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Complete chemical hydrolysis of cellulose into fermentable sugars via ionic liquids and antisolvent pretreatments

Silvia Morales-delaRosa, Jose M. Campos-Martin* and Jose L. G. Fierro*

This work describes a relatively simple methodology for efficiently deconstructing cellulose into monomeric glucose, which is more easily transformed into a variety of platform molecules for the production of chemicals and fuels. The approach undertaken here first involves the dissolution of cellulose in an ionic liquid (IL), followed by a second reconstruction step aided by an antisolvent. The regenerated cellulose exhibited strong structural and morphological changes, as revealed by X-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses. These changes dramatically affect the hydrolytic reactivity of the cellulose with dilute mineral acids. As a consequence, the glucose yield obtained from the deconstructed-reconstructed cellulose was substantially higher than that achieved via hydrolysis of the starting cellulose. Factors that affect the hydrolysis reaction include the type of cellulose substrate, the type of IL used in the pretreatment and the type of acid used in the hydrolysis step. The best results were obtained by treating the cellulose with IL and using phosphotungstic acid (0.067 mol/L) as a catalyst at 413 K. Under these conditions, the conversion of cellulose was almost complete (> 99 %), with a glucose yield of 87 % after only 5 h of reaction.

Introduction

The progressive increase in global oil consumption and the associated depletion of oil reserves has encouraged scientists to explore alternative routes to the synthesis of fuels and chemicals.[1] A promising feedstock for commercial-scale production of biofuels and chemicals is lignocellulosic biomass, which is abundant and readily available. Lignocellulose, which forms the structural framework of plants consisting of cellulose, hemicellulose and lignin, is first broken down and hydrolyzed into simple fermentable sugars.[2] A major bottleneck is the need to disarray lignin, which is present as a protective covering and makes cellulose and hemicellulose recalcitrant to enzymatic hydrolysis. A number of biomass deconstruction or pretreatment processes (physical, chemical, and biological) have been used to break the structural framework of plants and to depolymerize lignocellulose biomass. Some of these pretreatments include treatments with dilute sulfuric acid,[3, 4] aqueous ammonia at high temperature,[5, 6] lime[7, 8] or organic solvents,[9, 10] as well as treatments by oxidative delignification,[11] microwave irradiation,[12-14] ball milling[15, 16] or steam explosion.[17-19]

Examination of these cellulose deconstruction methods reveals that no pretreatment technology offers 100 % conversion of cellulose into fermentable C_5/C_6 sugars. Some biomass is always lost, which affects the final yield and increases the cost of the finished fuel or chemical product. Although pretreatment of lignocellulosic biomass with combination of two or more pretreatment processes has shown promising results, there is room for further development,[20] via either the development of a new efficient treatment process or the improvement of an existing process to provide better performance.

The conventional methodologies have technological limitations that compromise the efficiency of the separation processes, such as insufficient selectivity or partial degeneration of the products. Hence, the current and envisaged investigations are focused on understanding the pathways to improve the selective separation of lignocellulose compounds to achieve feasible and sustainable processes.[21]

In a pioneering work, Fort *et al.*[22] reported that solvent systems based on 1-buthyl-3-methylimidazolium chloride ([BMIM][Cl])-DMSO-d_6 mixed in a proportion of 84/16 wt% are capable of partially dissolving wood chips. These authors noted that, based on the color intensity and viscosity of the solution mixture, wood particles swelled and were reduced in size during the dissolution. Similarly, Kilpelainen *et al.*[23] reported the complete dissolution of 8 wt% dried wood sawdust samples (Southern pine) in both [BMIM][Cl] and [AMIM][Cl] (1-allyl-3-methylimidazolium chloride) ionic liquids (ILs) in the temperature range of 80 to 130 °C after 8 h. ILs have been recognized as promising solvents for the mild and rapid hydrolysis of biomass feedstocks.[24-28] However, the high cost of ILs can be a potential drawback. Therefore, ILs should be recovered from the hydrolyzate efficiently through the use of a cost-effective separation technology. Preliminary calculations show that at least 98% of the ILs should be recovered for an economically feasible process.[26] Extraction appears to be challenging because fermentable sugars and [EMIM][Cl] (1-ethyl-3-methylimidazolium chloride) exhibit similar solubilities in various solvents.[29]

For this reason, a different strategy has been proposed: the pre-treatment of lignocellulosic biomass using ILs. This

[a] *Ms. S. Morales-delaRosa, Dr. J. M. Campos-Martin*, Prof. Dr. J. L. G. Fierro**
Sustainable Energy and Chemistry Group (EQS), Instituto de Catálisis y Petroleoquímica, CSIC
Marie Curie, 2 Cantoblanco, 28049 Madrid, Spain,
http://www.icp.csic.es/eqsgroup/
E-mail: j.m.campos@icp.csic.es; jlgfierro@icp.csic.es

methodology can effectively remove the lignin and reduce the crystallinity of the cellulose to permit enzymatic hydrolysis at high solid loadings and low enzyme concentrations; hence, it substantially accelerates the rate of enzymatic hydrolysis and increases the yield of fermentable sugars.[30, 31] Indeed, pretreatment of cellulosic biomass using ILs can reduce the crystallinity of the cellulose to enable chemical hydrolysis at very low acid concentrations and thereby increase the yield of fermentable sugars. This approach allows the recovery of not only the precipitated cellulose but also the IL employed in the solubilization step.

With this idea in mind, we previously investigated[32] the hydrolysis of cellulose without solubilization in ILs. We observed that the crystallinity of the cellulose also affects its reactivity: well-crystallized cellulose is more resistant to acid hydrolysis than its less-crystalline counterpart. The highest selectivity for glucose over levulinic acid was recorded at a reaction temperature of 140 ºC and a H_2SO_4 concentration in the range of 0.2 to 0.5 mol/L. Under these reaction conditions, only a small concentration of levulinic acid was detected; however, the glucose yield reached only 20% in 2 h. Therefore, we undertook the present work to improve the yield of glucose by overcoming the recalcitrance of microgranular or fibrous cellulose. The approach undertaken here includes three steps: (i) deconstruction of cellulose by dissolution in an ionic liquid, (ii) reconstruction the cellulose structure by precipitation with the aid of an antisolvent (water), and (iii) hydrolysis of the resulting cellulose. The advantage of precipitating cellulose is that the IL can be completely recovered and is therefore not present during the hydrolysis step. Full recovery of ILs according to the methodology envisioned here is critically important when the techno-economic feasibility of a large-scale process for fermentable sugar production from IL-pretreated biomass is considered.

The importance of the methodology developed here is illustrated by the almost complete cellulose conversion (> 99%) with 87 % glucose yield being obtained after 5 h of reaction at 413 K using phosphotungstic acid (0.067 mol/L) as a cellulose hydrolysis agent of cellulose obtained via deconstruction with an IL and subsequent reconstruction by precipitation with water.

Results and Discussion

Modification of the cellulose during the pretreatment

The dissolution of cellulose, either fibrilar or microgranular, in the [EMIM][Cl] IL, followed by precipitation in water (antisolvent) induced important morphological and textural changes (see Figure 1). The original microfibrous (Figure 1 A) and granular (Figure 1 D) samples appear in powder form with no significant morphological differences among them. In contrast, the cellulose samples obtained via solubilization of microfibrilar cellulose in the [EMIM][Cl] IL followed by reconstruction upon precipitation with water as an antisolvent (Figure 1 B and Figure 1 C) exhibit a gel-like morphology. However, the color of the reconstructed cellulose appears to differ somewhat, depending on whether the water antisolvent was added at high temperature (408 K) or after the sample cooled (303 K). In the first case, the color of the reconstructed cellulose was white (Figure 1 B), whereas, in the latter case, it was almost transparent (Figure 1 C and E).

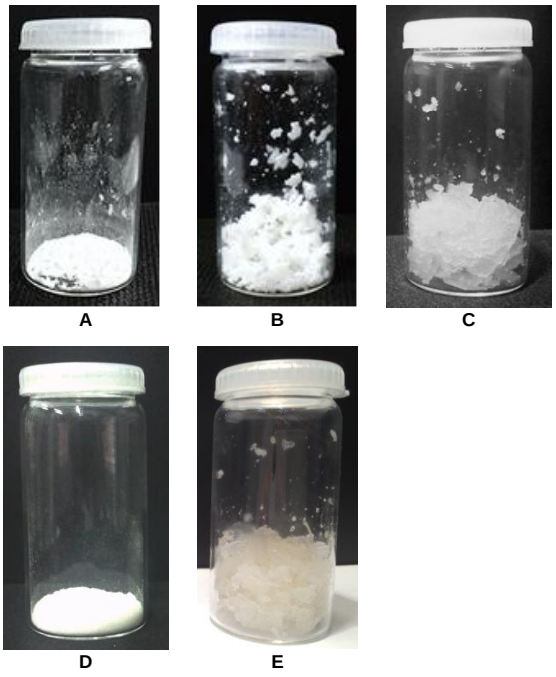


Figure 1. Original and IL-pretreated celluloses. (A), microfibrous cellulose; (B), pretreated microfibrous cellulose, white sample; (C), pretreated microfibrous cellulose, transparent sample; (D), microgranular cellulose; and (E), pretreated microgranular cellulose, transparent sample.

Morphology of pretreated cellulose

The micro- and submicrometric morphology of both the original and deconstructed-reconstructed cellulose samples was examined by scanning electron microscopy (SEM). The microfibrous and granular celluloses exhibit differences at low magnification: the microfibrous sample contains long cylindrical fibers with diameters of approximately 20 μm (Figure 2), whereas the microgranular sample contains smaller fragmented particles and fibers that are shorter than those of fibrous cellulose (Figure 3). However, when the SEM images were recorded at a higher magnification, both samples were observed to be composed of fibers with similar structures, although the microgranular sample contained shorter fibers together with some amorphous particles.

As previously mentioned, the deconstruction-reconstruction pretreatments led to a dramatic change in the structure and morphology of the starting cellulosic substrates. The morphology of the cellulose fibers disappeared after the pretreatments, irrespective of the cellulose source (Figure 4 and Figure 5). At low magnification, the surface appears rather smooth; however, at high magnification, some porous structures can be distinguished. The surface of the cellulose precipitated at lower temperature (transparent) is quite similar at low magnification to that of the cellulose precipitated at higher temperature; however, its porous structure observed at high magnification is less marked (Figure 6).

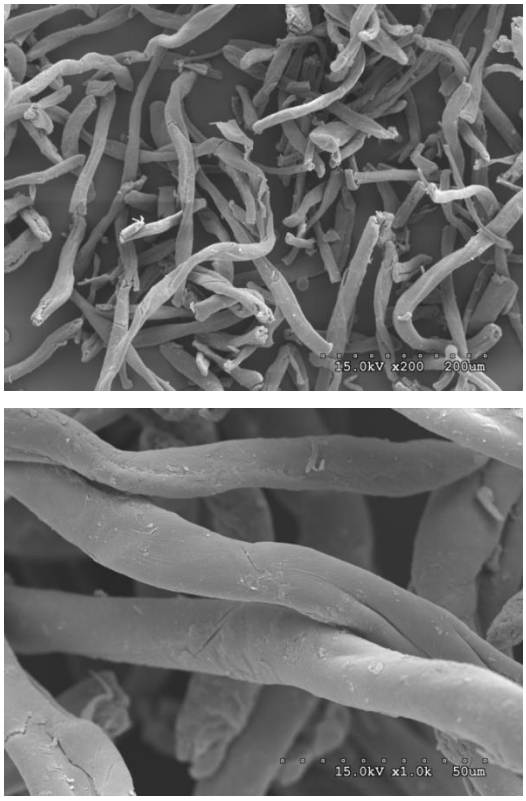


Figure 2. SEM micrographs of the starting microfibrous cellulose. The bottom panel depicts the same sample at higher magnification.

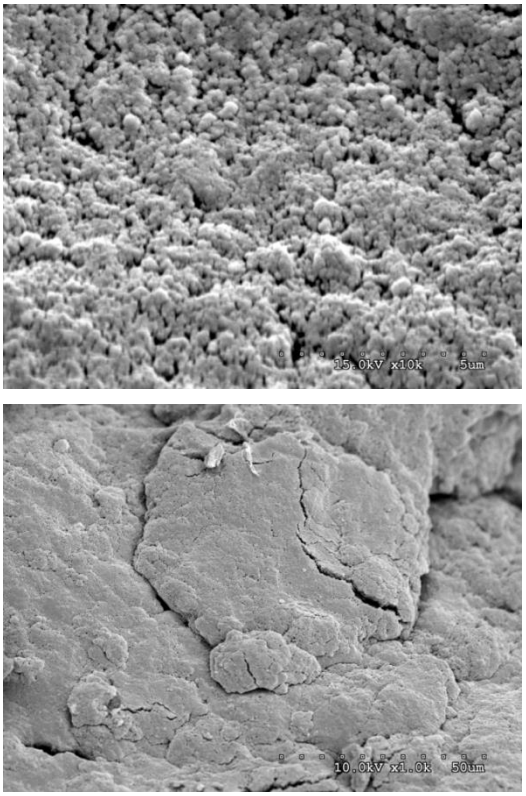


Figure 4. SEM micrographs of microfibrous cellulose pretreated with EMIMCl (15 min) and precipitated at high temperature (white sample).

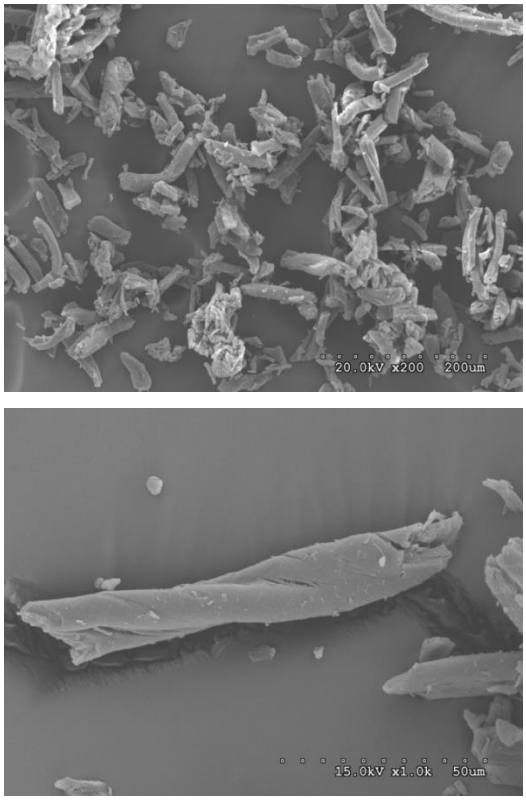


Figure 3. SEM micrographs of the starting microgranular cellulose. The bottom panel is an image of the same sample at higher magnification.

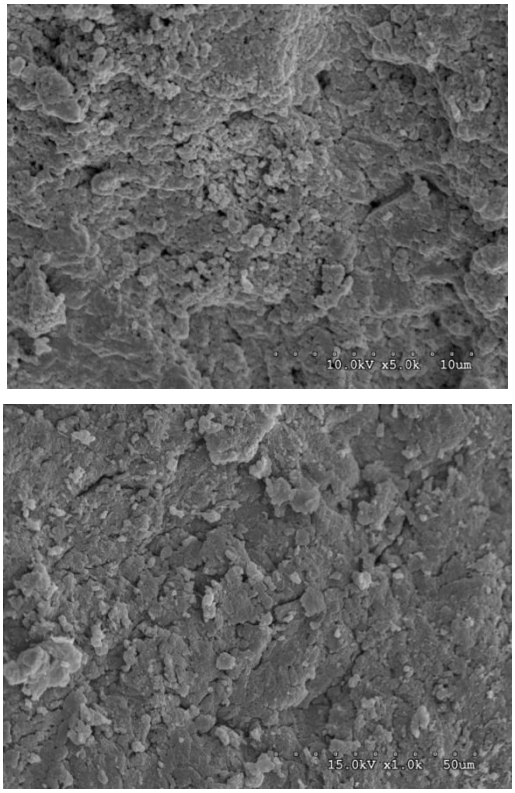


Figure 5. SEM micrographs of microgranular cellulose pretreated with EMIMCl (15 min) and precipitated at high temperature (white sample).

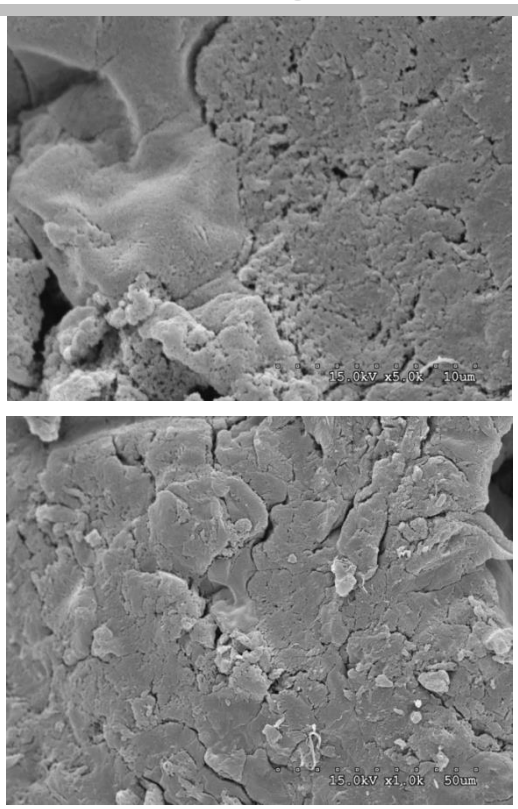


Figure 6. SEM micrographs of microfibrous cellulose pretreated with [EMIM]Cl (15 min) and precipitated at low temperature (transparent sample).

The crystalline structures of the original and pretreated cellulose samples were analyzed by X-ray diffraction (Figure 7). The XRD profiles show a prominent cellulose peak at 23º that corresponds to the (200) reflection; other less intense peaks appear at approximately 15º and 17º, which are characteristic of ($1\bar{1}0$) and (110) reflections, respectively, and a composite of several peaks that includes the (004) reflection at 34º[33, 34]. The intensity of the peaks is rather high, indicating high crystallinity of the samples. These diffraction peaks clearly disappears after the deconstruction-reconstruction pretreatment (Figure 7); the only diffraction line that still appears in the transparent samples is that at 22º, indicating that the solid retains some of its crystallinity.

Cellulose hydrolysis

After we subjected the cellulosic substrates to deconstruction-reconstruction processes, we subsequently tested them in the hydrolysis reaction with dilute acids to evaluate the influence of the morphology and crystallinity changes induced by the pretreatments of the raw cellulose substrate. For this purpose, very soft reaction conditions were selected to maximize the yield of sugars with a very low formation of by products such as levulinic acid.[32] The reaction temperature was fixed at 413 K, and the concentration of the homogeneous acid catalyst used was 0.2 mol/L.

Effect of cellulose type

The glucose yield of non-pretreated cellulose is very low, irrespective of the cellulose type used (Figure 8); simultaneously, the amount of unreacted solid is high (Table 1). However, a deep analysis of the results shows that the hydrolysis of the microgranular sample is more efficient than that of fibrous one. This finding is consistent with XRD and SEM results that showed a higher crystallinity and longer fibers for the fibrous sample. These characteristics make the fibrous sample more recalcitrant to hydrolysis because a higher order (i.e., greater crystallinity) and longer fibers impede the ability of H^+ ions to reach the β-glycosidic bonds; these characteristics thus inhibit the hydrolysis reaction.[35]

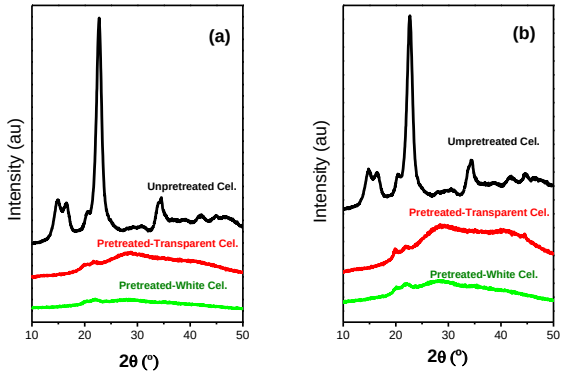


Figure 7. XRD patterns of both pretreated and unpretreated cellulose samples: (a) fibrous and (b) granular samples.

Table 1. Cellulose hydrolysis using H_2SO_4 as acid catalyst (0.2 mol/L) at 413 K for 2 h

Acid Catalyst	Cellulose Type	Conv. of Original Cellulose (%)	Conv. of Pretreated Cellulose (%)
H_2SO_4	Microfibrous	16	86
H_2SO_4	Microgranular	18	84

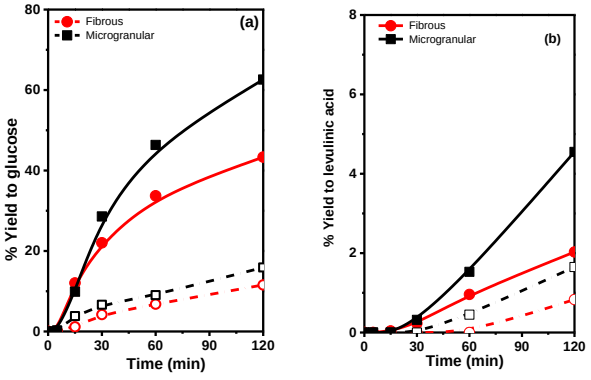


Figure 8. Yields of glucose (a) and levulinic acid (b) during the hydrolysis of microfibrous and microgranular celluloses that were either non-pretreated (empty symbols) or pretreated (full symbols) and with [EMIM][Cl] in the presence of 0.2 mol/L H_2SO_4 at 413 K.

However, the reactivity toward hydrolysis changes when IL pretreated samples are used. We observe a dramatic increase in the formation of glucose (Figure 8) and in the conversion of solid (Table 1). This behavior is quite similar for the two types of cellulose employed (microgranular and fibrous) (Figure 8). However, the yield of glucose is higher for the microgranular IL-pretreated sample than for the fibrous one. These differences are attributed to the differences in surface texture observed by SEM, where the microgranular IL-pretreated sample is more porous than its fibrous counterpart (Figure 4 and Figure 5).

Effect of precipitation procedure

The kinetics of the two celluloses (white and transparent celluloses) obtained according to the deconstruction-reconstruction methodology described here was studied. The white sample was obtained when cool water was added to the high-temperature IL-cellulose liquid phase (white sample), whereas the transparent sample was obtained when the IL-cellulose liquid phase was first cooled to ambient temperature before cool water was added.

The kinetics of hydrolysis of these two cellulose samples is displayed in Figure 9. For comparative purposes, the kinetics of hydrolysis of the unpretreated original cellulose are also included. Both the initial hydrolysis rates and the extent of glucose yields are much higher for the two cellulose samples prepared according to the deconstruction-reconstruction procedure. Notably, the glucose yield at 300 min of reaction time is somewhat higher for the white cellulose than for its transparent counterpart (70 %). Indeed, the glucose yield of these two samples is much higher than that of the untreated cellulose (21%), which indicates a strong influence of the cellulose morphology on the hydrolysis kinetics. These differences in reactivity are consistent with the morphology differences of the solids, as determined by SEM (Figure 4 and Figure 6), where the surface of the white sample clearly appeared more porous and accessible to reactant, which is a critical factor for the hydrolysis reaction.

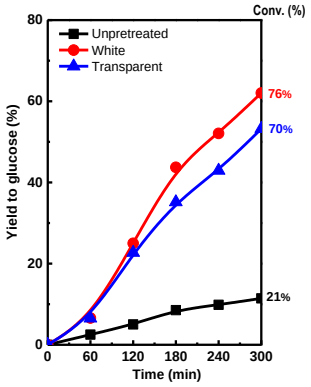


Figure 9. Hydrolysis of pretreated in EMIMCl and unpretreated microfibrous cellulose with H_2SO_4 (0.1 mol/L) at 413 K.

Effect of the IL type

The next steps consisted of using different ILs for the deconstruction of the cellulose. Three different imidazolium salts: 1-ethyl-3-methylimidazolium chloride [EMIM][Cl], 1-buthyl-3-methylimidazolium chloride [BMIM][Cl] and 1-ethyl-3-methylimidazolium acetate [EMIM][Ac] were used. Chloride salts are known to be slightly acidic, whereas [EMIM][Ac] is more inert toward cellulose hydrolysis than the chloride-based ILs counterparts and is able to solubilize a greater amount of biomass.[36]

Pretreated fibrous cellulose that was precipitated with water without the cellulose-IL mixture first being cooled (white sample) was selected for this comparison. The yield of glucose was higher for all of the IL-treated samples; however, some differences were observed, depending on the IL used. Glucose yield was higher for the cellulose treated with chloride IL than for that treated with acetate IL. A similar effect was observed with respect to the levulinic acid yield (Figure 10). These differences are more evident if the conversion of cellulose is compared (Table 2): the conversion is clearly higher for the samples treated with chloride ILs, reaching greater than 95 % at 5 h of reaction. This behavior is attributed to the acidity of the chloride ILs, which results in a pre-hydrolysis of the cellulose during the deconstruction-reconstruction treatment. The glucose yield is smaller for the cellulose treated with [EMIM][Ac]; however, in this case, the ratio of glucose/levulinic acid is higher than in the products generated using the other two ILs. Another advantage of using the [EMIM][Ac] IL is the absence of chloride ions, which makes the process safer, avoids corrosion and inhibits downstream processes such as fermentation of the sugars.

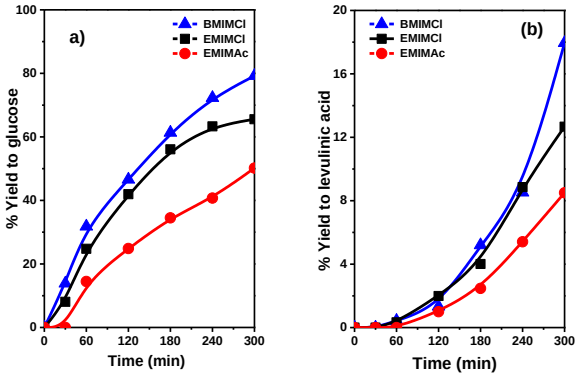


Figure 10. Hydrolysis of microfibrous white cellulose pretreated in different ILs (EMIMCl, BMIMCl, EMIMAc) with H_2SO_4 (0.2 mol/L) at 413 K for 5 h.

Table 2 Cellulose hydrolysis with different ILs in the presence of H_2SO_4 (0.2 mol/L) (413 K for 2 and 5 h)

Ionic Liquid	% conversion of white cellulose (2 h)	% conversion of white cellulose (5 h)
BMIMCl	78	97
EMIMCl	78	99
EMIMAc	36	63

Influence of the catalyst acid strength

Different acids such as p-TSA, H_2SO_4 and $H_3PW_{12}O_{40}$ were used as homogeneous catalysts to efficiently hydrolyze the β-1,4-glycosidic bonds.[27] The number of acidic protons liberated by these acids depends on the acid used. In the case of H_2SO_4, only one acidic proton should be considered because less than 1% of the bisulfate ions dissociate under the conditions employed for the hydrolysis of cellulose; therefore, only the first ionization of the H_2SO_4 appears relevant.[35] Similarly, p-TSA has only one acidic proton; however, all three protons of phosphotungstic acid are available, which make it a strong acid. For this reason, we added the same concentration of acid in the cases of pTSA and H_2SO_4, but we used a threefold lower molar concentration in the case of $H_3PW_{12}O_{40}$.

The glucose yield in the hydrolysis of untreated fibrous cellulose is very low, irrespective of the acid used (Figure 11). The glucose yield reaches 20% after 5 h of reaction only when phosphotungstic acid is used; however, the amount of unreacted solid is still rather high (Table 3), yielding a solid conversion of approximately 24-25%. The solid conversion percentages were similar for all three acids used.

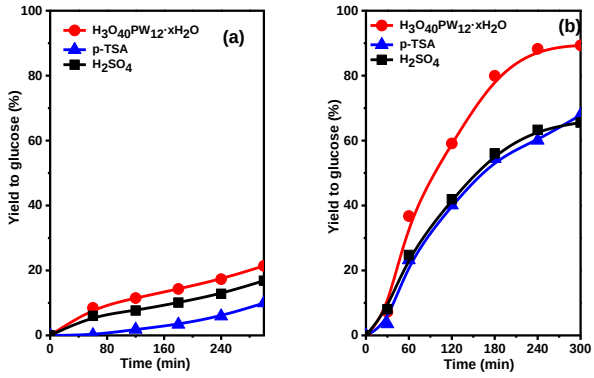


Figure 11. Glucose yield from the hydrolysis of cellulose with H_2SO_4, p-TSA (0.2 mol/L) and $H_3PW_{12}O_{40}$ (0.067 mol/L) at 413 K: (a) unpretreated cellulose; (b) cellulose pretreated with [EMIM][Cl].

Table 3 Cellulose hydrolysis in the presence of different homogeneous acid catalysts at 413 K, 5 h

Acid Catalyst	Catalyst Concentration (mol/L)	Conv. of Original Cellulose (%)	Conv. of Pretreated Cellulose (%)
$H_3PW_{12}O_{40}\cdot xH_2O$	0.067	24	98
*p-TSA[a]	0.20	24	99
H_2SO_4	0.20	25	99

[a] *p-TSA: para-toluenesulfonic acid*

Conversely, when the IL-pretreated cellulose is hydrolyzed under the same experimental conditions, a dramatic increase in the glucose yield is observed (Figure 11). The conversion of solid is also very high—approximately 98-99%—after only 5 h of reaction (Table 3). A comparison of the glucose yield profile shows that the amount of glucose produced increases with increasing acid strength. The glucose yield produced follows the order $H_3PW_{12}O_{40}\cdot xH_2O$ > H_2SO_4 > p-TSA. Notably, the $H_3O_{40}PW_{12}$ exhibited excellent performance in the hydrolysis of cellulose, leading to the conversion of more than 99 % of the starting cellulose and to a glucose yield of approximately 90 % in only 5 h of reaction time.

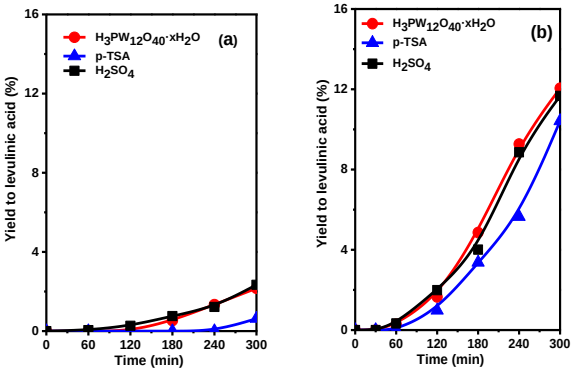


Figure 12. Yield of levulinic acid in the hydrolysis of cellulose with H_2SO_4, p-TSA (0.2 mol/L) and $H_3PW_{12}O_{40}\cdot xH_2O$ (0.067 mol/L) at 413 K: (a) unpretreated cellulose; (b) cellulose pretreated with [EMIM][Cl].

Another important finding is the low yield of levulinic acid (< 2.5 %) in all of the experiments that involved unpretreated cellulose (Figure 12), although small differences in levulinic acid yield were observed among the acids employed. The levulinic acid yield is higher when pretreated cellulose is used (Figure 12), most likely because of the higher concentration of glucose present in the reaction medium. This increase occurs for all three of the acids employed; however, the levulinic acid/glucose ratio appears somewhat higher for H_2SO_4 than for $H_3O_{40}PW_{12}\cdot xH_2O$ and p-TSA. This observation indicates that sulfuric acid performs better than its counterparts as a dehydrating acid. Given the glucose yield and the levulinic acid/glucose ratio, the most suitable catalyst among those investigated for cellulose hydrolysis is phosphotungstic acid.

Discussion

Cellulose deconstruction-reconstruction

Cellulose is a biopolymer in which the hydroxyl groups are oriented to form strong intra- and intermolecular hydrogen bonds that are integrated into micro- and macrofibrils networks. These molecular interactions define a complex and rigid structure forming a recalcitrant substrate against chemical or enzymatic hydrolysis. Deconstruction of this rigid structure requires harsh and expensive separation processes. Although numerous physical and chemical methods have been assayed,[37] no perfect pretreatment method has been discovered because the suitability of a given method varies with respect to the substrate. However, the recent discovery that ILs are good solvents for the mild and rapid hydrolysis of

biomass feedstocks has enabled the efficient conversion of cellulose into fermentable sugars.

With the objective of producing fibers from cellulose, researchers have devoted great effort to the development of solvents for the processing of lignocellulose. The use of ILs as solvents for cellulose is undoubtedly the most important example of such efforts.[36, 38] ILs are salts that melt at temperatures less than 100 °C. The 1-alkyl-3-methylimidazolium-based ILs with good H-bond-acceptor anions can dissolve cellulose and even wood.[22] The capability of ILs to dissolve cellulose was exploited in this work as a starting point to convert the solubilized fraction into useful products.

Cellulose dissolution is an industrially attractive application of ILs because of the good solubilities of cellulose in IL solvents (5–20 wt%). Complete cellulose dissolution in ILs is highly dependent on the temperature, type of the IL, time of dissolution and the water content, which, in turn, should be optimized for the specific IL-cellulose dissolution process. Nevertheless, when ILs dissolve carbohydrates, the ILs are considered to effectively disrupt the intricate network of non-covalent interactions between these polymers. Swatloski *et al*.[39] have suggested that the high chloride concentration and high activity of [BMIM][Cl] is responsible for breaking the extensive and well organized hydrogen-bonding network of cellulose and thus promoting dissolution. ILs not only disrupt the hydrogen-bonding interactions of crystalline cellulose in wood but also interact with and solvate the aromatic components of lignin by π-π and n-π interactions, generally via the IL cation.[40]

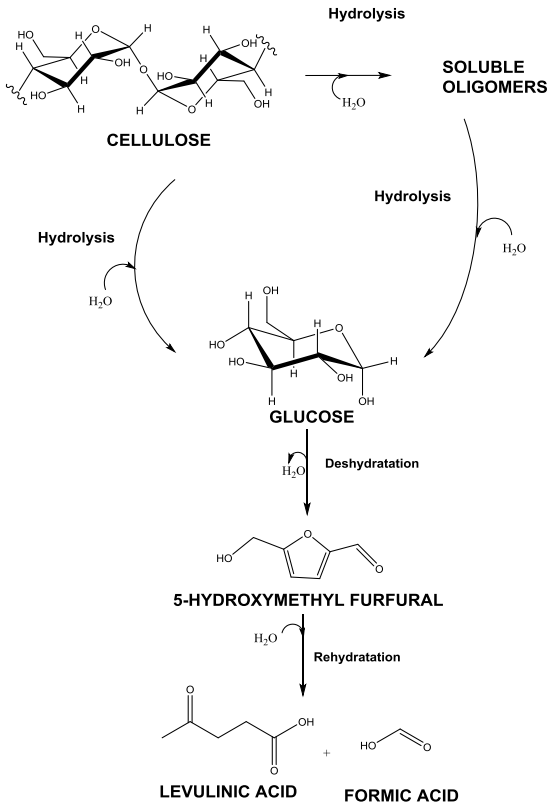
The dissolved cellulose can be modified in solution or regenerated (reprecipitated) by the addition of water, mixtures of water with organic solvents (*e.g.,* acetone) or protic organic solvents, such as ethanol, to form films and fibers.[39, 41] The ordering of the regenerated cellulose is reduced compared to the initial state, and it is transformed into cellulose II.[42] This transformation also results in significantly accelerated hydrolysis compared to that of native cellulose[43, 44]—an effect that is very attractive in terms of biorefineries and has sparked interest in the use of cellulose-dissolving ILs in lignocellulose deconstruction.

According to the literature, the interaction of cellulose–[BMIM][Ac] decreases in the order acetone > ethanol > water, with cellulose–$[Ac]_2$ forming the smallest number of H-bonds in water.[45] However, the interaction of cellulose–cellulose increases in the reverse order (acetone < ethanol < water), with the largest number of H-bonds between cellulose chains being observed in water. Thus, because water is an excellent antisolvent for cellulose, we have exploited this property to reconstruct the cellulose. As illustrated in Figure 1, where fibrilar or microgranular cellulose was dissolved in [EMIM][Cl] IL and then precipitated with water, a much more open structure was obtained compared to that displayed by the original cellulose. The morphology of the reconstructed cellulose is gel type; it offers a highly porous texture with a much greater exposed surface area that is prone to attack by mineral or organic acids, thus making acid hydrolysis easier.

Kinetics of hydrolysis

In the course of cellulose hydrolysis, breaking of the β-1,4-glycosidic linkages must occur. This reaction, which is catalyzed by strong homogeneous or heterogeneous acids, primarily yields glucose, a very useful fermentable monosaccharide. Interesting platform chemicals can be obtained from further conversion of reducing sugars.[46, 47] In addition, various fine chemicals and potential fuels (bio-ethanol) can also be directly obtained from acid processing of cellulose via a multistep fractionation process. Although cellulose hydrolysis can be catalyzed with either a heterogeneous catalyst or an acid, efficient acid-catalyzed hydrolysis has emerged recently because of the development of numerous fine and even homogeneous catalysts. In the present work, we focused only on the homogeneous process by using H_2SO_4, p-TSA, and $H_3O_{40}PW_{12}$.

In most of the previous studies, mineral acids (HCl, H_2SO_4) and organic acids (p-TSA, oxalic, maleic, fumaric) were observed to be particularly well suited to the production of glucose that can undergo further consecutive reactions to produce first hydroxymethyl furfural (5-HMF) and finally levulinic acid (LA) and formic acid (FA) (Scheme 1). Acid hydrolysis of cellulose is a kinetic process that is controlled primarily by (i) the nature of the cellulose precursor, (ii) the pKa of the acid, (iii) the acid concentration, and (iv) the reaction temperature.



Scheme 1. Selected products formed by acid-catalyzed reactions starting from cellulose. Adapted from Rinaldi et al.[46]

The acid hydrolysis of cellulose is a reaction catalyzed by protons (H^+) and also by hydroxide anions (OH^-) resulting from water dissociation; the protons and hydroxide ions react with cellulose molecules, yielding various products such as glucose, xylose, arabinose and cellobiose. In addition, oligosaccharides can be readily formed from the liquid-acid-catalyzed hydrolysis of cellulose.

The kinetics of the cellulose hydrolysis were found to be very fast when cellulose was deconstructed in ILs. The use of H_2SO_4 as a hydrolyzing agent at 413 K resulted in a solid conversion rate in the range of 97 to 99 % when cellulose deconstructed in [EMIM][Cl] and [BMIM][Cl] ILs was used. In contrast, the conversion rate was only 63 % in the case of cellulose deconstructed in [EMIM][Ac] (Table 3). In addition, under the same reaction conditions, hydrolysis of the deconstructed-reconstructed cellulose was fastest with the strongest acid. The observed trend in the glucose yield was $H_3O_{40}PW_{12}{\cdot}xH_2O$ > H_2SO_4 > p-TSA (Figure 11). Notably, the outstanding performance of the homogeneous $H_3O_{40}PW_{12}$ catalyst in the hydrolysis of cellulose, which led to a conversion rate of the starting cellulose greater than 99 % with a glucose yield of approximately 90 % in only 5 h of reaction time.

Conclusions

A simple methodology was used to make cellulose highly reactive toward acid hydrolysis. It basically includes a first solubilization of the cellulose in an IL, followed by the precipitation of solubilized cellulose with water. The cellulose is separated by filtration, and the ionic liquid is almost completely recovered. The X-ray diffraction pattern of the treated cellulose indicated that it was noncrystalline, and SEM images indicated that the fiber structure present in its untreated counterpart disappeared.

The major cause of the improvement in acid hydrolysis performance after cellulose deconstruction-reconstruction described here is the development of a completely different cellulose morphology. Although some aggregation of cellulose fibrils occurs at the end of the reconstruction process, the resulting cellulose substrate exhibits a much more accessible surface that enhances local acid reactivity.

Several factors influence the glucose yield, such as the type of IL employed, the precipitation procedure and the acid used in the hydrolysis. The best conditions were observed to be: ionic liquid, [EMIM][Cl] hydrolysis reaction temperature, 413 K; and phosphotungstic acid (0.067 mol/L). Under the experimental conditions, almost complete cellulose conversion was obtained (> 99 %) with 89 % glucose yield after only 5 h of reaction.

Experimental Section

Reagents

Sulfuric acid (H_2SO_4), para-toluensulfonic acid (p-TSA), phosphotungstic acid ($H_3PW_{12}O_{40}$), and two samples of cellulose powder from cotton linters: (fibrous cellulose (C6288) and microgranular cellulose (C6413)) were purchased from Sigma-Aldrich and used without any further purification. The ionic liquid that we used, are: 1-ethyl-3-methylimidazolium chloride [EMIM][Cl], 1-Buthyl-3-methylimidazolium chloride [BMIM][Cl] and 1-ethyl-3-methylimidazolium acetate [EMIM][Ac] also purchased from Sigma-Aldrich and used without any further purification.

Experimental Techniques

The scanning electron micrographs of untreated cellulose and cellulose pretreated with ionic liquid were taken with a Hitachi S-3000 N. The samples were treated with increasing concentrations of ethanol to fix the structure and to dehydrate the samples. We then proceeded to critical-point drying with a Polaron CPD7501 critical-point drier; finally, the samples were metallized in a Balzers SCD 004 gold sputter coater; they were sputter-coated with a thin layer of gold.

X-ray diffraction profiles of samples were recorded with an X'Pert Pro PANalytical diffractometer equipped with a Cu Kα radiation source (λ = 0.15418 nm) and an X'Celerator detector based on real-time multiple strip (RTMS). The samples were ground and placed on a stainless steel plate. The diffractograms were recorded in steps over a range of Bragg angles (2θ) between 4 and 90°, at a scanning rate of 0.02° per step and at an accumulation time of 50 sec. Diffractograms were analyzed with the X'Pert HighScore Plus software.

The pretreatment of the cellulose involved complete dissolution of the cellulose (0.5 g) in an ionic liquid (9.5 g) at 408 K using a continuously stirred tank reactor (Mettler Toledo Easy Max). Cellulose was completely dissolved within 15 min. After it was dissolved, the cellulose was precipitated by the addition of 50 mL of water. The obtained solid was washed several times with water to eliminate all remaining IL.

Hydrolysis reaction

Hydrolysis reactions were performed batch-wise in a magnetically stirred 100 mL thermostated Teflon-lined steel Berghof reactor equipped with a pressure addition funnel. In a typical run, 0.5 g of cellulose and 40 mL of water were mixed in the reactor and the suspension was heated to the reaction temperature (413 K). Then, 10 mL of acid solution was added dropwise to the reactor; the "reaction time" was measure from this moment. The total volume of liquid in the reactor was 50 mL. The acid concentration in the reactor was 0.2 mol/L. Aliquots were periodically collected from the reactor. In all cases, the reaction was stopped after 5 h, and the mixture was quickly cooled. The solution was collected by filtration, centrifuged and thoroughly washed with distilled water. The resulting solid was dried at 353 K overnight. The amount of solid isolated was determined by weighing.

The liquid was analyzed by HPLC (Agilent Technologies HPLC 1200 series). The chromatographic separations were conducted in an AMINEX HPX-87H column at 338 K using 0.6 mL/min of sulfuric acid aqueous solution (0.01 mol/L) as the mobile phase. The sugars and dehydration products (5-hydroxy-methylfurfural and levulinic acid) were analyzed using a refractive index detector and UV-Vis detector. The components were identified by comparing their retention times with those of reference samples. The products were quantified through the use of internal calibration curves.

In this paper, the results we obtained for 5-HMF in the hydrolysis of cellulose are not shown. We worked in the aqueous phase, where this compound readily decomposes to levulinic acid and formic acid, resulting in insignificant amounts of 5-HMF. For this reason, we only analyzed the results related to glucose and levulinic acid in the present work. The glucose and levulinic acid yields were calculated using the following equations:

% Glucose Yield = G_{con} *100 / GMx (1)
% Levulinic Acid Yield = L_{Con} *100 / L_{Mx} (2)

where G_{con} is the measured glucose concentration, G_{Mx} is the maximum concentration of glucose that can be obtained based on the amount of cellulose fed to the reactor, L_{con} is the levulinic acid concentration and L_{Mx} is the maximum concentration of levulinic acid that can be formed from the cellulose added.

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Keywords: Cellulose, hydrolysis, ionic liquid, antisolvent treatment, glucose, levulinic acid

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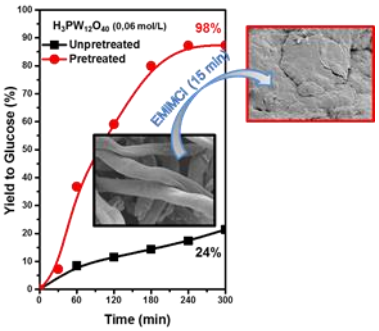
Entry for the Table of Contents

FULL PAPER

This work describes a relatively simple methodology for efficiently deconstructing cellulose into monomeric glucose, which is easier to transform into a variety of platform molecules for the production of chemicals and fuels.



Silvia Morales-delaRosa, Jose M. Campos-Martin and Jose L. G. Fierro**

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Complete chemical hydrolysis of cellulose into fermentable sugars via ionic liquids and antisolvent pretreatments