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Efficient Acid-Catalyzed Hydrolysis of Cellulose in Ionic Liquid

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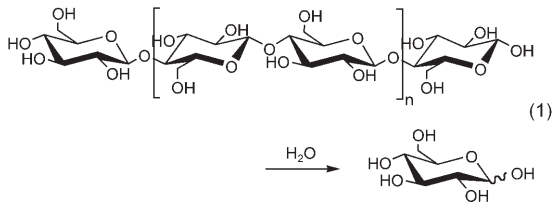
Abstract: A novel method for cellulose hydrolysis catalyzed by mineral acids in the ionic liquid 1-butyl-3-methylimidazolium chloride ([C_4mim]Cl) has been developed that facilitates the hydrolysis of cellulose with dramatically accelerated reaction rates at 100 °C under atmospheric pressure and without pretreatment.

Keywords: carbohydrates; green chemistry; hydrolysis; ionic liquids; polymers

Cellulose is the most abundant renewable carbon source which constitutes a large fraction of the lignocellulosic materials found in the world. Its efficient use is essential for the generation of biofuels and biomaterials.[1] It is a highly crystalline polymer of D-anhydroglucopyranose units jointed together in long chains by β-1,4-glycosidic bonds. The tight hydrogen-bonding network and van der Waals interactions greatly stabilize cellulose,[2] making it notoriously resistant to hydrolysis.

Cellulose gives rise to monomeric glucose upon complete hydrolysis with various processes catalyzed by mineral acids or enzymes [Eq. (1)].[3] Yet up to



(1)

now, these processes require extensive pretreatment.[4] The enzymatic process takes place under mild reaction conditions, but it is slow and the enzyme cost is high. The traditional dilute acid hydrolysis process is operated at elevated temperature under high pressure, yet the hydrolysis rate is slow and sugar degradation is substantial. Hydrolysis with concentrated sulfuric acid (H_2SO_4) can be operated under less harsh conditions, but requires expensive corrosion-resistant reactors and has major waste disposal problems. Furthermore, acid hydrolysis is known to generate degradation products, which significantly lowers glucose yield and interferes with downstream applications. Therefore, a method that can achieve the efficient and cost-effective hydrolysis of cellulose remains to be developed.

Studies by Rogers et al. showed that the ionic liquid (IL) 1-butyl-3-methylimidazolium chloride ([C_4mim]Cl) is a powerful solvent for cellulose. Up to 25 wt% of cellulose can be dissolved in this media to form a homogeneous solution.[5] Solubilization of cellulose in ILs has attracted much attention since.[6] We therefore envisioned that IL might be a superior solvent to be used for the acid hydrolysis of cellulose. In this report, we describe an efficient method for cellulose hydrolysis in [C_4mim]Cl catalyzed by H_2SO_4 without pretreatment.

Table 1 summarizes the hydrolysis conditions and yields of model substrate Sigmacell cellulose in solvent [C_4mim]Cl and with H_2SO_4 as the catalyst. According to the previous report, acid hydrolysis of cellulose under atmospheric pressure requires excess acid loading.[7] Therefore, our first reaction was performed by using an acid/cellulose mass ratio of 5 at

Table 1. Reaction conditions and yields of hydrolysis of Sigmacell cellulose in ionic liquid [C_4mim]Cl at 100 °C.

Entry	Acid/cellulose mass ratio	Time [min]	$Yield_{glucose}$ [%]	$Yield_{TRS}$ [%]
1	5	120	5	7
2	0.92	3	36	59
3	0.46	42	37	64
4	0.11	540	43	77
5[a]	0.92	1080	13	27

[a] Reaction was performed in water.

100 °C. Unfortunately, the yields of both total reducing sugars (TRS) and glucose were less than 10 % when the reactions were terminated either after 2 min or after 2 h (Table 1, entry 1). Because the cellulose would precipitate out from ILs upon mixing with water,[5] attempts were then made to recover the cellulose by diluting the reaction mixture with cold water. To our surprise, instead of precipitating, a homogeneous solution was formed, suggesting that cellulose deploymerization occurred. Next, we performed hydrolysis experiments with gradually reduced acid loading (see Experimental Section). TRS and glucose were obtained in 59 % and 36 %, respectively, within 3 min when the acid/cellulose mass ratio was 0.92 (Table 1, entry 2). Further reducing the acid/cellulose mass ratio to 0.46 produced higher yields after 42 min (Table 1, entry 3). When the mass ratio was dropped to 0.11, the yields of TRS and glucose reached 77 % and 43 %, respectively, in 9 h (Table 1, entry 4). In contrast, when water was used as the solvent, only 27 % of TRS and 13 % of glucose were obtained under otherwise identical conditions after 18 h (Table 1, entry 5). These results demonstrated that $[C_4mim]Cl$ as the solvent and a low content of H_2SO_4 as the catalyst was an efficient method for cellulose hydrolysis. This is an important finding because our reaction system was operated under mild conditions using essentially a catalytic amount of H_2SO_4 and no pretreatment was required.

To better understand the acid-catalyzed hydrolysis of cellulose in $[C_4mim]Cl$, we obtained the time course of TRS formation from Sigmacell cellulose at the acid/cellulose ratio of 0.46 for 130 min (Figure 1).

Regression analysis of the experimental data by non-linear least squares curve fitting with the software Origin 7.0 indicated that the kinetics most likely followed a consecutive first-order reaction sequence,[8] where k_1 for TRS formation and k_2 for TRS degradation were determined to be 0.073 min^{-1} and 0.007 min^{-1}, respectively. Therefore, cellulose hydrolysis proceeded significantly faster than TRS degradation. In the literature, a similar rate constant of 0.080 min^{-1} for TRS formation has been observed during the hydrolysis of α-cellulose at 180 °C under high pressure in 1.5 % aqueous H_2SO_4.[9]

Furthermore, we hydrolyzed cellulose samples from different origins and degrees of polymerization (DP) to explore the scope of this method. Under the same reaction conditions as in Figure 1, similar TRS yields were obtained for these cellulose samples with DP values ranging form 100 to 450 (Table 2). The reaction time that was needed to reach the maximal TRS yields showed some correlation with the DP values. The higher the DP value, the longer was the reaction time required. For α-cellulose with a DP value of 100, TRS yield reached 68 % in 9 min, but it took 25 min and 28 min, respectively, to reach similar TRS yields

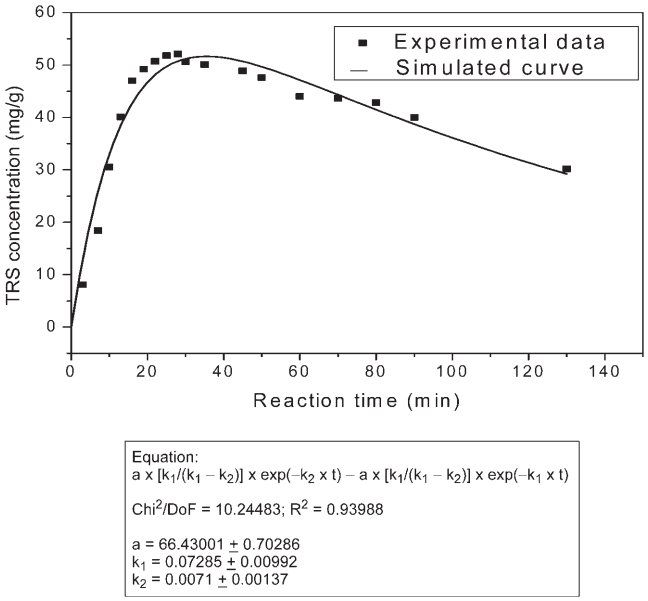


Figure 1. Time course of cellulose hydrolysis. *Reaction conditions:* Sigmacell cellulose (0.32 g) (initial concentration: 71 mg g^{-1}) in the mixture of H_2SO_4 (0.148 g), H_2O (0.063 g) and $[C_4mim]Cl$ (4.0 g) at 100 °C under atmospheric pressure.

for Avicel and Sigmacell cellulose (Table 2, entries 1, 3 and 7). It was also found that the longer was time to hydrolyze the cellulose with same DP, the higher was the yield glucose produced. Meanwhile, with the increase of the hydrolysis time, the yield of TRS slightly decreased. There was no significant effect of the reaction time on the TRS yield from cellulose with different DP values. Compared with over 60 % of TRS yield with our hydrolysis method, only 26 % TRS was obtained after 40 min hydrolysis at 175 °C and under high pressure when catalyzed by dilute H_2SO_4 and the reactant α-cellulose was pretreated by ball milling for 6 days (Table 2, entry 9).[10] Therefore, a significant improvement in TRS production has been achieved by our method.

Our data indicated that longer reaction times favored glucose formation, while the shorter reaction times produced more TRS (Table 2, entry 1, 3, 5, 7 *vs.* 2, 4, 6, 8). It was also found that glucose production did not vary with the cellulose origins (entry 2, 4, 6 and 8). These results implied that cellulose hydrolysis with this method most likely followed a random hydrolysis mechanism, as observed in the cellulose hydrolysis with concentrated acids.[11] During the hydrolytic process, both endoglycosidic and exoglycosidic scission occurred, but the endoglycosidic product, oligoglucoses, was the major one in the initial stage. Such phenomena may not be observed in the conventional hydrolysis of cellulose in a heterogeneous aqueous solution.

Other mineral acids, including HCl, HNO_3, and H_3PO_4, were tested for hydrolysis of cellulose with

Table 2. Reaction time and yields of acid-catalyzed hydrolysis of different celluloses in $[C_4mim]Cl$.[a]

Entry	Sample	DP	Time [min]	$Yield_{Glucose}$ [%]	$Yield_{TRS}$ [%]
1	α-cellulose	100	9	20	68
2	α-cellulose	100	24	39	63
3	Avicel	220	25	32	73
4	Avicel	220	35	39	66
5	Spruce	275	25	28	71
6	Spruce	275	42	36	64
7	Sigmacell	450	28	28	66
8	Sigmacell	450	45	38	62
9[b]	α-cellulose	100	40	$\leq$ 22	$\leq$ 26
10[c]	Avicel	220	540	31	58
11[d]	Sigmacell	450	11	21	65
12[e]	Sigmacell	450	10	13	50
13[f]	Sigmacell	450	420	16	54

[a] Unless otherwise noted, reactions were carried out with identical conditions to those of Figure 1.
[b] Hydrolysis of pretreated α-cellulose with 0.05 M H_2SO_4 at 175 °C in a sealed tubular reactor.[11]
[c] Hydrolysis of Avicel cellulose (1.0 g) in 70 wt % H_2SO_4 (3.0 mL) at 40 °C.[11]
[d] 0.285 g of 36 wt % HCl was employed.
[e] 0.278 g of 65 wt % HNO_3 was employed.
[f] 0.331 g of 85 wt % H_3PO_4 was employed.

$[C_4mim]Cl$ as the solvent. As shown in Table 2, entries 11, 12 and 13, all these acids afforded satisfactory results. However, the hydrolysis reactions catalyzed by HCl and HNO_3 resembled that of H_2SO_4, while H_3PO_4 was less effective. These results suggested that the strength of acidity played an important role in the hydrolysis of cellulose in $[C_4mim]Cl$.

When cellulose was completely dissolved in $[C_4mim]Cl$ and formed a homogeneous solution, it made the H^+ more accessible to the β-glucosidic bonds. This is likely the reason that the hydrolysis rate was much higher with $[C_4mim]Cl$ as the solvent when compared with those systems where hydrolysis occurred at the surface of cellulose. Therefore, a physical barrier for hydrolysis was overcome through formation of a solution. In addition, the dissociated Cl^- and the electron-rich aromatic π system of $[C_4mim]^+$ in $[C_4mim]Cl$ may also weaken the glycosidic linkage to faciliate hydrolysis. This method produced equal or higher yields of both glucose and TRS when compared with those reaction procedures at high temperature and/or using concentrated H_2SO_4 (65 wt % or higher).[7,12]

In conclusion, we have demonstrated, for the first time, that H_2SO_4 and other mineral acids in the ionic liquid $[C_4mim]Cl$, provided an effective method for the hydrolysis of cellulose without pretreatment. With this method, hydrolysis proceeded at a relatively lower temperature and under atmospheric pressure with reduced acid loading and without compromising the reaction yield. Since IL is a property-tunable solvent,[13] further studies on the use of other ILs in the hydrolysis of cellulose and other potential applications of the $H_2SO_4/[C_4mim]Cl$ system are warranted. Although more work, such as profiling the hydrolysis products and proof-testing them as feedstock for biorefinery, will be required to better understand the chemistry and to improve this technology, the method reported herein offers a potentially practical and efficient way to depolymerize cellulose to abstract biofuels and biochemicals from lignocellulosic materials.[1]

Experimental Section

Typical Procedure for the Acid-Catalyzed Hydrolysis of Cellulose in Ionic Liquid $[C_4mim]Cl$

The cellulose samples Avicel PH-101 (Cat. No. 11365), Sigmacell cellulose (Cat. No. S6790), cellulose powder from spruce (Cat. No. 22182) and α-cellulose (Cat. No. C8002) were purchased from Sigma (St. Louis, USA), and were dried under vacuum at 100 °C for 24 h before use. The IL $[C_4mim]Cl$ was prepared according to the procedures reported elsewhere.[14]

A mixture of cellulose (0.32 g) in $[C_4mim]Cl$ (4.0 g) was heated with stirring at 100 °C under atmospheric pressure until a clear solution was formed. To this solution was added H_2O (0.063 g, 1.75 mol equivs. to glucose unit) and the appropriate amount of 98 wt % H_2SO_4. The reaction mixture was vigorously stirred, quenched with cold water, neutralized with 0.5 mol/L NaOH, and filtered. The aqueous solution was collected and subjected to TRS analysis using a DNS method (see Supporting Information) and glucose analysis with a glucose analyzer. Isolation of TRS from the IL was realized by an ion exchange method using a cation resin (Dowex 50W × 8) (see Supporting Information).

Acknowledgements

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