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Graphical abstract

Unveiling the role of choline chloride on furfural synthesis from highly concentrated feeds of xylose

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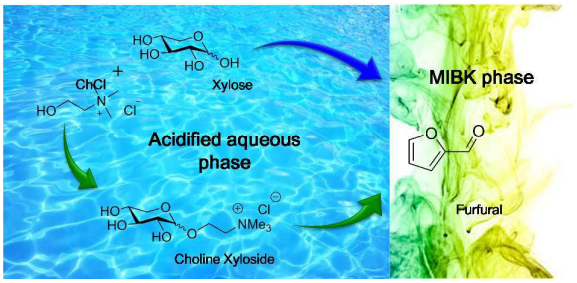

Choline chloride helps to convert high concentrated feeds of xylose to furfural through the formation of a choline xyloside intermediate.

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Furfural is a biomass derived compound being used for the synthesis of fuels and chemicals. Herein we show that choline chloride allows the conversion of highly concentrated feeds of xylose (up to 50 wt%) to furfural (up to 75%) and that it can be recyclable. Such a beneficial effect was explained by the formation of a choline xyloside intermediate exhibiting higher reactivity than xylose.

Introduction

Furfural is an attractive platform molecule identified as one of the top value added chemicals derived from biomass.[1] Valuable biobased chemicals and biofuels with huge market potential can be directly produced from furfural.[2] For instance, furfural can be converted into renewable fuels such as 2-methylfuran, 2-methyltetrahydrofuran, and valerate esters.[3] Furfural can be also used as a bio-based solvent for the synthesis of organic materials and as a building block for the synthesis of a broad range of valuable chemicals such as furfuryl alcohol,[4,5] 2-methylfuran,[6] succinic acid,[7] maleic acid[8] among others. Furfural is produced mainly from the hemicellulose part of lignocellulosic biomass through the sequential hydrolysis of hemicellulose to pentoses followed by their dehydration in the presence of an acid catalyst. China is the largest producer of furfural (around 70% world production capacity) followed by Dominican Republic (around 12% of the world production) and South Africa (around 7% of the world production). The furfural production by these three countries accounts for 90% of the world production (280 kTon).[9]

Furfural is traditionally produced at an industrial scale by the process earlier developed by the Quaker Oats Company using oat hulls as feedstock and sulfuric acid as catalyst. Due to the low capital intensity and relatively inexpensive feedstocks, this old process is still the main route to furfural and account for about 80% of the global furfural supply.[10] However, this process is limited by a low furfural yield (40-50%).[11] Alternative processes currently under evaluation also employ soluble mineral acid catalysts, such as sulfuric, phosphoric, or hydrochloric acid. These processes still show major shortcomings, in particular the formation of undesirable tar-like materials, commonly referred to as humins.[12,13] Several studies have also been reported using solid acid catalysts such as zeolites and related materials,[14-20] micro-mesoporous silica-supported acids,[21-24] Keggin-type hetero-polyacids,[25-26] and sulfonated metal oxides.[27-29] Although good furfural yields were claimed, catalyst deactivation and low productivity currently hamper the industrial deployment of these routes.

To improve the selectivity to furfural, media combining water and γ-valerolactone (GVL) or methyl isobutyl ketone (MIBK) have been investigated.[30-31] At low xylose concentration (below 5 wt%) a yield to furfural up to 70% was reported. Conversely, at high concentration, the process suffers from xylose degradation to resinous compounds, leading to low furfural yield. Being able to increase the concentration of furfural, while preserving the selectivity of the reaction is of outmost interest as regards industrialization, but still remain an important scientific question.[32]

This works explores the catalytic synthesis of furfural from concentrated feeds of xylose (up to 50 wt%). Particularly, we investigate the beneficial effect of choline chloride (ChCl), a relatively cheap and biodegradable compound that can form a deep eutectic solvent with carbohydrates[33] and that was employed recently as a solvent for fractionating lignocellulose.[34] Here we demonstrate that ChCl was used as an additive in acidified water, exhibiting an important role on the initial production rate of furfural. We isolated for the first

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time the *in situ* formation of a choline xyloside intermediate which is a key intermediate in the reaction mechanism.

Experimental

Chemicals

D-(+)-Xylose (≥99%), HCl (36.5-38.0%), Choline chloride (≥99%), Furfural (99%), Benzyltriethylammonium chloride (99%), 1-Butanol (≥99%), 4-Methyl-2-Pentanone (≥99%, FCC), 2-Chloroethanol (99%), Acetyl chloride (reagent grade, 98%), Dichloromethane (≥99.8%) and methanol (anhydrous, ≥99.8%) were all purchased from Sigma-Aldrich.

General procedure for the dehydration of xylose to furfural:

A mixture of xylose, acidified water (pH=1.28 measured at room temperature, 250 µL of HCl 37% in 250 mL of water), ChCl and methylisobutylketone (MIBK) with a weight ratio of acidified water : MIBK of 1 : 20 was heated at 120°C in a close reactor. The reaction was performed under biphasic conditions and the furfural was extracted continuously by MIBK and the MIBK phase was analysed. MIBK can be evaporated, recycled and the isolated yield of furfural was 5 to 10% below the yield observed before evaporation.

Synthesis of choline xyloside

Choline xyloside was prepared in two steps from xylose following a route already reported for glucose.[35] Xylosylation of chloroethanol followed by SN2 reaction with trimethyl-amine and precipitation led to choline xyloside as a mixture of anomers.

Intermediate 2-chloroethyl D-xylopyranoside (α/β 70 to 30). To a solution of D-xylose (8g, 53.33 mmol, 1 equiv.) in chloroethanol (24 mL, 9 equiv.) was added acetyl chloride (3 mL, 42 mmol, 0.8 equiv.) at 0°C. The reaction was stirred at room temperature for 24 h under nitrogen atmosphere. After completing the reaction, solid $NaHCO_3$ was added until no more bubbling was observed. The mixture was then filtered and the solid was washed with ethanol. After concentration of the filtrate, the crude reaction mixture was purified by column chromatography (DCM : MeOH (9 : 1)] to give chloroethyl xylopyranoside α and β, without separation (9.6 g, 85%, α/β 70 to 30).

N-[2-(D-Xylopyranosyl)ethyl]-N,N,N-trimethylammonium chloride (α/β 80 to 20). A solution of 2-chloroethyl xylopyranoside (2.87 g, 13.5 mmol) in anhydrous ethanol (7 mL) was placed in In a 25 mL sealable round bottom flask equipped with a magnetic stirrer. A 33 wt% solution of trimethylamine in EtOH (13 mL, 54.8 mmol, 4 equiv) was then added and the tube was sealed and placed at 65°C for 60h. The formation of a white precipitate was observed and the reaction was cooled to room temperature. The product was collected by filtration and washed with cold absolute ethanol. The resulting highly hygroscopic white powder was rapidly placed under vacuum to remove the volatiles, yielding compound (2.26 g, 8.3 mmol, 62% yield) as a mixture of anomers (α/β 80 to 20).

Analytical methods

Gas chromatography analyses were performed on a Bruker GC-456 equipped with a column injector (250), a FID detector (325) and an HP-5 ms column (30 m x 0.25 mm x 0.25 µm). The calibration was performed using *n*-dodecane as internal standard. Xylose was quantified by external calibration at 25°C using a HPLC equipped with a NH_2 column, a RID detector, and a mixture of water/acetonitrile (3:7) as mobile phase (0.8 mL/min). NMR spectra were recorded on a Bruker Advance DPX 400 spectrometer. Mass spectrometry analysis was conducted by LC-QExactive Mass Spectrometry (Thermo) (Source Type ESI, Scan Begin 50 m/z, Scan End 1000m/z, Ion Polarity Positive). Thermal analysis was performed using a TA instrument (SDT Q 600 model) under an airflow rate of 100 mL (STP)/min and a heating rate of 5°C/min up to 200°C.

DFT calculations

Proton affinity calculations were carried out by TURBOMOLE v7.1.[36] The proton affinity (PA) of a molecule, B, is defined as the opposite number of the enthalpy change for the reaction $B+H^+ \rightarrow BH^+$ at 393.15 K

$$\boldsymbol{PA} = \Delta \boldsymbol{E_{el}} + \Delta \boldsymbol{ZPE} + \Delta \boldsymbol{E_{vib}}(\boldsymbol{T}) + \frac{\boldsymbol{5}}{\boldsymbol{2}}\boldsymbol{RT}$$

where ΔE_{el}, ΔZPE and ΔE_{vib} are the differences between the total electronic energy, the zero-point energy and the temperature-dependent portion of the vibrational energy of the base molecule and its protonated form, respectively. The 5⁄2 RT value corresponds to changes of thermal translational and rotational energies. The PA of the different isomers was calculated within the SCS-MP2-F12/cc-pVTZ-F12//B3LYP/6-31G* level, which successfully reproduced the PA of water. As a matter of fact, the calculated PA of water was 163.9 kcal/mol compared to the experimental value which was 165 kcal/mol.[37]

Results and discussion

A first experiment was carried out in the presence of an aqueous solution of 33 wt% xylose (125 mg) acidified with HCl (pH = 1.28) at 120°C (Figure 1, Figure S1) in the presence of MIBK (biphasic medium) to extract continuously the furfural produced from the aqueous phase. The acidified water : MIBK weight ratio was 1 : 20. A maximum furfural yield of 58% was achieved after 12 h with 96% xylose conversion. A second experiment was conducted by adding 60 wt% ChCl relative to water (250 mg, xylose/ChCl molar ratio of 0.77) to the biphasic system under the same reaction conditions (Figure 1, Figure S1). A higher furfural yield (68%) was obtained after 12 h of reaction with a xylose conversion higher than 90%. However, the initial production rate of furfural (mol of furfural obtained after 1 h of reaction) was higher in the presence of ChCl (0.257 mmol/h) than without ChCl (0.149 mmol/h).

To rationalize the higher production rate of furfural in the presence of ChCl, a series of control experiments were carried out. In a first approximation, it could be assumed that ChCl might induce a salt out effect as reported earlier for NaCl.[38-40] To this aim, an experiment was carried out by replacing ChCl

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by an equimolar amount of NaCl resulting in the formation of furfural in a two times lower reaction rate (0.257 mmol/h with ChCl *vs* 0.108 mmol/h with NaCl) thus excluding a salt out effect for ChCl (Figure 1, Figure S1). From this result, it is clear that ChCl displays another role in the reaction mechanism. Two hypotheses can be considered: 1) a stabilizing effect of furfural by ChCl as in the case of deep eutectic solvent, and 2) formation of an intermediate between ChCl and xylose or furfural.

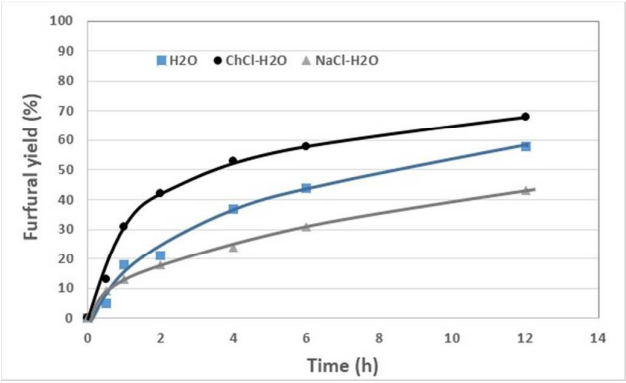


Figure 1. Effect of ChCl and NaCl on the furfural yield starting from xylose (33 wt%) in biphasic media (H_2O/MIBK = 1/20) at 120°C and a pH=1.28.

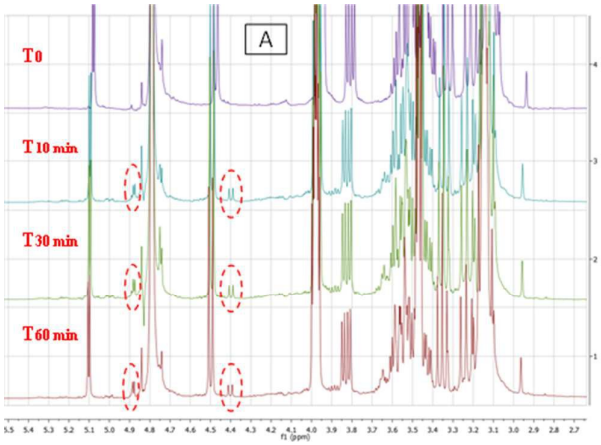
To assess if ChCl exerts a stabilizing effect on furfural, a series of thermogravimetry analyses were conducted keeping constant the xylose/ChCl/acidified water ratio (Table 1, Figure S2 A). The addition of ChCl to xylose revealed that the first weight loss was lower but at the same temperature than that observed without ChCl. The second weight loss occurred at a higher temperature (157°C *vs* 130°C), confirming an interaction between xylose and ChCl. When ChCl was added to the furfural, there was also a decrease of the first weight loss (39% *vs* 78%) and the third weight loss appeared at higher temperature (148°C *vs* 107°C) and the total weight loss was reduced from 100% to 76%. Relying on these results it seems that ChCl has also interaction with furfural. One can note that similar results were obtained in the absence of HCl (Figure S2 B, Table S1).

Table 1: Thermal analysis of different system (furfural/water, xylose/water with or without ChCl) in the presence of HCl.

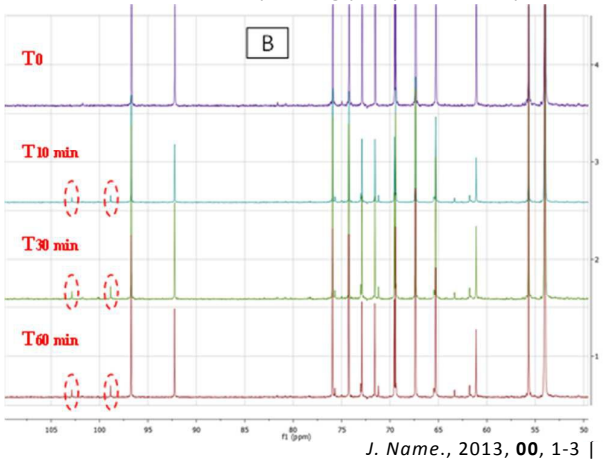
Entry	Compounds analysis	1stT weight loss (T°C/wt loss %)	2nd weight loss (T°C/wt loss %)	3rd weight loss (T°C/wt loss %)
1	Xylose/water/HCl	78/64	130/11	-
2	Xylose/water/ChCl/HCl	68/47	157/10	-
3	Furfural/water/HCl	80/78	96/9	107/13
4	Furfural/water/ChCl/HCl	83/39	98/19	148/18

To further understand the interactions between ChCl and xylose a series of dedicated NMR analyses were conducted. The ^{1}H NMR and ^{13}C NMR spectra were recorded for xylose/D_2O and xylose/D_2O/ChCl systems (Figure S3). Interestingly, at time = 0, a typical chemical shift belonging to C1Hα of xylose (Δδ = 0.0758 ppm ^{1}H NMR and Δδ = 0.1731 ppm ^{13}C NMR) and C1Hβ (Δδ = 0.0903 ppm ^{1}H NMR and Δδ = 0.2450 ppm ^{13}C NMR) of xylose was observed in both ^{1}H NMR and ^{13}C NMR spectra. This result confirms that ChCl has an interaction on xylose.

The reaction was then monitored at different reaction times (10 min, 30 min, 60 min) (Figure 2). Two additional doublets at 4.4 ppm and 4.9 ppm appeared after 10 min of reaction in ^{1}H NMR spectra, whereas two signals at 98 ppm and 102 ppm were clearly visible in the ^{13}C NMR spectra. The apparition of new signals corresponding to the anomeric positions of xylose cannot be ascribed to any isomer of xylose, such as xylulose which have different chemical shifts as reported earlier.[41] Hence, one may suspect that a chemical reaction between xylose and ChCl occurred. Fischer glycosylation of xylose with ChCl would be a rational explanation, ChCl bearing a primary -CH_2OH group. To confirm this hypothesis, choline xyloside intermediate was synthesized through a conventional route (ESI) and characterized by ^{1}H and ^{13}C NMR. The ^{1}H NMR spectrum of the as-obtained choline xyloside (Figure S7) showed a doublet centred at 4.4 ppm (β stereoisomer), while a second doublet appears at 4.9 ppm (α stereoisomer). Furthermore, the choline xyloside displays two typical signals at 98 ppm and 102 ppm in the ^{13}C NMR spectra which can be ascribed to the C1 of the xylose part belonging to the α and β choline xyloside (Figure S4). These chemical shifts



are strikingly similar to those obtained in Figure 2 providing evidence of an *in situ* and partial glycosydation of xylose with



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ChCl during the reaction.

Figure 2. NMR analysis (10 min / 30 min / 60 min). Condition: 250 mg xylose, 500 mg D_2O, 300 mg ChCl, 10 mL MIBK, pH=1.28, 120 °C; A) ^{1}H NMR spectra; B) ^{13}C NMR spectra.

The formation of choline xyloside during the reaction was further confirmed by HPLC-MS analysis of the reaction system with a peak at m/z = 236 clearly distinguished after 30 min (Figure 3).

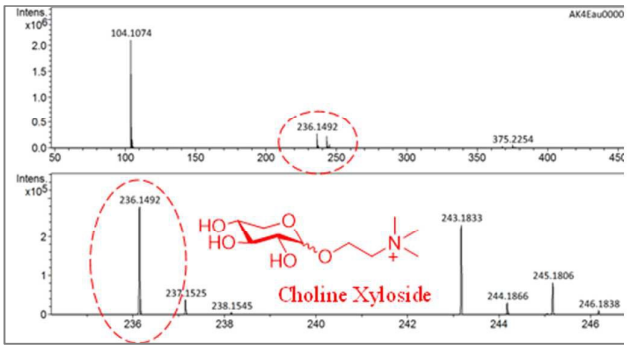


Figure 3. Mass spectrometry analysis of the reaction media after 30 min reaction starting from 33 wt% xylose, 60 wt% ChCl, water and MIBK at 120 °C and pH=1.28.

To assess the role of choline xyloside on the initial furfural production rate, a series of kinetic studies monitoring furfural formation from xylose or choline xyloside were conducted keeping rigorously the same reaction conditions (Figure 4, Figure S5).

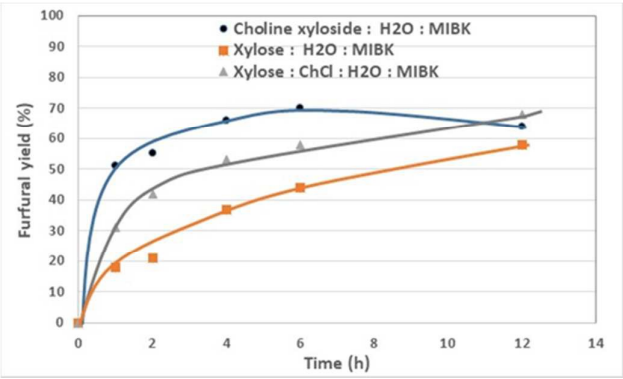


Figure 4. Comparison of the reactivity of choline xyloside and xylose at 120 °C and pH = 1.28.

The initial production rate of furfural was further improved (0.832 mmol/h) in the presence of choline xyloside without change of the maximum yield of furfural (70%). Replacing ChCl by a similar molar amount of benzyl triethyl ammonium chloride (BzTEACl, no possible glycosylation with xylose) during the reaction did not reveal any improvement of reaction rate confirming the particular behaviour of ChCl (Figure 5, Figure S6). One can mention that in the presence of an alkyl alcohol, the synthesis of furfural from xylose goes through the formation of an alkyl xyloside as reported in the literature but the concentration feed of xylose was very low (below 5 wt%).[42] For instance, using butanol in our conditions resulted in a viscous reaction media, which was very difficult to stir. The main advantage of using ChCl is its capability of converting a highly concentrated xylose feed to furfural compared to an alcoholic medium.

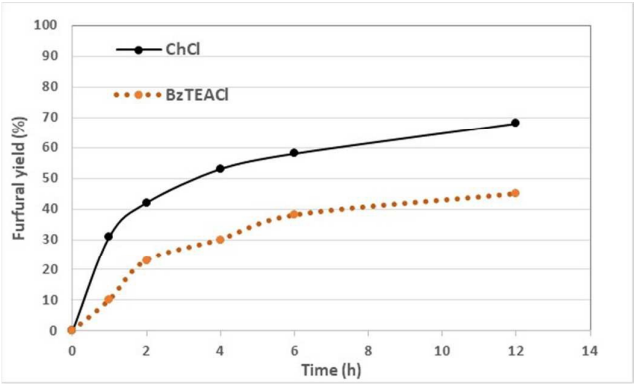
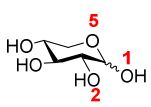


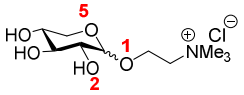
Figure5. Effect of the addition of BzTEACl (similar molar amount than ChCl) instead of ChCl in the synthesis of furfural from 33 wt% xylose, H_2O/MIBK weight ratio of 1 : 20, 120 °C and pH =1.28.

Different mechanisms have been reported in the literature for the synthesis of furfural from xylose, an acyclic mechanism (O-pryanose protonation followed by elimination) and two direct ring contraction mechanisms (triggered by either 1-OH or 2-OH protonation) :[43]

Table 2: DFT calculation of the proton affinity and pKa for xylose and choline xyloside



Xylose



Choline xyloside

	Oxygen	PA (method 1) kcal/mol	ΔPA (kcal/mol)
α-xylose	1-OH	185.0	-
	2-OH	184.5	-
	5-O	186.3	-
choline α-xyloside	1-O-ChXyl	175.0	-10
	2-OH	185.9	+1.4
	5-O	183.2	-3.1
β-xylose	1-OH	178.1	-
	2-OH	176.9	-
	5-O	183.3	-
choline β-xyloside	1-O-ChXyl	175.1	-3
	2-OH	188.2	+11.3
	5-O	183.0	-0.3

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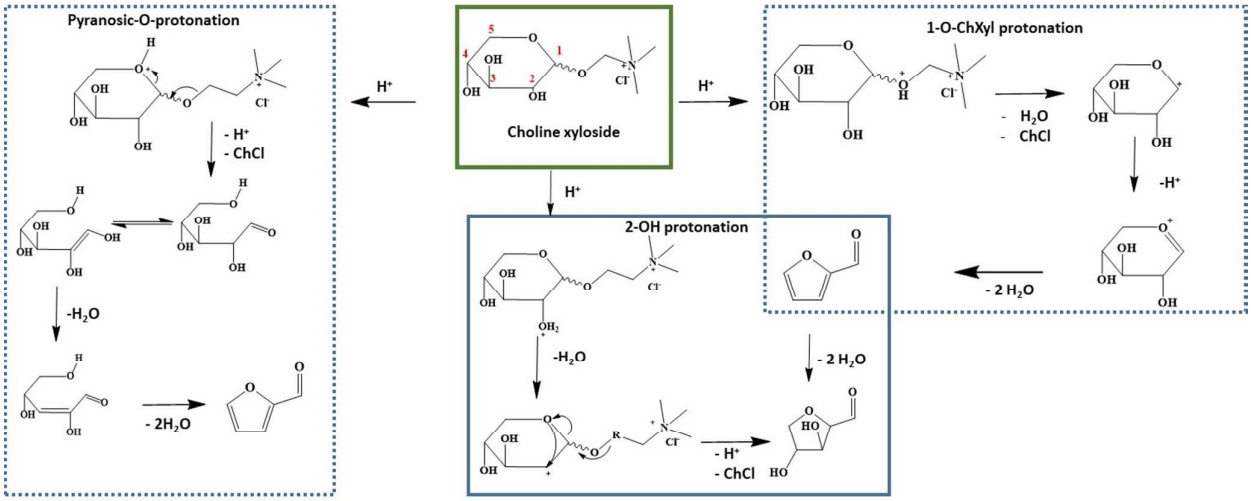
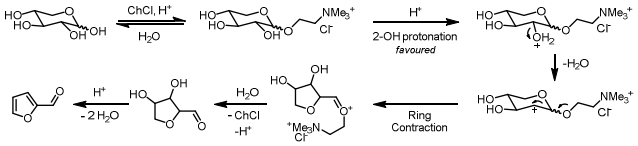


Scheme 1. Proposed mechanisms for choline xyloside dehydration to furfural through 1-O-ChXyl, 2_OH or pyranosic oxygen protonation

In the presence of ChCl, the formation of choline xyloside as an intermediate could be follow by the protonation of the pyranosic oxygen, or the 2-OH or the oxygen atom linked to xylose and choline chloride as described in scheme 1. For a sake of clarity this oxygen atom will be noted as 1-O-ChXyl. Three different possible reaction pathways can occur : (1) protonation of the pyranose oxygen which leads to ring opening, (2) a mechanism relying on 1-O-ChXyl protonation of choline xyloside followed by loss of a water molecule leads to the corresponding oxocarbenium, then a ring contraction generates a tetrahydrofuran derivative rapidly converted to furfural after double elimination of water (3) a mechanism where the 2-OH is protonated, generating the C-2 carbocation that undergoes ring-contraction, thus forming a tetrahydrofuran intermediate that dehydrates toward furfural.To determine the preferred reaction pathway in the presence of ChCl, the proton affinity (PA) was determined by single-point calculations by B3LYP/6-311G* structures using SCS-MP2-F12/cc-pVTZ-F12. Our aim was to rank O positions so we focused on the PA difference (ΔPA) between O positions instead of absolute PA values. The 2-OH positions of choline xyloside have higher PA than xylose. Indeed, the differences of PA for the α isomer and for theβ isomer are around 1 kcal/mol and 11 kcal/mol, respectively (Table 2). 2-OH positions of both xyloside isomers have the highest PA values among the three positions. Hence, in our conditions, the 2-OH position of choline xyloside is the most likely site for proton addition, and this step is followed by ring recombination. Moreover, the formation of a carbocation at C2 position was established in previous studies as the rate-limiting step for the conversion of xylose to furfural.[44-45]

Relying on these results and on the experimental data presented above, the mechanism suggested in the presence of ChCl follows the 2-OH protonation. First, the choline xyloside intermediate is generated. This intermediate can undergo ring contraction to form an oxonium-ion still incorporating the choline fragment. This classical intermediate of carbonyl chemistry is readily hydrolyzed in aqueous media to generate back the C-1 aldehyde and the choline chloride molecule (Scheme 2).



Scheme 2. Proposed mechanism for xylose dehydration to furfural through the formation of choline xyloside and 2-OH protonation.

The recovering of ChCl was then carried out. To this aim, the reaction was performed starting from 33 wt% xylose acidified with HCl (pH = 1.28) at 120°C in the presence of MIBK (acidified water : MIBK weight ratio was 1 : 20) and 60 wt% of ChCl. After the first catalytic run, the reaction medium was cooled down to room temperature and decanted. The MIBK phase was separated and the aqueous phase containing ChCl was washed again with MIBK to ensure the complete removal of organic soluble impurities from the aqueous phase. Then the aqueous phase was diluted with water, resulting in the

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precipitation of black materials formed during the reaction which were filtered off. Water was then evaporated and the recovered residue was dried overnight at 100 °C before analyzing by ^{1}H and ^{13}C NMR. It was shown that this solid was ChCl and that no structural modification was observed after the reaction since signals were similar to those obtained when commercial ChCl was analyzed (Figures S7, S8). One can mention that 95% of ChCl was recovered with high purity. The recycling of ChCl was then performed by adding fresh xylose (125mg) to an acidic solution of water in the presence of MIBK following the conditions described above. A 69% yield of furfural was obtained demonstrating the stability of ChCl under our working conditions and the possibility to recycle it.

Table 3: Effect of ChCl on the furfural yield starting from 50wt% of xylose in a biphasic media (H_2O/MIBK = 1/20) at 120°C and a pH of 1.28.

Entry	ChCl (wt%)	Initial formation rate of furfural (mmol/h)	Max. yield of furfural (%)	Time (h)
1	0	0.099	54	12
2	20	0.199	57	12
3	60	0.316	56	12
4	100	0.330	60 (60)*	6 (12)*
5	150	0.366	57	12

*The furfural yield was stable from 6 to 12 h.

We next explored the effect of choline chloride on the dehydration of a higher concentrated xylose solution (50 wt%). In these experiments, the ChCl concentration was kept at 60 wt%. We were delighted to see that the initial production rate of furfural was also enhanced (0.316 mmol/h, Table 3, entry 3) compared to the rate of the reaction medium without ChCl (0.099 mmol/h, Table 3, entry1). The maximum furfural yield was similar in both cases (60% *vs* 54%). Regardless on the concentration, ChCl exhibited a beneficial effect on the initial production rate of furfural (Table 3, Figure S9) a maximum rate being obtained for 150 wt% of ChCl (0.366 mmol/h). However, the highest furfural yield (60%) was achieved at a ChCl ratio of 100 wt% relative to water corresponding to a xylose : ChCl molar ratio of 0.93.

Based on all these results, it was interesting to see if the reaction time could be lowered to reach a furfural yield higher than 70%. A reaction was performed in an acid aqueous solution of a pH of 0.86 instead of 1.28 using 33.3 wt% of xylose at 120°C. We were pleased to see that after 3 h of reaction, 73% of furfural were obtained, for a total conversion of xylose and that after 4h of reaction the yield of furfural was 75% (Figure S10). This last result showed that by lowering the pH we could increase the reaction rate and the yield to furfural. The recycling of ChCl was also performed and similar yield to furfural (75% after 4h) was obtained with the recovered ChCl demonstrating again its recyclability.

Conclusions

Along this study, we have demonstrated that choline chloride can enhance the formation rate of furfural from a highly concentrated solution of xylose with a yield around 70% from 33 wt% xylose and 60% from 50 wt% xylose at a pH of 1.28 after 6h of reaction. If the pH was lowered to 0.86 the yield to furfural was enhanced to 75% after 4h of reaction showing that by decreasing the pH, the reaction rate and the yield of furfural could be increased. ChCl can be recovered after the reaction and was recycled successfully which is also of high interest. The formation of choline xyloside as an intermediate was found to promote the formation rate of furfural starting from a highly concentrated feed of xylose. The reaction mechanism was determined, relying first on the genesis of choline xyloside. This step is followed by the formation of a carbocation on the C2 position and ring con-traction, leading to furfural after further dehydration. To the best of our knowledge, it is the first time that such an intermediate is identified. Overall, the use of ChCl as a component of the biphasic medium appears as a beneficial approach for the synthesis of chemicals from highly concentrated feeds of carbohydrates, which will undoubtedly inspire research in the future.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

‡ For a sake of clarity, all the conversion curves are presented in the supporting information of the manuscript.

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