Tight control of cellulose depolymerization towards glucose in organic electrolyte solutions

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1. Introduction

Exploration and development of new, non-fossil energy sources for the production of automotive fuels is currently one of the most active scientific research areas [1–4]. From an industrial point of view, crude oil, the most used fossil source for fuels, is becoming more difficult to be exploded, not only because of reserves depletion, but mainly because these now...
display a lower quality in comparison to several decades ago. These facts complicate the extraction of the raw material and its processing into fuels and other valuable products. From an environmental point of view, the use of fossil fuel resources is directly linked to changes in earth’s climate [5], because of the massive delivery of carbon dioxide to the atmosphere and the subsequent unbalance of the natural greenhouse effect. Under these circumstances, the looking for new, renewable natural sources for energy and raw materials, as alternative to fossil ones, is becoming a priority in the fuels research field.

Lignocellulosic biomass, the most abundant renewable organic material on earth [6], has been widely described to be a potential candidate as raw material for the hypothetical substitution of fossil energy resources. This natural resource fulfills several of the requirements for a raw material liable to be considered as a potential substitute to fossil fuels, like being a plenty, renewable material. Lignocellulose is usually described to be formed by three major components: cellulose, hemicellulose and lignin, being the two first of them polysaccharides [7]. Both of them, the polysaccharides, cellulose and hemicellulose, have lately received much attention because of their aptitude as raw materials for the production of several highly versatile chemicals, known as platform molecules, which can be transformed into a large variety of chemical products and biofuels [8,9]. However, the first step in the production of platform molecules is the transformation of the polysaccharide fraction of lignocellulose into their monomeric units by the saccharification of biomass [10]. This transformation involves breaking down polysaccharides into their corresponding monomeric sugars [11], where the most abundant one is glucose. Enzymatic or biological hydrolysis of polysaccharides in aqueous media is one of the most desirable procedures to get saccharification, because the environmentally-friendly, mild reaction conditions needed by biological systems involves little energy consumption. However, this operation mode usually proceeds slowly, because of the hindered access of water molecules and enzymes to glucosidic bonds [12,13], making it less desirable. Chemically, either bases or acids can be used as hydrolysis catalysts, improving the depolymerization rate, though harsher reaction conditions, compared to biological systems, are required [14], leading to the formation of many different by-products [15]. Severe operation conditions are required because of the low reactivity of cellulose (recalcitrance), caused by existence of inter- and intra-molecular hydrogen bonds, leading to a highly packed structure [16] which hinders the access of reactants – both the hydrolysis catalysts and water molecules – to the 1,4-β glucosidic bonds.

Several authors have investigated how to overcome the low reactivity of cellulose by means of different alternatives [17] including chemical [18,19], thermochemical [20,21], mechanical [22–24], and thermomechanical [25] procedures. All of them pursue diminishing the crystallinity of cellulose to enhance the accessibility to the 1,4-β glucosidic bonds in order to make easier their hydrolysis [26]. A different strategy is the use of solvents able to separate the crystalline fibril bundles of cellulose into simple-discrete polysaccharide chains. This option is more attractive because of the higher efficiency than the reduction of crystallinity, since the separation of the linear cellulose polymer chains is achieved by destroying the interaction taking place between them. In this way, there is no hindered access of reactants to the glucosidic bondings, greatly enhancing the reactivity of cellulose in hydrolysis reactions. However, cellulose is not soluble in most of common solvents, because only those chemicals able to break down the hydrogen bondings, that keep the packed structure of cellulose, can dissolve this polysaccharide. Ionic liquids (ILs) are one kind of those solvents showing the ability to dissolve cellulose [27,28], and solutions containing up to 25% mass fraction of this polysaccharide can be prepared from these solvent. However, the solvating power of ionic liquids strongly depends on the nature of the same [27], being crucial the selection of the counter-ion or the structure of the cation. Nevertheless, the use of ILs as solvents offer multiple advantages such as being non-volatile solvents, so negligible loss occurs by evaporation, they display a great solvating behavior and they are easy to be recovered by different techniques. In this last case, the recovering of glucose by selective adsorption facilitates so much the reusability of the same [29]. On the contrary, ILs have to be carefully managed, it usually takes long times for complete dissolution of cellulosic materials [30], and they are also highly expensive, so that it is desirable to facilitate its recycling and to reduce their use. Several authors have overcome, at least partially, these drawbacks by developing alternative dissolution methods like the organic electrolyte solvent systems developed by Rinaldi [31] and Tian [32], in which a fraction of ILs is substituted by polar aprotic solvents to get mixtures able to dissolve cellulose in a quick manner. Several solvents can be used in this strategy, but it seems dimethyl sulfoxide (DMSO) and dimethyl formamide (DMF) display a superior solvating power than the rest, allowing a significant reduction of the amount required ionic liquid for solvating cellulose to a minimal fraction. Despite this advantage, the effect of combining ILs together with conventional solvents for the dissolution of cellulose on its reactivity has been scarcely investigated. Thus, the aim of our contribution is to bring new insights in the use of organic electrolyte solutions as a reaction media to promote the acid hydrolysis of cellulose. For this purpose, different mineral acids and a broad range of experimental conditions have been assayed.

2. Experimental

2.1. Materials and methods

Microcrystalline cellulose (Avicel) was dried under high vacuum conditions and stored in a dry box until use. Anhydrous 1-butyl,3-methylimidazolium chloride ([BMIM]Cl, Aldrich) was selected as ionic liquid for the preparation of the organic electrolyte solutions (OES) due to its superior solvating power and ability to dissolve cellulose [27]. For the same reasons, anhydrous dimethyl sulfoxide (DMSO, Aldrich) was selected as co-solvent, and because of the OES prepared from it needs a lower amount of [BMIM]Cl to completely dissolve cellulose. Both chemicals were fluxed with nitrogen and stored in a dry box to avoid water uptake from atmosphere. OES were prepared by combining both [BMIM]Cl and DMSO in a mole ratio 0.3/0.7, under nitrogen atmosphere. Both, the materials and
the prepared solutions, were manipulated in a dry box filled with a nitrogen atmosphere free from oxygen and moisture. Hydrochloric acid aqueous solution (Scharlab, 35% mass fraction) and sulfuric acid (Scharlab, 98% mass fraction) were used as catalysts for the cellulose hydrolysis tests.

2.2. Hydrolysis tests

Reaction media were prepared by dissolving 0.15 g of cellulose in 3 g of previously prepared OES and warming the resultant suspension at the reaction temperature. After the complete dissolution of cellulose, which occurs in less than 30 min, an aqueous solution of the hydrolysis catalyst (H2SO4 or HCl) is added to get mole theoretical ratio cellulose to protons of 100:1. Subsequently, an appropriate amount of water (Milli-Q grade) is added by dropping at a controlled rate by means of a syringe pump. The reaction is then allowed to evolve for 3 h before quenching it with the addition of water and sudden cooling in an ice-water bath. As a result, the remaining non-hydrolyzed cellulose precipitates as a white solid which is filtered off before analyzing the reaction media.

2.3. Analysis of the reaction products

Quantification of the extent of the cellulose hydrolysis was performed by means of the quantification of the products distribution by means of a Varian ProStar HPLC unit fitted with an Agilent Hi-Plex H⁺ column (7.7 x 300 mm, 8 μm, warmed at 65 °C) and a refraction index detector, using an aqueous solution of sulfuric acid (5 x 10⁻³ mol l⁻¹, 0.6 cm² min⁻¹), under isocratic conditions, as mobile phase. Product identification and quantification was based on a previous calibration of the analysis unit with standard stock solutions of pure commercially available chemicals. Products yields, on a molar basis, were calculated in accordance to the following equation:

\[ Y_{Product} = \frac{\text{Quantity of detected reaction product}}{\text{Quantity of starting glucose in cellulose form}} \times 100 \]  

Cellulose conversion, for the calculation of the selectivity towards each reaction product was not evaluated because of the formation of humins (dark-colored, tarry-solids derived from monosaccharides treated in presence of mineral acids) could interfere on its calculation. However, the slight coloring of recovered cellulose after the tests suggested that the formation of humins was not extensive.

3. Results & discussion

Organic electrolyte solutions prepared from [BMIM]Cl and DMSO have been assayed as solvents for the dissolution and subsequent hydrolysis of commercial cellulose. This investigation comprises several studies in which the effect of the main operation conditions has been investigated in order to maximize the production of glucose by this technique. Table 1 lists the main results achieved from the catalytic experiments performed under a wide range of experimental conditions. Analysis of the results provided data on the yield towards glucose, which is the main reaction product, but also several important by-products were also detected, such as cellobiose, a glucose dimer resultant from the incomplete hydrolysis of cellulose, anhydroglucose (1,6-Anhydro-β-D-glucopyranose), coming from the dehydration of glucose in 1,6 positions.

<table>
<thead>
<tr>
<th>#</th>
<th>Temperature (°C)</th>
<th>Water (mL)</th>
<th>Addition rate (mL h⁻¹)</th>
<th>Y_Cellobiose (%)</th>
<th>Y_Glucose (%)</th>
<th>Y_Anhydroglucose (%)</th>
<th>Y_HMF (%)</th>
</tr>
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<tr>
<td>1</td>
<td>100</td>
<td>—</td>
<td>—</td>
<td>0.0</td>
<td>0.0</td>
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<tr>
<td>2a</td>
<td>70</td>
<td>0.062</td>
<td>—</td>
<td>2.8 (0.9)</td>
<td>5.4 (1.4)</td>
<td>0.0 (0.0)</td>
<td>0.0 (0.0)</td>
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<tr>
<td>3a</td>
<td>90</td>
<td>0.062</td>
<td>—</td>
<td>3.3 (5.2)</td>
<td>22.4 (10.2)</td>
<td>7.3 (0.0)</td>
<td>6.8 (0.0)</td>
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<td>4a</td>
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<td>—</td>
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<td>7.0 (13.4)</td>
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</tr>
<tr>
<td>5a</td>
<td>110</td>
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<td>—</td>
<td>1.5 (4.2)</td>
<td>14.2 (14.5)</td>
<td>11.0 (12.8)</td>
<td>6.1 (2.9)</td>
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<td>6a</td>
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<td>—</td>
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<td>7a</td>
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<td>—</td>
<td>0.0 (1.7)</td>
<td>0.0 (2.8)</td>
<td>0.0 (0.0)</td>
<td>0.0 (0.0)</td>
</tr>
<tr>
<td>8a</td>
<td>100</td>
<td>0.900</td>
<td>0.67</td>
<td>10.8</td>
<td>42.6</td>
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<tr>
<td>9a</td>
<td>100</td>
<td>1.200</td>
<td>0.67</td>
<td>4.3</td>
<td>48.5</td>
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<td>1.600</td>
<td>0.67</td>
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<td>1.800</td>
<td>0.67</td>
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<td>1.00</td>
<td>3.5</td>
<td>58.8</td>
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<tr>
<td>13a</td>
<td>130</td>
<td>2.000</td>
<td>1.00</td>
<td>4.8</td>
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</tr>
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<tr>
<td>15a</td>
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</tr>
<tr>
<td>16a</td>
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<td>2.000</td>
<td>2.00</td>
<td>5.5</td>
<td>70.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

* Reactions performed in [BMIM]Cl:DMSO mixtures 1.4:1.6 wt/wt during 3 h.
* Total water volume added to the reaction media.
* Addition rate for water.
* Yield towards cellobiose.
* Yield towards glucose.
* Yield towards anhydroglucose.
* Yield towards HMF.

Results in brackets corresponds to reactions performed in presence of sulfuric acid as catalyst.
hydroxymethyl furfural (HMF), and formic and levulinic acid, which are produced from glucose by dehydration and hydrolytic transformations respectively.

Following, the main results achieved from the studies performed on the influence of several operation variables are described.

3.1 Effect of the reaction temperature

The influence of the reaction temperature on the extent of the controlled depolymerization of cellulose was assessed in the temperature range from 70 to 150 °C, using two types of mineral acids as catalysts: sulfuric and hydrochloric acid (Table 1, entries 2–7). The addition of these catalysts was adjusted to get the same concentration of protons in the reaction media in order to properly compare their influence on the depolymerization of the catalysts. Reactions were performed in presence of a stoichiometric amount of water to get a theoretical complete cellulose hydrolysis. For this purpose, the amount of water accompanying the mineral acid was taken into account. A blank reaction test was also carried out for comparison purposes (Table 1, entry 1). In this experiment no mineral acid was added to the reaction media, but performed at 100 °C and keeping constant the rest of the experimental conditions, including the addition of water. The first observed difference found in this experiment with regards to the rest of the tests performed in presence of mineral acid, is the readily precipitation of cellulose during the addition of water. This different behavior impossibilities the hydrolytic attack to the 1,4 glucoside bondings of cellulose, leading to a negligible yield towards glucose or any other by-product. These results suggest that simple presence of the ionic liquid species is not able to provide cellulose depolymerization, while revealing the needing of mineral acid to effectively maintain the cellulose in solution.

Four reaction products were detected by HPLC in these first reaction assays: cellobiose, glucose, anhydroglucose and 5-hydroxymethylfurfural (HMF) (Fig. 1). Cellobiose and glucose are both products coming from the hydrolysis of cellulose, though the former is a product of an incomplete hydrolysis—a glucose dimer. Their production, both of cellobiose and glucose, involves the consumption of water molecules added to the reaction media. On the contrary, anhydroglucose and HMF evolve from different glucose dehydrating transformations, and their production is favored in absence of water.

For both mineral acids used as catalysts, HCl and H2SO4, the achieved yields towards the hydrolysis products—cellobiose and glucose—are rather low, suggesting that the extension of hydrolysis reactions is limited, probably as consequence of using a low amount of water, just the stoichiometric amount to get complete hydrolysis of cellulose. Nevertheless, hydrolysis products are produced in a higher amount insofar as the temperature conditions get higher, up to reach maximum values at 100 °C. Above this temperature the yields toward the cellobiose and cellulose dramatically decrease, regardless the used acid catalyst. This fact could be related with the evaporation of water, quite scarce in the reaction media, at reaction temperatures over the water boiling point, making even lower the concentration of water in the liquid reaction media required for the hydrolysis of cellulose. In this way, the absence of water favors the formation of dehydration products, such as anhydroglucose and HMF, whose production follow the same trend with temperature than that observed for the hydrolysis products. However, some delay is observed in their maximum production, since these are produced at maximum rates at 110 °C. This temperature is probably low enough to provide water concentration in the reaction media able to provide the required production of glucose but quite low to favor the consumption of the produced monosaccharide by dehydration transformations. In this way, it seems that 100 °C is the optimal temperature to maximize the production of glucose while minimizing its consumption towards dehydration-derived products.

With regards to the effect of the nature of the mineral acid in the products distribution, hydrochloric acid produce higher amounts of hydrolysis products than sulfuric acid, whereas this latter is able to drive the transformation of cellulose quite further, providing higher amounts of dehydration products—anhydroglucose and HMF—. These differences could be due to the higher acid strength of sulfuric acid in comparison with hydrochloric acid. The superior strength of H2SO4 probably boost the depolymerization of cellulose into glucose, but also the transformation of the evolving monosaccharide into the corresponding dehydration products, leading to an overall higher yield towards solubilized products (47.3%) than HCl (40.5%) at 100 °C. However, glucose yield resulted to be, for all the tested temperature conditions, lower when using sulfuric acid than for hydrochloric acid. This has been the main reason why hydrochloric acid was selected as catalyst to perform the rest of hydrolysis assays in presence of organic electrolyte solutions.

3.2 Effect of the amount of water

The poor achieved yields towards hydrolysis products—cellobiose and glucose—when performing the hydrolysis reactions in presence of a stoichiometric amount of water, has prompted us to try to determine the influence of the effect of the amount of water in the hydrolysis of cellulose in OES. This

![Fig. 1](image-url)  
**Fig. 1** – Products distribution from the hydrolysis of cellulose in OES performed at different temperatures in presence of hydrochloric acid. Reaction conditions: cellulose = 0.15 g; [BMIM]Cl = 1.4 g; DMSO = 1.6 g; HCl = 77 mm³; H2O = 12 mm³; Total reaction time = 2 h.
variable plays a double critical role influencing the reaction in both a positive and negative way. Since water is one of the reactants in the breaking down of cellulose into glucose, increasing its concentration in the reaction media should lead to a higher extent in the depolymerization of cellulose. However, since cellulose is not soluble in water, a higher amount of water in the reaction media could precipitate the solubilized cellulose in the organic electrolyte solution. In this way, determining the optimized water amount to enhance the kinetics of cellulose depolymerization while preventing its precipitation would allow enhancing the yield towards glucose production.

Hydrolysis of cellulose in presence of different amounts of water were performed in presence of hydrochloric acid at 100 °C due to the better results achieved at this temperature (Table 1, entries 4 & 8–12). Addition rate of water was controlled by means of a syringe pump and set at 0.67 cm³ h⁻¹. Because the addition of different amounts of water led to different addition times, all the reaction tests were allowed to proceed the required time after the addition of water to complete a total reaction time of 3 h. This allows a proper comparison between the results achieved on each hydrolysis test.

Increasing the amount of water from 62 to 900 cm³ has a dramatic influence on the amount of hydrolysis products, since the total achieved yield towards these products is almost twice that obtained when using the stoichiometric amount of water (Fig. 2). Increasing the water content even more, displays a positive influence in the production of glucose. This positive effect is connected with the higher extension of hydrolysis reactions, while glucose-consuming by-reactions such as dehydration are limited. Thus, cellobiose, the other hydrolysis product, is produced in a lower extension when increasing the water content, because of its transformation into two glucose units by hydrolysis of the 1,4-glucoside bonding between the monosaccharide monomers. In addition, the detected amount of the anhydroglucose, coming from the dehydration of glucose, is below the quantification limit in this set of reactions, suggesting the inhibitory effect of water in this transformation, avoiding the consumption of glucose. Finally, HMF is produced in a higher extension as the amount of water increases, though it is produced by a dehydration transformation. This fact is most likely linked to the higher amount of glucose present in the reaction media acts a strong driving force to produce this glucose-derived product.

Increasing the amount of water in the reaction mixture up to 2 cm³ leads to a much better glucose yield, reaching values around ~60%. However, the influence of this variable is limited because higher amounts of water, above 2 cm³, produce lower glucose yields (not shown), because of the precipitation of cellulose. In this way, it seems that the optimal amount of water, under the tested conditions, is that corresponding to an initial loading of 2 cm³.

3.3. Effect of the water addition rate

As it has been previously assessed, the amount of water present in the reaction media plays a crucial role in the progress of the hydrolysis of cellulose and the glucose-consuming by-reactions. Therefore, the production of glucose by cellulose hydrolysis in OES seems to be tunable by means of the appropriate control of the water concentration in the reaction media. This variable depends on the addition of water and its consumption during the breaking down of the glucose polymer. Matching the rates of both processes should lead to a constant concentration of water in the reaction media. Maximizing the production of glucose involves the control of the water concentration in the required quantities to boost the hydrolysis rate while preventing the precipitation of cellulose and the consumption of glucose. This strategy has been partially followed by other authors through the addition of small quantities of water all along the reaction time, leading to good glucose yields [33].

Once the reaction temperature, which is also crucial in determining the reaction rates, has been previously set at 100 °C, and the amount of water at 2 cm³, the only variable to be tuned in order to match the water consumption rate with its addition rate is this last one. The influence of this variable has been studied in the range 0.67–2.00 cm³ h⁻¹, using a syringe pump to effectively control the addition of 2 cm³ of water (Table 1; entries 12–16) while the total reaction time has been kept, as in previous cases, in 3 h. The corresponding results are depicted in Fig. 3.

Fig. 3 shows the products distribution obtained in the hydrolysis of cellulose with a controlled addition of water. The glucose yield seems to be strongly dependent on the water addition rate, since the duplication of the water addition rate from 0.67 to 1.33 cm³ h⁻¹ leads to an increasing in the glucose yield from 58.8% to 92.4%. This increasing in glucose production is accompanied with a slight formation of cellobiose to yield 6.1% of the starting cellulose as this glucose dimer. This almost quantitative transformation of cellulose into hydrolysis products, accounting for 98.5% of the starting cellulose, is, to the best of our knowledge, one of the best ever reported value achieved by chemical hydrolysis of cellulose. Faster addition rates produce lower amounts of glucose, probably because of solubility of cellulose in OES decreases, diminishing its reactivity. As for the products coming from glucose dehydration – anhydroglucose and HMF – similarly to previous assays, these are not formed under the studied reaction conditions.
conditions, what means that the water addition rates used are high enough to maintain a rather high water content in the reaction media.

3.4. Hydrolysis of other cellulose-containing feedstocks

These results reveal the use of OES and the controlled addition of water as a promising technique to effectively control the quantitative hydrolysis of cellulose into glucose. However, in order to properly check the versatility of this methodology, several complex feedstocks containing cellulose, such as steam-exploded wheat straw (SE Wheat straw, 54.6% mass fraction cellulose [34]), Whatman filtering paper (W. filtering paper, Grade 1), and waste office paper (80 g/m² white paper), were used as starting materials to accomplish the hydrolysis into OES in a similar way to that previously described for crystalline cellulose. All the cellulose containing feedstock yielded cloudy solutions, probably as consequence of the precipitation of some substances such as lignin in wheat straw or inorganic loads, which precipitates in acid media [35], as well as to the presence of cellulose remained undissolved into OES in a similar way to that previously described for crystalline cellulose. Unlike crystalline cellulose, which was almost quantitatively hydrolyzed, the rest of the tested raw materials provided a lower amount of glucose after the hydrolytic treatment. In contrast to that expected for the steam exploded wheat straw, whose reactivity is supposed to be enhanced [38,39], the hydrolysis of this raw material provided 51.0% of the starting cellulose within the feedstock as glucose. One reason for this lack of performance of the hydrolysis method in comparison to the treatment of pure crystalline cellulose, could be the presence of substances such as lignin, which accounts for 30% of the starting material. This amorphous polymer, as well as the presence of structural inorganics, could interfere in the hydrolysis of cellulose, leading to a lower extent on its depolymerization [40]. As for the paper-based materials, the filtering and the office papers, both yielded a lower amount of glucose (29.0% and 27.0% respectively). In this case, the different additives used for the conformation of the paper sheets, such as different metal oxides used as loads in office paper, could negatively act as neutralizing agents of the mineral hydrochloric acid used as catalyst. Besides, the dissolution of these substances in the OES could be not complete, so that the total hydrolysis of the same is not possible, being another cause of the low glucose yields obtained when treating theses substances. Nevertheless, the performance of the method here described seems to be able to provide, with a low consumption of ionic liquids, the controlled depolymerization of cellulose – at least of pure cellulose, cellulose derived materials such as office or filtering paper or steam exploded wheat straw – in good yields with an outstanding selectivity towards the production of glucose.

### Table 2 – Reaction results obtained from the controlled hydrolysis of different cellulose-containing feedstocks in OES.\(^a\)

<table>
<thead>
<tr>
<th>#</th>
<th>Raw material</th>
<th>Y(_{\text{Celllobiose}})(^b) (%)</th>
<th>Y(_{\text{Glucose}})(^c) (%)</th>
<th>Y(_{\text{Anhydroglucose}})(^d) (%)</th>
<th>Y(_{\text{HMF}})(^e) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cellulose</td>
<td>6.1</td>
<td>92.4</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
<td>SE wheat straw</td>
<td>0.8</td>
<td>51.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>3</td>
<td>W. filtering paper</td>
<td>0.8</td>
<td>29.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>4</td>
<td>Waste office paper</td>
<td>0.0</td>
<td>27.0</td>
<td>0.0</td>
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</table>

\(^a\) Reactions performed in presence of hydrochloric acid, in [BMIM]Cl:DMSO mixtures 1.4:1.6 wt/wt at 100 °C, with a water addition rate of 1.33 mL h\(^{-1}\) during 3 h.
\(^b\) Yield towards celllobiose.
\(^c\) Yield towards glucose.
\(^d\) Yield towards anhydroglucose.
\(^e\) Yield towards HMF.

4. Conclusions

Organic electrolyte solutions (OES) formed by combination of [BMIM]Cl, as ionic liquid, and DMSO, as conventional solvent,
have been used as reaction media for the hydrolysis of cellulose. The use of these OES, as an effective strategy to save expensive ionic liquids in the solubilization of cellulose, provides also an excellent reaction media for the hydrolysis of this polysaccharide into glucose. In these experiments hydrochloric acid has revealed to be superior to sulfuric acid as catalyst in terms of selectivity towards glucose, because the stronger acidity of sulfuric acid seems to boost by-reactions leading to some consumption of the formed monosaccharides. Studies on the effect of the main operational reaction variables in the hydrolytic depolymerization of cellulose have revealed the importance of the water concentration in the reaction media. Driving this variable by controlling both the amount of water added to the reaction media as well as the rate in which water is incorporated to the mixture, allows increasing the glucose yield up to an outstanding 92% with a, extremely high selectivity towards this mono-saccharide and no glucose-derived by-products formation. Finally, this strategy has been successfully applied to the depolymerization of other cellulose-based materials such as steam explosion wheat straw and different paper-based materials. However, the glucose yield achieved for these starting feedstocks is lower than that obtained from pure crystalline materials. Further improvements would be required in order to increase the application scope of this strategy to the treatment of different polysaccharide-based materials.

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