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Sustainable Chemistry

Depolymerization of Cellulose Assisted by a Nonthermal Atmospheric Plasma**

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Concerns about the depletion of fossil carbon reserves and global warming have led to the progressive introduction of biomass as a renewable source of carbon in the chemical industry. Carbohydrates represent 75% of the annual production of biomass (estimated to 1×10^{11} tons) and thus appear as a central raw material for chemistry. In this context, the depolymerization of these carbohydrate-based biopolymers is a preliminary and necessary step from which fine chemicals, transportation fuels, and platform molecules can be more easily produced.[1] However, carbohydrates are mostly available as stable biopolymers thus making their depolymerization difficult.

Among the naturally available biopolymers, cellulose is the most valuable one especially because it is an inedible raw material, cheap, and available on a very large scale from biomass (45% of the annual production of biomass). For this reason, the depolymerization of cellulose to glucose is now witnessing a sort of renaissance, since glucose is used as a platform molecule for the production of a wide range of fine chemicals such as 5-hydroxymethylfurfural (HMF), levulinic acid, and alkylglucosides, among others.[2] However, the depolymerization of cellulose is strongly hampered by its highly crystalline structure, which makes cellulose insoluble in common solvents (including water) and recalcitrant to hydrolysis. To enhance its reactivity, cellulose is decrystallized prior to catalytic hydrolysis and two strategies are mainly employed. The first method consists in the solubilization/precipitation of cellulose in ionic liquids[3], liquid acids (H_3PO_4, triflic acid)[4], or alkaline solutions (NaOH/urea, ammonia).[5] The second method involves ball-milling of cellulose for 2–6 days.[6] Nowadays, most articles related to the catalytic hydrolysis of cellulose involve one of the above-mentioned pretreatments. Although these pretreatments definitely contribute to facilitating the catalytic depolymerization of cellulose to glucose, the cost, corrosiveness, and toxicity of these decrystallization processes and the large energy input required (in the case of ball-milling) hamper their industrial transposition. Clearly, the chemical industry is now seeking innovative technologies that are capable of enhancing the hydrolysis of cellulose through more efficient routes.

Herein, we show that a nonthermal atmospheric plasma (NTAP), which is widely used at an industrial level for surface treatments[7] (including biomass) and air depollution,[8] can be considered as a promising technology for enhancing the reactivity of recalcitrant cellulose towards hydrolysis. In particular, treatment by a NTAP was found to be more efficient than recently reported pretreatment methods (i.e., ball-milling or ionic liquid) while offering notable advantages, such as low energy consumption, low electric demand, ambient temperature, and absence of any solvent or catalyst, thus allowing bypassing of all the time-consuming purification workup required with ionic liquids, acid, or alkaline solutions.[9]

In a first set of experiments, we investigated the efficiency of the NTAP for the pretreatment of cellulose. To this end, microcrystalline cellulose (MCC) was subjected to NTAP treatment under air. MCC exhibits a very high purity to glucose but is also the most recalcitrant cellulose available on the market. In this study, Avicel PH 105 was chosen as the MCC. Avicel PH 105 exhibits an average degree of polymerization (DP) of 200, a particle size lower than 38 μm, and a water content of 5 wt%. Typically, 0.2 g of MCC was placed between two parallel square electrodes (copper) of area 25 cm^2 isolated from each other by a dielectric material. The electrodes were spaced by 2 mm to assure an optimal plasma discharge. In our experiments, the NTAP was formed by using a pulsed voltage waveform at a maximum voltage of 11.2 kV at frequency 2 kHz so that the power was continuously maintained at 26 W (see Figure S1 in the Supporting Information).

Remarkably, under air, we found that the NTAP was capable of partly cleaving the glycosidic bonds of MCC since, after 3 h of NTAP treatment, the DP of MCC was decreased from 200 to 120. Upon prolonged reaction time (up to 8 h), no further decrease of the DP was observed, which suggests that the NTAP only affected the most fragile part of the MCC, presumably the remaining amorphous area. This hypothesis was further supported by XRD analysis, which revealed that the crystallinity index of MCC was slightly increased from 78 to 81% after NTAP treatment (see Figure S2 in the Supporting Information). Partial depolymerization of MCC by NTAP might be attributed to the formation of hydroxyl radicals, which are generated during the NTAP treatment.[7] Because of formation of these highly reactive species, a partial oxidation of MCC cannot be ruled out.

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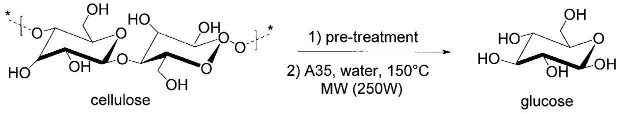
To check this possibility, MCC recovered after NTAP treatment was analyzed by infrared spectroscopy. A very weak band localized at 1724 cm^{-1} was observed showing that MCC was indeed partly oxidized during the NTAP treatment (see Figure S3 in the Supporting Information). Titration of carbonyl groups after the NTAP treatment of MCC revealed the presence of 0.6 and 0.5 $mmol\,g^{-1}$ of -CHO and -CO_2H groups, respectively, which suggests that oxidation of MCC occurs to a rather small extent. Additionally, no significant change in the C/O ratio before and after NTAP treatment was observed by elemental analysis, further supporting the view that oxidation or dehydroxylation of MCC did not occur to a large extent. Scanning electron microscopy showed that the particle size of MCC remained unchanged after the NTAP treatment (see Figure S4 in the Supporting Information). Note that no loss of weight was observed after the NTAP treatment.

Considering that a NTAP is capable of 1) lowering the DP of MCC and 2) slightly oxidizing MCC, it occurred to us that such a treatment could favor a better dispersion of MCC in water, thereby increasing its interaction with a solid catalyst. To highlight the contribution of NTAP treatment to enhancing the reactivity of recalcitrant MCC, a comparison with known pretreatment methods (ball-milling and ionic liquids) was carried out. In the literature, sulfonated carbon was reported as one of the best catalysts for the hydrolysis of ball-milled MCC in water.[10] However, a very large amount of catalyst (> 100 wt %) is required to obtain an acceptable yield of glucose (20 wt %). To be closer to industrial conditions, we decided to use only 40 wt % of Amberlyst 35 (A35), which is widely used in industry for many acid-catalyzed reactions. In a typical procedure, pretreated MCC (0.5 g) was suspended in water in the presence of A35 (0.2 g) and the mixture was heated for 1 h at 150 °C under microwave conditions (250 W).

As shown in Table 1, without any pretreatment MCC is recalcitrant to hydrolysis and glucose was detected only as a trace, thus highlighting the necessity to pretreat MCC prior to catalytic hydrolysis (Table 1, entry 1). In agreement with existing reports, pretreatment of MCC with ionic liquids ([BMIM]Cl (BMIM = 1-butyl-3-methylimidazolium), [BMIM]Et_2PO_4, and [BMIM]OAc)[3] or ball-milling led to a clear enhancement of the MCC reactivity and glucose was produced in yields of 3–14 wt % (Table 1, entries 2–5, see the Supporting Information for more details).

As expected, pretreatment of MCC with the NTAP also led to a significant enhancement of the MCC reactivity. In particular, catalytic hydrolysis of MCC pretreated by NTAP led to even higher yields of glucose than those obtained using ball-milling or ionic liquids. Indeed, when MCC was pretreated with the NTAP, glucose was obtained with 22 wt % yield (Table 1, entry 6) versus 14 and 13 wt % for [BMIM]Cl and ball-milling, respectively. The yield of glucose can even be increased to 25 wt % when using 10 mol % HCl as a homogeneous catalyst (Table 1, entry 7). The ^{13}C NMR spectrum recorded on the recovered aqueous phase is very similar to that of pure glucose, thereby supporting the facts that 1) MCC is not oxidized to a large extent during the NTAP treatment and 2) hydrolysis of NTAP-treated MCC is selective to glucose (see Figure S5 in the Supporting Information). It should be mentioned that a small formation of HMF and levulinic acid was detected in the ^1H NMR spectrum. However, HPLC analyses revealed that yields of these side products remained lower than 3 wt %.

Table 1: Effect of different pretreatments on the aqueous acid-catalyzed hydrolysis of MCC to glucose.[a]



Entry	MCC type	Pretreatment	Catalyst	Glucose yield [wt %]
1	Avicel PH 105	–	A35	< 1
2	Avicel PH 105	[BMIM]Cl	A35	14
3	Avicel PH 105	[BMIM]Et_2PO_4	A35	9
4	Avicel PH 105	[BMIM]OAc	A35	3
5	Avicel PH 105	ball-milling	A35	13
6	Avicel PH 105	NTAP	A35	22
7	Avicel PH 105	NTAP	HCl	25
8	Avicel PH 105	NTAP	–	5
9	Avicel PH 105	NTAP	–	14[b]
10	Avicel PH 105	NTAP[c]	A35	18
11	Avicel PH 101	NTAP[c]	A35	18
12	Avicel PH 102	NTAP[c]	A35	21
13	Avicel PH 200	NTAP[c]	A35	18

[a] Conditions of NTAP treatment: 0.2 g MCC, 11 kV, 2 kHz, 3 h. [b] Obtained after 3 h of hydrothermal treatment. [c] 0.5 g MCC, 11 kV, 2 kHz, 3 h. MW = microwave.

In all experiments, 1 h was the optimal time to reach the highest yield of glucose (see Figure S6 in the Supporting Information). Indeed, upon prolonged reaction time, the yield of glucose dropped because of its acid-catalyzed degradation to HMF, levulinic acid, and humins. Interestingly, when hydrolysis of NTAP-pretreated MCC was carried out under catalyst-free conditions (water, 150 °C, 250 W), glucose was obtained in 5 and 14 wt % yield after 1 and 3 h, respectively, which confirmed the significant contribution of the NTAP to enhancing the reactivity of recalcitrant MCC (Table 1, entries 8 and 9).

With the aim of increasing the interest in NTAP treatment, we then increased the amount of MCC treated per cm^2 of electrode from 8 $mg\,cm^{-2}$ (i.e., 0.2 g of MCC for an electrode of 25 cm^2) to 20 $mg\,cm^{-2}$. Note that in such a reactor configuration, 20 $mg\,cm^{-2}$ was found to be the maximum loading.[11] Under these conditions, only a slight decrease of the yield of glucose from 22 to 18 wt % was observed, thus showing that the NTAP treatment is also efficient with a larger amount of MCC (Table 1, entry 10). Figure 1 shows the effect of the NTAP treatment time on the yield of glucose when using an MCC loading of 20 $mg\,cm^{-2}$. In perfect agreement with the above-described results, the yield of glucose was gradually increased up to 18 wt % with an increase of the NTAP treatment time, which confirmed the effect of the NTAP on the reactivity of MCC. The efficiency of the NTAP treatment was found to be nearly optimal after 90 min since no significant increase of the yield of glucose was observed with prolonged NTAP treatment time.

Having these results in hand, we next checked the efficiency of the NTAP treatment for other MCCs differing

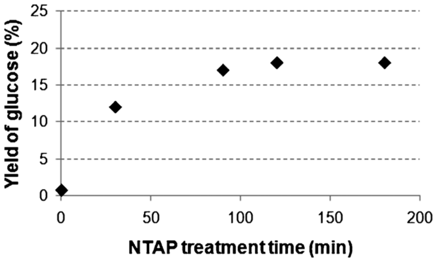


Figure 1. Effect of the NTAP treatment time on the acid-catalyzed conversion of MCC (loading 20 $mg\,cm^{-2}$) to glucose.

in their particle size. To this end, Avicel PH 101 (particle size $< 75\ \mu m$), PH 102 (particle size $> 75\ \mu m$), and PH 200 (particle size $> 150\ \mu m$) were subjected to the NTAP treatment prior to catalytic hydrolysis. As shown in Table 1, the efficiency of the NTAP treatment is not affected by a change of particle size and similar yields of glucose were obtained whatever the starting MCC (Table 1, entries 11–13).

To check the scope of NTAP treatment for the partial "deconstruction" of polysaccharides, other valuable biopolymers, namely α-cellulose, starch, and inulin, were subjected to the NTAP. First, α-cellulose was investigated. As compared to MCC, α-cellulose exhibits a larger DP (1000) and is less recalcitrant to hydrolysis than MCC owing to its lower crystallinity. To our delight, after NTAP treatment (3 h, 11 kV, 2 kHz), α-cellulose was depolymerized to a very large extent, since the DP of α-cellulose was decreased from 1000 to 160 (Table 2, entry 2). Such a DP is very close to that of MCC, further supporting the notion that the NTAP mostly affects the amorphous part of cellulose. After catalytic hydrolysis under the above-described conditions, glucose was obtained with 22 wt% yield and 6 wt% yield of xylose was also observed in accordance with the lower purity of α-cellulose than that of MCC.

Table 2: Effect of NTAP on the DP of various polysaccharides and on their subsequent catalytic hydrolysis to glucose.[a]

Entry	Polysaccharide	DP before NTAP treatment	DP after NTAP treatment	Glucose yield [wt%]
1	Avicel PH 105	200	120[b]	22
2	α-cellulose	1000	160[b]	22
3	starch (potato)	> 10000	< 20[c]	84[d]
4	inulin[e]	46	< 6[c]	16[f]

[a] NTAP conditions: 11 kV, 2 kHz, 3 h. [b] Determined by intrinsic viscosity measurements (normalized method: AFNOR NF G 06-037). [c] Determined by SEC and MALDI-TOF MS. [d] From starch, the maximum yield of glucose was obtained after only 30 min of hydrolysis. [e] 7 min of NTAP treatment. [f] Fructose directly obtained after NTAP treatment.

Next, the efficiency of NTAP treatment was extended to the depolymerization of starch (from potato). Starch is a biopolymer that is also available from biomass on a very large scale. As compared to MCC and α-cellulose, starch exhibits an even higher molecular weight ($DP > 10000$). Starch is not soluble in neat water whereas NTAP-treated starch was completely soluble (42 $g\,L^{-1}$), which is in agreement with an extensive depolymerization reaction (Table 2, entry 3, and Figure S7 in the Supporting Information). Depolymerization of starch was confirmed by size exclusion chromatography (SEC; see Figure S8 in the Supporting Information) and MALDI-TOF (Figure S9) analyses, which clearly showed that the DP of NTAP-treated starch was below 20 ($M_w < 3500$ Da). Note that with prolonged NTAP treatment time, recovered oligosaccharides were brown in color, which indicated the formation of undesirable products. As observed above with MCC, a slight oxidation of starch also occurred after 3 h of NTAP treatment. Nevertheless, oxidation of starch also remained rather low since after catalytic hydrolysis in the presence of A35 resin, 84 wt% of glucose was obtained and the presence of oxidized species in the recovered aqueous phase was not clearly evidenced (Table 2, entry 3).

Considering that the NTAP is itself capable of partly hydrolyzing biopolymers, we then evaluated the ability of this technology to produce valuable chemicals from biomass such as fructo-oligosaccharides (FOS). FOS exhibiting a DP lower than 10 are industrially relevant chemicals that are widely used in the food industry, especially for their high caloric value (replacement of corn syrup in food) and for prevention of yeast infections in the large intestine. Up to now, fermentation processes are preferred for the industrial production of FOS (either from inulin or sucrose). Indeed, all attempts to catalytically convert inulin to FOS failed because of the huge difficulty in selectively stopping the depolymerization process at the FOS step. In all reported catalytic routes, inulin was converted to HMF, levulinic and formic acids, or humins.[12]

To propose an alternative route for the synthesis of FOS, inulin (from chicory) was subjected to a NTAP treatment (11 kV, 2 kHz). Under these conditions, we found that inulin ($DP = 46$) was selectively converted to FOS within only 7 min of NTAP treatment (Table 2, entry 4) along with the production of fructose in 16 wt% yield. This very fast depolymerization of inulin induced by NTAP treatment was attributed to the higher reactivity of inulin than that of MCC or α-cellulose. The formation and DP of FOS were monitored by MALDI-TOF and SEC analyses (see Figures S10 and S11 in the Supporting Information). Both analyses confirmed that the DP of FOS was in the range of 1 to 6, which is the targeted DP in industry. Interestingly, whether the air was dry or wet, inulin was depolymerized to a similar extent, which suggests that water contained in the polysaccharide backbone plays an important role in the depolymerization observed under NTAP treatment. As observed above with starch, upon prolonged reaction time the FOS were degraded. It is noteworthy that, owing to the very short NTAP treatment time, no oxidation of FOS was observed. As compared to the traditional aqueous catalytic routes, the recovered FOS was colorless, thus avoiding extensive and costly bleaching post-treatment (see Figure S12 in the Supporting Information).

In conclusion, we have reported that NTAP treatment allowed the partial hydrolysis of valuable polysaccharides. In particular, we showed that the NTAP can be considered as a very promising pretreatment technology for enhancing the reactivity of recalcitrant polysaccharides such as MCC and α-cellulose. Such pretreatment was found to be even more efficient than the recently studied pretreatment methods involving ionic liquid or ball-milling. Indeed, after hydrolysis of NTAP-pretreated cellulose over A35, glucose was obtained with 22 wt % yield, which represents an improvement of 60 % in the yield of glucose relative to the pretreatment methods involving [BMIM]Cl or ball-milling. The NTAP was also efficient for the deconstruction of other valuable polysaccharides, such as starch and inulin. In particular, industrially relevant chemicals, such as water-soluble gluco- and fructo-oligosaccharides, were obtained without the assistance of any solvent or catalyst, thereby offering an alternative route to fermentation processes.

From the viewpoint of sustainable chemistry, the NTAP offers notable advantages such as short reaction time, absence of solvent or catalyst, low energy input (26 W), and production of colorless carbohydrates.

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