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# High Yielding Acid-Catalysed Hydrolysis of Cellulosic Polysaccharides and Native Biomass into Low Molecular Weight Sugars in Mixed Ionic Liquid Systems

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Ionic media comprising 1-butyl-3-methylimidazolium chloride and the acidic deep eutectic solvent choline chloride/oxalic acid as co-solvent-catalyst, very efficiently convert various cellulosic substrates, including native cellulosic biomass, into water-soluble carbohydrates. The optimum reaction systems yield a narrow range of low molecular weight carbohydrates directly from cellulose, lignocellulose, or algal saccharides, in high yields and selectivities up to 98%. Cellulose possesses significant potential as a renewable platform from which to generate large volumes of green replacements to many petrochemical products. Within this goal, the production of low molecular weight saccharides from cellulosic substances is the key to success. Native cellulose and lignocellulosic feedstocks are less accessible for such transformations and depolymerisation of polysaccharides remains a primary challenge to be overcome. In this study, we identify the catalytic activity associated with selected deep eutectic solvents that favours the hydrolysis of polysaccharides and develop reaction conditions to improve the outcomes of desirable low molecular weight sugars. We successfully apply the chemistry to raw bulk, non-pretreated cellulosic substances.

## 1. Introduction

Biomass is the principal renewable resource for sustainable industrial production of high-volume and high-value chemicals.[1,2] Within natural sources, cellulose is the most abundant substrate with the scale to reduce reliance on fossil fuel-derived bulk chemicals.[3] There is an intense effort to efficiently transform polysaccharides into small organic building block molecules (platform chemicals) generating a source of renewable replacements to crude oil-based products.[3–5] In the presence of an acid catalyst, cellulose hydrolyses into low molecular weight glucans and monomer glucose, which are convertible into a range of value added molecules with high potential for manufacturing applications (Scheme 1). Platform chemicals are readily accessible on industrial scale but the present production is mostly based on refined edible sugars (such as glucose, fructose, sucrose, or starch). This reliance undermines the sustainability of the biorefinery and becomes a source of controversy and public concern.[3–5] Cellulose-derived low molecular weight sugars can potentially provide an inexhaustible source of substrates for useful chemicals (Scheme 1). Cellulose is composed of monomer units suitable for conversion into platform chemicals but cellulose has an intractable structure which renders challenging the direct transformation thereof into platform chemicals. The synthesis of platform chemicals directly from cellulose thus remains mostly industrially unviable.[3,6,7] The ongoing major challenge relates to the efficient depolymerisation of cellulose and its concomitant hydrolysis into low molecular weight water-soluble saccharides under green processing conditions.

An excellent example of the direct transformation of biomass into platform chemicals is the Biofine Process.[8] High temperature reaction of cellulosic biomass with dilute mineral acids yields levulinic acid, formic acid, furfural and biochar. Stage 1 processing of a high cellulose-content substrate at 210 °C affords low molecular weight saccharides and 5-(hydroxymethyl)furfural (HMF), while Stage 2 reaction at below 200 °C converts the sugars into levulinic and formic acids as major products.[8] Importantly, the procedure requires the pre-processing of the lignocellulosic raw material to remove hemicellulose and generate the high cellulose-content feed for the reactors. Equally importantly, the two-stage process requires the hydrolytic formation of low molecular weight sugars from cellulose, which are converted into the desired platform products. The hydrolysis of cellulose is therefore a critical step in the chemical transformation of this substance.[2,3,8]

Ionic liquids (ILs) are efficient solvents for reactions of cellulosic materials.[9a] These ionic media can fully dissolve polysaccharides, and thereby can promote chemical transformations into highly desirable products under mild reaction conditions; in contrast, common aqueous media cannot dissolve cellulose and require forcing processing conditions to

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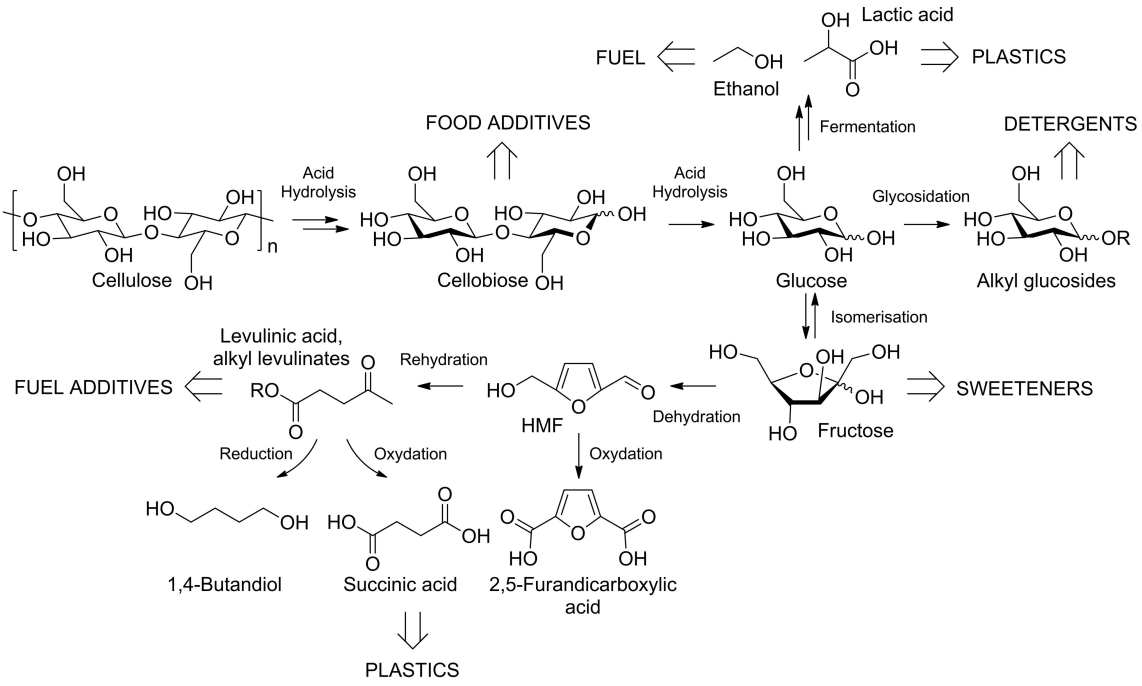



**Scheme 1.** Catalytic conversion of cellulose into value added molecules. n = integer, R = H, or alkyl.

promote catalytic reactions.[3,9b,c] In particular, mineral acids (e.g., hydrochloric, sulfuric or phosphoric acids) or solid acid catalysts (e.g., acidic resins or carbonaceous acids) in imidazolium-based ILs have been heavily explored in the hydrolysis of microcrystalline cellulose (MCC) to low molecular weight reducing sugars and sometimes for its conversion directly into platform chemicals such as HMF.[10–12] In some instances the imidazolium quaternary salts possess acidic functional groups, which avoids the need to add catalysts.[13] Importantly, ionic solvents and saccharides can be fully recovered after catalytic processing by potentially scalable methods.[14a]

The low molecular weight sugars so produced are amenable to fermentation into alcohols.[14] Much of the work presented in the current literature relating to the hydrolysis of cellulose employs pretreated cellulose such as MCC, obtained by the treatment of cellulose with mineral acids, or ball-milled cellulose.[9b,c,10,11,13,15,16] Some works present the use of unfractionated biomass. However, many chemical treatments detailed in the literature have not been demonstrated on native- or raw biomass, or even the type of cellulose that is available via the large volume cellulose refining technologies applied in the paper and pulp industry.[3,14]

While common imdazolium-based systems present some advantages in the processing of cellulose, deep eutectic solvents (DESs) are somewhat overlooked in this arena. DESs are alternative media (to common ILs) usually formed from eutectic mixtures of Lewis or Brønsted acids and bases under solvent-free conditions.[3] These solvents can be produced from inexpensive plant-based substances and many DESs are considered to be environmentally benign reaction systems for the processing of carbohydrates.[17,18] Especially, the combinations of choline chloride (ChCl) with organic acids prove to be useful green media for chemical conversions of some poly- and oligosaccharides.[18] The intrinsic acidity of such DESs facilitates the transformation of inulin and hemicellulose into monomer sugars and ultimately into furan-type molecules in a single solvent system.[19,20] Despite the promising characteristics of DES systems, cellulose largely resists dissolution in DES. The optimum conditions deliver solutions containing a maximum of 6.5 wt% cellulose. In this instance, a specific cotton linter pulp with a low degree of polymerisation is used and the observations are not generalised (this material is known as a dissolving pulp, which is soluble in aqueous solutions of mineral bases).[18,21,22] If native cellulose can be dissolved and selectively chemically transformed in the presence of DESs then substantial progress would have been made in the processing of biomass into useful products, offering an area with significant scope for exploration.

The present work uncovers and demonstrates the functionality of DESs as reactive (catalyst) co-solvents in imidazolium-based solvents for the conversion of cellulose and native biomass into low molecular weight carbohydrates under green processing conditions. It researches the chemistry associated with catalytic reactions of polysaccharides, and develops novel acidic systems for their effective employment in biorefinery settings. Most importantly, we successfully apply the optimised conditions to the hydrolysis of raw bulk cellulosic substrates of terrestrial and marine origin, including an example of an agricultural waste product. Many current state-of-the-art systems employ vigorous pretreatment methods such as extensive ball milling.[9b,c] Such energy intensive techniques are more suited to scientific studies than to large scale industrial manufacture. In contrast to most related studies which typically report for glucose, we track the formation of $(glucose)_n$

saccharides for n = 1–4 by LC-MS, thereby improving our understanding of the course of the hydrolysis chemistry.

## 2. Results and Discussion

To explore the course of the hydrolytic reaction of cellulose in various ILs, we investigated the conversion of MCC and of typical low-molecular-weight sugars that commonly appear during the hydrolysis of cellulose (i.e., cellobiose, glucose, fructose; Scheme 1). Reactions were conducted in 1-butyl-3-methylimidazolium chloride ([$C_4$mim]Cl) or in DESs based on ChCl and oxalic or citric acids, or on ChCl and TsOH, at 120 °C for 2 h (Table 1 and in Table S1). Neither the imidazolium IL nor the DES systems were suited to the task, for different reasons. While MCC is freely soluble in [$C_4$mim]Cl, it does not hydrolyse notably in this solvent under our conditions, and the masses of the input and recovered cellulose were practically identical (Table 1, entry 1). Within the low molecular weight saccharides, cellobiose was hydrolysed into glucose in [$C_4$mim]Cl in only low yield (8 wt%), while glucose or fructose provided a little HMF (up to 6 mol%), but were otherwise unchanged (Table S1). The imidazolium-based solvent clearly possesses some Brønsted acidity which catalyses certain reactions to a limited extent (e.g., hydrolysis of glycosidic bonds, dehydration into HMF), but this solvent-derived acidity is insufficient to catalyse the transformation of cellulose into products.[3] On the other hand, DES systems based on ChCl/oxalic acid or ChCl/TsOH promoted more comprehensive transformation of MCC under the selected reaction conditions (conversion up to 46%, Table 1, entries 2 and 4) but mostly into undesirable high molecular weight humins (even though MCC remained as a suspension in the DES). Humins are thought to form by the condensation of intermediate sugars and aldehydes.[23,24] Similarly, low molecular weight carbohydrates in ChCl/oxalic acid DES were almost completely transformed (total conversion to product of 96, 97, and 99% for cellobiose, glucose, and fructose, respectively, Table S1) into a bulk of undesirable humins and small amounts of HMF (yields up to 11 mol%). The results clearly suggest that neither imidazolium-based solvent nor the acidic DESs are suitable reaction media under our conditions, due to a) the low acidity of [$C_4$mim]Cl which fails to promote the catalytic conversion of cellulose and b) the high acidity of DESs inducing the formation of by-products. These drawbacks are likely to be mutually exclusive and a combined solvent system based on [$C_4$mim]Cl and acidic DESs should favour the more selective transformation of cellulose into desirable low molecular weight sugars.

To test this hypothesis, the transformation of MCC was conducted in mixed [$C_4$mim]Cl/DES systems, in which the intention was to employ the acidic DES to catalyse the hydrolysis (Table 1, entries 5–7, 9–14). A combination of [$C_4$mim]Cl and ChCl/oxalic acid 10:1 w/w showed high selectivity towards low molecular weight carbohydrates (total selectivity is 81% for the products glucose, cellobiose, cellotriose, and cellotetraose) after reaction of MCC at 120 °C for 2 h (Table 1, entry 5). This mixed solvent readily dissolves cellulose and, based on observation, has lower viscosity than neat

**Table 1.** Acid-catalysed conversion of cellulose in single and combined ILs.[a]

| Entry | IL | Time [h] | *X* [%] | *S* [%] | Yield glucose [wt%] | Yield cellobiose [wt%] | Yield cellotriose [wt%] | Yield cellotetraose [wt%] | Yield HMF [mol%] |
|---|---|---|---|---|---|---|---|---|---|
| 1 | [$C_4$mim]Cl | 2 | 4 | 0 | 0 | 0 | 0 | 0 | 0 |
| 2 | ChCl/oxalic acid | 2 | 43 | 0 | 0 | 0 | 0 | 0 | 2 |
| 3 | ChCl/citric acid | 2 | 10 | 0 | 0 | 0 | 0 | 0 | 2 |
| 4 | ChCl/TsOH | 2 | 46 | 0 | 0 | 0 | 0 | 0 | 2 |
| 5 | [$C_4$mim]Cl/ChCl/oxalic[b] | 2 | 31 | 81 | 3 | 1 | 7 | 14 | 0 |
| 6 | [$C_4$mim]Cl/ChCl/citric[b] | 2 | 3 | 33 | 0 | 0 | 0 | 1 | 0 |
| 7 | [$C_4$mim]Cl/ChCl/TsOH [b] | 2 | 68 | 0 | 0 | 0 | 0 | 0 | 8 |
| 8 | [$C_4$mim]Cl/oxalic acid [c] | 2 | 23 | 74 | 0 | 1 | 4 | 12 | 0 |
| 9 | [$C_4$mim]Cl/ChCl/oxalic [b] | 4 | 80 | 89 | 12 | 8 | 20 | 31 | 0 |
| 10 | | 6 | 85 | 98 | 16 | 16 | 20 | 31 | 2 |
| 11 | | 8 | 87 | 92 | 21 | 12 | 20 | 27 | 3 |
| 12 | | 12 | 90 | 79 | 28 | 11 | 16 | 16 | 5 |
| 13 | | 16 | 94 | 46 | 26 | 5 | 7 | 5 | 7 |
| 14 | | 20 | 96 | 30 | 23 | 2 | 2 | 2 | 9 |

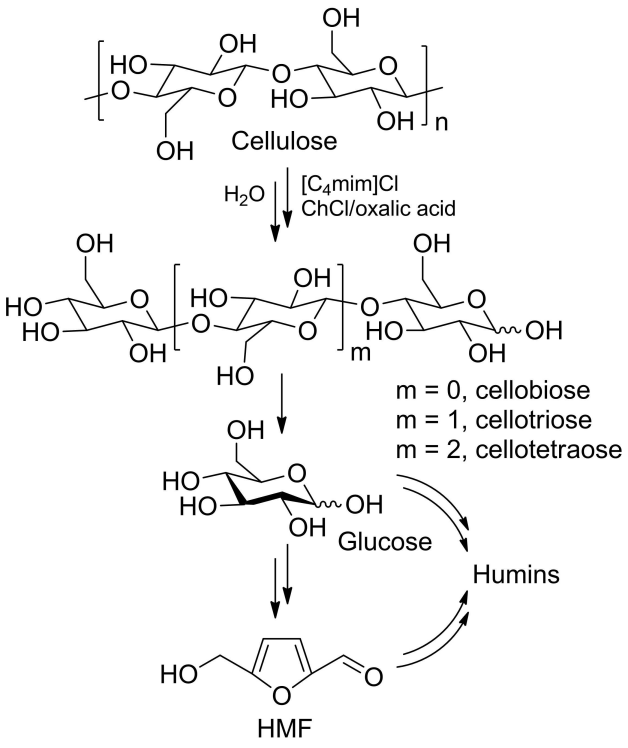
[a] Yields are specified in wt% based on input of cellulose for carbohydrates and in mol% based on anhydroglucose units present for HMF; '0' means that product was identified in trace amounts based on HPLC analysis; *X* = conversion; *S* = total selectivity of carbohydrates (glucose, cellobiose, cellotriose, and cellotetraose). Reaction conditions: MCC (50 mg), IL or DES (1.000 g), 120 °C. [b] Reaction conditions: MCC (50 mg), [$C_4$mim]Cl (1.000 g), DES (0.100 g), 120 °C. [c] Reaction conditions: MCC (50 mg), [$C_4$mim]Cl (1.000 g), oxalic acid dihydrate (48 mg), 120 °C.

[$C_4$mim]Cl, which alleviates one of the downsides attributed to the use of imidazolium-based ILs.[25] Other DESs based on citric acid or TsOH, combined with [$C_4$mim]Cl, are less effective for the hydrolysis of cellulose under similar conditions (Table 1, entries 6 and 7). Possibly, the solvent system with ChCl/citric acid possesses insufficient acidity to catalyse the hydrolysis under the prevailing conditions (see Table 2 below, for pH measurements and the discussion relating thereto), while the higher acidity of ChCl/TsOH caused the formation of HMF and humins. It is worth noting that the combined solvent [$C_4$mim]Cl/ChCl/oxalic acid provided higher yield and selectivity for sugars than [$C_4$mim]Cl/oxalic acid (Table 1, entries 5 and 8). The hydrolysis of MCC in [$C_4$mim]Cl/ChCl/oxalic acid showed very high conversions of polysaccharide (up to 96%) and selectivity to low molecular weight reducing sugars (up to 98%, Table 1). Cellotriose and cellotetraose appeared as major products in the range 2–8 h (Table 1, entries 5, 9–11), while extended reaction times (12 h, Table 1, entry 12) favoured the production of glucose. These results show that cellulose hydrolyses predominantly into 'chunks' rather than directly to glucose, i.e., low molecular weight oligosaccharides (cellotetraose, cellotriose and cellobiose) from which glucose emerges. The longest reactions (16 and 20 h, Table 1, entries 13 and 14) led to the formation of HMF and by-product humins, which reduced the overall selectivity. HMF likely derives from fructose, the isomerisation product of glucose, while humins form by condensation of sugars and HMF.[23,24] Scheme 2 summarises the findings.

**Table 2.** pH readings of ionic liquids and single acids.[a]

| Source | pH/0.15 M |
|---|---|
| ChCl | 4.89 |
| Oxalic acid | 1.58 |
| ChCl/oxalic acid | 1.37 |
| Citric acid | 2.03 |
| ChCl/citric acid | 1.87 |
| TsOH | 1.29 |
| ChCl/TsOH | 1.28 |
| [$C_4$mim]Cl | 7.15 |
| $La(OTf)_3$ | 7.43 |
| $La(OTf)_3$/oxalic acid | 1.52[b] |
| | 1.39[c] |
| $La(OTf)_3$/ChCl/oxalic acid | 1.33[b] |
| | 1.29[c] |

[a] pH readings were performed in triplicate in water at room temperature. The molar concentration of DES solutions and combined acid solutions is calculated based on the content of the Brønsted acid comonent. OTf = trifluoromethanesulfonate. [b] The molar ratio of oxalic acid and La$(OTf)_3$ is 12:1. [c] The molar ratio of oxalic acid and La$(OTf)_3$ is 1:1.




**Scheme 2.** Acid-catalysed conversion of cellulose in solvent system [$C_4$mim]Cl/ChCl/oxalic acid.

We sought to better understand the origins of the catalyst activity in the ChCl systems. pH readings of dilute aqueous solutions of the DES systems and of their parent acids revealed that the ionic solvents possess enhanced Brønsted acidity compared to the parent acids, in the cases of the organic acids (Table 2). All readings were performed at the same concentration of the components being measured and are therefore a measure of acid strength. ChCl, which is considered to be a Lewis acid, apparently forms a Lewis acid-assisted Brønsted acid complex[26,27] with oxalic acid; this complexation assists to deliver the higher acidity of the DES (Scheme S1). Most likely, the complex so formed consists of choline cation and oxalate anion, as proposed in Scheme S1. Interestingly, the induced Brønsted acidity catalyses the esterification[28] of oxalic acid with ChCl (Scheme S1). The esterification of carboxylic acids with ChCl in molten media, especially with added hydrochloric acid, has been previously noticed by Florindo et al.[29] In our hands, $^{13}$C NMR analysis of ChCl/oxalic acid (1:1 mixture, dissolved in deutero acetonitrile) demonstrates three chemical shifts associated with the carboxylic groups of oxalic acid (one peak associated with free oxalic acid at 160.2 ppm, and two new peaks at 158.9 and 158.7 ppm that are consistent with the formation of the ester, Figure S1), along with six chemical shifts assigned to the carbon atoms of choline cation (three peaks associated with free ChCl at 68.5, 56.5 and 54.7 ppm, and three new peaks assigned to the ester at 64.8, 60.5, and 54.6 ppm, Figure S1). Integration of the peaks in the $^1$H NMR spectrum of ChCl/oxalic acid diluted in deuterated solvents ($CD_3CN$ or $D_2O$, Figure S2) or using neat DES (with DMSO-$d_6$ for external lock employing a coaxial insert tube, Figure S2), showed the ester and ChCl to be present in a ratio 1:10. The FTIR spectrum of the DES indicates a band at 1723 $cm^{-1}$ characteristic of the asymmetrical C=O stretching mode and a band at 1185 $cm^{-1}$ corresponding to asymmetrical vibration of C–C(=O)–O (Figure S3).[30] Free oxalic acid or ChCl do not provide these vibrations, which we propose to be associated with the ChCl/oxalic acid ester.

Now with reference to the experimental results (Table 1) and the pH measurements (Table 2), while Table 2 shows only incremental differences between the various acidic systems, there are distinct experimental outcomes associated with the

different reaction media (Table 1). Of the media probed, the acidity secured through ChCl/oxalic acid is optimal for the conversion of cellulose into water-soluble low molecular weight carbohydrates. Other DESs showed either high Brønsted acid activity leading to the rapid conversion of cellulose into by-products, or too low acidity for the effective hydrolysis of glycosidic bonds. The experimental data point to a need for sufficient acidity to cause the hydrolysis but for a tight balancing act such that the acidity is not so high as to cause secondary reactions under the conditions.

Although cellulose-derived oligoglucans (such as those produced as described above: cellobiose, cellotriose, cellotetraose) are valuable products, glucose is usually considered to be *the* desired product of the hydrolysis of polysaccharides.[9,31] Metal triflates are efficient green Lewis acidic catalysts for a range of chemical transformations, including the processing of cellulose, especially when mixed with Brønsted acids to form Lewis acid-assisted Brønsted acid complexes.[3,32,33] Because DESs possess intrinsic Brønsted acidity as shown above (Table 2, Scheme S1), in theory, it is possible to advantage the conversion of cellulose in favour of glucose by modifying solvent/catalyst system with Lewis acid. Accordingly, the activity of metal triflates ($Al(OTf)_3$, $Y(OTf)_3$, AgOTf, $In(OTf)_3$, $Sn(OTf)_2$, $La(OTf)_3$, $Yb(OTf)_3$ and $Hf(OTf)_4$) in mixed ionic solvent $[C_4mim]Cl$/ChCl/oxalic acid was investigated for the conversion of MCC. Table 3 presents that metal triflates, specifically AgOTf, $In(OTf)_3$, $Sn(OTf)_2$, $La(OTf)_3$, and $Yb(OTf)_3$, promote the rapid hydrolysis of cellulose into low molecular weight sugars. Those that afford higher acidity ($Al(OTf)_3$, $Y(OTf)_3$ and $Hf(OTf)_4$) favour the formation of HMF and the unwanted by-product humins. $La(OTf)_3$ possessed the highest activity to catalyse the transformation of MCC directly into desired monomer glucose in high yield (35 wt% based on cellulose), and in shorter reaction time compared to the process without metal triflate catalysts. $La(OTf)_3$ and oxalic acid formed a Lewis acid-assisted Brønsted acid in the DES, improving the overall activity of the catalytic media for hydrolysis of glycosidic bonds. The addition of $La(OTf)_3$ leads to slightly higher acidity (Table 2). This is caused by complexation of the La to the oxalic acid, thereby providing a complementary form of Lewis acid-assisted Brønsted acidity. This complexation was unambiguously demonstrated by FTIR analyses of $[C_4mim]Cl$ ionic liquid solutions of $La(OTf)_3$ mixed with oxalic acid and separately $La(OTf)_3$ mixed with ChCl/oxalic acid (Figure S4). Both mixtures showed the appearance of an asymmetrical stretching band at 1620–1600 $cm^{-1}$ of the carboxylate anion[30] confirming the complexation. As we have already discussed for the $La(OTf)_3/H_3PO_4$ system,[23,27,34] La holds a special place relating to Lewis acid-assisted Brønsted acidity, providing a complex acid system with exceptional catalyst activity in several different chemical transformations. pH readings of the mixed acid systems ($La(OTf)_3$ + oxalic acid) show the increased acidity, albeit that it too appears incremental in dilute solution. Notwithstanding this incremental change to the pH, the experimental results (Table 3) provide strong evidence for the benefits brought by the addition of the Lewis acid, leading to 73% conversion of cellulose within two hours into 69% low molecular weight saccharides (w/w based on the input cellulose) and 95% selectivity for such saccharides. Care needs to be taken with reaction times, though. The heightened activity of the reaction media with $La(OTf)_3$ is detrimental after extended periods due to the transformation of glucose into HMF and ultimately into humins (Table 3, Scheme 2).

The hydrolytic conversion of cellulose in ILs is more efficient in the presence of water, favouring the formation of glucose.[10,14,15] We therefore conducted the transformation of MCC in the mixed ionic solvent $[C_4mim]Cl$ / ChCl/oxalic acid at 120 °C with the addition of water (Figure 1). MCC was first dissolved in the ionic solvent at 100 °C for 2 h, after which the temperature was raised to 120 °C to cause the reaction, and water was added to the reaction media after 0.5 h (water content 20 wt% based on IL) and 1 h (water content 30 wt% based on IL) of reaction time. The glucose yield is dramatically enhanced in the presence of water. Recall that in the absence of added water, cellulose yielded (with a maximum at 12 h) 28 wt% glucose, along with 43 wt% oligosaccharides consisting of 11, 16 and 16 wt% of cellobiose, cellotriose and cellotetraose,

**Table 3.** Acid-catalysed conversion of MCC in $[C_4mim]Cl$ / ChCl/oxalic acid in the presence of metal triflates.[a]

| Catalyst | Time [h] | *X* [%] | *S* [%] | Yield glucose [wt%] | Yield cellobiose [wt%] | Yield cellotriose [wt%] | Yield cellotetraose [wt%] | Yield HMF [mol%] |
|---|---|---|---|---|---|---|---|---|
| none | 2 | 31 | 81 | 3 | 1 | 7 | 14 | 0 |
| $Al(OTf)_3$ | 2 | 66 | 5 | 3 | 0 | 0 | 0 | 10 |
| $Y(OTf)_3$ | 2 | 65 | 15 | 10 | 0 | 0 | 0 | 10 |
| AgOTf | 2 | 76 | 89 | 13 | 8 | 18 | 29 | 1 |
| $In(OTf)_3$ | 2 | 79 | 85 | 15 | 8 | 18 | 26 | 1 |
| $Sn(OTf)_2$ | 2 | 60 | 70 | 6 | 4 | 8 | 24 | 0 |
| $La(OTf)_3$ | 1 | 71 | 92 | 14 | 7 | 17 | 27 | 1 |
| | 2 | 73 | 95 | 35 | 6 | 10 | 18 | 4 |
| | 4 | 75 | 21 | 16 | 0 | 0 | 0 | 10 |
| | 6 | 76 | 8 | 6 | 0 | 0 | 0 | 11 |
| $Yb(OTf)_3$ | 2 | 69 | 41 | 17 | 10 | 1 | 0 | 8 |
| $Hf(OTf)_4$ | 2 | 65 | 0 | 0 | 0 | 0 | 0 | 9 |

[a] Yields are specified in wt% based on input of cellulose for carbohydrates and in mol% based on anhydroglucose units present for HMF; '0' means that product was identified in trace amounts based on HPLC analysis; *X* = conversion; *S* = total selectivity of carbohydrates (glucose, cellobiose, cellotriose, cellotetraose); HMF = 5-(hydroxymethyl)furfural; OTf = trifluoromethanesulfonate. Reaction conditions: MCC (50 mg), $[C_4mim]Cl$ (1.000 g), DES (0.100 g), catalyst (10 mol% based on anhydroglucose unit present), 120 °C.

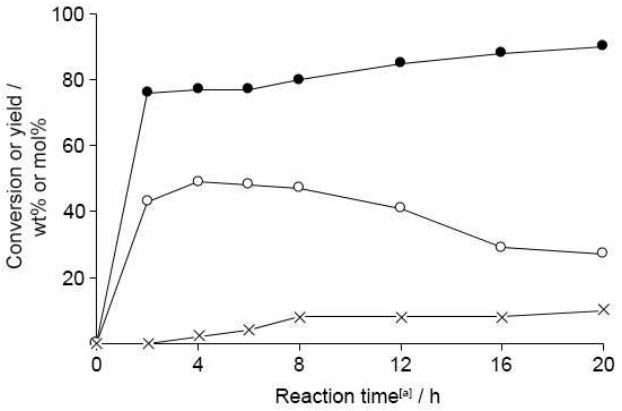



**Figure 1.** Acid-catalysed conversion of MCC in [$C_4$mim]Cl/ChCl/oxalic acid with gradually added water. ● conversion, ○ glucose yield (wt% based on MCC), × HMF yield (mol% based on anhydroglucose units present). [a] Dissolution of MCC (50 mg), [$C_4$mim]Cl (1.000 g), DES (0.100 g), 100 °C, 2 h. Reaction of cellulose: T = 120 °C; addition of water in two steps (step 1: 0.220 mL, water content 20 wt%, based on IL, $t$ = 0.5 h; step 2: 0.110 mL, total water content 30 wt%, based on IL, $t$ = 1 h).

respectively (Table 1, entry 12). In contrast, in the presence of water, glucose was the major product (maximum at 4 h, 49 wt %, Figure 1), with only little accumulation of oligosaccharides (maximum at 2 h, 8, 9, 7 wt% of cellobiose, cellotriose and cellotetraose, respectively). These results suggest that added water improved the rates of hydrolysis of glucans. Other studies also note that water suppresses the conversion of glucose into HMF in ILs, most likely related to the reduced acidity of the diluted media.[14,15] Longer reaction times nonetheless led to diminished yields of glucose by the formation of HMF and humins (Figure 1).

All of the reactions performed to this stage had been conducted using MCC as a substrate. MCC is a polysaccharide obtained after the acid-catalysed depolymerisation of native cellulose and is a commodity product for many industries.[35] However, the conversion of non-pretreated substrates is desirable. A subsequent set of reactions was performed employing non-pretreated cellulose of various origins (cotton linter, cellulose extracted from eucalyptus and *Pinus*, microalgal biomass, macroalgal biomass). Processing of non-pretreated bulk cellulose in the co-solvent system [$C_4$mim]Cl / ChCl/oxalic acid at 120 °C for 6 h afforded lower yields of low molecular weight reducing sugars compared to MCC (Table 4, entries 1, 3, 5, 8, 10), showing the difficulties experienced when working with native biomass, and the need to improve and modify reaction conditions. Depolymerisation of bulk cellulose requires more forcing conditions compared with MCC, and therefore the overall rate of hydrolysis is lower.[36] The addition of $La(OTf)_3$ slightly improved the transformation of cellulose extracted from eucalyptus to glucose (yield 20 wt%, Table 4, entry 6), but the effect of the Lewis acid is less prominent, when compared to the conversion of MCC under identical reaction conditions (glucose yield 35 wt%, Table 3). Similar to the processing of MCC, longer reactions were accompanied by the formation of humins. Pleasingly, the addition of water in two steps as before, improved the hydrolysis of polysaccharides, affording excellent yields of glucose (45–50 wt%, based on substrate, Table 4, entries 4, 7, 9, 11). This is an efficient process for the conversion of a range of non-pretreated cellulosic substrates into glucose, involving environmentally benign solvent-catalyst media. The results compare favourably with outcomes in the literature where mineral acids or zeolites are employed as catalysts for cellulose hydrolysis in [$C_4$mim]Cl (Table 4, entries 21–23).[11,15]

The conversion of native cellulosic biomass is a significant challenge, and we applied our hydrolysis protocols to biomass derived from terrestrial (chips obtained from softwood or corncob) and marine sources (macroalgae *Ulva lactuca* and microalgae *Porphyridium cruentum*), respectively. Optimal conditions for each source of cellulose or biomass and the reaction outcomes are given in Table 4, entries 12–20. The direct processing of biomass is inherently difficult because native cellulose is usually entangled into plant cell walls with other polysaccharides (e.g., hemicellulose, polymannosides, glycoproteins, etc.) and aromatic polymers (e.g., lignin) forming a rigid polymer system.[3,6] In our hands, the transformation of softwood chips (Table 4, entry 13) in the mixed solvent [$C_4$mim]Cl/ChCl/oxalic acid yielded low molecular weight carbohydrates (glucose + glucosyl oligosaccharides) in a respectable 38 wt% yield based on the glucan content in the biomass. This required processing of wood chip biomass at 120 °C for 6 h, followed by further processing for 4 h after the addition of water (30 wt% of water, based on solvent, added as detailed in Table 4, entry 13). Under these conditions, the xylans (part of the hemicellulose) were hydrolysed into monomer xylose in 25 wt% yield (based on xylan content in the biomass), demonstrating the hydrolysis of both linear and branched polysaccharides (Table 4, entry 13). Most likely, the lower yields of low molecular weight carbohydrates are caused by complicated depolymerisation of wood biomass in ILs. Nevertheless, higher yields of glucose (25 wt%) and xylose (30 wt%, Table 4, entry 14) were attainable after somewhat extended processing of the wood chips (120 °C, 12 h) before addition of water and further heating. In distinct contrast to softwood, the conversion of corncob provided excellent yields of glucose (54 wt%) and xylose (35 wt%) under milder processing conditions before the dilution (100 °C, 2 h, Table 4, entry 16), likely due to the less rigid molecular structure and larger amount of structurally branched polysaccharides present (e.g., hemicellulose and starch).[37] For the same reason,[38–40] marine cell walls were more amenable to hydrolysis. For example, the conversion of the seaweed *Ulva lactuca* in [$C_4$mim]Cl / ChCl/oxalic acid at 120 °C for 6 h, followed by addition of water (30 wt% of water) and further heating at 120 °C for 4 h, provided glucose in 40 wt% yield (based on the glucan content, Table 4, entry 17). This yield can reach 43 wt% when adding water at the 4 h mark (instead of at 6 h, Table 4, entry 18). The experimental data confirm that the branched saccharides which are predominant in marine plant cell walls require less forcing reaction conditions for selective conversion into desirable low molecular weight saccharides. In a remarkable example, the direct processing of microalgae *P. cruentum*, as raw biomass, in [$C_4$mim]Cl / ChCl/oxalic acid, yielded 55 wt% of glucose and 40 wt% of xylose (based on the content of glucans and xylans in biomass, respectively, Table 4, entry 20),

**Table 4.** Acid-catalysed conversion of bulk cellulose and cellulosic biomass in [$C_4$mim]Cl / ChCl/oxalic acid.[a]

| Entry | Substrate | *X* [%] | *S* [%] | Yield xylose [wt%] | Yield glucose [wt%] | Yield cellobiose [wt%] | Yield cellotriose [wt%] | Yield cellotetraose [wt%] | Yield HMF [mol%] |
|---|---|---|---|---|---|---|---|---|---|
| 1 | MCC | 85 | 98 | – | 16 | 16 | 20 | 31 | 2 |
| 2[b] | | 91 | 73 | – | 37 | 9 | 11 | 9 | 6 |
| 3 | Cotton linter | 93 | 73 | – | 19 | 8 | 19 | 22 | 3 |
| 4[b] | | 95 | 60 | – | 45 | 7 | 8 | 5 | 6 |
| 5 | Eucalyptus cellulose | 85 | 64 | – | 11 | 7 | 16 | 20 | 1 |
| 6[c] | | 68 | 85 | – | 20 | 8 | 14 | 16 | 4 |
| 7[b] | | 91 | 74 | – | 48 | 7 | 7 | 5 | 4 |
| 8 | *Pinus* cellulose | 82 | 73 | – | 11 | 8 | 17 | 24 | 5 |
| 9 [b] | | 92 | 77 | – | 50 | 7 | 8 | 6 | 6 |
| 10 | *Pinus* cellulose (unbleached) | 80 | 73 | – | 12 | 7 | 16 | 23 | 1 |
| 11[b] | | 91 | 80 | – | 46 | 9 | 10 | 8 | 4 |
| 12 | Wood chips (softwood) | 36 | – | 1 | 8 | 4 | 9 | 12 | 0 |
| 13[b] | | 65 | – | 25 | 20 | 5 | 7 | 6 | 0 |
| 14[d] | | 75 | – | 30 | 25 | 5 | 6 | 4 | 2 |
| 15 [b] | Corncob | 73 | – | 2 | 18 | 0 | 0 | 0 | 10 |
| 16[e] | | 74 | – | 35 | 54 | 0 | 0 | 0 | 10 |
| 17[b] | *Ulva lactuca* | 86 | – | 3 | 40 | 2 | 3 | 2 | 0 |
| 18[f] | | 83 | – | 4 | 43 | 5 | 4 | 4 | 0 |
| 19[b] | *P. cruentum* | 99 | – | 3 | 16 | 0 | 0 | 0 | 0 |
| 20[e] | | 98 | – | 40 | 55 | 0 | 0 | 0 | 0 |
| 21[g,11] | Sigmacell | – | – | – | 38 | – | – | – | – |
| 22[h,11] | | – | – | – | 21 | – | – | – | – |
| 23[i,15] | MCC | – | – | – | 50 (mol%) | 5 (mol%) | – | – | 24 |

[a] Yields are specified in wt% based on input of cellulose for carbohydrates and in mol% based on anhydroglucose units present for HMF; yields of glucose, cellobiose, cellotriose and cellotetraose obtained from lignocellulose, or algal biomass, are specified in wt% based on the glucans content in substrate; yields of xylose are specified based on the xylans content in biomass; '0' means that product was identified in trace amounts based on LC analysis; *X* = conversion; *S* = total selectivity of carbohydrates (glucose, cellobiose, cellotriose, cellotetraose). Reaction conditions: substrate (50 mg), [$C_4$mim]Cl (1.000 g), DES (0.100 g), 120 °C, 6 h. [b] Reaction conditions: substrate (50 mg), [$C_4$mim]Cl (1.000 g), DES (0.100 g), 120 °C, 6 h, then addition of water in two steps (step 1: 0.220 mL, water content 20 wt%, based on IL, $t = 0$; step 2: 0.110 mL, water content 30 wt%, based on IL, $t = 0.5$ h), 120 °C, 4 h. [c] Reaction conditions: substrate (50 mg), [$C_4$mim]Cl (1.000 g), DES (0.100 g), La(OTf)$_3$ (10 mol% based on anhydroglucose unit present), 120 °C, 2 h. [d] Reaction conditions: substrate (50 mg), [$C_4$mim]Cl (1.000 g), DES (0.100 g), 120 °C, 12 h, then addition of water in two steps (step 1: 0.220 mL, water content 20 wt%, based on IL, $t = 0$; step 2: 0.110 mL, water content 30 wt%, based on IL, $t = 0.5$ h), 120 °C, 4 h. [e] Reaction conditions: substrate (50 mg), [$C_4$mim]Cl (1.000 g), DES (0.100 g), 100 °C, 2 h, then temperature increase to 120 °C and gradual addition of water in two steps (step 1: 0.220 mL, water content 20 wt%, based on IL, $t = 0$; step 2: 0.110 mL, water content 30 wt%, based on IL, $t = 0.5$ h), 4 h. [f] Reaction conditions: substrate (50 mg), [$C_4$mim]Cl (1.000 g), DES (0.100 g), 120 °C, 4 h, then addition of water in two steps (step 1: 0.220 mL, water content 20 wt%, based on IL, $t = 0$; step 2: 0.110 mL, water content 30 wt%, based on IL, $t = 0.5$ h), 120 °C, 4 h. [g] Sigmacell is a commodity cellulose that typically consist of cotton linters. Reaction conditions: substrate (0.32 g), [$C_4$mim]Cl (4.0 g), $H_2SO_4$ (98 wt%, 0.184 g), water (0.063 g), 100 °C, 45 min.[11] [h] Reaction conditions: substrate (0.32 g), [$C_4$mim]Cl (4.0 g), HCl (36 wt%, 0.285 g), water (0.063 g), 100 °C, 11 min.[11] [i] Reaction conditions: substrate (0.1 g), [$C_4$mim]Cl (2.0 g), 130 °C, to complete dissolution, then addition of HY-zeolite (11 mol%) and water in three steps (step 1: water content 5 wt%, based on IL, $t = 0$; step 2: water content 20 wt%, based on IL, $t = 0.5$ h; step 3: water content 33 wt%, $t = 60$ min ), 130 °C, 2 h.[15]

giving 98% conversion of the biomass. These experimental outcomes shine light on the exquisite promise held by the direct conversion of biomass into significantly higher value and useful monosaccharides. One persistent drawback is the need to employ large volumes of the IL solvent, and this challenge remains to be solved. Nevertheless, the results serve as a springboard towards scalable processes to manufacture sustainable and renewable chemicals (Scheme 1).

## 3. Conclusions

The combined ionic liquid mixture of [$C_4$mim]Cl/ChCl/oxalic acid is an excellent solvent-catalyst system for the high yielding and selective conversion of cellulose and native biomass, of terrestrial and marine origin, into the low molecular weight saccharides glucose, cellobiose, cellotriose, cellotetraose and xylose. We demonstrate that the acid-catalysed transformation of cellulose in mixed solvents occurs predominantly into glucan oligomer 'chunks' (cellotetraose, cellotriose and cellobiose) from which glucose emerges. The conversion into glucose can be improved by modifying the natural acidity of the DES with added Lewis acid, producing a Lewis acid-assisted Brønsted acid complex, or by the addition of water during the course of the reaction. Importantly, the mixed system avoids the need for pretreatment of the native cellulosic materials. While efficient in this process, the need for large volumes of the ionic system remains to be solved.

## Experimental Section

### Materials

Reagents and metal trifluoromethanesulfonate (metal triflate) catalysts (Al(OTf)$_3$, Y(OTf)$_3$, AgOTf, In(OTf)$_3$, Sn(OTf)$_2$, La(OTf)$_3$, Yb(OTf)$_3$, or Hf(OTf)$_4$) were used as supplied from commercial sources. Cotton linter, and cellulose extracted from eucalyptus and *Pinus* (unbleached and bleached, BKT, Kinleith, New Zealand) were a

generous gift from Dr Simon Hinkley, The Ferrier Research Institute, Victoria University of Wellington (New Zealand). Lignocellulose (softwood chips and corncob) was sourced from local growers (Australia). Macroalgae *Ulva lactuca* was provided as a generous gift by Dr Wayne O'Connor, Department of Primary Industries Fisheries, Port Stephens Fisheries Institute (Australia). Microalgae *Porphyridium cruentum* was grown and supplied by Climate Change Cluster (C3), University of Technology Sydney (Australia). Biomass for acid-catalysed reactions was vacuum oven-dried (60 °C, 12 h). Compositional analysis of biomass was performed using standard analytical procedures: NREL/TP-510-42618[41] for lignocellulose, NREL/TP-5100-60957[42] for algal biomass. The total amount of carbohydrates in the given biomass is specified in the Supporting information Table S2. [$C_4$mim]Cl was prepared according to reference,[43] while ChCl/acid (1:1 molar ratio for oxalic acid dihydrate or *p*-toluenesulfonic acid monohydrate, respectively; 1:0.5 for citric acid monohydrate, respectively) solvents were prepared according to reference.[44]

### High Performance Liquid Chromatography

Carbohydrates were analysed using liquid chromatography-mass spectrometry (LC/MS) on a Shimadzu LCMS-8060 instrument with electrospray ionisation source in negative ion mode. The separation was conducted on a Supelco apHera NH2-Polymer analytical column (150 mm × 4.6 mm, 5 μm) using a mixture of acetonitrile and water (65:35 v/v) as the mobile phase at a flow rate 0.6 mL $min^{-1}$ and a run time of 18 min. Five transitions *m/z* 149.10→89.05 (fragmentor voltage 12 V, collision energy 7 eV), *m/z* 178.85→89.15 (fragmentor voltage 19 V, collision energy 8 eV), *m/z* 341.30→161.20 (fragmentor voltage 16 V, collision energy 8 eV), *m/z* 503.35→161.20 (fragmentor voltage 24 V, collision energy 13 eV) and *m/z* 665.25→503.10 (fragmentor voltage 26 V, collision energy 12 eV) were monitored for detection of xylose, glucose, cellobiose, cellotriose and cellotetraose, respectively. A representative chromatogram is shown in Figure S5. HPLC analysis of HMF was performed using an Agilent 1290 LC instrument equipped with an Agilent Zorbax Eclipse XDB-C18 analytical column (150 mm × 4.6 mm, 3 μm) and Agilent 1260 DAD VL+ detector (detection wavelength: 278 nm). The mobile phase was a mixture of methanol and water (15:85 v/v) at a flow rate of 1.1 mL $min^{-1}$ with a run time of 20 min. Quantitative analysis was performed with the use of a standard curve plotted with analytical standards. The standard curves were generated using measured HPLC-peak area at appropriate concentration of the analytical standard; all figures provided linear correlation coefficient $>0.99$.

### NMR Spectroscopy

NMR spectra of the products were recorded on an Agilent 500 MHz NMR spectrometer using deuteroacetonitrile-$d_3$ ($CD_3CN$), or deuterium oxide ($D_2O$) as solvents. 2D NMR spectroscopy (HSQC and COSY) were used to unambiguously assign the peaks. Samples were dissolved in the selected solvents in a 5 mm NMR tube and the spectra were collected at 25 °C with chemical shifts referenced relative to residual solvent for samples recorded in $CD_3CN$ ($^1$H: $\delta=$ 1.96 ppm; $^{13}$C: $\delta=118.2$ ppm), or to deuterated sodium 3-trimethylsilylpropionate ([$D_4$]TMSP, $^1$H, $^{13}$C: $\delta=0.00$ ppm) for samples recorded in $D_2O$. NMR spectra of the neat DESs were collected at 25 °C in a 5 mm NMR tube equipped with coaxial inserts containing deuterodimethyl sulfoxide ([$D_6$]DMSO, $^1$H: $\delta=2.49$ ppm; $^{13}$C: $\delta=$ 39.7 ppm) as an external lock.

### IR Spectrometry

IR spectra were collected using a thin film on a Thermo Scientific Nicolet 6700 spectrometer in a range 4000–450 $cm^{-1}$.

### pH Readings

pH Readings were recorded at room temperature (22–23 °C) using a Mettler Toledo pH meter adapted with a standard glass electrode with prior calibration by two buffer solutions (pH = 4.00, pH = 7.00). Measurements were performed in triplicate and the average values are presented.

### Acid-Catalysed Conversion of Cellulosic Substrates

MCC, cellobiose, glucose, or fructose (50 mg) and solvent ([$C_4$mim]Cl, or DES, 1.000 g) were loaded to a glass pressure tube equipped with a magnetic follower and the reactor was sealed. The mixture was heated and stirred at 120 °C for 2 h. After completion of the process, the reaction mixture was cooled and diluted with deionised water (9.00 mL) to precipitate any unreacted cellulose. The mixture was centrifuged (10,000 × g for 15 min) and decanted. The recovered solids were washed with deionised water (3 × 10 mL), vacuum oven-dried (60 °C, 1 mbar, 12 h) and weighed to calculate the conversion of cellulose. The decanted liquid phase was quenched by the addition of an aqueous solution of sodium hydrogen carbonate (1.00 mL, 0.05 M) and centrifuged (10,000 × g for 15 min). The recovered solutions were diluted with a known volume of deionised water, if required, and analysed by HPLC. To recover HMF from the diluted and neutralised ILs (50.0 mL, combined aqueous phases after conversions of carbohydrates), an extraction with ethyl acetate (3 × 100 mL) was performed. The ethyl acetate layers were combined and dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was subjected to flash column chromatography (hexane/ethyl acetate, 60:40 v/v) to isolate HMF, which gave satisfactory analytical data.[23]

For the conversions in mixed ionic solvent, cellulose (50 mg), [$C_4$mim]Cl (1.000 g) and DES (0.100 g), and in some instances metal triflate catalyst ($Al(OTf)_3$, $Y(OTf)_3$, AgOTf, $In(OTf)_3$, $Sn(OTf)_2$, $La(OTf)_3$, $Yb(OTf)_3$, or $Hf(OTf)_4$, 10 mol% based on the number of anhydroglucose units present in cellulose), were introduced to a glass pressure tube equipped with a magnetic follower and the reactor was sealed. The mixture was heated and stirred at the predetermined temperature for a fixed period of time. The products were recovered and analysed as detailed above.

For the conversions with gradually added water, cellulosic substrate (cellulose, lignocellulose, or algal biomass, 50 mg), [$C_4$mim]Cl (1.000 g) and DES (0.100 g) were charged to a glass pressure tube equipped with a magnetic follower and the reaction mixture was heated and agitated for a fixed amount of time. After this fixed period of time (which varied from case to case), deionised water was added (0.220 mL, water content 20 wt%, based on IL) followed by heating, and 30 minutes later a second portion was added (0.110 mL, total water content 30 wt%, based on IL) and the reaction system was additionally heated and stirred for a fixed period of time. The products were recovered and analysed as detailed above.

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## Conflict of Interest

The authors declare no conflict of interest.

**Keywords:** biomass · carbohydrates · ionic liquids · acid catalysis · green chemistry

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