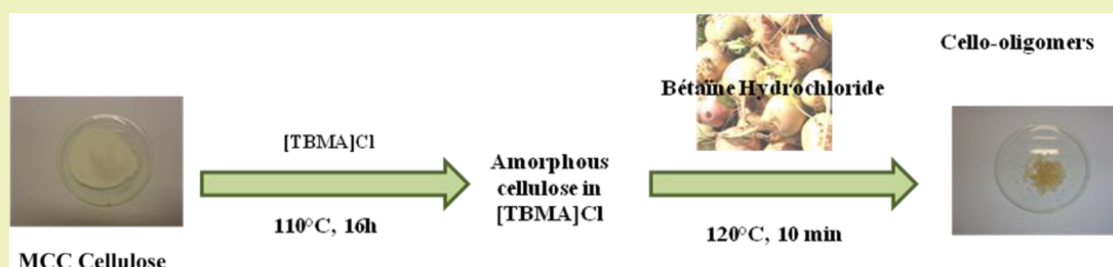# Selective Depolymerization of Cellulose to Low Molecular Weight Cello-Oligomers Catalyzed by Betaïne Hydrochloride

Florent Boissou, Karine De Oliveira Vigier,* Boris Estrine, Sinisa Marinkovic, and François Jérôme

Institut de Chimie des Milieux et Matériaux de Poitiers, CNRS/Université de Poitiers, 1 Rue Marcel Doré, 86022 Poitiers, France

S *Supporting Information*

ABSTRACT: This study aims to demonstrate that depolymerization of cellulose can be closely controlled in a reaction media made of betaïne hydrochloride (BHC) and [TBMA]Cl opening the route to low molecular weight cello-oligomers that exhibit a high potential for marketing in the production of surfactants and thickener agents. The main advantages of this process rely on (1) the sustainability of BHC, (2) convenient isolation of cello-oligomers, and (3) recyclability of BHC and [TBMA]Cl. On the other hand, we demonstrate that this work can be also considered as an efficient pretreatment process of cellulose. Indeed, whereas in water cellulose is recalcitrant to hydrolysis, we show here that recovered cello-oligomers can be subsequently readily converted in water to glucose.

KEYWORDS: *Cellulose, Catalysis, Depolymerization, Betaïne hydrochloride, Ionic liquid*

INTRODUCTION

Cellulose is the most abundant biopolymer available on Earth with an annual production estimated to about 1×10^{10} ton.[1] Cellulose is industrially produced in large scale from different raw materials such as wood, cotton, and wastes, among many other renewable sources.[2] Nowadays, cellulose and its derivatives find a large variety of applications. For instance, cellulose is commonly used as fibers or for the production of tissues, paper, membranes, polymers, paints, and medicines.[3,4]

In the field of fine chemistry, a plethora of articles is currently dedicated to the conversion of cellulose to relevant chemicals such as 5-hydroxymethylfurfural, γ-valerolactone, levulinic acid, tetrahydrofuran derivatives, etc. All of these processes rely on a complete depolymerization of the cellulosic backbone. The selective depolymerization of cellulose to low molecular weight cello-oligomers has been however scarcely investigated, although it also provides a direct access to valuable chemicals with an important market potential especially in the field of surfactants, thickener agents, glues, etc.[5] The reason for this lack of documentation stems from the huge difficulty of selectively controlling the depolymerization of cellulose. In particular, due to a robust intra- and intermolecular hydrogen bond network, the depolymerization of cellulose requires harsh conditions of pressure and temperature that are unfortunately not compatible with the stability of cello-oligomers.[6−8] Hence, yields of cello-oligomers are generally low, and the purification workup is too costly for an industrial use. Recently, physical[9] and mechanical treatments[10] of cellulose have been proposed

for the production of cello-oligomers from cellulose. Although of great interest, one should comment that optimization is still needed to reduce the energy consumption of these processes prior to making these technologies mature for an industrial use. Alternatively, cello-oligomers can be produced through enzymatic routes generally by controlled repolymerization of glucose (named as the reversion reaction).[11] Despite a wide range of cello-oligomers with different chemical structures and a controlled degree of polymerization (DP) produced, this fermentation process is subject to important limitations such as (1) the price and recyclability of enzymes, (2) the higher price of glucose (~650 €/ton) than cellulose (~60 €/ton), and (3) a costly workup procedure hampering their use in the field of fine chemistry.

Since the pioneering works of Rogers in 2002,[12] ionic liquids (ILs) have become of great interest for the dissolution of cellulose, and ILs are now rapidly emerging as attractive solvents for cellulose processing.[12−15] In this field of research, much effort is now being paid to the design of ILs with lower price, lower toxicity, and improved biodegradability and recyclability. Schüth and co-workers were the first to demonstrate that cello-oligomers can be selectively produced from cellulose in 1-butyl-4-methylimidazolium chloride and [BMIM]Cl and in the presence of a cation exchange resin as a

solid acid catalyst.[16] In such a process, high molecular weight cello-oligomers were produced (DP = 150). The partial exchange between the proton supported on the resin and the imidazolium cation of [BMIM]Cl is however a drawback of this process (liberation of HCl) hampering the recycling of the resin. Moreover, the toxicity of the ionic liquid is still under controversy as described by different authors.[17−21]

Here, we propose an alternative route based on the association of tributylmethylammonium chloride ([TBMA]Cl) and glycine betaïne hydrochloride (BHC) (Scheme 1). Both

Scheme 1. Betaïne Hydrochloride (BHC)

- Renewably-sourced
- Cheap
- Biocompatible
- pKa value : 1.9
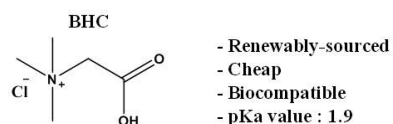
chemicals have been selected not only because of their higher availability, lower price, and higher biocompatibility than [BMIM]Cl but also because (1) BHC is a weak organic Brønsted acid ($pK_a \sim 1.9$), thus avoiding the proton exchange with the ammonium cation leading to the side liberation of HCl, and (2) BHC can be conveniently recycled, a limitation of current mineral acids. Under optimized conditions, low molecular weight cello-oligomers with an average DP of 65 were produced with 85% yield in this work. These cello-oligomers were conveniently isolated opening the route to poorly explored chemicals in the literature. Finally, we wish to demonstrate in the last part of this report that this methodology can be also used as an efficient pretreatment process for the catalytic production of glucose from cellulose for which the demand of new technologies/processes is highly researched.

■ EXPERIMENTAL SECTION

Materials. Microcrystalline cellulose (MCC cellulose, Avicel PH200), DP = 200, crystallinity index of 54% (measured by CP MAS ^{13}C NMR) was kindly provided by FMC Corp. Tributylmethylammonium chloride ([TBMA]Cl = 98%) was purchased from Fluka, and betaïne hydrochlorie was purchased from Sigma-Aldrich. Phosphoric acid (85%) was purchased from Sigma-Aldrich. [BMIM]Cl was synthesized by adding 119.39 g of methylimidazole to 161.54 g of 1-chlorobutane. This mixture was heated to reflux for 24 h at 100 °C. Two phases were obtained. The upper phase containing nonconverted 1-chlorobutane was eliminated. To the residual phase, 200 mL of anhydrous acetone was added to crystallize [BMIM]Cl. [BMIM]Cl was filtered and washed with diethyl ether. The ionic liquid was hence dried under vacuum at room temperature.

Depolymerization of Cellulose. A totalof 12 g of [TBMA]Cl was heated under stirring at 110 °C prior to adding 5 to 10 wt % of cellulose AVICEL PH200 (MCC). When cellulose was completely dissolved (after 16 h under stirring), a clear and highly viscous solution was obtained. The temperature was then increased to 120−150 °C, and 5 to 10 wt % of BHC was added. After 10 min, cello-oligomers and BHC were precipitated by adding acetone (100 mL); the solubility of BHC in acetone is 0.5 g L^{-1}. The acetone phase was dried under vacuum to recover [TBMA]Cl. The solid containing cello-oligomers and BHC was washed with water to remove BHC. Cello-oligomers were obtained as a white powder. The water phase containing BHC can be then evaporated under vacuum, yielding BHC with a sufficient purity to be reused (see text for more details on the procedure). Prior to analysis, cello-oligomers were washed with ethanol and acetone to remove residual [TBMA]Cl/BHC.

Catalytic Hydrolysis of Cello-Oligomers in Presence of A35 Cation Exchange Resin. Hydrolysis of MCC was performed in an automated multimode microwave oven (MicroSynth from Milestone s.r.l., Italy). This oven operates at 2.45 GHz, and temperature is controlled by a fiberoptic sensor. Temperature was monitored by insertion of the calibrated fiberoptic sensor in the reaction mixture while stirring properly. The maximum power input could be adjusted between 0 and 1000 W. Under microwave heating, the internal temperature of the reaction vessel reached the reaction set points in 20 min and was maintained at a temperature of ±5 °C using a power compensation feedback control. In a typical procedure, cello-oligomers (0.1 g), A35 (0.04 g), and 5 mL of H$_2$O were introduced into a microwave reactor and sealed and heated with a magnetic stirring bar at 150 °C for 1 h. At the end of the reaction, the microwave heating was stopped, and the reaction vessel was cooled to room temperature. The reaction mixture was then filtered, and the recovered aqueous solution was analyzed by HPLC.

Characterization Methods. ^{1}H NMR spectra were recorded on a 400 MHz Bruker Advance DPX spectrometer using D$_2$O as solvent.

The degree of polymerization (DP) of cellulose was determined by intrinsic viscosity measurements using a copper ethylenediamine complex as solvent for the cellulose dissolution (normalized method: AFNOR NF G 06-037). Typically, 0.125 g of cellulose was dissolved in 20 mL of cupriethylenediamine and stirred for 2 h at room temperature. Viscosity data were determined in a UBBELOHDE thermostated capillary tube viscosimeter (25 °C). The relation between the viscosity and DP is given in the NF G 06-037 norm using a normalized abacus. One can note that after 0.5 h of reaction, the DP of cellulose was not determined anymore due to the side production of insoluble black materials preventing the determination of the DP by viscosimetry. The margin of error for the DP measurements is ±5.

SEC analyses were performed on a Shimadzu Prominence LC equipped with a degasser DGU-20A3, pump system (LC-20AQ), thermostated autosamplor SIL-20AC (samples were maintained at 15 °C), and oven CTO-20AC maintained at 40 °C. Saccharides with a DP lower than 10 (glucose, cellobiose, etc.) were analyzed on a Shodex KS-802 column using water as eluent (1 mL/min) and quantified by a refractor indice detector. Note that external calibration of the LC was performed using glucose, cellobiose, cellotriose, cellotetraose, cellopentaose, and cellohexaose as standards.

Glucose was analyzed on a Simadzu HPLC equipped with a pump system (LC-20AD), autosamplor SIL-10A, and controller CBM 20A. Products were separated on a Varian 100-5 amino S 250 mm × 4.6 mm (NH$_2$) column using a mixture of water/acetonitrile (2/8) as eluent with a flow rate of 0.8 mL/min. Quantification was by a refractor indice detector (Waters 2410). External calibration of the LC was performed using standards of glucose. The margin of error for the glucose yield is ±2%.

XRD patterns of cellulose were recorded on a Bruker D5005 Bragg−Brentano ($\theta-$) diffractometer operated with a copper tube powered at 40 kV and 40 mA (Cu$_{K\alpha1}$ = 1.54060 Å and Cu$_{K\alpha2}$ = 1.54443 Å). Measurements were performed from 2θ = 5° to 50° in step mode, with steps of 0.068 and a fixed acquisition time of 10 s/step.

^{13}C CP/MAS NMR analyses were performed on a Brüker Avance III 400 WP apparatus with A CP MAS 4 mm probe.

■ RESULTS AND DISCUSSION

Dissolution/depolymerization experiments were conducted using microcrystalline cellulose (MCC) of the type PH-AVICEL 200 in neat [TBMA]Cl to investigate its ability to dissolve cellulose. MCC has a DP of 200, particle size lower than 200 μm, water content lower than 5 wt %, glucose content higher than 99%, and crystallinity of 54% (measured by CP MAS ^{13}C NMR). At 110 °C, up to 10 wt % of MCC was successfully dissolved in [TBMA]Cl after 16 h. Next, cellulose was regenerated by the addition of ethanol, used here as an antisolvent, to measure the DP of dissolved cellulose. XRD analysis of regenerated cellulose indicated an important decrease in the cellulose crystallinity index supporting the

dissolution of MCC in [TBMA]Cl (Figure S1, Supporting Information). In addition, as expected, under neutral conditions, similar DP (190 vs 200 for MCC) was obtained, which is also classically observed in the presence of imidazolium-based ILs. Hence, the dissolution of 5 wt % of MCC cellulose was also carried out in 12 g of [BMIM]Cl with a water content of 1 wt %. Cello-oligomers with a DP of 200 were obtained. However, one can note that under optimized conditions (see below) the recycling of [BMIM]Cl was not possible, and the recovery of BHC was less than 14 wt %.

To induce the partial depolymerization of MCC to low molecular weight cello-oligomers, various amounts of BHC were added in [TBMA]Cl. First, solutions of [TBMA]Cl containing 20−50 wt % of BHC were heated at 110 °C prior to adding 5 wt % of MCC. Note that water contained in [TBMA]Cl (1 wt %), BHC, and MCC (7 wt %) was in sufficient quantity to promote the theoretical complete depolymerization of MCC. After 16 h under stirring, no dissolution of MCC was observed. This result is in agreement with previous works that highlighted that protic species prevent the dissolution of cellulose in ILs.[17] Although no dissolution occurred under these conditions, the DP of cellulose was however decreased from 200 to 120 in a [TBMA]Cl/BHC (8:2) solution supporting that BHC was capable of partly hydrolyzing the glycosidic bond of cellulose. Note that prolonged heating did not result in the depolymerization of MCC to a larger extent. Even worse, it led to the formation of side dark brown products. Although these insoluble cello-oligomers with a DP of 120 are of course of interest, one should comment that their DP and crystallinity are still too high to facilitate their processing in fine chemistry.

To overcome this problem, the process was optimized to ensure the complete dissolution of MCC and thus to facilitate its depolymerization in a larger extent. When employing this strategy, a balance has to be found between the DP of in situ produced cello-oligomers and their recovery. Indeed, cello-oligomers with a low DP (<40) are highly soluble in [TBMA]Cl/BHC and thus very difficult to extract. In a typical procedure, 5 wt % of MCC was dissolved in neat [TBMA]Cl at 110 °C prior to adding 10 wt % of BHC. Note that a higher BHC content led to the precipitation of dissolved cellulose. Next the solution was heated at 150 °C to promote the depolymerization of cellulose by BHC. The depolymerization process was monitored by measuring the DP (viscosimetry) of recovered cello-oligomers at different periods of time. In a typical procedure, at the desired time, acetone was added to the reaction medium leading to the coprecipitation of cello-oligomers and BHC ([TBMA]Cl is soluble in acetone). BHC was then separated from cello-oligomers by washing with water. Note that for recovered cello-oligomers with a DP higher than 40, no soluble carbohydrate was detected in the aqueous wash.

At 150 °C, the average DP of cellulose was rapidly decreased from 200 to only 65 and 40 after 10 and 20 min of reaction, respectively (Figure 1). At such a low reaction time, glucose was produced with a yield lower than 0.5% (after 10 min) and 2.5% (after 20 min). Prolonging the reaction time from 20 min to 1 h increased the yield of glucose from 2.5% to 9%, suggesting in this case an important depolymerization of cellulose. Prolonging again the reaction time was detrimental for the reaction selectivity, and even glucose was decomposed in this case (production of brown colored products). Hence, reaction times lower than 20 min were selected in our study.
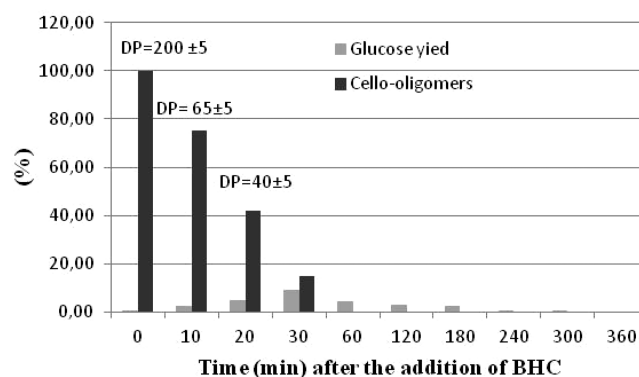

Figure 1. DP of cellulose as a function of time in a [TBMA]Cl/BHC (9/1) solution heated at 150 °C.

Next, we focused on the extraction efficiency of cello-oligomers from the [TBMA]Cl/BHC media. After 20 min of reaction, only 42 wt % of cello-oligomers with an average DP of 40 was extracted. This low extraction efficiency was mostly due to the extensive depolymerization of cellulose leading to the concomitant presence of (1) low molecular weight oligosaccharides that remained soluble in the reaction media and (2) partial degradation of cello-oligomers to soluble unidentified side products. When the reaction was stopped at 10 min, cellulose was depolymerized to a lower extent, and in this case, 75 wt % of cello-oligomers were recovered with an average DP of 65, opening an interesting route for the fabrication of novel commodities from cellulose.

Having all these data in hand, we then characterized more in detail the recovered cello-oligomers. To this end, cello-oligomers were characterized by ^{13}C CP/MAS NMR on a Brüker Avance III 400 WP apparatus with A CP MAS 4 mm probe (Figure 2). The chemical shift of carbon 2 and 6 of the glucose unit unambiguously revealed that recovered cello-oligomers with a DP of 65 are of type cellulose II, indicating a change in the cellulose crystalline structure during the dissolution/depolymerization of cellulose.[22] The crystallinity index of recovered cello-oligomers, measured by CP/MAS ^{13}C NMR, revealed that it was lower than that of MCC (28% vs 54% for MCC), which is also supported by XRD analysis.

Although this NMR study is consistent with a linear structure of cello-oligomers, possible reorganization of cello-oligomers during the depolymerization of cellulose (ramification of glucose units) cannot be however totally ruled out because it has been already observed feasible in the acid-assisted ball-milling hydrolysis of cellulose.[23,24] One can note in Figure 2 that cello-oligomers contain BHC and [TBMA]Cl as contaminants. By means of elemental analyses, we found that the nitrogen contamination of cello-oligomers was however rather low (20 μmol/$g_{cellulose}$).

Although [TBMA]Cl is much cheaper than [BMIM]Cl, its recyclability was then investigated to improve again the eco-efficiency of this process. As mentioned above, addition of acetone led to the coprecipitation of cello-oligomers and BHC. The acetone phase containing [TBMA]Cl was evaporated under reduced pressure allowing [TBMA]Cl to be recovered. BHC was then separated from the cello-oligomers by washing with water. After removal of water under vacuum, 94 wt % of BHC with a purity higher than 95% was recovered. Next, recovered [TBMA]Cl and BHC were combined and reengaged in the dissolution/depolymerization of fresh MCC (Scheme 2).
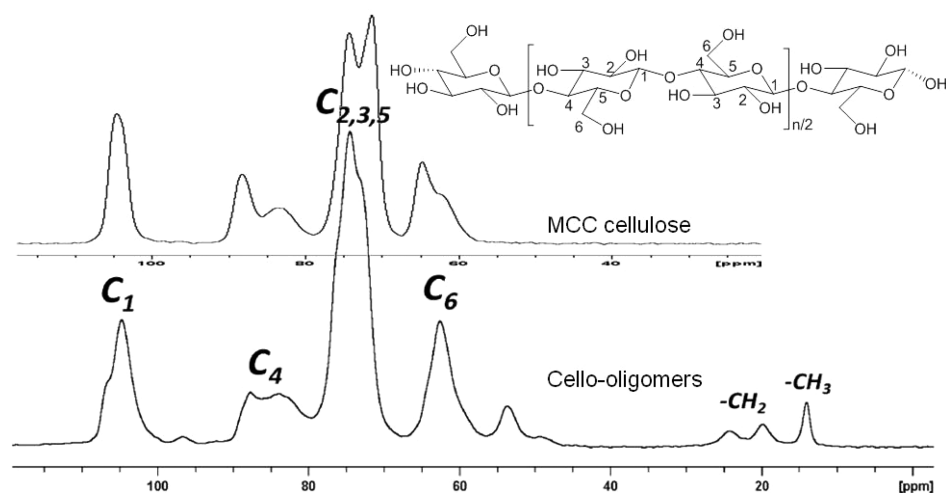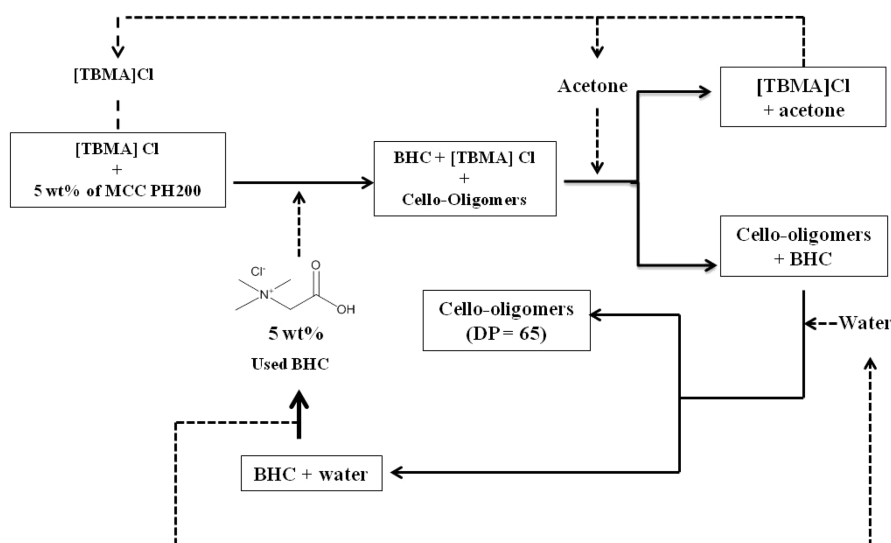
Figure 2. ^{13}C CP/MAS NMR spectra of MCC cellulose and cello-oligomers with a DP of 65.

Scheme 2. Representation of Procedure Employed for Recovery of Cello-Oligomers and Recycling of [TBMA]Cl and BHC

Using this procedure, cello-oligomers with an average DP of 65 were still obtained during the second cycle. However, after the third recycling, the efficiency of the process was decreased, and the average DP of recovered cello-oligomers was found to be 140 (Figure S2, Supporting Information). This decrease in efficiency after three cycles was attributed to the accumulation of impurities (soluble carbohydrates and degradation product) in [TBMA]Cl hampering the long-term dissolution of cellulose. Although these species are difficult to observe on the ^{1}H and ^{13}C NMR spectra of used [TBMA]Cl, the important coloration of the reaction medium after only two cycles corroborated this hypothesis.

In order to limit the degradation of carbohydrates and to facilitate the recycling of the [TBMA]Cl/BHC mixture, the reaction temperature of the process was progressively dropped from 150 to 110 °C (Figure 3). Interestingly, at a temperature ranging from 120 to 140 °C, cello-oligomers with an average DP of 65 were still obtained after 10 min of reaction. More importantly, at 110 °C, the depolymerization of cellulose still took place, but in this case, the average DP of recovered cello-oligomers was slightly higher (DP = 85) due to a slower depolymerization rate in accordance with the Arrhenius' law.
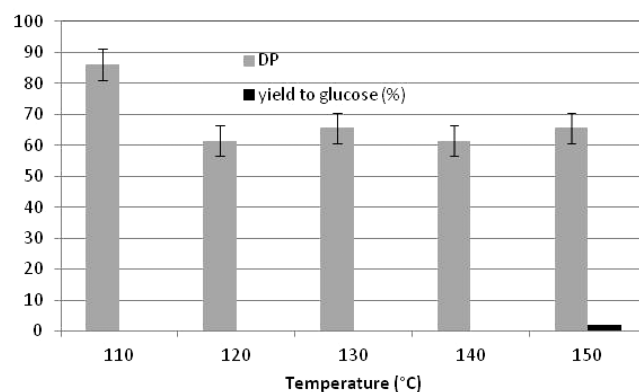

Figure 3. Influence of reaction temperature on the depolymerization of cellulose in a [TBMA]Cl/BHC (9/1) mixture after 10 min of strirring.

This slower depolymerization rate of cellulose observed at 110 °C was also supported by HPLC analysis. Indeed, whereas trace of glucose was observed after 10 min of reaction at 150 °C, glucose was not detected anymore at 110 °C, and only traces of

cello-oligomers with a DP within the range of 2−6 were detected.

The possible decrease in reaction temperature is expected to limit the formation of side products and thus to facilitate recycling of [TBMA]Cl. One should however comment that a decrease in the reaction temperature from 150 to 120 °C led to a concomitant increase in the reaction viscosity making the stirring of the solution more difficult. Hence, recycling experiments were performed at 120 °C but in the presence of only 5 wt % of BHC and 5 wt % of cellulose. As shown in Table 1, at 120 °C both [TBMA]Cl and BHC were successfully

Table 1. Recycling of [TBMA]Cl and BHC after 10 min of Heating at 120°C

number of run	wt % of recovered [TBMA]Cl	wt % of BHC recovered	DP
1	100	94 ± 5	65 ± 5
2	97 ± 2	86 ± 5	70 ± 5
3	93 ± 2	88 ± 5	65 ± 5
4	91 ± 2	90 ± 5	65 ± 5
5	89 ± 2	80 ± 5	100 ± 5

recycled at least four times (vs two times at 150 °C) without an appreciable decrease in their efficiency. After each run, more than 90 wt % of BHC and [TBMA]Cl were recovered demonstrating the chemical stability of these ionic species under our working conditions. The weight percentage of cello-oligomers recovered after each cycle was 85%, which is higher than the value provided above at 150 °C (75 wt %). However, after the fourth run, the efficiency of the [TBMA]Cl/BHC solution started to drop, presumably due to the unavoidable long-term contamination of [TBMA]Cl with side products even at 120 °C. Nevertheless, the overall productivity of the process after four runs reached 180 mg of cello-oligomers (DP = 65) per gram of [TBMA]Cl/BHC.

One can note that when [BMIM]Cl was used instead of [TBMA]Cl, cello-oligomers with a DP of 65 were also obtained after the addition of BHC. The recovery of [BMIM]Cl was performed by adding ethanol. A second run was carried out by adding 5 wt % of MCC cellulose to the recovered [BMIM]Cl. After 16 h of stirring at 110 °C, the dissolution of cellulose was not observed showing that [BMIM]Cl cannot be recycled. The DP of the cello-oligomers obtained was 140, showing that BHC still remained in [BMIM]Cl. Hence, only 14 wt % of BHC was recovered after the addition of water.

To prove the interest of using BHC for the production of cello-oligomers, BHC was replaced in the procedure described above by phosphoric acid (85% of purity). To this end, in the first step, 5 wt % of cellulose was dissolved for 16 h in [TBMA]Cl at 110 °C. The temperature was then raised to 120 °C, and the same molar amount of H_3PO_4 than BHC was added. Stirring continued for 10 min. Cello-oligomers (70 wt % of recovery) with a DP of 90 were recovered at the end of the process. The formation of glucose and cello-oligomers with a DP lower than 6 was not observed. The recovered [TBMA]Cl

was used in another cycle for the dissolution of 5 wt % of MCC cellulose. After 16 h of stirring at 110 °C, no dissolution of cellulose was observed, and the recovered cellulose had a DP of 140, showing that phosphoric acid was still present in the recovered [TBMA]Cl, leading to a partial depolymerization of cellulose. This result shows that BHC is a convenient acid because it can be separated from [TBMA]Cl, allowing for recycling of [TBMA]Cl. Moreover, BHC can be recycled more conveniently than H_3PO_4. All these results demonstrate that this [TBMA]Cl/BHC mixture allows the formation of cello-oligomers with DP of 65, with the recycling of [TBMA]Cl and BHC.

The flexibility of the process was then checked by testing other cellulose sources such as cellulose extracted from soft (coniferous, DP = 1050) and hard wood (broadleaf, DP = 900) (Table 2). Interestingly, these cellulose grades were also converted to cello-oligomers by dissolution and heating at 120 °C for 10 min in the [TBMA]Cl-BHC system. In such a case, 80 wt % of cello-oligomers with a DP of 150 and 210 were conveniently obtained from coniferous and broadleaf wood, respectively, showing the efficiency of the [TBMA]Cl/BHC mixture for the partial depolymerization of cellulose.
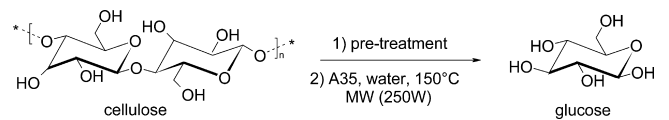
Beside the fact that this process conveniently afforded cello-oligomers from which a valuable chemistry can be done, this process can be also considered as a promising pretreatment for the complete depolymerization of cellulose to glucose (Table 3). Acid-catalyzed depolymerization of cellulose to glucose is difficult, and most chemical processes provide glucose in a rather low yield. For instance, when MCC was heated for 1 h in water at 150 °C (under microwave irradiation, 250W) and in the presence of Amberlyst-35 as a solid acid catalyst, glucose was produced only as a trace (<5%). In such a case, the catalytic reaction was strongly limited by a very weak solid−solid interaction between cellulose and Amberlyst-35. When MCC was dissolved and regenerated from [TBMA]Cl or ball milled according to a previous work,[25] cellulose with a low crystallinity index was obtained. As expected, in this case, cellulose was more prone to hydrolysis (due to a better swelling in water), and glucose was obtained with 15−22% yield. When a similar catalytic test was carried out with cello-oligomers with a high DP (150) and crystallinity index (obtained by treatment of cellulose in a [TBMA]Cl/BHC mixture (1/1)), yield of glucose remained in a similar range than those obtained using ball-milled cellulose or cellulose dissolved and regenerated from [TBMA]Cl.

This result showed that the crystallinity index of cellulose, often considered as a key parameter governing the catalytic depolymerization of cellulose in water, is not the only one that has to be considered; the degree of polymerization of cellulose definitely plays a crucial role also. As evidence, using now cello-oligomers with a DP of 65, more than 43% yield of glucose (along with 3% of cellobiose and 1% of cellotriose) was obtained showing a noticeable advantage over the [TBMA]Cl/BHC system for the production of glucose from cellulose.

Table 2. Controlled Depolymerization of Different Sources of Cellulose in [TBMA]Cl/BHC Mixture after Heating at 120°C

cellulose	time (min)	DP before treatment	DP after treatment in the [TBMA]Cl/BHC mixture
MCC	10	200 ± 5	65 ± 5
cellulose from coniferous	10	1050 ± 5	150 ± 5
cellulose from broadleaf	10	900 ± 5	210 ± 5

Table 3. Pretreatment of Cellulose in [TBMA]Cl/BHC Mixture

entry	pretreatment	crystallinity	DP	glucose yield (%)
1	no	high	200 ± 5	<5
2	dissolution in [TBMA]Cl	low	190 ± 5	22 ± 2
3	ball milling	low	200 ± 5	15 ± 2
4	dissolution in [TBMA]Cl/BHC (1/1)	high	150 ± 5	22 ± 2
5	dissolution in [TBMA]Cl/BHC (9/1)	low	65 ± 5	43 ± 2

■ CONCLUSION

In this study, we report that the combination of [TBMA]Cl and renewably sourced BHC affords reaction media capable of solubilizing and depolymerizing cellulose. By controlling the reaction time and temperature, it was possible to produce cello-oligomers with a DP as low as 65. At such a low DP, more than 85 wt % of cello-oligomers were conveniently extracted from the reaction media opening the route to valuable chemicals that have not been explored yet. Besides their higher availability, lower price, and higher biocompatibility than traditional imidazolium-based ionic liquids, it is our opinion that this media offers noticeable advantages such as (1) low temperature (120 °C), (2) convenient isolation of cello-oligomers, and (3) convenient recycling of BHC and [TBMA]Cl. On the other hand, the possibility to control the depolymerization of cellulose to low molecular weight cello-oligomers can be also considered as an efficient pretreatment process allowing cellulose to be converted to glucose, a reaction for which the demand of new technologies/processes is highly demanded. In particular, whereas cellulose is recalcitrant to hydrolysis, low molecular weight cello-oligomers produced in this work were readily converted to glucose (43% yield) in water and in the presence of a cation exchange resin as a solid acid catalyst.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

XRD analyses of cellulose and cello-oligomers and recycling of [TBMA]Cl and BHC at 150 °C. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: karine.vigier@univ-poitiers.fr. Phone: + 33 (0)5 49 45 39 51.

Present Address

F. Boissou, B. Estrine, and S. Marinkovic: Agro-Industrie Recherches et Développement, Green Chemistry Department, 3 F-51110 Pomacle, France.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ ABBREVIATIONS

TBMACl, tributylmethylammonium chloride; BHC, betaïne hydrochloride; ILs, ionic liquids

■ REFERENCES

(1) Klemm, D.; Heublein, B.; Fink, H. P.; Bohn, A. Cellulose: Fascinating biopolymer and sustainable raw material. *Angew. Chem., Int. Ed.* **2005**, *44*, 3358−3393.

(2) Ragauskas, A. J.; Williams, C. K.; Davison, B. H.; Britovsek, G.; Cairney, J.; Eckert, C. A.; Frederick, W. J.; Leak, D. J.; Liotta, C. L.; Mielenz, J. R.; Murphy, R.; Templer, R.; Tschaplinski, T. The path forward for biofuels and biomaterials. *Science* **2006**, *311*, 484−489.

(3) Moutos, F. T.; Freed, L. E.; Guilak, F. A biomimetic three-dimensional woven composite scaffold for functional tissue engineering of cartilage. *Nat. Mater.* **2007**, *6*, 162−167.

(4) Fan, L. T.; Gharpuray, M. M.; Lee, Y. H. *Cellulose Hydrolysis*; Springer-Verlag: Berlin, 1987.

(5) Monsan, P.; Paul, F. Enzymatic synthesis of oligosaccharides. *FEMS Microbiol. Rev.* **1995**, *16*, 187−192.

(6) Nishiyama, Y.; Sugiyama, J.; Chanzy, H.; Langan, P. Crystal structure and hydrogen bonding system in cellulose I_α from synchrotron X-ray and neutron fiber diffraction. *J. Am. Chem. Soc.* **2003**, *125*, 14300−14306.

(7) Jarvis, M. Cellulose stacks up. *Nature* **2003**, *426*, 611−612.

(8) Langan, P.; Nishiyama, Y.; Chanzy, H. X-ray structure of mercerized cellulose II at 1 angstrom resolution. *Biomacromolecules* **2001**, *2*, 410−416.

(9) Benoit, M.; Rodrigues, A.; Zhang, Q.; Fourré, E.; De Oliveira Vigier, K.; Tatibouët, J.-M.; Jérôme, F. Depolymerization of cellulose assisted by nonthermal atmospheric plasma. *Angew. Chem., Int. Ed.* **2011**, *50*, 8964−8967.

(10) Rinaldi, R.; Meine, N.; vom Stein, J.; Palkovits, R.; Schüth, F. Which controls the depolymerization of cellulose in ionic liquids: The solid acid catalyst or cellulose? *ChemSusChem* **2010**, *3*, 266−176.

(11) Thiem, J. Applications of enzymes in synthetic carbohydrate chemistry. *FEMS Microbiol. Rev.* **1995**, *16*, 193−199.

(12) Swatloski, R. P.; Spear, S. K.; Holbrey, J. D.; Rogers, R. D. Dissolution of cellulose with ionic liquids. *J. Am. Chem. Soc.* **2002**, *124*, 4974−4975.

(13) Wang, H.; Gurau, G.; Rogers, R. D. Ionic liquid processing of cellulose. *Chem. Soc. Rev.* **2012**, *41*, 1519−1537.

(14) Brandt, A.; Gräsvik, J.; Hallett, J. P.; Welton, T. Deconstruction of lignocellulosic biomass with ionic liquids. *Green Chem.* **2013**, *15*, 550−583.

(15) Zhu, S.; Wu, Y.; Chen, Q.; Yu, Z.; Wang, C.; Jin, S.; Ding, Y.; Wu, G. Dissolution of cellulose with ionic liquids and its application: A mini-review. *Green Chem.* **2006**, *8*, 325−327.

(16) Rinaldi, R.; Palkovits, R.; Schüth, F. Depolymerization of cellulose by solid catalysts in ionic liquids. *Angew. Chem., Int. Ed.* **2008**, *120*, 8047−8050.

(17) Marlair, G.; Diallo, A. O.; Benaissa, W.; Vignes, A.; Blanc, L.; Len, C. Developing dedicated methods and tools for safe use and processing of key chemicals in biorefining. *Chem. Eng. Trans.* **2013**, *31*, 859−864.

(18) Chancelier, L.; Diallo, A. O.; Santini, C. C.; Marlair, G.; Gutel, T.; Mailley, S.; Len, C. Targeting adequate thermal stability and fire safety in selecting ionic liquid-based electrolytes for energy storage. *Phys. Chem. Chem. Phys.* **2014**, *16*, 1967−1976.

(19) Diallo, A. O.; Fayet, G.; Len, C.; Marlair, G. Evaluation of heats of combustion of ionic liquids through use of existing and purpose built models. *Ind. Eng. Chem. Res.* **2012**, *51*, 3149−3156.

(20) Diallo, A. O.; Len, C.; Morgan, A. B.; Marlair, G. Revisiting physico-chemical hazards of ionic liquids. *Sep. Purif. Technol.* **2012**, *97*, 228−234.

(21) Diallo, A. O.; Morgan, A. B.; Len, C.; Marlair, G. An innovative experimental approach aiming to understand and quantifiy the acual fire hazards of ionic liquids. *Energy Environ. Sci.* **2013**, *6*, 699−710.

(22) Boissou, F.; Mühlbauer, A.; De Oliveira Vigier, K.; Leclercq, L.; Kunz, W.; Marinkovic, S.; Estrine, B.; Nardello-Rataj, V.; Jérôme, F. Transition of cellulose crystalline structure in biodegradable mixtures of renewably sourced levulinate alkyl ammonium ionic liquids, gamma valerolactone and water. *Green Chem.* **2014**, *16*, 2463−2471.

(23) Shrotri, A.; Lambert, L. K.; Tanksale, A.; Beltramini, J. Mechanical depolymerisation of acidulated cellulose: Understanding the solubility of high molecular weight oligomers. *Green Chem.* **2013**, *15*, 2761−2768.

(24) Hilgert, J.; Meine, N.; Rinaldi, R.; Schüth, F. Mechanocatalytic depolymerization of cellulose combined with hydrogenolysis as a highly efficient pathway to sugar alcohols. *Energy Environ. Sci.* **2013**, *6*, 92−96.

(25) Benoit, M.; Rodrigues, A.; De Oliveira Vigier, K.; Fourré, E.; Barrault, J.; Tatibouët, J.-M.; Jérôme, F. Combination of ball-milling and non-thermal atmospheric plasma as physical treatments for the saccharification of microcrystalline cellulose. *Green Chem.* **2012**, *14*, 2212−2215.