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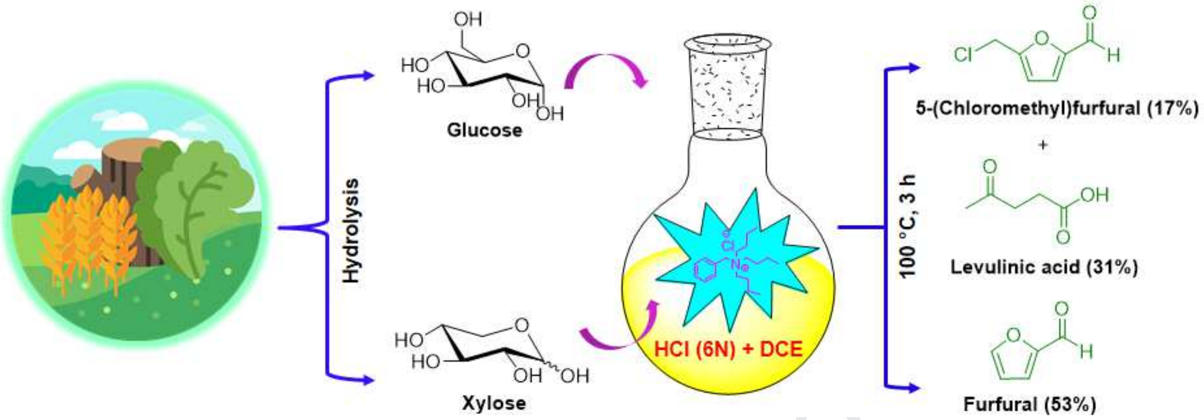
Graphical Abstract



Hydrochloric Acid-Catalyzed Coproduction of Furfural and 5-(Chloromethyl)furfural Assisted by a Phase Transfer Catalyst

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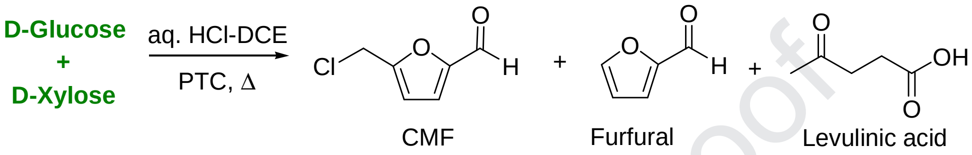
Abstract: Furfural has been produced in 53% isolated yields from D-xylose within an aqueous HCl-1,2-dichloroethane biphasic reaction mixture using benzyltributylammonium chloride (BTBAC) as a phase transfer catalyst. The use of BTBAC noticeably improved the yield of furfural compared to that in the control reaction. The reaction was optimized on the reaction temperature, duration, concentration of HCl, and the loading of BTBAC. Furfural and 5-(chloromethyl)furfural (CMF) have also been coproduced from a mixture of pentose and hexose sugars. Under optimized conditions (100 °C, 3 h, 20.2% HCl, 10 wt% BTBAC), CMF and furfural were isolated in 17% and 53% yield, respectively, from a mixture of glucose and xylose. In addition, levulinic acid was isolated from the aqueous layer in 31% yield.

Keywords: biomass, 5-(chloromethyl)furfural, furfural, phase transfer catalyst, renewable synthesis.

1 Introduction

The renewable and carbon-neutral character of biomass makes it an environment-friendly alternative to the exhaustible fossilized carbon sources for the production of liquid transportation fuels and chemicals [1]. A major challenge for the conversion of biomass into fuels and chemicals is the depolymerization and selective deoxygenation of the complex, oxygen-rich biopolymers [2]. The chemocatalytic value addition of biomass in the biorefinery realm is of particular interest since they are fast, selective, biomass agnostic, and could potentially be integrated into the existing petrorefinery infrastructure [3]. Feedstock plays a pivotal role in the commercial feasibility of a biorefinery. In this regard, carbohydrates in the form of cellulose and hemicellulose constitute more than half of the total mass of terrestrial and algal biomasses [4]. Glucose receives special interest since it is abundant, inexpensive, and the monomer of the most abundant biopolymer cellulose. Hemicellulose is the second most abundant polysaccharide (20-35% of lignocellulosic biomass), where xylose is one of the major constituents [5]. The acid-catalyzed dehydration of sugars is an elegant strategy that allows selective removal of the oxygen atoms and excessive functionalities from the sugar moiety in the form of water. Since the transformations do not involve any carbon-carbon bond scission reactions, the carbon efficiency is quantitative. The production of furfural and 5-(hydroxymethyl)furfural (HMF) from xylose and glucose, respectively, are known for over a century, and the commercial production of furfural was realized in as early as 1921 [6]. Furfural and HMF retain some of the reactive functional groups of the parent sugars that can be exploited for downstream value-addition pathways [7]. Both furfural and HMF have been demonstrated as renewable chemical building blocks that can be transformed into fuels, specialty chemicals, and materials by selective chemical transformations [8, 9]. Over the past three decades, hundreds of publications and patents have been dedicated to the production and application of furfural and HMF, and several comprehensive reviews have summarized these works [10-12]. Although HMF is routinely obtained in high yields from simple sugars like fructose, the high-yielding production of HMF from cellulosic biomass often requires special reaction conditions [13]. The commercial production of HMF is plagued by the hydrophilicity and inherent instability of HMF in aqueous acid [14]. The coproduction of HMF and furfural from a mixture of pentose and hexose sugars, as well as lignocellulosic biomass, is also reported [15]. In recent years, 5-(chloromethyl)furfural (CMF), a hydrophobic congener of HMF, has been explored as a functional substitute for HMF. CMF can be synthesized in high isolated yields even from carbohydrates and untreated cellulosic biomasses, alike [16]. CMF has been demonstrated as a renewable chemical platform for the synthesis of a diverse range of specialty chemicals [17]. Therefore, an efficient coproduction of furfural and CMF from the mixture of glucose and xylose could work as a working model for terrestrial and algal biomasses. An aqueous-organic biphasic reaction is frequently adopted for the production of furanics from biomass [18]. The idea is to sequester the furanic molecules into the organic phase as soon as they form and slow down their decomposition in aqueous acid. Benzyltributylammonium chloride (BTBAC) is a known phase transfer catalyst (PTC) for various organic synthetic applications [19]. In a recent report, we had shown that CMF could be prepared from various carbohydrates in concentrated hydrochloric acid-1,2-dichloroethane (DCE) biphasic reaction using BTBAC) as a PTC [20]. The use of BTBAC afforded higher isolated yields of CMF when compared to the control reactions. We reasoned that the hydrophobic environment created by the PTC shielded the reactive intermediate species during the formation of CMF, thereby increasing the selectivities and yields of the same. We envisaged that the process could also be extended for the production of other furanic molecules such as furfural. In this work, we report the production of furfural from biomass-derived pentose sugars like xylose in aq. HCl-DCE biphasic system using BTBAC as a phase transfer catalyst. The reaction was optimized on reaction temperature, duration, loading of BTBAC, and concentration of HCl. The optimized reaction condition was then applied for the one-pot coproduction of furfural and CMF from a mixture of pentose and hexose sugars such as glucose and xylose (Scheme 1). The 20.2%HCl-DCE biphasic reaction was conducted in a glass pressure reactor in the presence of BTBAC (10 wt.%) as additive. The azeotropic concentration of HCl was used to allow straightforward recovery of the aqueous acid by distillation while minimizing the decomposition of BTBAC.



Scheme 1. Coproduction of CMF and furfural from a mixture of glucose and xylose in the presence of a phase transfer catalyst.

2 Results and Discussion

Initially, the preparation of furfural from xylose was attempted using aqueous HCl (20.2%)-DCE biphasic medium. The use of azeotropic HCl helped to avoid degassing of hydrogen chloride during the reaction. The acid catalyst could be recovered conveniently via distillation without altering the concentration. DCE was chosen as the solvent due to its availability in bulk, intermediate boiling point, chemical inertness under the reaction conditions used, and recoverability by distillation. The loading of xylose was initially fixed at 5 wt.% compared to the amount of aqueous HCl used. In a typical reaction, xylose was dissolved in aqueous HCl (20.2%) taken in a sealed round-bottomed glass pressure reactor fitted with a Teflon screw-top and a magnetic stir bar. The solvent (i.e., DCE) and BTBAC (10 wt.% of xylose) were added before the reactor was sealed. The reactor was then placed in a pre-heated (100 °C) oil-bath and stirred magnetically at 400 rpm for 3 h. The reactor was then cooled down to RT, opened, and the mixture was transferred into a separatory funnel. The DCE layer was separated, dried, and distilled off under reduced pressure to isolate furfural. The control reaction was carried out under the same reaction conditions, except no BTBAC was added. The reaction with BTBAC as the PTC afforded furfural in 53% isolated yield, whereas the yield of furfural in the control reaction was only 34% (Table 1). The mass balance is the soluble and insoluble humin formation, which was noticeably more in the control reaction.

Table 1. Preparation of furfural from D-xylose using various Brønsted acid catalysts. Reaction Conditions: Xylose (1 g), aqueous acid (20 mL), DCE (40 mL), BTBAC (0.1 g)

S/N	Catalyst	Reaction conditions	Yield (%)[b]
1	HCl (20.2%, 6M)	100 °C, 3 h	53 (34)[c]
2	H_2SO_4 (6M)	100 °C, 3 h	35 (20)
3[a]	CF_3CO_2H (6M)	100 °C, 20 h	19 (08)
4	CH_3SO_3H (6M)	100 °C, 3 h	28 (21)
5	H_3PO_4 (6M)	100 °C, 5 h	22 (15)

[a] The yield of furfural was poor (<5%) after 3 h. [b] Isolated yield. [c] The yield of furfural in the control reaction.

Various frequently used Brønsted acid catalysts were examined for the preparation of furfural as described in Table 1. When sulfuric acid was used as the acid catalyst (entry 2), furfural was isolated in 35% yield within 3 h at 100 °C, whereas the control reaction provided only 20% yield under identical conditions. Methanesulfonic acid (entry 4) provided marginally lower yield, but the positive effect of BTBAC on the furfural yield was still pronounced. Weaker acids, like trifluoroacetic acid (entry 3) and orthophosphoric acid (entry 5), provided lower yields of furfural even after significantly longer reaction time. Interestingly, the yields of furfural in the control reactions were still noticeably lower. The results may be explained by the continuous decomposition of furfural during the course of the reaction, even when the conversion of xylose remain low.

Since aqueous hydrochloric acid (20.2%) was found to be the most effective catalyst, the reaction was further optimized on other reaction parameters for the best selectivity and yield of furfural starting from xylose.

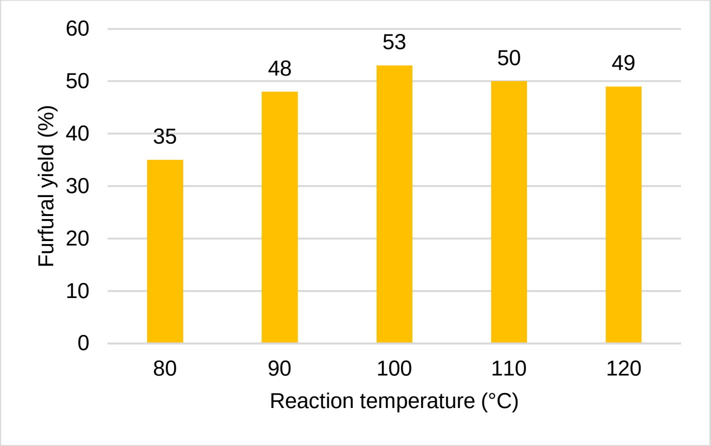


Figure 1. The effect of reaction temperature on furfural yield. Reaction conditions: xylose (1 g), BTBAC (0.1 g), DCE (40 mL), aq. HCl (20.2%, 20 mL), 3 h.

At first, the effect of reaction temperature was studied by keeping the other reaction parameters unchanged. When the reaction was conducted at 80 °C, only a 35% yield of furfural was isolated (Figure 1). Increasing the reaction temperature to 100 °C increased the yield significantly to 53%. Further increase in temperature marginally decreased the yield of furfural. The results may be explained by the incomplete conversion of xylose at lower temperatures, whereas faster decomposition at higher temperatures. When the reaction was carried out under reflux, furfural was isolated in only 23% yield after 3 h, which increased up to 29% after 6 h of reaction time. The control reaction under identical conditions (reflux, 3 h) provided 14% yield of furfural.

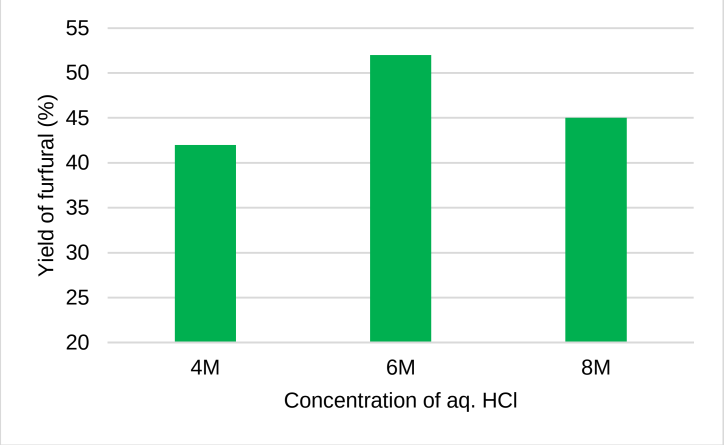


Figure 2. The effect of aqueous HCl concentration on furfural yield. Reaction conditions: xylose (1 g), BTBAC (0.1 g), DCE (40 mL), aq. HCl (20 mL), 100 °C, 3 h.

The effect of the concentration of aqueous HCl on the isolated yield of furfural was then explored. The use of 4M HCl provided only 42% of furfural (100 °C, 3 h) (Figure 2). The result may be rationalized by the incomplete conversion of xylose at lower acid concentration. Increasing the acid concentration to 8 M also lowered the yield of furfural to 45% compared to 53% in 20.2% (6 M) HCl. The result may be explained by the instability of the BTBAC catalyst at higher concentrations of HCl [21].

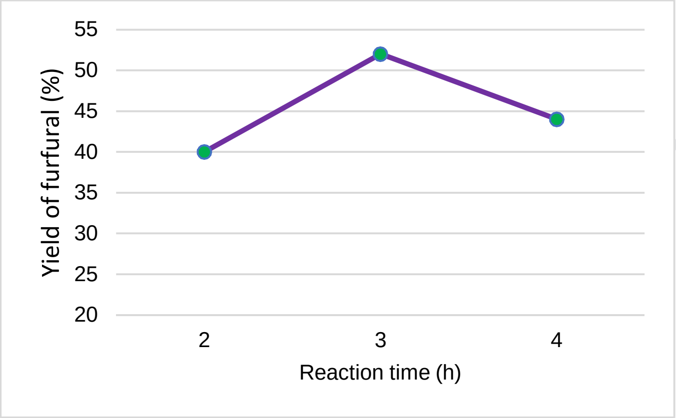


Figure 3. Effect of the duration of reaction on the yield of furfural. Reaction conditions: xylose (1 g), BTBAC (0.1 g), DCE (40 mL), HCl (20.2%, 20 mL), 100 °C.

The effect of the duration of reaction, keeping the reaction temperature fixed at 100 °C (Figure 3). After 2 h of reaction time, the yield of furfural was only 40% due to incomplete reaction. However, prolonged reaction time (ca. 4 h) also lowered the yield of furfural due to more decomposition. Though the use of less BTBAC (5 wt.%) led to lower yield of furfural (ca. 48%), higher loadings of BTBAC (10 wt.%) did not show any discernible improvement in the yield of the same. The formation of insoluble humin as black solid was found to be only 0.036 g for 1 g of xylose under the optimized conditions.

The optimized reaction was then applied for the coproduction of CMF and furfural starting from a mixture of xylose and various hexoses. The products could be separated by column chromatography in the laboratory scale or by fractional distillation in a larger scale. The relative ratio of products was also calculated by the integration of peaks in the ^{1}H-NMR spectrum. The isolated mass of CMF and furfural conformed well to the NMR data. When a mixture of glucose and xylose was used as the feedstock, CMF, and furfural were isolated in 17% and 53% yields, respectively, under the optimized conditions (Table 2, entry 1). Interestingly, when glucose was used alone, CMF was isolated in similar yields (ca. 18%).

Therefore, the use of physical mixture of pentose and hexose sugars did not affect the individual yields of furfural and CMF. Due to low concentration of chloride ion, the yields of CMF remained low for all the hexoses studied. When NaCl was used in excess, the yield of CMF improved to 29% (with BTBAC). We envisioned that instead of forming CMF, the HMF intermediate would likely tranform into LA in the aqueous layer. Extraction of the aqueous acid with ethyl acetate afforded 31% of LA in the reaction using BTBAC. The yields of CMF and furfural in the control reaction were 12% and 34%, respectively. When the combination of sucrose and xylose was used (entry 2), CMF and furfural were isolated in 16% and 51% yields. The combination of fructose and xylose (entry 3) provided comparable yields. The yields of CMF were nearly same for all the polymeric carbohydrates (entry 4-6) and higher than those in the control reactions. Interestingly, furfural was isolated in similar yields from all the mixtures of sugars examined. The insoluble humin formation is noticably higher in the control reaction compared to reactions using BTBAC. For example, the mixture of glucose and xylose (entry 1) produced 0.025 g of insoluble humin as black solid compared to 0.052 g of the same in the control reaction. The BTBAC catalyst was separated from the product by column chromatography (Silica Gel 60-120 mesh) eluting with 20% MeOH in $CHCl_3$. Alternatively, selective dissolution of the furanics in hot petroleum ether (60-80 °C) left behind BTBAC in excellent mass balance (>95%). The use of recovered BTBAC for the preparation of furfural or for the coproduction of CMF and furfural did not show any noticeable change in isolated

Table 2. Coproduction of furfural and CMF. Reaction conditions: HCl (20.2%, 20 mL), DCE (40 mL), 100 °C, 3 h, 0.5 g of each substrate, 0.1 g BTBAC.

S/N	*Substrate*	*Yield (%) with BTBAC*		*Yield (%) without BTBAC*	
		CMF	*Furfural*	*CMF*	*Furfural*
1[a]	Glucose+Xylose	17	53	12	34
2	Sucrose+Xylose	16	51	10	34
3	Fructose+Xylose	16	52	12	35
4	Inulin+Xylose	15	49	11	32
5	Starch+Xylose	16	48	11	33
6	Cellulose+Xylose	15	48	10	32

[a] LA was isolated from the aqueous layer in 31% (with BTBAC) and 15% (without BTBAC) yields, respectively.

yields up to three consecutive cycles. The chemical stability of BTBAC was confirmed by NMR spectrocpy and no perceptible chemical decomposition was observed.

3 Experimental Section

3.1 Production of furfural from xylose

Xylose (1 g) was taken in a 100 mL round-bottomed glass pressure reactor fitted with a Teflon screw-top. To this, aqueous HCl (20.2%, 20 mL), DCE (40 mL), and BTBAC (0.100 g) were added. A magnetic stirring bead was added, and the pressure reactor was sealed. The reactor was placed in a pre-heated oil bath (100 °C) the reaction mixture was magnetically stirred continuously for 3 h. After the reaction, the reactor was removed from the oil bath and cooled down to room temperature. The reactor was opened, and the reaction mixture was transferred into a separating funnel. The DCE layer was separated, and the aqueous phase was extracted with fresh DCE (2×10 mL). The DCE layers were combined, dried over anhydrous Na_2SO_4, and passed through a plug of silica gel (60-120 mesh). Evaporation of DCE in a rotary evaporator under reduced pressure provided furfural as light yellow oil (0.340 g, 53%). The control reactions were performed as described above, except no BTBAC was used. The FTIR and ^{1}H-NMR spectroscopy confirmed the identity and purity of furfural. The FTIR and ^{1}H-NMR spectroscopy confirmed the identity and purity of furfural. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 9.67 (s, 1H), 7.70 (s, 1H), 7.27 (d, 1H, *J* = 3.6 Hz), 6.61 (d, 1H, *J* = 3.6 Hz); ^{13}C{^{1}H}-NMR ($CDCl_3$, 75 MHz) δ (ppm): 177.8, 152.9, 148.1, 121.2, 112.6; FTIR (ATR, cm^{-1}): 3133, 2924, 2852, 2811, 1669, 1463, 745.

3.2 Coproduction of CMF and furfural from the mixture of glucose and xylose

Xylose (0.500 g) and glucose (0.500 g) were taken in a 100 mL round-bottomed glass pressure reactor fitted with a Teflon screw-top. To this, aqueous HCl (20.2%, 20 mL), DCE (40 mL), and BTBAC (0.100 g) were added. A magnetic stirring bead was added, and the pressure reactor was sealed. The reactor was placed in a pre-heated oil bath (100 °C) the reaction mixture was magnetically stirred continuously for 3 h. After the reaction, the reactor was removed from the oil bath and cooled down to room temperature. The reactor was opened, and the reaction mixture was filtered through a filter paper. The filtrate was transferred into a separating funnel. The DCE layer (bottom) was separated, and the aqueous phase was extracted with fresh DCE (2×10 mL). The DCE layers were combined, dried over anhydrous Na_2SO_4, and evaporated in a rotary evaporator under reduced pressure to provide the crude mixture of CMF and furfural as a brown oil. The components were separated by column chromatography (Silica gel) using a mixture of petroleum ether and ethyl acetate as eluent. Evaporation of the solvent produced furfural (0.170 g, 53%) and CMF (0.068 g, 17%) as a light yellow oil. The control reactions were performed as described above, except no BTBAC was used. The ^{1}H-NMR spectrum of the mixture of CMF and furfural showed the same molar ratio of products as calculated by the integrals of the relevant peaks of each compound.

3.3 Isolation of Levulinic Acid:

The aqueous layer was filtered through a filter paper, and the filtrate was saturated by adding solid sodium chloride. The saturated solution was cooled and extracted with ethyl acetate (6×20 mL). The ethyl acetate layers were combined, dried over anhydrous Na_2SO_4, and evaporated in a rotary evaporator under reduced pressure to yield a brown liquid. The liquid was chromatographed over silica gel (60-120 mesh) using diethyl ether as eluent. Evaporation of the solvent provided levulinic acid (LA) as light yellow oil (0.099 g, 31%). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 2.75 (t, 2H, *J* = 6.3 Hz), 2.62 (t, 2H, *J* = 6.3 Hz), 2.20 (s, 3H); ^{13}C{^{1}H}-NMR ($CDCl_3$, 75 MHz) δ (ppm): 206.6, 177.8, 37.7, 29.8, 27.7; FTIR (ATR, cm^{-1}): 3163, 2923, 1702, 1236, 1161.

3.4 Quantification of Humin:

The aqueous layer was passed through a filter paper, and the filter paper was washed with excess distilled water. The filter paper was dried in a hot-air oven at 60 °C till a constant weight was achieved.

3.5 Recovery and Characterization of BTBAC:

After isolating CMF from the silica-gel column, the column was eluted with 20% methanol/DCM to recover the BTBAC. A 97% recovery of BTBAC was obtained using this technique. Alternatively, the mixture of furfural, CMF, and BTBAC was triturated with petroleum ether under reflux. Both CMF and furfural dissolved in hot petroleum ether and decanted, whereas BTBAC is recovered as a beige solid in near quantitative yield. The recovered BTBAC was characterized by FTIR and ^{1}H-NMR spectra and compared with literature data. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.33 (m, 5H), 4.68 (s, 1H), 3.15 (m, 6H), 2.98 (s, 1H), 1.65 (m, 6H), 1.28 (m, 6H), 0.84 (t, 9H); FTIR (ATR, cm^{-1}): 3300, 2928, 1704, 1211, 1161.

Conclusions

The use of BTBAC afforded significantly higher yields of furfural starting from xylose when compared to the control reaction. The insoluble humic matter formed in noticeably lower quantities in reactions using BTBAC. CMF and furfural were coproduced from a physical mixture of xylose and hexose carbohydrates. The yields of CMF and furfural were higher when using BTBAC as PTC. The azeotropic concentration of HCl allowed conducting the reaction under the refluxing condition without evaporative loss of the HCl gas. No chemical decomposition of BTBAC was observed, and it was recovered in near-quantitative yield after the reaction BTBAC was conveniently separated from the product mixture by chromatography or trituration with petroleum ether.

Supporting Information Summary

The spectral data are provided as supporting information.

Acknowledgments

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Conflict of Interest

The authors declare no conflict of interest

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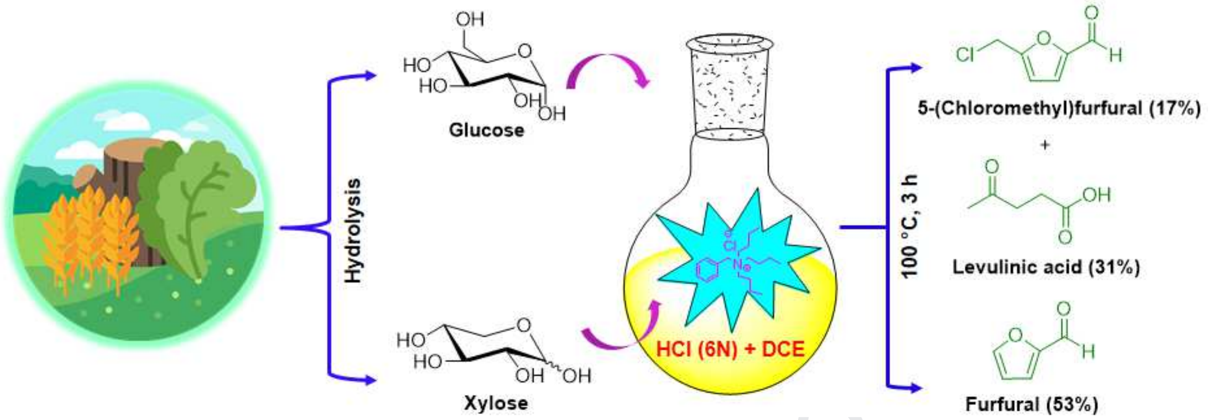
[21] The ^{1}H-NMR spectrum of the recovered BTBAC showed peaks of benzyldibutylammonium salt.

Graphical Abstract



Highlights

- Furfural has been produced in good isolated yield from xylose in an aqueous-organic biphasic batch reactor using benzyltributylammonium chloride (BTBAC) as a surface-active agent.
- Hydrochloric acid was found to be the most active catalyst that provided furfural in 53% yield within 3 h at 100 °C under 10 wt% loading of xylose and 1,2-Dichloroethane (DCE) as the organic extractant.
- BTBAC improved the yield of furfural noticeably compared to the control reaction.
- Furfural and 5-(chloromethyl)furfural (CMF) were coproduced starting from a mixture of xylose and glucose. In addition, levulinic acid (LA) was isolated from the aqueous phase.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: