High enhancement of the hydrolysis rate of cellulose after pretreatment with inorganic salt hydrates

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We study the use of inorganic salt hydrates as solvents in the dissolution/precipitation pretreatment of cellulose. The dissolution of cellulose was very fast (15 min in some cases) at the low temperature of 70 °C. ZnCl₂·4H₂O, ZnBr₂·4H₂O, LiCl·8H₂O and LiBr·4H₂O were studied as solvent. The dissolution/precipitation process dramatically modified the cellulose structure, which was completely deconstructed, as corroborated by both XRD and SEM. The nature of these salts affects cellulose dissolution. The change in cellulose morphology after dissolution/precipitation pretreatment produced an increase in the rate of hydrolysis with respect to that of untreated cellulose. The acidic catalyst employed in hydrolysis had a moderate effect on the reaction results. The best performance was obtained with H₄SiW₁₂O₴₀ (0.05 M) at 140 °C for 300 min, where the cellulose conversion was close to 99% and the glucose yield was 90%.

Introduction

At present, the search for new sources of energy as substitutes for fossil fuels is required because fossil fuels are a finite resource. A new alternative is the use of lignocellulosic waste from energy crops because such waste offers a high potential for the production of bioproducts and biofuels that can be used as raw materials or energy sources in agricultural activities within a circular economy. However, due to its recalcitrance and low activity, lignocellulosic biomass must be pretreated to obtain products selectively at mild temperatures in an efficient way. The three main components of lignocellulosic biomass are cellulose, hemicellulose and lignin. Among them, cellulose is a very interesting feedstock, that can be transformed in compounds of high interest. Cellulose is a polymer of glucose linked by β-1,4-glycosidic bonds. It has a crystalline structure, which was completely deconstructed, as corroborated by both XRD and SEM. The nature of these salts affects cellulose dissolution. The change in cellulose morphology after dissolution/precipitation pretreatment produced an increase in the rate of hydrolysis with respect to that of untreated cellulose. The acidic catalyst employed in hydrolysis had a moderate effect on the reaction results. The best performance was obtained with H₄SiW₁₂O₴₀ (0.05 M) at 140 °C for 300 min, where the cellulose conversion was close to 99% and the glucose yield was 90%.

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Dissolution and precipitation

Cellulose (1.5 g) was added slowly to 28.5 g of each inorganic salt hydrate at 70 °C in a Mettler-Toledo Easy Max 102® reactor equipped with mechanical stirring. The complete dissolution of the added solute was determined by direct visual observation. Then, the material was precipitated by the addition of water (25 mL). The obtained solid was separated by vacuum filtration with a nylon membrane and was washed several times with HCl (0.1 N) and distilled water to eliminate all remaining inorganic salt hydrate.

Hydrolysis

Hydrolysis reactions were carried out batchwise in a magnetically stirred 100 mL thermostatic Teflon-lined steel Berghof reactor equipped with a pressure addition funnel. In a typical run, 0.5 g of material and 40 mL of water were mixed in the reactor, the suspension was heated to the reaction temperature (140 °C), and the appropriate amount of catalyst to obtain a concentration of 0.2 M was added. The “reaction time” was measured from this moment. The total volume of liquid in the reactor was 50 mL. Aliquots were periodically taken from the reactor. In all cases, the reaction was stopped after 5 h, and the mixture was quickly cooled. The solution was filtered off, and the solid was washed with distilled water and dried at 80 °C overnight. The amount of solid isolated was determined by weighing.

The liquid was analyzed by HPLC (Agilent Technologies HPLC 1200). The chromatographic separations were carried out in a Hi-PLEX H column at 60 °C using 0.6 mL min⁻¹ sulfuric acid aqueous solution (0.01 M) as the mobile phase.

Characterization

X-ray diffraction profiles of samples were recorded with an X’Pert Pro PANalytical diffractometer equipped with a CuKα radiation source (λ = 0.15418 nm) and X’Celerator detector based on real-time multiple strip (RTMS) technology. The samples were ground and placed on a stainless steel plate. The diffraction patterns 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 an accumulation time of 30 s. Diffractograms were analyzed with X’Pert HighScore Plus software.

Scanning electron micrographs of original and pretreated cellulose were taken with a Hitachi S-3000 N instrument. The samples were treated with increasing concentrations of ethanol to fix the structure and to dehydrate the samples. The samples were metallized in a Balzers SCD 004 gold-sputter coater.

The composition of original and recovered inorganic hydrate salts was determined by inductively coupled optical emission spectrometry (ICP-OES) using an Analytik Jena ICP-OES PlasmaQuant PQ 9000 spectrometer.

Results and discussion

Pretreatment with inorganic salts hydrates

The dissolution capacity of cellulose depends on the water content, the state of the solution and the species of the in-
organic salts used.\(^4\) The molten salt hydrates reported to be able to dissolve cellulose are ZnCl\(_2\)·4H\(_2\)O, ZnBr\(_2\)·4H\(_2\)O, LiCl·8H\(_2\)O, and LiBr·4H\(_2\)O. These salts were chosen to be able to compare the relationship between cations with different anions and between two cations with the same anions. However, LiCl has \(R = 8\) due to the need to add more water to form a liquid salt hydrate.\(^2\) The amount of water added to this inorganic salt has been studied in other works, which revealed that the relationship with \(R = 4\) is an interesting option for the dissolution of lignocellulosic biomass.\(^3\)

Table 1 shows the time it took the different molten salt hydrates used to dissolve the cellulose Avicel®. ZnBr\(_2\)·4H\(_2\)O dissolved the cellulose sample in only 15 min, being the fastest of all used, followed by LiBr·4H\(_2\)O in 25 min and finally ZnCl\(_2\)·4H\(_2\)O in 30 min, which may indicate that bromides are better solvents and more effective than chlorides. Possibly, the larger size of the anion Br\(^-\) favors the opening of the cellulose chains, causing faster dissolution. However, in the case of LiCl·8H\(_2\)O after 60 min, the cellulose was not able to dissolve, so the solution pretreatment was stopped. A possible explanation for this result is that LiCl·8H\(_2\)O is twice as hydrated as the other salts, and as already described in previous works, an excess of water present in solution makes it difficult or impossible to dissolve cellulose.\(^2,3\) The amount of cellulose recovered after the pretreatment is almost quantitative for all solvent employed (Table 1).

**Table 1** Dissolution time of cellulose in different hydrated ionic salts at 70 °C, proportion of cellulose recovered after precipitation and crystallinity index (Cl) obtained from XRD measurements

| Sample          | Dissolution time (min) | Cellulose recovered (%) | Cl (%) |
|-----------------|------------------------|-------------------------|--------|
| Original Avicel PH-101 | —                      | —                       | 82     |
| ZnCl\(_2\)·4H\(_2\)O | 30                     | ≈ 100                   | 45     |
| ZnBr\(_2\)·4H\(_2\)O | 15                     | 97                      | 21     |
| LiCl·8H\(_2\)O | >60                    | ≈ 100                   | 79     |
| LiBr·4H\(_2\)O | 25                     | 99                      | 36     |

**X-ray diffraction**

The XRD profiles of the samples in Fig. 2 show the morphological differences between the untreated cellulose samples and those pretreated with the different ionic salts. The dissolution treatment modified the shape of the crystal structure. The profile of untreated cellulose shows typical peaks of the crystal structure. The prominent peak at 23° shows a reflection corresponding to (200) and a peak width from 15–17°, which represents the combination of the two reflections corresponding to (110) and (110).\(^4\) After the process of dissolution/ regeneration, the diffraction profiles of the pretreated samples exhibit a clear change: the peaks of original cellulose disappear, and we detect only a doublet at 22.0° and 20.3° that indicates a loss of the original crystallinity (cellulose type I) and the formation of an incipient type II cellulose with low crystallinity.\(^4\) However, the samples treated with LiCl·8H\(_2\)O gave an XRD profile quite similar to the original, with a small decrease in intensity, which implies that the loss of crystallinity is very small. This result is consistent with the low dissolution of the cellulose sample in LiCl·8H\(_2\)O.

The crystallinity index has been measured according to the following expression after the normalization of the different XRD profiles. \(CI = (I_{23} − I_{18})/I_{23}\) where \(I_{23}\) and \(I_{18}\) are the intensities diffractogram at 23° and 18° respectively.\(^4\)

The CI of starting cellulose is relatively high (Table 1), but the treatment of dissolution/precipitation produces a tremendous decrease in the CI, the order of CI is the following ZnBr\(_2\)·4H\(_2\)O < LiBr·4H\(_2\)O < ZnCl\(_2\)·4H\(_2\)O < LiCl·8H\(_2\)O. The sample treated with LiCl·8H\(_2\)O has a CI similar to the starting material, as consequence of the low dissolution of the cellulose in this solvent. A lower dissolution time yields a lower CI in the cellulose recovered.

**Scanning electron microscopy**

The morphology of the original and pretreated cellulose samples with different inorganic salt hydrates was examined by SEM (Fig. 3). The micrographs in the upper part of the figure show the original cellulose without pretreatment. This sample contains small fragmented fibers, typical of cellulose structure, which are more apparent in the SEM images recorded at a higher magnification (right side).

The morphology of the cellulose samples after dissolution/precipitation with salts (ZnCl\(_2\)·4H\(_2\)O, ZnBr\(_2\)·4H\(_2\)O and LiBr·4H\(_2\)O) suffers a dramatic change; the fibers disappear, and the solid material presents porous structures and spongy particles (Fig. 3). The details are clearer in the higher-magnifi-
cation micrographs (on the right). However, with the salt LiCl·8H₂O, the structure of cellulose observed in the SEM micrographs is quite similar to that of the starting material (Fig. 3), and the small fragmented fibers of cellulose present in the micrographs are quite similar to untreated Avicel PH-101 cellulose. This observation agrees with the XRD analysis and dissolution experiments: dissolution of the cellulose sample in LiCl·8H₂O did not occur.

The changes observed in pretreated cellulose are quite similar to those observed in previous works, where pretreatment by dissolution/precipitation in ionic liquids led to a dramatic change in the structure and morphology of cellulosic substrates.

Cellulose hydrolysis

After dissolution/precipitation pretreatment, we tested the samples in a hydrolysis reaction with H₂SO₄ to evaluate the influence of the changes in morphology and crystallinity induced by pretreatment. For comparison purposes, we used the original cellulose as a reference. We selected the reaction conditions, a temperature of 140 °C and an acid catalyst (H₂SO₄) concentration of 0.2 M, based on previous works.

The hydrolysis results for the celluloses pretreated with ZnCl₂·4H₂O, ZnBr₂·4H₂O and LiBr·4H₂O present a higher conversion of cellulose and yield of glucose than those of the reference untreated cellulose (Table 2). As expected, the sample pretreated with LiCl·8H₂O, which exhibited no dissolution crystallinity or morphology changes, the reaction results were quite similar to those of untreated samples. These results agree with the lack of changes in the structure of cellulose based on the characterization data (XRD and SEM). The reactivity trend has the opposite to the CI (Tables 1 and 2) samples with lower CI yields higher reactivity.

The highest conversion and yield of glucose were obtained with pretreatment with ZnBr₂·4H₂O (88% and 80%, respectively), followed by the sample pretreated with LiBr₂·4H₂O and the sample pretreated with ZnCl₂·4H₂O. These results seem to be related to the dissolution time and CI. Treatment with salt hydrates that are able to dissolve cellulose quickly is more effective and reduces the CI. The salt hydrates that contain Br⁻ anions are better solvents of cellulose, yielding a more accessible structure, which is more porous and spongier. These changes make easier to hydrolyze to glucose because access to β-O-glycosidic bonds is facilitated by changes in the structure of the cellulose.

The most efficient pretreatment was when ZnBr₂·4H₂O was employed as a solvent. Thus, we selected this pretreatment to compare the performance of different acidic homogeneous catalysts to study the efficiency of the hydrolysis of the β-glycosidic bonds of cellulose. The catalysts employed were heteropolyacids, which are very strong acids (H₃PW₁₂O₄₀ and H₄SiW₁₂O₄₀), and their performance was compared with that of H₂SO₄ as a reference catalyst. However, the number of protons released by these acids was different in the reaction conditions, and if we used the same concentration, the number of protons involved in the reaction would be different.

| Samples treated with             | Conversion of cellulose (%) | Yield of glucose (%) | Selectivity of glucose (%) |
|----------------------------------|-----------------------------|---------------------|---------------------------|
| Original Avicel PH-101           | 25                          | 12                  | 48                        |
| ZnCl₂·4H₂O                       | 60                          | 54                  | 90                        |
| ZnBr₂·4H₂O                       | 88                          | 80                  | 91                        |
| LiCl·8H₂O                        | 26                          | 12                  | 46                        |
| LiBr·4H₂O                        | 74                          | 63                  | 85                        |

Fig. 3 SEM micrographs of the original cellulose (Avicel PH-101) without pretreatment and the solids obtained after pretreatment with different inorganic salt hydrates. The left panel depicts the samples at lower magnification, and the right panel depicts the same samples with higher magnification.
In the case of H$_2$SO$_4$ (0.2 M), only one acidic proton should be considered (the first ionization) under the conditions employed for this hydrolysis of cellulose.$^{25,44}$ However, we consider that all protons are active in the heteropolyacids; for this reason, we employed a lower concentration for these acids than sulfuric acid. For H$_2$SO$_4$, we used 0.2 M (1 proton), for H$_3$PW$_{12}$O$_{40}$, 0.067 M (3 protons), and for H$_4$SiW$_{12}$O$_{40}$, 0.05 M (4 protons).

All the catalysts exhibited a high conversion of cellulose and glucose yield in the hydrolysis of pretreated samples. The cellulose conversion ranged between 88 and 99% (Table 3), and the glucose yield ranged between 80 and 90% (Fig. 4). The main byproduct obtained was levulinic acid, which is produced by the dehydration of glucose, we detected also the presence of small amounts of 5-hydroxymethylfurfural (<3% yield) and small amounts of furfural (<0.5% yield). The yields of levulinic acid were low in all samples (Fig. 5), but the yield of levulinic acid can be related to the concentration of glucose in the reaction media. The original sample produced a low amount of glucose in dissolution, and the yield of levulinic acid was very low (<2%); however, when the samples were pretreated, the concentration of glucose in solution was high, and the levulinic acid content increased to approximately 8% at the end of the reaction in all reactions. However, we detected some differences in the levulinic acid yield among the acids employed as catalysts. The highest glucose/levulinic acid ratio was obtained for H$_4$SiW$_{12}$O$_{40}$, followed by H$_3$PW$_{12}$O$_{40}$ and finally H$_2$SO$_4$. In all cases, the amount of other by-products was very low.

### Table 3
Hydrolysis of cellulose in samples treated with ZnBr$_2$·4H$_2$O at 140 °C for 300 min

| Catalyst          | Conversion of cellulose (%) |
|-------------------|-----------------------------|
| H$_2$SO$_4$       | 88                          |
| H$_3$PW$_{12}$O$_{40}$ | 95                          |
| H$_4$SiW$_{12}$O$_{40}$ | 99                          |

Salt hydrate reuse

Finally, we studied the reuse of ZnBr$_2$·4H$_2$O. Although this solvent is not expensive and has a low environmental impact, the reuse of solvents is an important point to be studied. The liquid obtained after precipitation of cellulose, filtration and washing was collected. This solution contained the salt hydrate (ZnBr$_2$·4H$_2$O) and an excess of water. The excess water was evaporated under reduced pressure, and the original amount of salt hydrate was almost completely recovered, the amount of salt hydrate recovered is higher than 96% (Table 4), then the salt hydrate can be reused without any additional supply of fresh salt. The recovered solvent was employed in cellulose pretreatment, and the reused salt hydrate was recovered again. The second recovery was similar to the first one, and the newly recovered salt hydrate was also employed in the pretreatment of cellulose.

### Table 4
Reuse of ZnBr$_2$·4H$_2$O. Recovery of salt hydrate and hydrolysis of cellulose in samples treated at 140 °C for 300 min using H$_2$SO$_4$ (0.2 M)

| Samples treated with | ZnBr$_2$·4H$_2$O recovered (%) | Conversion of cellulose (%) | Yield of glucose (%) |
|----------------------|-------------------------------|----------------------------|----------------------|
| ZnBr$_2$·4H$_2$O fresh | 88                           | 88                         | 80                   |
| 1$^{st}$ reuse       | 97                           | 87                         | 81                   |
| 2$^{nd}$ reuse       | 96                           | 89                         | 80                   |
The time required for the dissolution of cellulose was almost the same for the original salt hydrate and the once- and twice-reused solvents. The obtained pretreated cellulose was employed in hydrolysis with sulfuric acid at 140 °C. The conversion values and yield of glucose were quite similar for all three experiments, showing a high reusability of the salt hydrate.

Conclusions

Inorganic salt hydrates are good alternative solvents for cellulose, are an economical alternative to other solvents such as ionic liquids and are less noxious to the environment. In addition, the dissolution of the samples was very fast and at the low temperature of 70 °C, cellulose dissolved in 15 min. The dissolution/precipitation process dramatically modified the cellulose structure, which was completely deconstructed, as corroborated by both XRD and SEM. The nature of these salts affects cellulose dissolution. Bromide salt hydrates (ZnBr₂·4H₂O and LiBr·4H₂O) are more efficient and dissolve cellulose faster than their chloride counterparts.

The change in cellulose morphology after dissolution/precipitation pretreatment produced an increase in the rate of hydrolysis with respect to that of untreated cellulose. The acidic catalyst employed in hydrolysis had a moderate effect on the reaction results. The best performance was obtained with H₂SiW₁₂O₄₀ (0.05 M) at 140 °C for 300 min, where the cellulose conversion was close to 99% and the glucose yield was 90%.

Salt hydrates can be reused after the evaporation of the excess water used in the precipitation and washing of treated samples.

Conflicts of interest

The authors declare no conflicts of interest.

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