatively high efficiency.[13] Industrial furfural production processes, developed as early as the 1920s, have long relied on xylose-rich feedstocks such as corncobs, oat hulls, and sugarcane bagasse.[14] Under optimized conditions, furfural yields from D-xylose can exceed 80–85%, while L-arabinose, although somewhat less reactive, can still provide competitive yields with appropriate catalytic systems.[15] The consistent reactivity and availability of these sugars make them ideal model substrates for mechanistic studies and process development, especially in the context of green chemistry and biomass valorization.[16] Furfural, in particular, has gained significant industrial relevance owing to its use in the synthesis of furan-based resins, biodegradable plastics, lubricants, and as a potential biofuel additive.[17,18] Nevertheless, despite its importance, current production methods remain suboptimal, often relying on corrosive acid catalysts, pressurized systems, or non-renewable solvents.[19–22] These methods typically require high energy input and pose safety and environmental concerns, while also suffering from poor selectivity and costly downstream processing. The development of more benign, efficient, and scalable approaches to furfural synthesis therefore represents a key challenge.[23]

In recent years, hydrated iron(III) sulfate [$Fe_2(SO_4)_3 \cdot xH_2O$] has emerged as an effective and low-cost Lewis acid catalyst in a variety of carbohydrate transformations, including the synthesis of furan derivatives, per-*O*-acetylation reactions, and acylal formation from aldehydes. Its non-toxic nature,

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commercial availability, and catalytic versatility make it a promising alternative to conventional mineral acids and corrosive metal salts.[24–26]

Carbohydrates such as pentoses (*e.g.*, D-xylose and L-arabinose) are abundant in hemicellulosic biomass and have been shown to yield higher furfural conversions compared to direct processing of raw lignocellulosic feedstocks, which often require extensive pre-treatment.[27,28]

In our previous study on fructose dehydration under atmospheric distillation conditions, $Fe_2(SO_4)_3 \cdot xH_2O$ was shown to be a low-cost, readily available catalyst for converting a food-related hexose into furfural.[29] In contrast, the present work represents the first application of $Fe_2(SO_4)_3 \cdot xH_2O$ to hemicellulose-derived pentoses (D-xylose and L-arabinose) under continuous atmospheric distillation. Dehydration of pentoses presents distinct kinetic and selectivity challenges compared to hexoses, particularly for L-arabinose, which, to the best of our knowledge, has not previously been reported to yield furfural at such high efficiency. In this study, we achieve isolated yields of up to 92% from D-xylose and 85% from L-arabinose, with improved selectivity and at lower catalyst loading (30% mol) than in our fructose study (40% mol). The only by-product of the reaction is water, whereas reactions starting from fructose produced formaldehyde as a secondary by-product. Moreover, the feedstocks employed here are non-edible and directly obtainable from lignocellulosic biomass, enhancing both the industrial applicability and sustainability of the method.[30,31]

While low catalyst loadings (<5 mol%) are often desirable in industrial processes, it is important to consider the overall process impact of the catalyst choice. Strong mineral acids such as $H_2SO_4$ or HCl, even at low loadings, can induce severe corrosion of reactor materials, require costly corrosion-resistant alloys, and generate large quantities of acidic effluents that demand neutralization and treatment.[32,33] In contrast, benign salts such as $Fe_2(SO_4)_3 \cdot xH_2O$, even at higher loadings, are eco-compatible, inexpensive, and non-corrosive, producing only water as a by-product. This feature can offset the need for ultra-low catalyst loadings, providing an attractive balance between safety, sustainability, and process feasibility. Recent studies on green catalysts for pentose dehydration emphasize this trade-off, highlighting that higher loadings of non-corrosive catalysts can be justified when compared to low-loadings of corrosive acids.[34,35]

## Results and discussion

A significant difficulty in producing furfural lies in its intrinsic chemical instability across different reaction environments.[36–38] These characteristics render furfural prone to breakdown and side reactions, which result in reduced selectivity and the generation of various unwanted by-products, including 5-hydroxymethylfurfural (HMF), methylfurfural, levulinic acid, and other polymeric or resin-like compounds.[39,40] To address these challenges, biphasic reaction systems have been introduced, allowing the immediate transfer of furfural from the aqueous layer into an organic solvent upon formation. This method helps to minimize further breakdown and side reactions. Although biphasic systems are effective in delivering high yields and selectivity for furfural and related furan compounds, they pose considerable difficulties when it comes to scaling up. Typically, these reactions are conducted in sealed Pyrex vials or autoclaves under elevated pressure, conditions that are less suitable for industrial-scale or continuous-flow processes.[41,42] Building upon insights from our earlier work, we aimed to develop a more feasible and scalable method for producing furfural that overcomes the limitations of harsh reaction conditions and pressurized setups. Our objectives included creating a process that (1) operates at atmospheric pressure, (2) employs a catalyst that is non-toxic, cost-effective, and readily available, and (3) utilizes straightforward distillation apparatus suitable for both laboratory and pilot-scale applications. This configuration also enables the immediate separation of furfural from the reaction mixture, thereby limiting its exposure to elevated temperatures and reducing decomposition.

To identify the most effective catalyst, we conducted a screening of various metal halides and compared their catalytic efficiency to that of corresponding metal sulfates. The evaluation focused on furfural yield and selectivity, using D-xylose and L-arabinose as representative pentose sugars. Experiments were performed at an initial temperature of 170 °C, above furfural's boiling point, with a catalyst loading of 30 mol% and a reaction time of two hours. The comparative results of this screening are presented in Table 1, showcasing the differences in catalyst performance.

Table 1 reports the furfural (FF) yields and selectivities obtained from the catalytic conversion of D-xylose and L-arabinose using different metal halides and metal sulfates under the established reaction conditions. Among the catalysts tested, hydrated iron(III) sulfate [$Fe_2(SO_4)_3 \cdot xH_2O$] exhibited the highest catalytic performance, delivering furfural yields of 92% from D-xylose and 85% from L-arabinose, with corresponding selectivities of 94% and 90%, respectively. The performance of $Fe_2(SO_4)_3 \cdot xH_2O$ significantly surpasses that of iron(II) chloride ($FeCl_2$) and iron(III) chloride ($FeCl_3$), which achieved furfural yields below 55% and slightly lower selectivities. Similarly, zinc chloride ($ZnCl_2$) and copper sulfate pentahydrate [$Cu(SO_4) \cdot 5H_2O$] showed moderate activity, with furfural yields ranging between 44% and 62% for both pentoses. Iron(II) sulfate heptahydrate [$Fe(_{SO4}) \cdot 7H_2O$] also performed well, but still underperformed relative to $Fe_2(SO_4)_3 \cdot xH_2O$, indicating the crucial role of the iron oxidation state and sulfate coordination environment in enhancing catalytic activity and selectivity.[43]

The higher catalytic activity of $Fe_2(SO_4)_3 \cdot xH_2O$ can be rationalized by its stronger Lewis acidity compared to the other tested salts, as indicated by the lower $pK_{a1}$ value of its hydrated $Fe^{3+}$ species. A comparison of the acidity descriptors ($pK_{a1}$ values and qualitative Lewis acidity rankings) for all catalysts used in this study is provided in Table S1 of the SI.

These results highlight the superior catalytic efficiency and selectivity of hydrated iron(III) sulfate, which can be attributed to its strong Lewis acidity, thermal stability, and

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**Table 1** Comparison of metal halides with metal sulfates. Yields are referred to as isolated yields (%)

| Catalyst[a] | FF yield | FF yield | FF selectivity | FF selectivity |
|---|---|---|---|---|
| | D-Xylose | L-Arabinose | D-Xylose | L-Arabinose |
| $FeCl_2$ | $40 \pm 3$ | $35 \pm 3$ | $94 \pm 2$ | $91 \pm 2$ |
| $FeCl_3$ | $52 \pm 3$ | $46 \pm 3$ | $92 \pm 2$ | $88 \pm 2$ |
| $ZnCl_2$ | $50 \pm 3$ | $44 \pm 3$ | $93 \pm 2$ | $90 \pm 2$ |
| $Cu(SO_4) \cdot 5H_2O$ | $62 \pm 3$ | $53 \pm 3$ | $93 \pm 2$ | $89 \pm 2$ |
| $Fe(SO_4) \cdot 7H_2O$ | $76 \pm 3$ | $69 \pm 3$ | $91 \pm 2$ | $88 \pm 2$ |
| $Fe_2(SO_4)_3 \cdot xH_2O$ | $92 \pm 3$ | $85 \pm 3$ | 94 | $90 \pm 2$ |
| $H_2SO_4$ | Char | Char | — | — |

[a] Reaction conditions: 170 °C, 120 minutes, 30 mol% catalyst. All the experiments were performed in triplicate.

the ability to facilitate the selective dehydration of pentoses to furfural while minimizing side reactions leading to by-products. Furthermore, the use of $Fe_2(SO_4)_3 \cdot xH_2O$ aligns well with the goals of sustainable chemistry, given its low cost, non-toxic nature, and commercial availability.

The results show that furfural selectivity remains high for both pentoses (94% for D-xylose and 90% for L-arabinose), indicating minimal formation of side products. Furthermore, the calculated conversions of 98% for D-xylose and 95% for L-arabinose, demonstrate that nearly all of the starting sugar is consumed under the optimized reaction conditions. This combination of high selectivity and conversion supports the conclusion that water is indeed the sole by-product in this transformation, in agreement with the stoichiometry of the reaction. The slightly higher performance observed with D-xylose is consistent with its more favorable isomerization kinetics and dehydration pathway compared to L-arabinose, as discussed later.

To benchmark the performance of our benign Lewis acid system against the industry standard and to justify the necessity of a non-corrosive catalyst under these conditions, we attempted a control experiment using 30 mol% concentrated sulfuric acid ($H_2SO_4$) under the same optimized solvent-free and temperature (170 °C) conditions.

The results with $H_2SO_4$ were decisively negative for both pentose feeds: when reacting D-xylose and L-arabinose under these conditions, the mixture evolved rapidly and uncontrollably into a charred mass (charring), yielding no appreciable furfural. This failure highlights that the extreme acidity and strong dehydrating power of concentrated $H_2SO_4$ are fundamentally incompatible with the high-temperature, solvent-free reaction regime, promoting destructive polymerization and carbonization over selective dehydration. This result validates the critical role of the modulated Lewis acid activity provided by $Fe_2(SO_4)_3 \cdot xH_2O$ in achieving high yields and selectivity without solvent.

After that, we examined how varying the catalyst loading influences the reaction yield, and the results are presented in Fig. 1.

The data reported in Fig. 1 show a significant increase in furfural yield with increasing catalyst loading up to 30 mol% for both sugars. For D-xylose, the yield rises from 30% at 10 mol% to a maximum of 92% at 30 mol%, beyond which

further increases in catalyst concentration do not enhance the yield, indicating a plateau. A similar trend is observed for L-arabinose, with yields increasing from 8% to 85% between 10 mol% and 30 mol%, and remaining constant thereafter. These results suggest that 30 mol% of Fe(III) sulfate hydrate is sufficient to reach optimal catalytic activity under the experimental conditions.

Several attempts have been made to reduce the quantity of catalyst, even by extending the reaction time. A 10 mol% loading resulted in insufficient kinetics, yielding only 30% in 120 minutes. Furthermore, a 5 mol% loading required a prohibitively long reaction time (6 hours) to achieve a 26% yield from xylose and 8% from arabinose, thus rendering the process uncompetitive on a productivity basis.

The present work employs $Fe_2(SO_4)_3 \cdot xH_2O$ at 30 mol%. While this may appear high, it is important to consider the advantages of using a non-corrosive and eco-compatible catalyst. Unlike HCl or $AlCl_3$, $Fe_2(SO_4)_3 \cdot xH_2O$ does not produce corrosive chloride ions, avoiding costly materials and neutralization steps, and generates only water as a by-product.[44,45]

In fact, our primary objective was the development of a sustainable, non-corrosive, and *solvent-free* process, focused on achieving maximum yield in minimum time (≤90 minutes).

Industrial pentose dehydration processes, such as the classic Quaker Oats process (dilute sulfuric acid), typically operate at temperatures exceeding 150 °C and are limited to
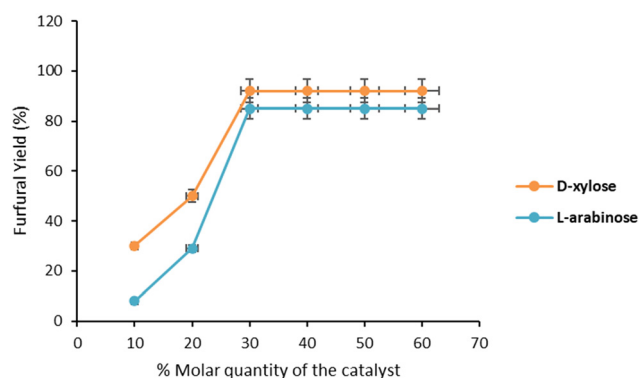


**Fig. 1** Catalyst effect on furfural yield from D-xylose and L-arabinose. Yields are referred to isolated yields. Reaction conditions: 170 °C, 120 minutes. All the experiments were performed in triplicate.

furfural molar yields of only about 50%. This low yield is an inherent consequence of mineral acid catalysis, which promotes severe side reactions (condensation and homopolymerization) between the furfural product and unreacted starting material, leading to humin formation and drastically reduced overall yield.[46,47]

Our performance of 92% yield in just 90 minutes stands out even when compared to modern high-yield systems:

• Mineral acids under biphasic conditions: while biphasic conditions can improve product extraction, these processes often demand extended reaction times and high acid concentrations. For instance, one study reported an 83% yield after 5 hours, using $10\%(w/w)H_2SO_4$ in a boiling toluene/water mixture.[48]

• Non-conventional systems and high loads: other advanced catalytic systems often show high loading requirements for lower or merely comparable yields:

- The ionic liquid $[Bmim]HSO_4$ requires a $10:1$ catalyst-to-xylose weight ratio to achieve a yield of only 63.87%.[49]

- The HPA-preyssler catalyst demands a significant weight loading of 15–45% for a 75% furfural yield.[50]

- While the $HCOOH/AlCl_3$ system can achieve a high yield (92.2%), it requires a $1:1$ molar ratio (equivalent to $\approx 100$ mol%) and necessitates a complex microreactor apparatus.[51]

In summary, the adopted strategy successfully delivered one of the best yields ($\approx 92\%$) in one of the shortest times ($\leq 90$ min) among reported catalytic systems, all while operating under solvent-free conditions with a non-corrosive catalyst.

After that, we investigated how pentose conversion varies with time (Fig. 2) and temperature (Fig. 3) to identify the most energy-efficient conditions. Furfural yield increases markedly with reaction time for both pentoses. For D-xylose, the yield rises from 32% at 10 minutes to 92% at 90 minutes, after which it remains constant up to 180 minutes, indicating that maximum conversion is achieved within 90 minutes. Similarly, L-arabinose shows an increase from 25% to 85% between 10 and 90 minutes, with no further improvement at
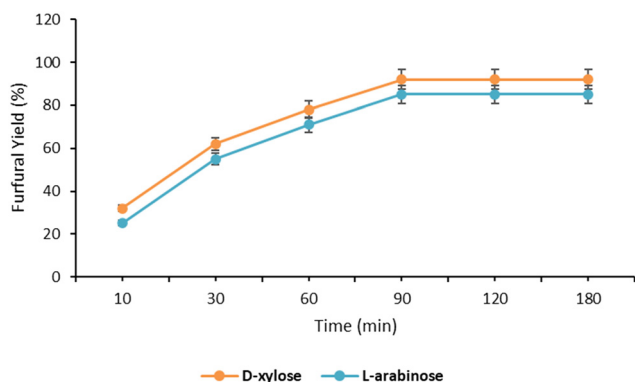
**Fig. 2** Effect of reaction time on furfural yield from D-xylose and L-arabinose. Yields are referred to isolated yields. Reaction conditions: 170 °C, 30 mol% catalyst. All the experiments were performed in triplicate.
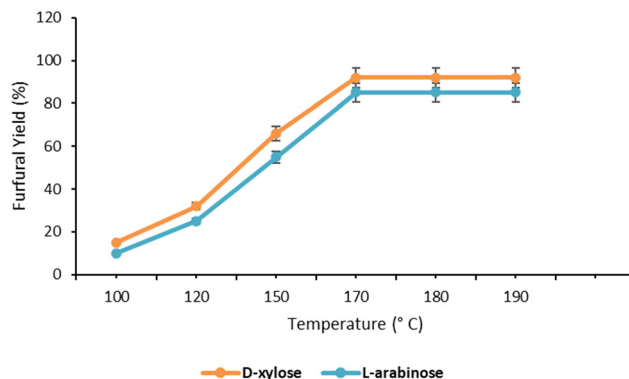
**Fig. 3** Effect of reaction temperature on furfural yield from D-xylose and L-arabinose. Yields are referred to isolated yields. Reaction conditions: 90 minutes, 30 mol% catalyst. All the experiments were performed in triplicate.

longer times. These findings suggest that, under the tested conditions, the optimal reaction time for achieving maximum furfural yield from both D-xylose and L-arabinose is 90 minutes. Extending the reaction beyond this point does not lead to increased productivity and may result in unnecessary energy consumption.

To precisely address whether the superior performance of $Fe_2(SO_4)_3 \cdot xH_2O$ stems from sustained reactivity or a mere kinetic advantage, we conducted a comparative temporal study (furfural yield *versus* time) under the optimized conditions, testing our catalyst against two representative alternatives: $FeCl_3$ and $Cu(SO_4) \cdot 5H_2O$.

The full kinetic profiles, presented in the SI, conclusively demonstrate that the low final yields observed for the alternative catalysts are not merely due to slower kinetics but to a premature termination of the reaction. While $Fe_2(SO_4)_3 \cdot xH_2O$ reached its maximum yield of 90% within 90 minutes, the reactions catalyzed by $FeCl_3$ and $Cu(SO_4) \cdot 5H_2O$ rapidly reached a plateau at 52% and 62%, respectively. Extending the reaction time up to 360 minutes yielded no further increase in furfural production.

This crucial observation confirms that the reactions utilizing $FeCl_3$ and $Cu(SO_4) \cdot 5H_2O$ suffer from insufficient sustainable reactivity. The inferior catalytic systems are unable to maintain the necessary reaction rate to fully consume the substrate before the high-temperature (170 °C), solvent-free environment causes rapid functional deactivation through the accelerated formation and accumulation of carbonaceous by-products (humin/char), thereby terminating the catalytic cycle. This highlights the indispensable role of the non-coordinating sulfate anion ($SO_4^{2-}$) in sustaining the high activity and stability of the $Fe_2(SO_4)_3 \cdot xH_2O$ system.

The furfural yield from both pentoses increases notably with rising temperature, a common behavior for a carbohydrate dehydration reaction (Fig. 3).

The furfural yield from D-xylose increases from 15% at 100 °C to a maximum of 92% at 170 °C, where it plateaus. For L-arabinose, the yield similarly rises from 10% to 85% between 100 °C and 170 °C, with no further improvements
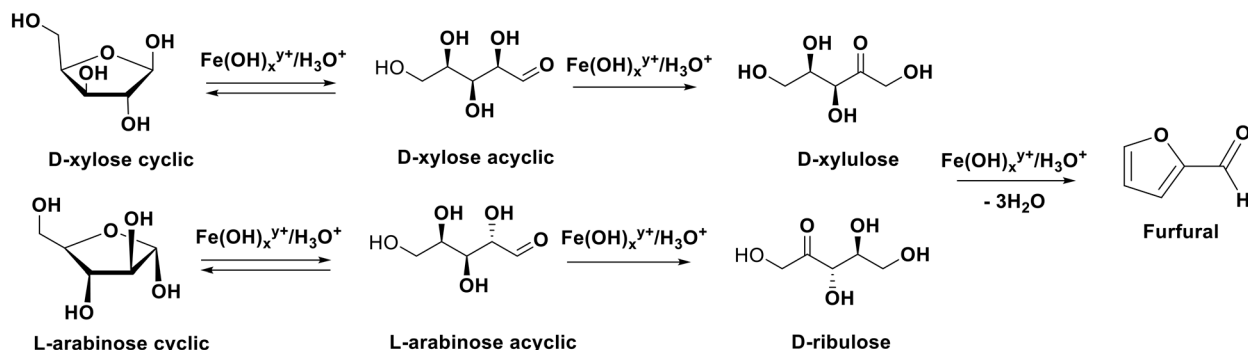
**Fig. 4** Proposed mechanism for furfural formation from D-xylose and L-arabinose *via* isomerization and dehydration under [$Fe_2(SO_4)_3 \cdot xH_2O$] catalysis.

above this temperature. It is important to note that 170 °C corresponds to the boiling point at which furfural can be effectively distilled from the reaction mixture. Below approximately 160 °C, the furfural formed is not distilled but rather recovered through extraction using an organic solvent (ethyl acetate) from the reaction mixture. The significant increase in yield observed at and above 170 °C can therefore be attributed to the onset of efficient *in situ* furfural distillation, which facilitates its continuous removal from the reaction environment, minimizing degradation and boosting overall yield.

Based on the previous findings reported in the literature, in the following Fig. 4 a hypothesis of reaction mechanism is depicted.

The iron(III) species acts as a Lewis acid to facilitate the isomerization of aldopentoses into keto forms, followed by sequential dehydration to form the furan ring.[52]

The reaction starts from the cyclic forms of D-xylose and L-arabinose, both five-carbon aldopentoses. The first step involves the acid-catalyzed isomerization of these sugars from their cyclic (furanose or pyranose) forms to their open-chain (linear) forms. In the linear form, D-xylose undergoes an aldose-ketose isomerization to yield D-xylulose, while L-arabinose is isomerized to D-ribulose.

Once D-xylulose and D-ribulose are formed, both compounds undergo acid-catalyzed dehydration steps. Each molecule loses three molecules of water through a series of enolization, condensation, and elimination steps. This cascade leads to the formation of furfural.[53,54]

The slightly higher yield of furfural from D-xylose compared to L-arabinose can be attributed to differences in stereochemistry and reaction pathway efficiency between the two sugars. Both D-xylose and L-arabinose are aldopentoses, but they differ in the configuration of the hydroxyl group at carbon 2 (C-2): for D-xylose the OH at C-2 is equatorial in the pyranose form, and this configuration tends to favor faster and more efficient isomerization to D-xylulose, while for L-arabinose, the OH at C-2 is axial, which can introduce more steric hindrance or less favorable transition states during isomerization to D-ribulose. As a result, the aldose-to-ketose isomerization of D-xylose to D-xylulose is typically more efficient than that of L-arabinose to D-ribulose, likely due to

more favorable enediol intermediate formation and less steric strain. D-Xylulose may also form more stable intermediates during the dehydration steps compared to D-ribulose, contributing to higher furfural yields. The rate of dehydration of D-xylulose might be slightly faster due to better alignment of functional groups necessary for water elimination and ring closure to form the furan ring.[55,56]

HPLC analysis of the reaction mixture starting from D-xylose sampled after 20 minutes conclusively identified D-xylulose as a key intermediate (see SI for chromatogram details). This evidence confirms that the Fe(III) catalyst successfully drives the selective isomerization of the aldose (D-xylose) to the highly reactive ketose (D-xylulose), which subsequently undergoes rapid triple dehydration to furfural.

The true catalytic species is probably not the bare $Fe^{3+}$ ion, but rather the hydrolyzed aquo- and hydroxo-species formed in aqueous solution. Literature confirms that the strong Lewis acidity of the $Fe^{3+}$ cation leads to significant hydrolysis in water ($pK_{a1} = 2.2$), generating $Fe(OH)^{2+}$, $Fe(OH)_2^+$ and others. This species acts as an effective Lewis acid site, coordinating the sugar's hydroxyl groups to facilitate the initial isomerization step, while the $H^+$ ions generated from the hydrolysis contribute to the subsequent Brønsted acid-catalyzed dehydration steps.[57–59]

The Lewis acid catalyst is represented in Fig. 4 by the generic form $Fe(OH)_x^{y+}$. The generic formula acknowledges that the active catalytic agent in the dehydration mechanism is the $Fe^{3+}$ center which has been partially hydrolyzed.

The importance of the counter-ion is demonstrated by the vastly different yields obtained with $Fe_2(SO_4)_3 \cdot xH_2O$ and $FeCl_3$ (Table 1). The high performance is critically dependent on the use of the non-nucleophilic sulfate anion ($SO_4^{2-}$). Unlike the coordinating chloride anion ($Cl^-$), sulfate does not coordinate strongly with the Fe(III) metal center, thereby maintaining the high intrinsic Lewis acidity of the $Fe(OH)^{2+}$ site. Furthermore, the non-nucleophilic nature of sulfate prevents the promotion of unwanted side reactions or degradation pathways that are often catalyzed by halides.[60,61] This optimized chemical environment, combined with the continuous removal of furfural by reactive distillation, ensures that the product is protected from secondary
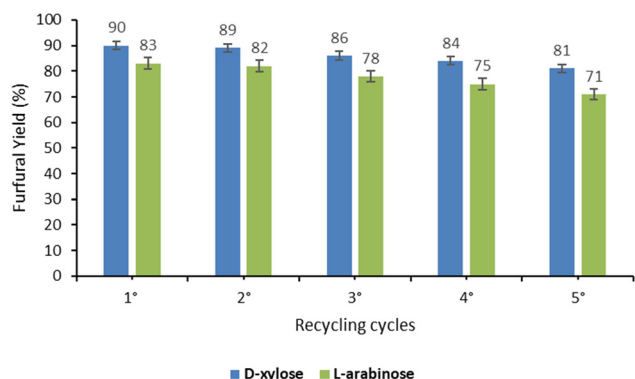
**Fig. 5** Catalyst recycling. Yields are referred to isolated yields. Reaction conditions: 90 minutes, 30 mol% catalyst, 170 °C. All the experiments were performed in triplicate.

reactions (such as humin formation), maximizing both selectivity and productivity.

We also tested the recycling to verify the stability of the catalyst in this reaction environment, and after five cycles the yields of furfural starting from D-xylose and L-arabinose are reported in the following (Fig. 5).

After each run, the freshly produced furfural was distilled off. The subsequent cycle was initiated by simply adding a fresh batch of pentose substrate to the reactor residue, which contained the entire catalyst load. No isolation, washing, or purification of the catalyst was performed between runs, maintaining the solvent-free nature of the process.

This recycling approach demonstrated good stability over the first few cycles, with the yield experiencing only a moderate, gradual decrease: from 90% to 81% for D-xylose and 83% to 71% for L-arabinose over five cycles.

Since the $Fe_2(SO_4)_3 \cdot xH_2O$ catalyst remains entirely within the concentrated, viscous residue, the decrease in activity is primarily attributed to catalyst fouling rather than significant metal leaching.

The reaction conditions (170 °C in a solvent-free environment) inevitably promote the formation of minor carbonaceous by-products, specifically humins and char, from the condensation of unreacted sugars and furfural.[62,63]

As these materials accumulate on the catalyst surface over successive cycles, they block the active Lewis acid sites, thus inhibiting substrate access and causing the observed deactivation.

This hypothesis was confirmed by thermogravimetric analysis (TGA) of the spent catalytic residue (see the SI file). Compared to the fresh catalyst, the spent residue exhibited a substantial mass loss between 200 °C and 400 °C, which is characteristic of the thermal decomposition and combustion of accumulated carbonaceous organic material. This analysis strongly supports fouling as the dominant deactivation mechanism under these high-temperature, solvent-free conditions.

Beyond delivering excellent yields and selectivity under mild conditions, this protocol also demonstrates several key benefits from a green chemistry perspective. Compared to our previous study on D-fructose dehydration using $Fe_2(SO_4)_3 \cdot xH_2O$ under similar distillation conditions,[29] the current process delivers superior performance (92% yield vs. 78%) with lower catalyst loading (30 mol% vs. 40%), and avoids the formation of formaldehyde, a toxic and volatile by-product observed in fructose conversion. Here, water is the only by-product, simplifying purification and minimizing health and environmental hazards. Furthermore, the use of D-xylose and L-arabinose, which are derived directly from non-edible hemicellulosic biomass, enhances the sustainability of the approach. These pentoses are more abundant, less expensive, and more compatible with biorefinery streams than D-fructose, making the process not only greener but also more practical for future scale-up. Overall, these results represent a meaningful advancement in the development of solvent-free, safe, and efficient strategies for furfural production.

To further contextualize the performance of $Fe_2(SO_4)_3 \cdot xH_2O$, we compared its efficiency and operational characteristics with commonly used industrial catalysts for pentose dehydration (Table 2). This comparison highlights not only the high furfural yield achievable with $Fe_2(SO_4)_3 \cdot xH_2O$, but also its practical advantages in terms of safety, sustainability, and process feasibility.

These results demonstrate that, conventional acids, although in smaller quantities, can provide lower furfural

**Table 2** Comparison of $Fe_2(SO_4)_3 \cdot xH_2O$ with conventional industrial catalysts for pentose dehydration to furfural

| Catalyst | FF yield | Key features | Ref. |
|---|---|---|---|
| $Fe_2(SO_4)_3 \cdot xH_2O$ | 92% (D-xylose), 85% (L-arabinose) | Non-corrosive, only water by-product, easy to handle, compatible with non-edible lignocellulosic biomass | Present study |
| $H_2SO_4$ (0.05 M) | 80% (xylose) | Corrosive, requires resistant materials, generates side-products (e.g., formaldehyde), needs neutralization | 64 |
| HCl (100 Mm) | 85% (xylose) | Corrosive, generates side-products, requires resistant materials, environmental issues | 65 |
| Formic acid (50 mM) | 65% (xylose) | Less corrosive, but still requires neutralization and produces side-products | 66 |
| Solid acid catalysts | 85.9% (xylose) | Less corrosive, lower efficiency, requires harsher conditions (pressures) | 67 |
| HCl (1000 mM) | 26% (arabinose) | — | 68 |
| $H_2SO_4$ (1 g $L^{-1}$) | 43% (arabinose) | . | 69 |
| Formic acid (75 wt/vol%) | 60% | . | 70 |

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**Table 3** Green metrics for pentose dehydration to furfural using $Fe_2(SO_4)_3 \cdot xH_2O$

| Pentose | FF yield (%) | Atom economy | $E$-factor | RME(%) | PMI |
|---|---|---|---|---|---|
| D-Xylose | 92 | 100 | ~0.1 | 92 | 1.11 |
| L-Arabinose | 85 | 100 | ~0.13 | 85 | 1.15 |

yields. $Fe_2(SO_4)_3 \cdot xH_2O$ instead, offers significant advantages for sustainable and safe operation, with only water as by-product, reduced equipment constraints, and compatibility with non-edible biomass.

Table 3 summarizes the green metrics for the dehydration of D-xylose and L-arabinose to furfural using $Fe_2(SO_4)_3 \cdot xH_2O$. The high yields (92% and 85%) and 100% atom economy demonstrate efficient conversion of pentoses with minimal waste. The reaction mass efficiency (RME) values of 92% and 85%, and the low process mass intensity (PMI $\approx$ 1.1–1.15) further highlight the resource efficiency of the process. Water is the only by-product, and the reaction proceeds under ambient pressure using a non-corrosive, inexpensive catalyst. These metrics collectively support the environmental and practical advantages of $Fe_2(SO_4)_3 \cdot xH_2O$, demonstrating its potential as a sustainable alternative to conventional mineral acids.

Therefore, this method represents a clear green advance by combining operational simplicity, abundance of pentose raw materials, eco-friendly and reusable catalyst, solvent-free conditions, and high efficiency into a scalable and environmentally benign approach to furfural production, with water as the sole by-product.

## Conclusions

In this study, we developed a simple, efficient, and sustainable method for the direct production of furfural from hemicellulosic pentoses, specifically D-xylose and L-arabinose, using hydrated ferric sulfate [$Fe_2(SO_4)_3 \cdot xH_2O$] as a catalyst under atmospheric pressure distillation. The proposed approach, free of organic solvents and based on moderate operating conditions (170 °C, 90 minutes), demonstrated high efficiency in terms of conversion (98% for D-xylose and 95% for L-arabinose) and selectivity toward furfural (94% and 90%, respectively), with water as the major by-product. Compared to other metal salts and mineral acids, hydrated ferric sulfate showed superior catalytic performance due to its strong Lewis acidity, thermal stability, and ability to selectively promote the dehydration of pentoses to furfural. These results suggest that $Fe_2(SO_4)_3 \cdot xH_2O$ is a promising, cost-effective, and environmentally benign catalyst for the valorization of biomass-derived carbohydrates, offering a viable route for the sustainable production of platform chemicals.

## Author contributions

## Conflicts of interest

There are no conflicts to declare.

## Data availability

The data underlying this study are available in the published article and its online supplementary information (SI).

Supplementary information is available. See DOI: **https://doi.org/10.1039/d5re00371g**.

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