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FULL PAPER

Acid-Catalysed Conversion of Carbohydrates into Furan-Type Molecules in Zinc Chloride Hydrate

Iurii Bodachivskyi,[a] Unnikrishnan Kuzhiumparambil,[b] and D. Bradley G. Williams *[a]

Abstract: Acid-catalysed conversion of biomass, specifically cellulose, holds promise to create value-added, renewable replacements for many petrochemical products. We investigated an unusual acid-catalysed transformation of cellulose and cellobiose in the biphasic solvent system zinc chloride hydrate (ionic liquid)/anisole. Here, furyl hydroxymethyl ketone and furfural are obtained as major products, which are valuable but less commonly formed in high yields in transformations of cellulosic substrates. We explored this chemistry in small-scale model reactions and applied the optimised methods to the conversion of cellulose in bench-scale processes. The optimum reaction system and preferred reaction conditions are defined, to select for highly desirable furanoid products in the highest known yields (up to 46%) directly from cellulose or cellobiose. The method avoids the use of added catalysts: the ionic solvent zinc chloride hydrate possesses the intrinsic acidity required for the hydrolysis and chemical transformation steps. The process involves inexpensive media for the catalytic conversion of cellulose into high-value products under mild processing conditions.

Introduction

In the past few decades there has been a significant and growing interest in acid-catalysed transformations of carbohydrates into value-added organic building block chemicals (platform molecules). These molecules are diverse and represent a platform with the potential to replace a large portion of crude oil-based products such as fuels, plastics, coatings, detergents, and other useful commodities.[1–6] The application of ionic liquids (ILs), as alternative reaction media to common aqueous and organic solvents, in the valorisation of polysaccharides has enabled substantial progress towards mild reaction conditions and improved yields and selectivities.[5,6] That many ILs fully dissolve cellulosic material under mild conditions is a primary enabler towards high yields and selectivity, although secondary reasons exist for the success of ILs in this context.[6] Pertinent examples of successful applications of ILs include the transformation of cellulose into low-molecular-weight reducing sugars in 99% yield within 1 h at 100 °C (solvents 1-methyl-3-butylimidazolium chloride and triethyl-(3-sulfopropyl)-ammonium hydrogen sulfate),[7] into 5-(hydroxymethyl)furfural (HMF) in 79% yield within 2 h at 120 °C (solvent 1-butyl-3-methylimidazolium chloride),[8] or into levulinic acid in 40% yield in 2 h at 120 °C (solvent 1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate),[9] all of which are arguably benchmark instances of the chemical processing of cellulose into target platform molecules. Drawbacks of the use of ILs include the complexity of recovery of ionic solvents and products from the reaction media, along with their high cost, and these pose potential hurdles to their widespread acceptance in industrial scale processes.[6] There is thus an imperative to develop and employ inexpensive ILs that are able to facilitate the efficient processing of polysaccharides and which are easy, or relatively so, to recover; this remains a goal for workers in this field.

While common ILs suffer some drawbacks as mentioned, inorganic molten salt hydrates show promise to avoid some of these issues. Such ionic systems possess inherent acidity, as well as low viscosity compared to common quaternary ammonium salts, and have been demonstrated to be suitable media for the dissolution of cellulose.[10–12] With commodity level pricing of some inorganic salts and the ease of preparation of their hydrates, these ILs are budding candidates for the chemical conversion of cellulose. Zinc chloride hydrate with the formula $ZnCl_2{\cdot}nH_2O$ (n = 3–4; this system is considered to be an IL. Although the conventional presentation of the molecular formula of zinc chloride hydrate is $ZnCl_2{\cdot}nH_2O$, its formula is more accurately represented as $[Zn(OH_2)_6][ZnCl_4]$ in the case of n = 3, based on solid state and liquid state determinations.[13,14]) is useful in the conversion of polysaccharides into furan-type molecules, typically into HMF.[15–18] The processes detailed in these papers require lengthy pretreatment of the substrates, the use of microwave irradiation, or high loading of acid catalyst, all of which inhibit the ability to scale up such processes.[6] It remains an unsolved problem to convert polysaccharides in such IL solvent systems into one or two major products under mild reaction conditions using techniques that are potentially scalable.

The present work discloses the functionality and potential of zinc chloride hydrate solvent in the catalytic conversion of carbohydrates into unusual furan-type molecules (i.e. products that are valuable but less seldom obtained during the conversion of cellulose) under mild reaction conditions.

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Results and Discussion

To explore the course of the hydrolytic conversion of polysaccharides towards platform molecules in $ZnCl_2{\cdot}3H_2O$, the processing of microcrystalline cellulose (MCC) was performed. Firstly, MCC was dissolved in this IL (loading of cellulose 1 wt% based on IL, 80 °C, 1 h) and then the solution was heated under constant agitation at 120 °C for 1 h during which the mixture became dark-brown coloured. Dilution of the reaction medium after completion of the process, with aqueous sodium hydrogen carbonate, led to precipitation of the unreacted cellulose and conversion of zinc chloride into insoluble zinc salts. The aqueous phase yielded three main products, being HMF, its isomer furyl hydroxymethyl ketone (FHK), and furfural (FF), each in yields below 3.0 mol% based on the number of anhydroglucose units present in the cellulose substrate. It is worth noting that low-molecular-weight sugars, and the product of rehydration of furanoids, namely, levulinic acid, were identified in trace amounts only. However, there was a mass of dark-brown colour solids in the water phase: these are typically considered to be high-molecular-weight by-product humins.[6] The portfolio of products suggests that cellulose hydrolyses into monomer glucose under these reaction conditions, and that the glucose transforms rapidly into HMF and FHK in the acidic reaction media. We propose that this process proceeds, under our conditions, via hydrolysis of cellulose into glucose, followed by isomerisation of glucose into ketohexoses and their subsequent dehydration into furanoid products. To test this proposal, we performed liquid chromatography-mass spectrometry (LC-MS) analysis of the recovered reaction media. The results confirmed the presence of glucose and its two isomers fructose and an unidentified ketohexose sugar, as proposed in Scheme 1 and presented in Figure S1. FF is most likely formed in a sequence that involves conversion of the intermediate hexose sugar fructose into one or more pentose products (e.g., arabinose) followed by dehydration into furan derivatives, as has been disclosed in the literature.[19] This dehydration process would be catalysed by the $ZnCl_2$, which is acidic in nature, and is driven by aromatic stabilisation. The furan-type molecules are unstable in $ZnCl_2{\cdot}3H_2O$ and are converted into high-molecular-weight by-products, arguably by condensation with low-molecular-weight sugars as was recently highlighted.[20]

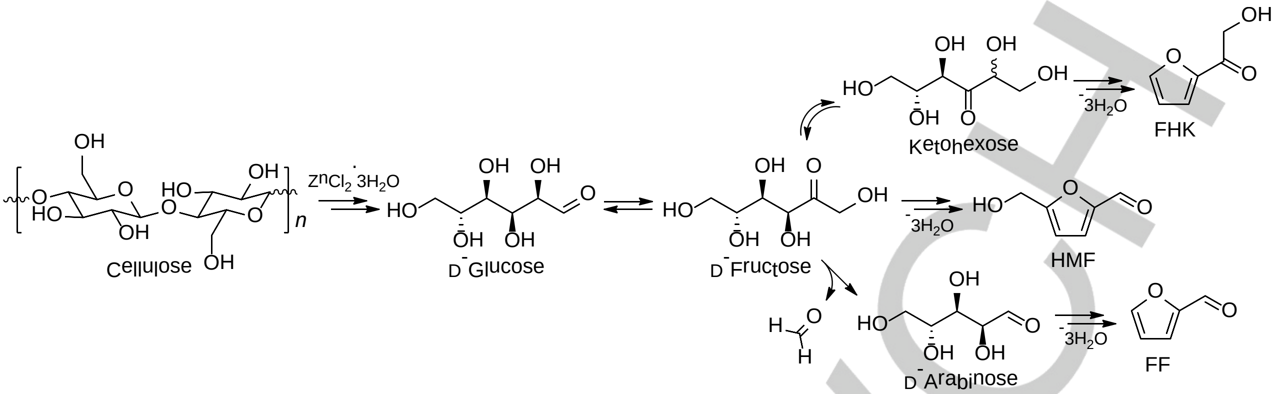
To improve the outcome towards platform molecules, we investigated the influence of loading of cellulose in the medium, and reaction temperature and time. In no case did the reaction afford products in yields higher than 5 mol%, persistently accompanied by humins. The only useful strategy was the continuous extraction of furan derivatives by *m*-xylene during the process, which separates reactive furan derivatives from the acidic medium/catalyst. This was accomplished by the addition of this solvent-extractant from the start of the reaction. Additionally, we identified that dilution of $ZnCl_2{\cdot}3H_2O$ with a small amount of water (1 equivalent volume based on the weight of IL) after completion of the process serves to better extract products into the organic solvent phase, likely due to disruption of the ionic solvent and a salting out effect. Analysis of the products in the polar and *m*-xylene phases showed improved yields of FHK and FF of 16 and 13 mol%, respectively, but HMF was present only in trace amounts (Table 1). It is worth noting that FF was found predominantly in the xylene phase, while FHK was present in both the organic solvent and the polar aqueous phase. The incomplete separation of the polar product FHK from the acidic IL by xylene would prolong its exposure to the acidic conditions, leading to its partial decomposition.

Table 1. Yields of furan derivative from the processing of cellulose in the biphasic system $ZnCl_2{\cdot}3H_2O$/organic solvent and partition coefficients of products.

Solvent	FHK yield, [mol%][a]	log P[b]	FF yield, [mol%][a]	log P[c]
m-Xylene	16	–0.93	13	0.64
tert-Butylbenzene	16	–0.45	11	0.48
Anisole	20	0.03	8	0.98
4-Methylanisole	14	–0.37	1	0.97
1,2-Dimethoxybenzene	12	–0.57	11	–0.63
2-*sec*-Butylphenol	6	0.79	2	1.79

[a] mol% based on anhydroglucose unit. [b,c] Logarithm of partition coefficient of product between the organic solvent and the water-diluted ionic liquid (1:1 wt/v IL/water) for FHK and FF, respectively. Reaction conditions: MCC (5 mg), $ZnCl_2{\cdot}3H_2O$ (500 mg), solvent-extractant (2.00 mL), 120 °C, 1 h.

It had become clear that one method to improve the yield of desirable products, FHK in particular, was to extract them into a phase separate from the reaction medium, such as into an organic solvent. But a more efficient means of removal of products from the IL phase was required, and so we investigated various organic solvents for this purpose. It is worth noting that common polar high boiling solvents, such as dimethylformamide, dimethylsulfoxide, γ-valerolactone, and methyl isobutyl ketone, which are useful for the conversion of carbohydrates in water-based biphasic systems,[4,6] are miscible with $ZnCl_2{\cdot}3H_2O$, and cause precipitation of cellulose. In turn, aromatic solvents like *tert*-butylbenzene, anisole, 4-methylanisole, 1,2-dimethoxybenzene, or 2-*sec*-butylphenol form a second phase, and therefore maintain the polar phase of the reaction system, in which cellulose remains dissolved. All of these aromatic solvents were applied to the conversion of MCC in a biphasic system; among them, anisole afforded high overall yields of and selectivity to FHK and FF (20 and 8 mol%, respectively, Table 1). This result may be rationalised by the higher partition coefficients of products in anisole, which serves to efficiently remove them from the catalytic system and therefore limits side reactions. A measure of miscibility between the ionic solvent and the organic solvent is deleterious to the course of the reaction. For instance, the occurrence of humins was observed when 1,2-dimethoxybenzene, or 2-*sec*-butylphenol, was used as the organic phase; the partial



Scheme 1. Catalytic conversion of cellulose into furan-type molecules in $ZnCl_2 \cdot 3H_2O$.

miscibility led to degradation of the furan-type products with concomitant diminished yields. Conversely, the less polar aromatic solvent anisole demonstrates lower miscibility with the IL, which protects the extracted products from side reactions.

Aiming to improve the conversion of cellulose into FHK and FF in the biphasic system $ZnCl_2 \cdot 3H_2O$/anisole, we conducted some parameter testing. Firstly, the influence of the loading of cellulose to IL (1, 1.25, 1.5, 1.75 and 2 wt% based on the IL) with a low amount of extractant (2 v/w based on IL) was examined. While the yields of FHK and FF remained essentially unchanged in these reactions (Figure S2), ranging from 18–20 mol% and 7–8 mol%, respectively, there was an increase in the amount of humins formed when employing higher concentrations of cellulose. This is most likely due to longer residence times of furanoids in the IL phase, consistent with the literature,[21] which would promote acid-catalysed by-product formation. This occurs because of non-exhaustive extraction of the FHK and FF into the organic phase, leaving open the possibility of reaction between the furanoids and sugars present.

In response, and to enhance the efficiency of the extraction, the conversion of MCC at a loading of 1 and 2 wt% in $ZnCl_2 \cdot 3H_2O$ was performed making use of larger volumes of anisole. The yields of FHK and FF are slightly improved to 23 mol% and 10 mol%, respectively, at 6 v/wt (based on IL) of anisole and 1 wt% cellulose in the IL (Figure S3). The overall yields of FHK are lower at 2 wt% loading of MCC, and the formation of humins was observed in all instances. Overall there was no significant difference in yield between the two loadings of cellulose nor in the formation of humins.

Reaction temperature and the time for which the reactions were conducted substantially influence the outcomes (Figure 1, 2). For instance, the highest yields of FHK and FF were produced at 120 °C (Figure 1) and yields of FHK reached a peak at 1.5 h (24 mol%, Figure 2). Longer reaction times led to diminished yields through by-product formation. At 100 °C (low temperature) we identified small amounts of HMF (2 mol%), and only at that temperature. Presumably, elevated temperatures favour reaction pathways leading to FHK and FF, in preference to those producing HMF (Scheme 1).

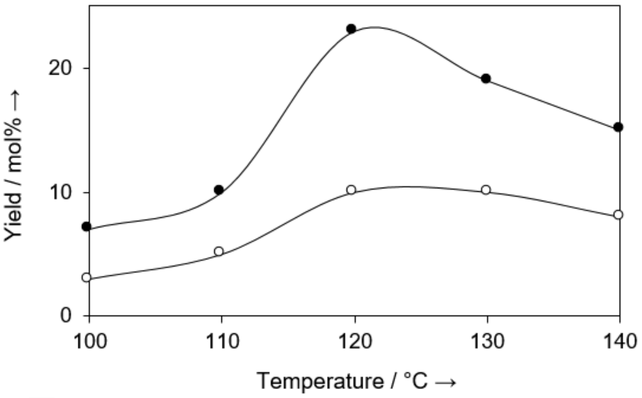


Figure 1. Production of furanoids from reaction of cellulose in the biphasic system $ZnCl_2 \cdot 3H_2O$/anisole at various reaction temperatures. Reaction conditions: MCC (5 mg), $ZnCl_2 \cdot 3H_2O$ (500 mg), anisole (3.00 mL), 1 h. ●: yield of FHK; ○: yield of FF.

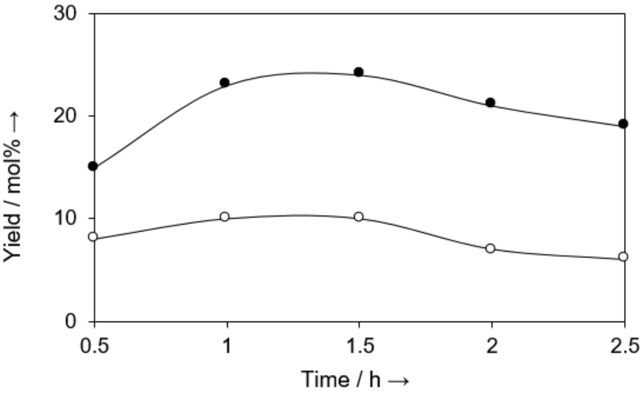


Figure 2. Production of furanoids from reaction of cellulose in the biphasic system $ZnCl_2 \cdot 3H_2O$/anisole at various reaction times. Reaction conditions: MCC (5 mg), $ZnCl_2 \cdot 3H_2O$ (500 mg), anisole (3.00 mL), 120 °C. ●: yield of FHK; ○: yield of FF.

To test this proposal, low molecular-weight sugars, such as cellobiose, glucose, and fructose, respectively, which putatively appear during the course of the transformation of cellulose,[6] were subjected to reaction in the IL. As is evident from Figure 3, HMF is one of the products of the conversion of sugars at temperatures below 100 °C, reaching yields up to 16 mol% (based on sugar substrate) from cellobiose or glucose. At higher temperatures FHK and FF become the dominant furanoid products, with yields of HMF falling away dramatically above 100 °C.

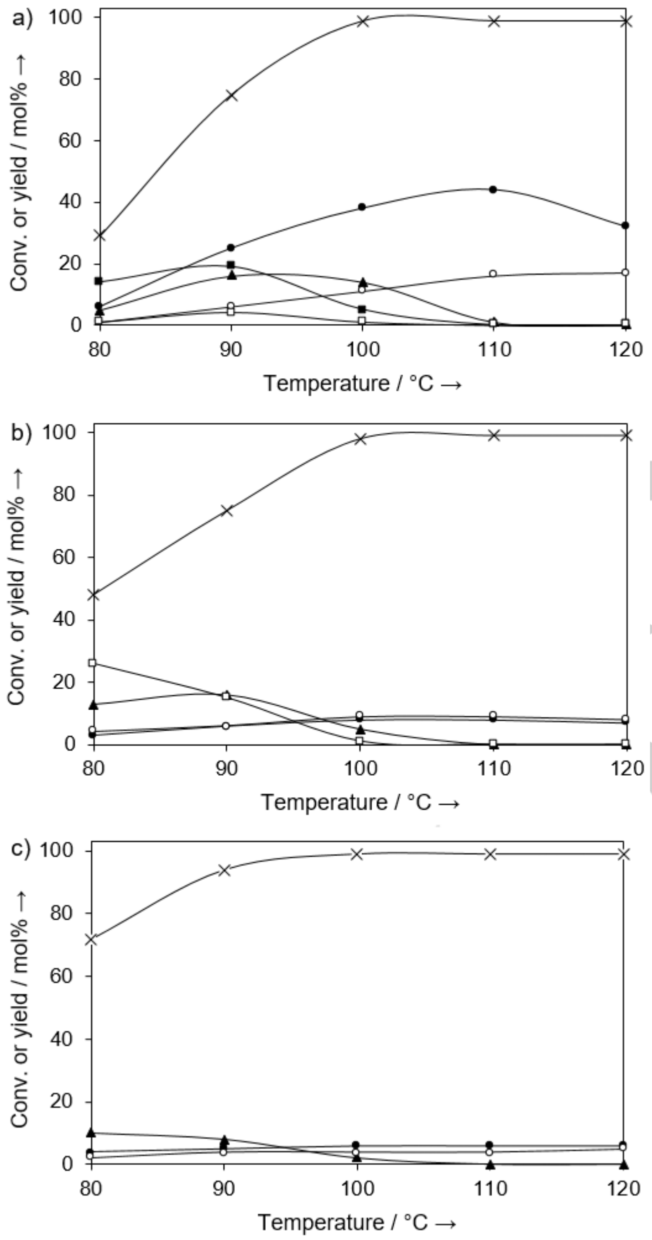


Figure 3. Conversion of carbohydrates (a: cellobiose; b: glucose; c: fructose) and the yields of the major products obtained in the biphasic system $ZnCl_2 \cdot 3H_2O$/anisole at various reaction temperature. Reaction conditions: sugar (5 mg), $ZnCl_2 \cdot 3H_2O$ (500 mg), anisole (3.00 mL), 1 h. ×: conversion; ■: yield of glucose; □: yield of fructose; ●: yield of FHK; ○: yield of FF; ▲: yield of HMF.

The processes with cellobiose, glucose and fructose at elevated temperature was accompanied by complete conversion of substrates (99% conversion of all substrates at the temperature above 100 °C, Figures 3a-c). Losses in yields of desirable products is most likely associated with the formation of humins, which were noted in some instances. Apart from furan derivatives and humins, we identified glucose and fructose during the transformation of cellobiose at lower temperatures (yields up to 19 and 4 mol%, respectively, Figure 3a); the occurrence of fructose (yield up to 26 mol%) is also apparent during the conversion of glucose (Figure 3b). The portfolio of compounds identified maps perfectly onto the acid-catalysed cascade of cellulose conversion proposed in Scheme 1, involving hydrolysis, aldose-ketose isomerisation and dehydration steps, respectively. It is likely that the dehydration of fructose into HMF is only favourable at temperatures below 100 °C. At higher temperatures the rates of fructose isomerisation into ketohexose or the pentose intermediate are increased, leading to FHK and FF becoming major products. From the outcomes it appears that the rates of the fructose isomerisation and further dehydration into FHK are higher, relative to the processes forming FF, accounting for the fact that FHK often appears in somewhat higher yields than FF. There is an interesting contrast in this set of reactions compared to those involving cellulose. With cellulose, a reaction temperature of 120 °C affords highest yields of furan derivatives; with low molecular weight substrates the optimum temperature is 110 °C. This finding presumably reflects the need for elevated temperatures to hydrolyse the glycosidic bonds in cellulose at an appreciable rate compared to subsequent reactions that lead to furan derivatives. Reactions converting glucose into furans appear to proceed at higher rate than the hydrolysis reaction of cellulose into glucose, and the optimum temperature that we identified is likely a trade-off between optimised hydrolysis, optimised formation of furans and minimised conversion into humins.

It is possible, in theory, to advantage the hydrolysis of polysaccharides by the addition of water or an acid catalyst, and thus improve the yields of target products. However, reaction of cellulose in zinc chloride with higher ratios of water ($ZnCl_2 \cdot 3.25H_2O$ and $ZnCl_2 \cdot 3.5H_2O$), or $ZnCl_2 \cdot 3H_2O$ with added acid catalysts (*p*-toluenesulfonic acid, oxalic acid, aluminium(III)-, lanthanum(III)-, gadolinium(III)-, ytterbium(III)- or hafnium(IV) trifluoromethanesulfonates, or lanthanum(III)- or gadolinium(III) chlorides) afforded similar or diminished yield of furanoids (Table S1). Arguably, the excess of water, or added catalyst, increases the overall acidity of the reaction media leading to decomposition of the ketone before its extraction, or to rehydration reactions potentially affording levulinic acid.[2,6] However, levulinic acid was not detected during the analysis of the reaction media and so this process appears not to prevail. Overall, the conversion in neat $ZnCl_2 \cdot 3H_2O$ remains the best process to date.

All of the reactions performed to this stage had been conducted at 5 mg scale. A subsequent set of reactions was performed at 10× this scale under identical reaction conditions (Table 2). The scaling operations revealed that the yields of the desired products were reduced to 15% for FHK and remained relatively stable at

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Table 2. Results of scaling and comparative literature data of the conversion of carbohydrates in $ZnCl_2{\cdot}nH_2O$[a]

Entry	Substrate	Time [h]	Temp [°C]	FHK yield [mol%]	FF yield [mol%]	S [%]	X [%]
1[b]	MCC	1.5	120	15	9	33	73
2[c]	MCC	1.5	115	20	9	48	61
3[c]	Cellobiose	1.5	115	32	14	46	99
4[d,15]	Cotton fibre	5 min	135	12	–	–	–
5[e,17]	Cotton cellulose	1.67	190	1	1	–	–
6[f,22]	Cellulose	2.5	270	–	6	–	–

[a] S = total selectivity of furan-type molecules. X = conversion of substrate. [b] Reaction conditions: MCC (50 mg), $ZnCl_2{\cdot}3H_2O$ (5,000 mg), anisole (30.0 mL). [c] Reaction conditions: MCC or cellobiose (50 mg), $ZnCl_2{\cdot}3H_2O$ (5,000 mg), anisole (40.0 mL). [d] Reaction conditions: cotton fibre (1,000 mg), $ZnCl_2{\cdot}3.36H_2O$ (140 mL), heating under microwave irradiation 600 W.[15] [e] Reaction conditions: cotton cellulose (650 mg), $ZnCl_2{\cdot}3.56H_2O$ (100 mL), *n*-butanol (600 mL).[17] [f] Reaction conditions: cellulose (1,000 mg), compressed steam and nitrogen (2.5 MPa), calcined $Ca(H_2PO_4)_2$ (0.1 mmol).[22]

9% for FF (Entry 1). Arguably, this relates to reduced mass transfer of products into the anisole phase leading to decomposition of unstable molecules in the polar acidic reaction media. To improve the outcome, the volume of anisole was increased to 8 vol/wt of IL and the reaction temperature was slightly reduced (by 5 °C). This improved the yield of FHK to 20% while the yield of FF remained constant at 9% (Entry 2). It is noteworthy that total selectivity of furan-type molecules was 48% (Entry 2), based on conversion of substrate (recovered unreacted substrate), indicating that the transformation of MCC in $ZnCl_2{\cdot}3H_2O$ is a reasonably selective process. Even higher yields of FHK and FF can be achieved from cellobiose in bench-scale processes. The total yield of furan products is excellent (46% yield of furan products, being a combination of 32% FHK and 14% FF, Entry 3). To the best of our knowledge, these outcomes set the benchmark in terms of yields of FHK and FF during the conversion of poly- or oligoglucans under mild reaction conditions. For comparison purposes, the targeted synthesis of FHK from polysaccharides was hitherto possible only for processes conducted under microwave heating in comparably lower yield than those achieved in this work (12% yield of FHK, Entry 4).[15] Otherwise, FHK and FF are attainable only in small amounts as by-products of the degradation of cellulose (Entries 5, 6);[17,22,23] usually, the major product secured from cellulose is HMF. It is worth noting that zinc chloride hydrate solvent is amenable to recovery and can potentially be reused, as has been shown in the reproducible conversion of cellulose into HMF in 4 catalytic runs in aqueous zinc chloride solvent.[18]

Conclusions

This work details the one-pot transformation of cellulose, into the furan-type platform products FHK and FF in high yield, in biphasic media containing $ZnCl_2{\cdot}3H_2O$ and anisole. These two products are valuable but are less commonly formed in high yield in the transformation of cellulosic substrates. The optimum method avoids the use of added catalysts because the ionic solvent possesses the intrinsic acidity required to facilitate all requisite transformations, namely hydrolysis, isomerization, and dehydration. In turn, anisole promotes the extraction of products from acidic media and preserves them from decomposition. These outcomes improve on the state of the art and provide a framework, involving inexpensive, recoverable media for the efficient direct conversion of cellulose into platform chemicals under mild conditions. The work highlights the ongoing challenge of removal of the reactive (under the reaction conditions) furanoid products from the catalyst, which is likely the current major obstacle to larger scale reactions and improved yields and selectivities.

Experimental Section

Preparation of ionic liquids and processing of carbohydrates were performed in oven-dried glassware at atmosphere pressure. Reagents were used as supplied from commercial sources. All details about analytical methods and equipment are specified in the Supporting Information (SI).

Preparation of zinc chloride hydrate solvent and dissolution of carbohydrates

Anhydrous zinc chloride and deionised water in a molar ratio 1 to 3.0, 3.25 or 3.5, to form $ZnCl_2{\cdot}3H_2O$, $ZnCl_2{\cdot}3.25H_2O$ or $ZnCl_2{\cdot}3.5H_2O$ (Table S2), respectively, were introduced to a round-bottom flask equipped with a thermometer and magnetic follower. The mixture was heated and agitated at 80 °C for 30 minutes, resulting in a transparent colourless ionic liquid. Then the microcrystalline cellulose (100–200 mg, to form a 1–2 wt% solution based on the solvent) was introduced to the flask with the prepared zinc chloride hydrate solvent (10.00 g) and the mixture was heated and agitated at 80 °C for 1 h, resulting in a yellowish transparent solution. The same method was employed for the dissolution of low-molecular-weight carbohydrates (cellobiose, glucose, or fructose) but the processing temperature was 60 °C.

Microscale model reactions

A solution of microcrystalline cellulose or low-molecular-weight sugars (cellobiose, glucose or fructose, 5–10 mg) in $ZnCl_2{\cdot}nH_2O$ (n = 3.0–3.5, 500 mg, 1–2 wt% solution of carbohydrate based on the ionic liquid) and organic solvent (2.00–6.00 mL of *m*-xylene, *tert*-butylbenzene, anisole, 4-methylanisole, 1,2-dimethoxybenzene or 2-*sec*-butylphenol, respectively) were introduced to a two-neck round-bottom flask equipped with a condenser, thermometer and magnetic follower. The mixture was heated and stirred at a predetermined reaction temperature and for a fixed period of time. In some instances, Brønsted acids (*p*-toluenesulfonic acid or oxalic acid, 1–20 mol% based on the number of anhydroglucose units present in cellulose) or Lewis acids (aluminium(III)-, lanthanum(III)-, gadolinium(III)-, ytterbium(III)- or hafnium(IV) trifluoromethanesulfonates, or lanthanum(III)- or gadolinium(III) chlorides, 1–20 mol% based on the number of anhydroglucose units present in cellulose) were added to the reaction media when investigating the role of the catalyst on the outcome of the conversion of cellulose. Recovery of the product included dilution of the ionic liquid with 1 equivalent volume of water based on the weight of ionic liquid in the reactor, followed by agitation of the biphasic system at room temperature for 30 minutes, after which the organic solvent phase was removed from the reactor. Work-up of the aqueous phase was performed by the addition of aqueous sodium hydrogen carbonate (0.50 mL, 1 M), followed by centrifugation and decantation (20,000 × g for 10 minutes) to remove precipitated zinc salts. The aqueous and organic solvent phases were analysed using high performance liquid chromatography (HPLC), as detailed in SI, to provide the results described in the main text. All microscale reactions were repeated at least three times.

Bench scale processes

A solution of microcrystalline cellulose or cellobiose (50 mg) in $ZnCl_2 \cdot 3H_2O$ (5.00 g, 1 wt% solution of carbohydrate based on the ionic liquid) and anisole (30.0 or 40.0 mL) were introduced to a two-neck round-bottom flask equipped with a condenser, thermometer and magnetic follower. The mixture was heated and stirred at a predetermined reaction temperature (115 or 120 °C) for 1.5 h. Recovery of the products included dilution of ionic liquid with 1 equivalent volume of water based on the weight of ionic liquid in reactor followed by agitation of the biphasic system at room temperature for 30 minutes. The two phases were separated and a small amount of each (0.5 mL) was processed, as detailed above, before chromatographic analysis using an HPLC system to provide the outcome shown in the main text. The remaining aqueous phase was diluted with aqueous hydrochloric acid (25.0 mL, 0.2 M) to precipitate the unreacted cellulose, which was recovered, washed with deionised water (3 × 25.0 mL), vacuum oven-dried (60 °C, 1 mbar, 12 h) and weighed to provide the conversion of cellulose detailed in the manuscript.

Isolation of furan-type molecules and recovery of solvents

Isolation of furan-type molecules from anisole phase comprised adsorption of products on the solid adsorbents. A solution of products in anisole (40.0 mL, combined anisole phases after microscale conversion of carbohydrates) was diluted with 1 equivalent volume of hexane and was passed through a glass funnel containing silica gel (10.00 g) and activated carbon (1.00 g) under ambient pressure. The polar products were trapped on the solid adsorbents, while the anisole and hexane were removed as a filtrate. Then furan-type molecules were desorbed with ethyl acetate (3 × 20.0 mL) and collected as a mixture. The recovery of products from the diluted with 1 equivalent volume of water ionic liquid (10.0 mL, combined aqueous phases after microscale conversion of carbohydrates) comprised extraction with ethyl acetate (3 × 20.0 mL) under vigorous agitation at room temperature for 10 min. The achieved solutions of products in ethyl acetate after recovery from anisole and aqueous phases were combined and dried over $MgSO_4$ and the solvent was removed under reduced pressure. The mixture of furan-type molecules was subjected to flash column chromatography (hexane–ethyl acetate, 1.5:1) to isolate FHK, FF and HMF. The HPLC analysis of the recovered anisole and diluted with water ionic liquid showed only trace amounts of furanoids remained in both solvents implying almost complete recovery.

Furyl hydroxymethyl ketone.[15] TLC: R_f = 0.308 (1.5:1 hexane/EtOAc; UV, $KMnO_4$); ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.63 (dd, *J* = 1.5, 0.5 Hz, 1H), 7.30 (dd, J = 3.5, 0.5 Hz, 1H), 6.60 (dd, J = 3.5, 1.5 Hz, 1H), 4.74 (s, 2H), 3.27 (br s, 1H, OH); ^{13}C NMR: (125 MHz, $CDCl_3$, 25 °C): δ = 187.6, 150.1, 147.0, 117.9, 112.6, 65.1; IR (neat): ν_{max} = 3331, 3133, 3115, 1678, 1563, 1468, 1421, 1321, 1270, 1168, 1113, 1029, 976, 912, 880, 774, 636, 590, 504 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_6H_6O_3H$ [M+H]$^+$: 127.0390, found: 127.0378.

Furfural.[24] TLC: R_f = 0.532 (1.5:1 hexane/EtOAc; UV, $KMnO_4$); ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 9.63 (s, 1H), 7.68 (t, J = 1.0 Hz, 1H), 7.23 (dd, J = 3.5, 1.0 Hz, 1H), 6.58 (dd, J = 3.5, 1.0 Hz, 1H). ^{13}C NMR: (125 MHz, $CDCl_3$, 25 °C): δ = 177.8, 152.9, 148.0, 121.0, 112.5. IR (neat): ν_{max} = 3132, 2807, 1673, 1568, 1473, 1394, 1367, 1278, 1157, 1081, 1021, 930, 883, 759, 595 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_5H_4O_2H$ [M+H]$^+$: 97.0284, found: 97.0278.

Hydroxymethylfurfural.[25] TLC: R_f = 0.213 (1.5:1 hexane/EtOAc; UV, $KMnO_4$); ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 9.56 (s, 1H), 7.21 (d, J = 3.5 Hz, 1H), 6.51 (d, J = 3.5 Hz, 1H), 4.70 (s, 2H), 2.97 (br s, 1H, OH). ^{13}C NMR: (125 MHz, $CDCl_3$, 25 °C): δ =177.7, 160.7, 152.3, 123.0, 110.0, 57.6. IR (neat): ν_{max} = 3339, 3120, 2841, 1657, 1582, 1519, 1396, 1368, 1336, 1278, 1188, 1070, 1017, 986, 965, 806, 768, 511 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_6H_6O_3H$ [M+H]$^+$: 127.0390, found: 127.0379.

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Keywords: biomass • carbohydrates • catalysis • ionic liquids • sustainable chemistry

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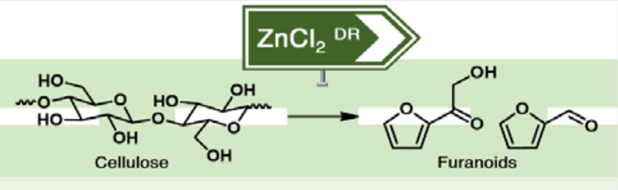

Cellulose is abundant and renewable, and is converted into value-added small molecules to be employed for chemical synthesis, replacing some reliance upon petrochemical sources. In the present work, furyl hydroxymethyl ketone and furfural are obtained as major products, which are valuable but less commonly formed in high yields in transformations of cellulosic substrates.

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Acid-Catalysed Conversion of Carbohydrates into Furan-Type Molecules in Zinc Chloride Hydrate