

Conversion of Xylan and Xylose into Furfural in Biorenewable Deep Eutectic Solvent with Trivalent Metal Chloride Added

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Transformation of the hemicellulose fraction in an environmentally benign manner to deliver high value-added chemicals is critical for the integrated utilization of biomass. Amongst all the chemicals derived from hemicellulose, furfural (produced by hydrolysis of xylan into xylose and successive dehydration of the latter) is a promising option. In this manuscript, a catalytic approach for converting xylan and xylose into furfural co-catalyzed by choline chloride-citric acid·H₂O, a deep eutectic solvent (DES) synthesized from biorenewable building blocks, and trivalent metal chloride was developed. Choline chloride-citric acid·H₂O acted as both reaction medium and Brønsted acid catalyst. Both monophasic route and biphasic route (with methyl isobutyl ketone as extractant for *in situ* extraction of furfural) were proposed. The highest furfural yields obtained from xylose and xylan in monophasic approach were 59.3% and 54.2%, respectively, at 140 °C, and these values increased to 73.1% and 68.6% when biphasic system was applied for the reaction. Moreover, in biphasic system, choline chloride-citric acid and metal chloride could be recycled and reused for 5 runs with stable catalytic ability.

Keywords: Xylan; Xylose; Furfural; Metal chloride; Deep eutectic solvent

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INTRODUCTION

Biomass is a renewable and carbon-neutral resource that can be used in the production of fuels and other high value-added chemicals that could eventually replace those derived from petrochemical resources (Ma *et al.* 2012; Zhang *et al.* 2012). The transformation of lignocellulosic biomass to deliver biofuels and valuable platform chemicals has great potential economic and social benefits. The main chemical compositions of biomass are cellulose, hemicellulose, and lignin. Specifically, the chemical catalytic conversion of hemicellulose is of substantial significance because the biological conversion of hemicellulose is not as efficient as the conversion of cellulose. Among the chemicals derived from hemicellulose, furfural is a promising option, as it is one of the key industrial chemicals, with applications in many industries (such as oil refining, plastics, pharmaceuticals, and agrochemical industries) and in the development of next-generation biofuels and bioplastics (Mamman *et al.* 2008; Xing *et al.* 2011). In particular, furfural is proposed as one of the top 10 biobased products from biorefinery carbohydrates in a recent U.S. Department of Energy report (Bozell and Petersen 2010). However, there is no chemical synthetic route available for furfural production; the

commercial processing approach that has been used for converting lignocellulose into furfural using mineral acid as catalyst is not only energy intensive but also inefficient. Moreover, it results in relatively low furfural yields, causes corrosion to equipment, and suffers from serious environmental problems due to the acidic effluent, which is difficult to handle. Therefore, it would be highly desirable to look for a new route that mitigates all the shortcomings for the transformation of lignocellulose into furfural.

Up to now, optimization investigations in the use of biomass for furfural production have been carried out in the presence of alternative reaction solvents, such as dimethylsulfoxide, DMA (dimethylacetamide) (Binder *et al.* 2010) and supercritical fluid (Gairola and Smirnova 2012) instead of water in monophasic systems. Additionally, biphasic systems using organic solvents, *e.g.*, MIBK (methyl isobutyl ketone) (Weingarten *et al.* 2010), THF (tetrahydrofuran) (vom Stein *et al.* 2011), or CPME (cyclopentyl methyl ether) (Campos Molina *et al.* 2012) as reagents to extract furfural simultaneously with satisfactorily achieved yields have also attracted much attention. These approaches have made some progress in improving furfural yield and selectivity; however, conversion of lignocellulose into furfural with a “green” route remains a challenging issue.

Compared to most commonly used volatile organic solvents, ionic liquids (ILs) are considered to have minimal environmental impact due to their extremely low volatility. Several researchers recently have investigated the utilization of ILs for converting biomass into furfural (Binder *et al.* 2010; Zhang *et al.* 2013a; Zhang and Zhao 2010). Nevertheless, the most commonly used ILs are not readily biodegradable, and their high cost limits their application on industrial scale. Additionally, if measured against the 12 principles of green chemistry, whether the commonly used ionic liquids themselves can be claimed to be “green” reaction media is still open to debate. From the viewpoints of both environmental and economical concerns, a “fully green” reaction medium must meet the following conditions: be environmentally benign, biorenewable, inexpensive, generated from non-toxic starting materials, and easily prepared. Recently, deep eutectic solvents (DESs) are being considered as promising candidates for green media (Durand *et al.* 2013; Yang *et al.* 2013). They share many of the unique properties of ILs; for example, DESs are not flammable, they have negligible volatility and high thermal stability, and they also have the added advantages of being economical, biodegradable, and having low toxicity. Particularly, ChCl-citric acid·H₂O (choline chloride-citric acid·H₂O), an acidic DES obtained by mixing choline chloride with citric acid monohydrate, has been employed as both catalysts and solvents for the production of 5-HMF from fructose and inulin (Hu *et al.* 2008; Hu *et al.* 2009). There are similarities in some aspects of the conversions of C₆ sugars and C₅ sugars; thus ChCl-citric acid·H₂O could be a candidate for converting pentose or pentosan into furfural.

Another key issue involving the conversion of C₅ sugars to furfural is the development of environmentally benign catalysts. There have been many studies on the application of different types of solid acid catalysts (Rinaldi and Schüth 2009; Weingarten *et al.* 2011) in the conversion of xylan and xylose into furfural. More recently, the effectiveness of metal chlorides for catalyzing furfural production from xylose, xylan, and untreated biomass has been proposed (Mao *et al.* 2012, 2013; Yang *et al.* 2012b; Zhang *et al.* 2013b), and both Cl⁻ ions and cations of metal chlorides have been shown to be responsible for producing furfural. Specifically, metal chlorides induce a change in the reaction mechanism for furfural production *via* xylose isomerization to xylulose (Binder *et al.* 2010; Yang *et al.* 2012b), and the dehydration rate of xylose with

metal chloride is significantly higher than the reaction carried out in Brønsted acids alone (Choudhary *et al.* 2012). Moreover, while it has been confirmed that metal chlorides could facilitate the isomerization reaction of xylose, the presence of a Brønsted acid is indeed necessary for the dehydration reactions and furfural selectivity (Marcotullio and De Jong 2010; Marcotullio and de Jong 2011). Furfural is produced by hydrolysis of xylan (the major component of hemicellulose and the most abundant non-cellulosic component in the secondary cell walls of many plants (Li *et al.* 2013)) into xylose and the successive cyclodehydration of the latter. Thus, investigations involving the conversion of xylan and xylose into furfural are needed to achieve a clear understanding of the furfural formation pathway and better furfural yields.

Given these reasons, investigations were conducted in an attempt to use trivalent metal chlorides as co-catalyst for converting xylose and xylan into furfural with ChCl-citric acid·H₂O employed as both reaction medium and Brønsted acid catalyst (tricarboxylic acids are the functional parts). ChCl-citric acid·H₂O is an acidic DES prepared from inexpensive, natural, and biorenewable starting materials, and it is also a Cl⁻ ion donor. The combination of ChCl-citric acid·H₂O with a metal chloride could be an attractive green option for transforming xylan and xylose to furfural.

EXPERIMENTAL

Materials

Xylan (from birch wood, $\geq 90\%$) was supplied by Sigma-Aldrich. D-Xylose ($\geq 98\%$) and choline chloride ($\geq 99\%$) were supplied by Acros. CrCl₃·6H₂O, FeCl₃·6H₂O, AlCl₃·6H₂O and citric acid monohydrate (hereinafter referred to as citric acid) were supplied by Tianjin Jiangtian Chemical Co. Ltd. (Tianjin, China); these chemicals were reagent-grade and used without further purification. All other chemicals were purchased from Sigma-Aldrich. ChCl-citric acid was synthesized according to procedures reported in the literature (Abbott *et al.* 2004; Hu *et al.* 2009). The molar ratio of choline chloride to citric acid was 2:1 (lowest melting point for this DES could be obtained at this ratio).

Standard Procedure for Xylose/Xylan Conversion into Furfural in Monophasic System

First, 2.97 g of ChCl-citric acid, 38.3 mg of xylose, and 6 mg of AlCl₃·6H₂O were loaded into a glass vessel (10 mL). The reaction mixture was then heated in a preheated oil bath and stirred at specified temperatures for different reaction times. After the desired residence time, the reaction was terminated by immediately quenching the reactor in cooling water. Samples were then diluted, filtered, and analyzed using HPLC.

The standard procedure for furfural formation from xylan was similar to that from xylose mentioned above, but with 10 mg of H₂O added into each reactor.

Standard Procedure in Biphasic System

A thick-walled glass vessel (10 mL) was charged with 2.97 g of ChCl-citric acid, 0.25 mmol of feedstock (38.3 mg of xylose, 36.7 mg of xylan), and 6 mg of metal chloride, and these materials were then stirred at 65 °C for 1 min. Afterwards, 4 mL of MIBK was added to the vessel and the mixture was heated in a preheated oil bath and stirred at different temperatures for desired times. After the desired residence time, the

reaction was terminated by quenching the reactor in cooling water, thus the two phases were separated and collected for analysis.

Analytical Methods

Furfural was determined using high-performance liquid chromatography (HPLC, Agilent 1200) at 280 nm with an ultraviolet detector and an XDB-C18 column. The column oven temperature was 30 °C, and acetonitrile/water (15/85v/v) at a flow rate of 1 mL/min was used as the mobile phase. Xylose was determined using HPLC (Waters 1525) with an aminex HPX-87H column and a refractive index detector (Waters 2412). The column oven temperature was 65 °C. The mobile phase was a solution of H₂SO₄ (5 mM) at a flow rate of 0.6 mL/min. For HPLC analysis, all the samples were filtered with a syringe filter (0.22 μm) prior to analysis.

The byproducts were analyzed by GC/MS (GC: HP 7890, MS 5975, Column: DB-Wax, 30 m × 0.25 mm × 0.25 mm) with ionization achieved by electron impact at 70eV. The operating conditions were as follows: injection port temperature, 250 °C; interface temperature, 280 °C; column oven temperature, 60 °C for 5 min, ramped at 10 °C min⁻¹ to 250 °C with a 5 min hold; and helium carrier gas (flow rate of 1.2 mL min⁻¹).

The unreacted xylan was determined using NREL LAP “Determination of Structural Carbohydrates and Lignin in Biomass” (NREL 2006). All reaction products were quantified using calibration curves constructed with authentic samples. Each experiment was performed three times, and the averaged value was used for analysis.

Conversion of reactants and yield of furfural

The following equations were used:

$$\text{xylose conversion} = \frac{\text{moles of xylose reacted}}{\text{moles of starting xylose}} \times 100\% \quad (1)$$

$$\text{xylan conversion} = \frac{\text{moles of xylan reacted}}{\text{moles of starting xylan}} \times 100\% \quad (2)$$

$$\text{furfural yield (from xylose)} = \frac{\text{moles of furfural produced}}{\text{moles of starting xylose}} \times 100\% \quad (3)$$

$$\text{furfural yield (from xylan)} = \frac{\text{moles of furfural produced}}{\text{moles of starting xylan}} \times 100\% \quad (4)$$

RESULTS AND DISCUSSION

Conversion of Xylose into Furfural in ChCl-Citric Acid in the Presence of Metal Chlorides

Experiments were started by applying a monophasic process for xylose dehydration into furfural. Reactions at 90 °C without metal chloride added yielded only 8% furfural with 53% xylose conversion within 30 min. However, the process efficiency of xylose dehydration into furfural was substantially improved with the combination of metal chlorides in ChCl-citric acid from 90 °C to 140 °C, affording furfural yields in the range of 15% to 59% (Table 1). The positive effect of metal chlorides could be attributed to the metal chlorides acting as weak bases and assisting in the formation of 1,2-enediol

via proton transfer, thus accelerating the dehydration of xylose leading to furfural (Marcotullio and de Jong 2011). In addition, metal chlorides promote xylose isomerization via the formation of xylulose (Yang *et al.* 2012b). Specifically, the optimal furfural yield (59%) was obtained by the addition of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ at 140 °C for 15 min. Moreover, the furfural yield decreased with increased amount of humins when increasing $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ dosage at 140 °C (Table 1, entries 6 and 7). This trend can be ascribed to $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, as a Lewis acid catalyst, favoring not only xylose isomerization but also furfural degradation. The proportion of Lewis acid to Brønsted acid is essential for maximizing the furfural yield in a mixed Lewis and Brønsted acid catalyst system (Weingarten *et al.* 2011), and excess $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ could accelerate the yield-loss reactions (fragmentation of furfural, resinification reactions between furfural molecule, and condensation reactions between furfural and xylose or other intermediates) that result in undesired compounds. In addition, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ achieved comparable furfural yields to that of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, but with longer residence time or increased dosage (Table 1, entries 9 and 10). $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ was less effective than $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ or $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, affording 44% furfural yield with 82% xylose conversion when the reaction was conducted under conditions similar to that used successfully with $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$. Subsequently, to compare the catalytic effect of different metal cations, conversions of xylose were conducted by adding metal chlorides in equimolar quantities to eliminate the influence of different Cl^- ion levels (Table 1, entries 11 and 13). The effect of chlorides on furfural production followed this order: $\text{AlCl}_3 \cdot 6\text{H}_2\text{O} > \text{FeCl}_3 \cdot 6\text{H}_2\text{O} > \text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, probably because the metal cations catalyzed the transformation of carbohydrates into furfural proportionally to their ionization potential (Al^{3+} : 119.99 V, Fe^{3+} : 54.8 V, Cr^{3+} : 49.1 V) (Gravitis *et al.* 2001); the catalytic effect of different metal cations on xylose conversion into furfural is of great interest and deserves more detailed studies in the future.

Table 1. Conversion of Xylose into Furfural in ChCl-Citric Acid with the Addition of Metal Chlorides^[a]

Entry	T (°C)	t (min)	Co-catalyst	Xylose conv.(%)	Furfural yield (%)
1	90	30	None	53.4±0.8	8.3±0.2
2	90	30	$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$	64.3±0.3	15.3±0.1
3	100	30	$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$	69.8±1.2	22.8±0.4
4	120	25	$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$	86.1±0.3	36.5±0.3
5	140	10	$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$	90.5±0.7	49.8±0.4
6	140	15	$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$	96.1±1.3	59.3±0.2
7 ^b	140	15	$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$	99.3±0.4	45.1±0.3
8	140	15	$\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$	82.1±0.9	44.6±0.2
9 ^b	140	15	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	95.4±0.7	58.3±0.4
10	140	25	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	96.1±0.4	58.5±0.1
11 ^c	140	15	$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$	95.9±0.8	57.5±0.1
12 ^c	140	15	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	92.2±0.1	53.6±0.2
13 ^c	140	15	$\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$	88.2±0.2	48.7±0.3

[a] Reaction conditions: 2.97 g of ChCl-citric acid, 38.3 mg of xylose, and 6 mg of metal chloride. [b] 12 mg of metal chloride was employed. [c] 0.04 mmol of metal chlorides were used.

Conversion of Xylan into Furfural in ChCl-Citric Acid with the Addition of Metal Chlorides

Next, the reaction system was further extended by employing xylan as the starting material. Conversion of xylan was challenging at low to moderate temperatures (vom Stein *et al.* 2011). Binder *et al.* (2010) reported that the furfural yield from xylan was very low (1%) with acid and chromium catalysts and halide additives at 100 °C in DMA. Nevertheless, a particularly interesting observation in this work was that xylan was hydrolyzed into furfural even at 100 °C, with furfural yields of 23% and 8% achieved with or without the presence of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, respectively. In contrast, when using water as reaction solvent, no furfural was produced from xylan at 100 °C, even with $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ added, probably because non-aqueous media facilitates a higher furfural yield (Lange *et al.* 2012; Takagaki *et al.* 2010). Subsequently, reactions of xylan transformation were conducted at 140 °C by optimizing the reaction parameters; the yield of furfural increased by prolonging the residence time from 15 min to 25 min (Table 2, entries 5 and 4) or increasing the $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ dosage from 6 mg to 12 mg (Table 2, entries 9 and 4), giving the highest furfural yield of 54%. However, further increasing the reaction time (with 12 mg of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$) did not result in a further increase in furfural yield (Table 2, entries 9 and 10). In addition, the furfural yield decreased, while the formation of solid humins increased with the longer residence time. The result indicated that optimizing the residence time is necessary to achieve a maximum furfural yield in this batch reactor because furfural underwent several unwanted secondary reactions with increasing reaction time after the optimal time, which led to the formation of degradation products (Lessard *et al.* 2010). Besides, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ achieved comparable results (53% furfural yield) to that of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ by optimizing the reaction conditions. This trend is similar to the results from xylose discussed before.

Table 2. Conversion of Xylan into Furfural with the Addition of Metal Chlorides in ChCl-Citric acid ^[a]

Entry	T (°C)	t (min)	Co-catalyst	Furfural yield (%)
1	100	40	None	8.3±0.4
2	100	40	$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$	23.2±0.6
3 ^b	100	40	$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$	Not detected
4	140	15	$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$	47.3±0.1
5	140	25	$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$	54.2±0.2
6	140	25	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	45.3±0.1
7	140	40	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	53.4±0.2
8 ^c	140	25	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	50.1±0.3
9 ^c	140	15	$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$	51.3±0.2
10 ^c	140	25	$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$	46.2±0.1

[a] Reaction conditions: 2.97 g of ChCl-citric acid, 36.7 mg of xylan, 6 mg of metal chloride, and 10 mg of water. [b] Water was used as reaction medium with an equal volume of DES. [c] 12 mg of metal chloride was employed.

Putative Route for the Hydrolysis of Xylan into Furfural in ChCl-Citric Acid with the Addition of Trivalent Metal Chlorides

The reaction mechanism for xylan hydrolysis into furfural is complex and still debated, and the reaction pathways may differ in the case of different types of catalysts in different reaction conditions. It has been inferred that metal chlorides could accelerate the isomerization of xylose (Mao *et al.* 2013; Marcotullio and De Jong 2010; Yang *et al.*

2012a), and the presence of a metal chloride also induces an alternative mechanism for xylose dehydration into furfural *via* the formation of xylulose, which is different from that using a single Brønsted acid as catalyst (Binder *et al.* 2010; Choudhary *et al.* 2012; vom Stein *et al.* 2011; Yang *et al.* 2012b). Specifically, both metal chloride and Brønsted acid are present in this reaction system, and ChCl-citric acid is also a Cl⁻ ion donor. The mechanism by which a metal chloride plus ChCl-citric acid catalyzes xylose dehydration may differ from that catalyzed by Brønsted acid or metal chloride alone. A plausible reaction pathway for xylan conversion into furfural co-catalyzed by a trivalent metal chloride and ChCl-citric acid is presented in Fig.1.

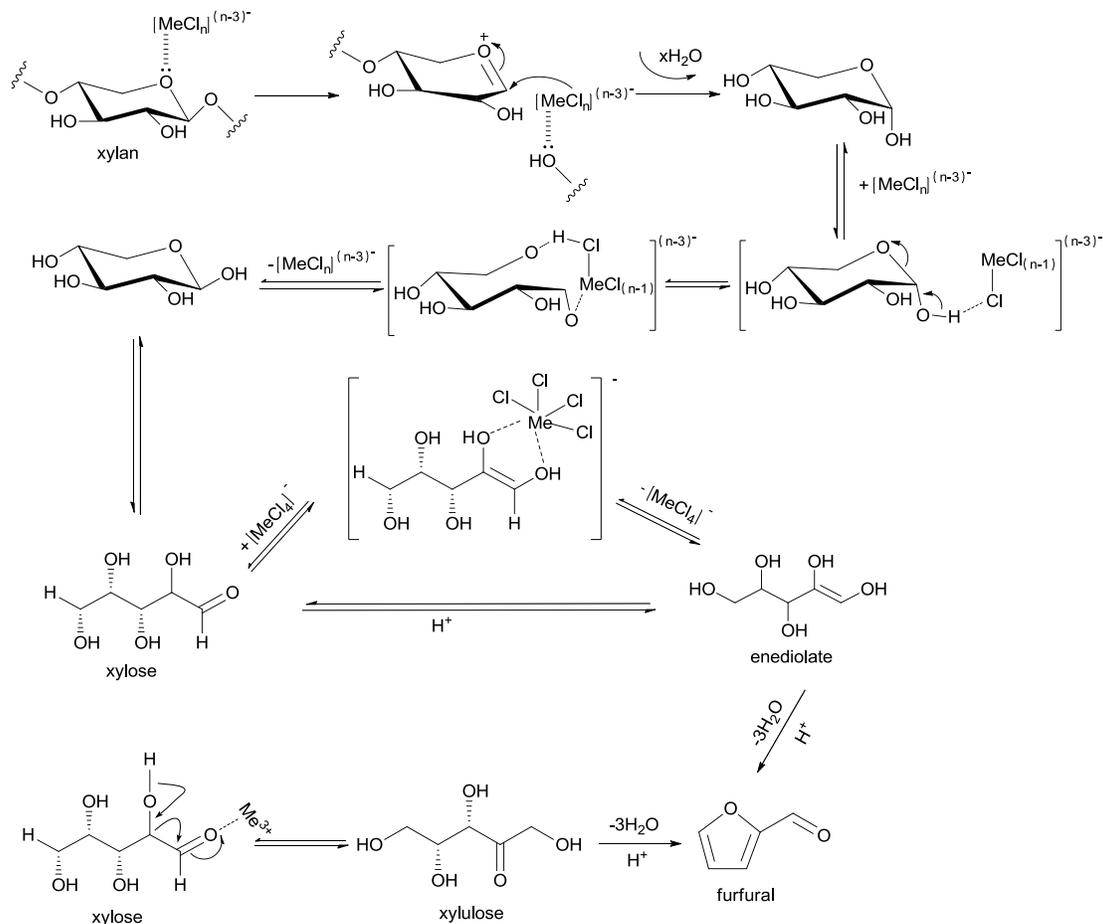


Fig. 1. Putative mechanism for the conversion of xylan into furfural in ChCl-citric acid with a trivalent metal chloride added. Me^{3+} represents trivalent metal cation

A trivalent metal chloride in ChCl-citric acid forms $[\text{MeCl}_n]^{(n-3)-}$ complexes in a manner similar to LnCl_3 (Hines *et al.* 2008; Zhang and Zhao 2010). By bonding with a glycosidic oxygen atom, $[\text{MeCl}_n]^{(n-3)-}$ complexes weaken the glycosidic bonds and lead to the hydrolysis of xylan to xylose. Then, $[\text{MeCl}_n]^{(n-3)-}$ facilitates the conversion of α -xylopyranose anomers to β -xylopyranose anomers through hydrogen bonding between the hydroxyl groups and the chloride anions (Zhang and Zhao 2010). Next, the xylose isomerization to an enolate structure is promoted by $[\text{MeCl}_4]^-$ or by H^+ after the cyclic aldoses reverse to acyclic form. Moreover, through bonds between oxygen atoms and metal cations, the isomerization of xylose to xylulose is also promoted (Binder *et al.* 2010), followed by dehydration to produce furfural.

Effect of Initial Feedstock Loading on Conversion of Xylan and Xylose into Furfural in ChCl-Citric Acid

The initial feedstock loading in all the treatments above was 0.25 mmol. To study the effects of feedstock loading on the conversion of xylose/xylan into furfural, the initial substrate concentration in the presence of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ in ChCl-citric acid was further increased. As shown in Fig. 2, the furfural yields obtained from xylose and xylan were 56.8% and 50.1%, respectively, with 0.3 mmol initial loadings; these values were slightly lower than those obtained with 0.25 mmol initial loadings. Moreover, the furfural yields decreased gradually, and more insoluble humins were observed with increasing feedstock concentration. A significant decline to 29.6% and 20.5% furfural yields from xylose and xylan, respectively, was observed when 0.9 mmol of substrates were added. The decrease in furfural yield with increasing feedstock concentration may be associated with an increased probability that catalyzed or uncatalyzed cross-polymerization reactions had occurred between two or more product molecules in the system, and the cross-polymerization reactions that favored the formation of undesired by-products were more likely to occur when a monophasic system was employed. Other byproducts (such as formaldehyde, formic acid and acetaldehyde) were observed for both xylose and xylan samples using GC/MS. However, the yields of these compounds were low, and humins were the major by-products.

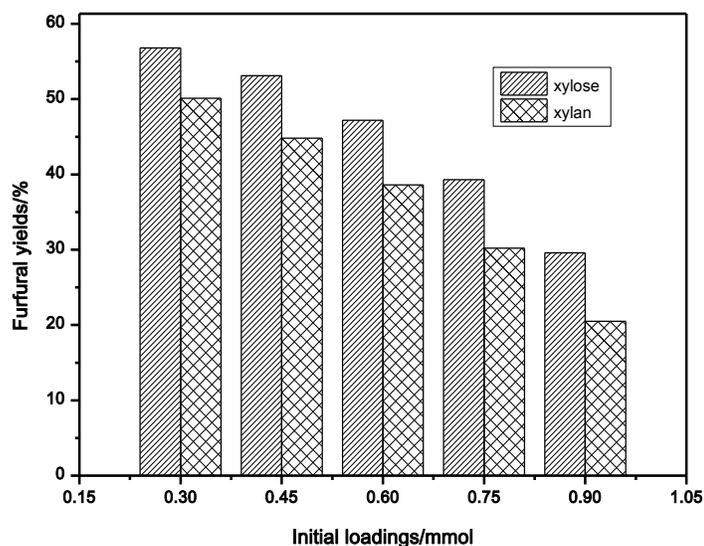


Fig. 2. Effect of initial substrate loading on xylose/xylan conversion into furfural. Conditions: 2.97 g of ChCl-citric acid, 6 mg of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, 140°C, 15 min for xylose, 25 min for xylan

Conversion of Xylan and Xylose into Furfural in DES/MIBK Biphasic System

Next, attempts to improve the efficiency of xylan/xylose conversion into furfural were conducted. Once formed, furfural could be rapidly converted to other degradation products. To avoid further yield-loss reactions, overcome humin formation, and facilitate higher furfural yield and selectivity, an efficient method of separating furfural from the reaction system in a timely manner is required. Recently, biphasic processing approaches focusing on the simultaneous extraction of furfural by employing an organic solvent as extracting reagent have been demonstrated to be effective for avoiding furfural degradation reactions (Xing *et al.* 2011; Yang *et al.* 2012b). Considering the subsequent

separation, a solvent with a low-boiling point (such as MIBK) is energetically more advantageous in a biphasic system. Besides, the solubility of ChCl-citric acid, metal chloride, and the reactants (xylose and xylan) in MIBK is negligible. Therefore, the biphasic route with MIBK as extractant was further explored in this work for the *in situ* extraction of furfural from the DES phase to the MIBK phase. As expected, the simultaneous extraction of furfural by MIBK significantly increased the total furfural yields in all cases (Table 3), mainly because furfural yield-loss reactions between two or more product molecules were more likely to occur in a monophasic reaction system, biphasic systems facilitated the continuous product removal by extracting furfural to the organic phase once it is produced, and side reactions were suppressed. In addition, the ChCl-citric acid and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ could be recycled and reused (Fig. 3) by removing the MIBK phase and further extracting the furfural in the DES phase with fresh MIBK ($3\text{ mL} \times 3$). After extraction, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ remained in the DES phase. Before reuse, the DES/ $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ phase was dried at 80°C in a vacuum drier to remove water in the system. Subsequently, the DES/ $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ phase was reused by adding new substrate into the reactor and replacing the organic phase.

Table 3. Furfural Formation in DES/MIBK Biphasic Systems^[a]

Entry	t (min)	Conversion (%)	Total furfural yield (%)	Furfural yield in MIBK (%)	Extraction rate (%)
1	25	99.8	73.1	58.3	79.8
2 ^b	35	99.7	71.4	57.5	80.5
3 ^c	35	99.4	68.6	54.4	79.3

[a] Reaction conditions: 2.97 g of ChCl-citric acid, 4 mL of MIBK, 38.3 mg of xylose, and 6 mg of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ at 140°C . [b] 6 mg of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was used as catalyst. [c] 36.7 mg of xylan was employed as feedstock.

The recycled ChCl-citric acid and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ still showed reasonable activity in Runs 1 and 2 with the addition of fresh xylose. Notably, cycles without the addition of feedstock (Runs 3 and 4) afforded much lower furfural yields. Nevertheless, the yield of furfural returned to its initial value once fresh xylose was added again to the system (Runs 5 and 6), indicating that the ChCl-citric acid and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ were still active.

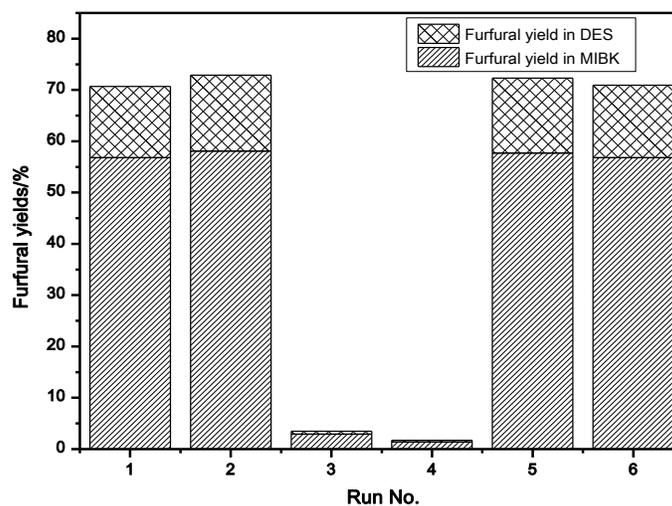


Fig. 3. Results of recycling of ChCl-citric acid and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$. The conditions were the same as that of entry 1 in Table 3

CONCLUSIONS

1. The conversion of xylan and xylose into furfural co-catalyzed by trivalent metal chloride and ChCl-citric acid were developed in both monophasic process (DES) and biphasic process (DES/MIBK). ChCl-citric acid acted as both reaction medium and Brønsted acid catalyst.
2. By optimizing the reaction parameters for the conversion of xylan and xylose into furfural, a furfural yield of 73.1% was achieved by biphasic route with the addition of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$.
3. In biphasic approach, the ChCl-citric acid and metal chloride could be recycled and reused with stable catalytic effect for five successive runs.
4. The present process provides a more ecologically benign route than commercial process for furfural production because ChCl-citric acid is cheap and biorenewable. Meanwhile, ChCl-citric acid in this catalytic approach was not stable when the reaction temperature was higher than 146 °C; thus, future work should focus on developing an acidic green DES that exhibits better thermostability, as this appeared to be a key limiting issue of this route.

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