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# Thermochemical saccharification of cellulose: The benefit of adding a scavenger

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ABSTRACT

The solid acid-catalysed saccharification of cellulose was studied under elevated temperatures. Pretreatment of cellulose was necessary to obtain high glucose selectivity at high yields. Dissolution-regeneration from 1-butyl-3-methylimidazolium yielded more reactive cellulose compared to ball-milling. The highest glucose productivity was obtained from regenerated cellulose in the presence of Norit CAP Super (NCS), 685.7 g $h^{-1}$ $kg^{-1}$ catalyst at a glucose yield of 61.2% and a selectivity of 73.8%. The carbon catalyst, however, is not stable and leaches acidic species. The observed activity is higher than may be expected from the leached species alone. In addition, NCS is able to steer the reaction selectively towards glucose, especially when brought into close contact with the substrate. The highest glucose selectivity observed was 94.5% at a glucose yield of 38.9% and was obtained after co-milling cellulose with NCS. The effects are thought to be related to the ability of NCS to trap by-products, thus preventing the formation of humins and reducing glucose losses due to condensation reactions.



## 1. Introduction

Glucose is considered a green precursor for chemicals and fuels [1–6]. Currently, most glucose comes from starch and is in competition with food supply. Alternatively, cellulose can be used as a source for glucose. The parallel alignment of linear anhydroglucose chains in cellulose enables a vast network hydrogen bonding, contributing to the overall stability of the structure [7–9]. As a result, cellulose is recalcitrant and insoluble in water and common organic solvents. Glucose is thus locked in the robust, crystalline structure and controlled depolymerisation to D-glucose is challenging.

One way to liberate glucose is by enzymatic hydrolysis. However, enzymatic hydrolysis is expensive, time-consuming and suffers from disadvantages, such as enzyme loss through non-productive binding, shear deactivation of enzyme, and product inhibition [10,11]. To improve the economics a faster and cheaper route for the production of glucose is desired. Key in the valorisation of cheap feedstock such as lignocellulose is to improve the productivity rather than to pursue an incremental increase in yield and/or selectivity. Much faster, but intrinsically less selective, is hydrolysis catalysed by mineral acids [4,11,12]. The use of mineral acids, however, is associated with potential corrosion problems, hazard issues, catalyst loss and significant saline waste streams.

To overcome these problems, the use of solid acid catalysts was suggested [13–16]. Solid acids would simplify catalyst reuse and therefore minimise costs, reduce the amount of waste, and facilitate continuous flow operation. Conversely, due to the insolubility of cellulose in common solvents, problems with diffusion limitations may arise when using solid acid catalysts. Indeed, previous studies showed the necessity of large catalyst loadings and prolonged reaction times in order to produce glucose from microcrystalline cellulose, resulting in low glucose productivities [13–18]. To a certain extent, the productivity can be increased by applying more severe reaction conditions at the cost of selectivity due to simultaneously accelerated glucose degradation reactions [19].

Cellulose may be pretreated in various ways to enhance its reactivity [8,20–22]. Onda et al. [14,15] reported enhanced cellulose hydrolysis activity over sulfonated active carbon after ball-milling. They achieved a glucose yield of 41% at a maximum glucose productivity of 18.8 g $h^{-1}$ $kg^{-1}$ catalyst. Pang et al. [17] optimised the sulfonation procedure, yielding sulfonated activated carbons with an increased acid density and a superior performance. The authors reported maximum 94.4% cellulose conversion after 24 h reaction at 150 °C, yielding 74.5% glucose at a productivity of 34.5 g $h^{-1}$ $kg^{-1}$ catalyst. At nearly similar conditions, Van de Vyver et al. [18] reported 50% glucose yield over sulfonated silica/carbon at a glucose productivity of 23.2 g $h^{-1}$ $kg^{-1}$ catalyst. The energy intensive character of ball-milling, however, makes it a less attractive method for large scale cellulose pretreatment.

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Another method to enhance the reactivity of cellulose is through the use of ionic liquids. Swatloski et al. [23] reported that certain ionic liquids, such as 1-butyl-3-methylimidazolium chloride, [bmim]Cl, were capable of dissolving cellulose. The dissolution process disrupts the cellulosic fibres, leaving the hydroxyl groups and the β-glycosidic linkages accessible, thus improving the reactivity of the cellulose. Indeed, dissolved in ionic liquid, cellulose can easily be hydrolysed to glucose in high yields by mineral acids [24,25]. Herein, the ionic liquid can be acidic, thus serving as both solvent and catalyst, making addition of a mineral acid redundant [26–28]. However, efficient methods for extracting glucose from such solutions remain challenging. Only recently, Feng et al. [29] demonstrated the use of alumina column chromatography for the separation of glucose from *N*-methyl-*N*-methylimidazolium di-methyl phosphate and Caes et al. [30] reported on the recovery of 3-methyl-1-(2′-2′-3′-3′-3′-pentafluoropropyl)-imidazolium chloride after cellulose hydrolysis.

Apart from their use as a (catalytic) medium for cellulose hydrolysis, ionic liquids have also been used for cellulose pretreatment prior to enzymatic hydrolysis. Precipitation of cellulose from an ionic liquid solution by addition of an anti-solvent, such as water or methanol, results in a cellulose, termed regenerated cellulose, with a less crystalline and more accessible structure and is significantly more susceptible to enzymatic hydrolysis relative to untreated cellulose [31–34]. Still, due to the restricted maximum temperature that can be applied when using enzymes, the glucose productivity is limited. The incubation time, temperature and nature of the anti-solvent had little effect on the improved enzymatic digestibility of the resultant regenerated celluloses [32,33].

Studies on the use of both ionic liquids and solid acid catalysts remain sparse. Particularly Rinaldi et al. [35,36] reported on the hydrolysis of α-cellulose in [bmim]Cl using Amberlyst™ 15Dry. Rather than complete saccharification they stopped the reaction at the cellooligomer stage, allowing recycling of the ionic liquid while obtaining solid, regenerated cellulose with a decreased degree of polymerisation. The maximum cellulose recovery was 91% after 1 h of reaction and decreased with prolonged reaction time. Amberlyst™ was not stable in [bmim]Cl and $H_3O^+$ was released into the liquid. The leached species were responsible for the observed catalytic activity.

Kim et al. [37] proposed complete disentanglement of the ionic liquid pretreatment and the solid acid mediated hydrolysis reaction. Microcrystalline cellulose was first regenerated from [bmim]Cl and subsequently hydrolysed over Nafion NR50 for 4 h at 160 °C. Although solid acid catalysed hydrolysis of cellulose was facilitated by the pretreatment, the maximum glucose yield was limited to 16% based on the initial amount of cellulose, considerably lower compared to those reported on ball-milled cellulose [14–18]. The glucose productivity, 88.9 g $h^{-1}$ $kg^{-1}$ catalyst, however, was higher as a result of the relatively short hydrolysis time and lower substrate to catalyst ratio. The overall low yields were accredited to solid–solid mass transfer limitations.

Previously, we have demonstrated the effectiveness of a [bmim]Cl pretreatment for the solid acid mediated hydrolysis of Avicel cellulose as monitored by in situ ATR-IR spectroscopy [19]. The glucose productivity from regenerated cellulose was 21.6 g $h^{-1}$ $kg^{-1}$ at 150 °C and 150.3 g $h^{-1}$ $kg^{-1}$ catalyst at 180 °C. The glucose selectivity was 64% in both cases. In this work, we report on the progress made on the solid acid mediated hydrolysis of cellulose to glucose. Herein, we will discuss the ionic liquid pretreatment conditions in more detail. The hydrolysis of ball-milled and regenerated cellulose is studied over various solid and mineral acids and the glucose productivity is optimised.

## 2. Experimental

### 2.1. Materials

The cellulose used was Avicel PH 101 (Fluka, particle size ~50 μm, $DP_w$ 200–240 AGU), the ionic liquid used was 1-butyl-3-methylimidazolium chloride (Basionic ST 70, purity ≥95%). Both were purchased from Sigma–Aldrich. Beta zeolite and mordenite used were obtained from Zeolyst. Sulphated and tungstated zirconia were kindly provided by Saint-Gobain NorPro, Amberlyst™ 15Dry and Amberlyst™ 70 by Rohm and Haas, Y Zeolite by Albemarle, and phosphoric acid activated carbon CAP Super by Norit. The Si/Al atomic ratios of the zeolites are indicated by a number in parentheses, for example H-beta (75) is the proton-form of beta zeolite with a Si/Al atomic ratio of 75.

### 2.2. Cellulose pretreatment

A portion of the Avicel cellulose (25 g) was dry milled in a zirconia pot (2 L), for one third filled with zirconia balls (diameter 1.5 cm). The vessel was closed, placed on a roller bank and the cellulose was milled at approximately 60 rpm for 48 h. The milled cellulose was recovered and stored at RT in a closed vessel, in the absence of moist. The recovered material is referred to as ball-milled cellulose. In one experiment cellulose was milled in the presence of Norit CAP Super in a 1:1 weight ratio.

For cellulose pretreatment in ionic liquid, 1-butyl-3-methylimidazolium chloride, [bmim]Cl, was heated above its melting point before cellulose was added. In some experiments [bmim]Cl was pre-dried at 150 °C for 2 h under a nitrogen flow before adding the cellulose. In other experiments extra water and Amberlyst™ 15Dry was added. After the predetermined incubation period the heating was removed and the cellulose was precipitated by adding 5 parts (v/v) of hot demineralised water (>80 °C). During pretreatment, precipitation and initial cooling, the liquid [bmim]Cl solutions were stirred at all times. The solutions were stored at 4 °C overnight to allow the precipitate to settle. The clear solution was decanted and the precipitates were separated by centrifugation (Thermo Scientific SL 40R, 10 min at 4000 rpm) and washed three times with hot (>80 °C) and once with cold demineralised water. The moisture content of the freshly prepared sample was determined (Mettler Toledo HR83 Halogen). The regenerated cellulose samples were diluted with water yielding a colloidal aqueous suspension with 5.0% (w/w) regenerated cellulose and stored at 4 °C until tested. Prior to testing the sample was homogenised and the moisture content was determined again.

### 2.3. Cellulose hydrolysis experiments

Hydrolysis experiments were performed in six parallel 125 mL batch reactors (acid digestion bomb type 4748, SS 316 with Teflon liner, Parr Instrument Company, Moline, IL). An exact amount of substrate was mixed with demineralised water. In catalysed experiments a liquid or insoluble catalyst was added. The closed reactor vessels were placed in a heating block (adapted RS600, Thermo Fisher Scientific, Rochford, UK) and the block temperature was typically set at temperature ranging from 150 to 180 °C. The suspensions were stirred by a magnetic rod at the bottom of the vessels (1000 rpm). Visual tests with model slurries showed that the mixing in the reactor was adequate, for typical experiments. All experiments were carried out at autogenous pressure. After the pre-set incubation time, the heating block was switched off and the reactors in the block were allowed to cool passively.

**Table 1**
Cellulose recovery from [bmim]Cl. Reaction conditions: Avicel cellulose (as supplied, 4% moist w/w), 5.00 g, [bmim]Cl (as supplied), 100 g.

| Entry | Temperature (°C) | Incubation (min) | Precipitate (%, w/w) | Glucose yield (%, w/w) |
|---|---|---|---|---|
| 1[a] | 100 | 15 | 85 | 1.4 |
| 2[a] | 100 | 30 | 75 | 3.6 |
| 3[a] | 100 | 45 | 59 | 7.1 |
| 4[a] | 100 | 60 | 38 | 10.9 |
| 5 | 100 | 30 | >100 (gel) | –[c] |
| 6 | 130 | 30 | >100 (gel) | –[c] |
| 7 | 150 | 30 | 99 | 0.0 |
| 8[b] | 150 | 30 | 96 | 0.0 |

[a] Added: Amberlyst™ 15Dry (1.0 g), water (2.0 g).
[b] Prior to cellulose dissolution, [bmim]Cl dried for 2 h at 150 °C under dry $N_2$.
[c] Not measured.

### 2.4. Liquor composition analysis and definitions

After reaction the samples were separated by centrifugation (Thermo Scientific SL 40R, 10 min at 4000 rpm). The supernatants were analysed for glucose, fructose, 5-(hydroxymethyl)-2-furaldehyde (HMF), furan-2-carbaldehyde (furfural), acetic, formic and levulinic acid (HPLC, Agilent 1100 series, equipped with a RI analyser and UV-detector and a Biorad AMINEX HPX-87H column). Compounds were identified by elution times and quantified by calibration standards. The solid residue was washed three times with water to remove water soluble species and dried (50 °C, vacuum) until no further mass changes were observed.

Products yields are expressed in C-mol% and are calculated as follows: product yield = (moles of product × number of carbon atoms in the product)/(moles of carbon in initially present in the substrate). The glucose productivity is expressed as the yield of glucose (g) per hour of hydrolysis per kg catalyst (dry weight). The degree of cellulose solubilisation is calculated from the dry mass loss after reaction, corrected for the dry weight of the catalyst. For further calculations, it was assumed that solid humins formation is negligible and the catalyst weight is constant. Then, cellulose solubilisation in weight percent is approximately the solubilisation in C-mol% and the total yield of water soluble organic compounds not being glucose (WSOC) can be estimated from the difference between the cellulose solubilisation and the glucose yield. The glucose selectivity is calculated by dividing the glucose yield by the estimated yield of all solubilised organic species including glucose.

## 3. Results and discussion

### 3.1. Cellulose pretreatment in ionic liquid

Microcrystalline Avicel cellulose ($DP_w$ 200–240 AGU) was regenerated by dissolution in [bmim]Cl followed by precipitation with demineralised water. A first pretreatment series was carried out in the presence of Amberlyst™ 15Dry as is described by Rinaldi et al. [35]. The amount of recovered regenerated cellulose was relatively low (Table 1). Rinaldi et al. reported yields of 91% after 1 h of incubation starting from α-cellulose ($DP_w$ > 2000 AGU). In our experiments no induction period was observed; the solid mass loss and glucose production appeared instantaneous. The dissimilarities may be explained by the differences in degree of polymerisation of the starting material, since an equal amount of scissions in Avicel cellulose would lead to higher fractions of soluble sugars than in α-cellulose.

To ensure optimum utilisation of the raw cellulose material, the amount of recovered precipitate should be maximised while the duration of the pretreatment should be kept to a minimum to obtain high glucose productivities in the overall envisaged process. In an attempt to increase yield the incubation time was shortened,

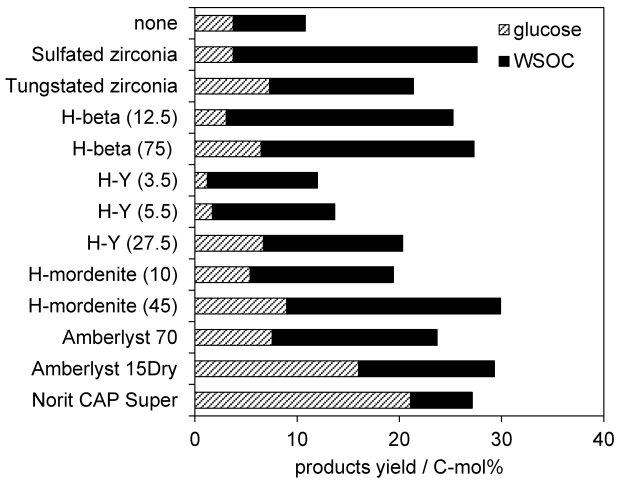


**Fig. 1.** Cellulose hydrolysis over various solid acid catalysts at 150 °C. Reaction conditions: milled cellulose 1.0 g, catalyst 1.0 g, demineralised water 50 mL, 24 h (WSOC = water soluble organic compounds).

the catalyst loading was decreased, and the pretreatment temperature lowered. Both shortening the pretreatment and lowering the catalyst loading led to the formation of gels after addition of the anti-solvent. Precipitation with hot water under vigorous stirring reduced the tendency to form gels, but only to a certain extent. Upon formation, the gels encapsulated most of the Amberlyst™ and part of the ionic liquid and were difficult to purify. Pretreatment temperatures below 100 °C led to mixtures that were too viscous to be mixed sufficiently and slow cellulose dissolution rates. Addition of a mixing agent, such as DMSO, DMAc or little water, lowered the viscosity, but also limited the cellulose dissolution capacity of the liquid mixture.

A second pretreatment series was carried out in the absence of a catalyst between 100 and 150 °C (Table 1). Without catalyst, 30 min incubation up to temperatures of 130 °C led to the formation of gels, immediately upon addition of the anti-solvent. Within the range studied, the tendency to form gels was not affected by the duration of the incubation, as it was by increasing the pretreatment temperature. In addition, a higher temperature lowered the viscosity of the mixture and benefited the cellulose solubility (rate). After 30 min of incubation at 150 °C over 95% (w/w) of the cellulose could be recovered as a colloid. The liquid phase of the colloidal suspension was slightly discoloured, indicative of some cellulose degradation. Shorter incubation (15 min) led to a clear, predominantly colloidal system, however, with some residual gel. Longer incubations resulted in progressive discolouration and lower cellulose recoveries. Drying the ionic liquid prior to pretreatment had certainly a positive effect on the dissolution rate of cellulose, but not on the cellulose recovery.

For Avicel, 30 min incubation in dry [bmim]Cl at 150 °C followed by precipitation with hot water yielded the best regenerated cellulose in terms of recovery and reactivity. These conditions were chosen to prepare the regenerated cellulose used in this study. The recovered cellulose was centrifuged, washed, and diluted with water yielding a colloidal aqueous suspension with 5% (w/w) regenerated cellulose. The suspension was stable for weeks when stored at 4 °C.

### 3.2. Catalyst screening

Screening experiments were carried out with ball-milled Avicel cellulose at 150 °C (Fig. 1). The cellulose was milled for 48 h, similarly to the work of Onda et al. [14,15]. The results obtained for the none-catalysed reaction are comparable with those of Onda

et al., whereas hydrolysis in the presence of comparable solid acids all resulted in lower glucose yields and typically a lower degree of cellulose solubilisation, except for H-mordenite (10) and H-beta (75). In any case, the degree of cellulose solubilisation seems to be limited to about 30%. The reasons for the observed differences are not known, but may be related to a less effective cellulose milling pretreatment or the different scale of reaction.

Similarities were observed as well, such as the relatively low glucose selectivity over sulphated zirconia and H-beta (12.5). Herein, circa 80% of the converted carbon was recovered in water soluble organic compounds (WSOC) other than glucose, such as soluble cellooligomers, humins, 5-hydroxymethylfurfural (HMF), levulinic acid, formic acid, and small quantities of furfural and acetic acid. Levels of cellobiose and fructose were below the detection limit.

The H-form zeolites with lower Si/Al molar ratio such as H-beta (75), H-mordenite (45) and H-Y (27.5) are less acidic in nature and resulted in higher glucose selectivities as compared to their corresponding, more acidic zeolite relatives (Fig. 1). An explanation may be that glucose, once it is formed, is less likely to be converted into its degradation products, once trapped in the micropores of zeolites with lower Si/Al ratios. This does not hold for the macroreticular Amberlyst™ ion exchange resins, in which the more acidic Amberlyst™ 15Dry (≥4.7 mmol $H^+$/g) resulted in both a higher degree of cellulose solubilisation and a higher glucose selectivity as compared to Amberlyst™ 70 (≥2.55 mmol $H^+$/g). Probably, the open structure of these materials also allow cellooligomers to enter and get hydrolysed yielding relatively more glucose with a higher density of acid sites. However, Amberlyst™ 15Dry is hydrothermally unstable under the applied conditions [14,35] and leached acidic species may be responsible for the observed higher cellulose solubilisation and glucose yield. Still, the higher glucose selectivity in comparison with the also leaching sulphated zirconia is remarkable.

The best performing catalyst in terms of glucose yield and selectivity were obtained with non-neutralised Norit CAP Super (NCS), a chemically activated carbon using the phosphoric acid process. Nonetheless, the glucose yield (21.1%) and productivity (9.8 g $h^{-1}$ $kg^{-1}$ catalyst) obtained after 24 h at 150 °C are a factor 2–4 lower in comparison with similar studies [14–18]. Nonetheless, NCS was chosen to evaluate the effect of substrate pretreatment on the saccharification of cellulose. The results are compared to H-mordenite (45), the best performing zeolite in the screening experiments, in terms of glucose yield.

It was noted that the hydrolysate, typically coloured light-yellow to dark-brown due to the presence of HMF derived breakdown products and condensates, was colourless in the presence of NCS. In the hydrolysate with NCS no HMF and only little levulinic acid was found. It is known from literature that active carbons can selectively adsorb HMF in the acid catalysed dehydration of fructose and thus slow down consecutive reactions towards levulinic and formic acid [38]. The adsorption hypothesis was tested qualitatively at RT by addition of NCS to samples of coloured hydrolysates obtained from the screening experiments. Addition of NCS indeed led to discolouration of the hydrolysates. Similar behaviour was observed by addition of other activated carbons, such as Vulcan XC72, Norit ZN2, and Norit PAC200.

### 3.3. Effect of cellulose pretreatment

The effect of the optimum cellulose [bmim]Cl treatment on the saccharification over NCS and H-mordenite (45) at 150 °C were investigated and the results were compared to experiments starting from untreated and ball-milled Avicel (Fig. 2a). In all cases the presence of a solid acid led to an increase in glucose yield and for pretreated cellulose also to improved substrate solubilisation. The solubility of untreated cellulose was limited at 5–6% (w/w), whether or not a catalyst was present. Ball-milling led to an increase in solubilisation and a slight increase in glucose selectivity, however, even in the presence of a catalyst the solubilisation was limited to just below 30% (w/w). Interestingly, large differences in glucose selectivity were obtained, in which NCS showed superior performance. Regenerated cellulose was found most susceptible to solubilisation, especially in the presence of NCS. The solid substrate mass loss in the presence of NCS was 76.5% (w/w) versus 39.1% (w/w) in the case of mordenite (45). Also here, the presence of NCS resulted in the higher glucose yield and selectivity. Still, the productivity was only 25.1 g $h^{-1}$ $kg^{-1}$ catalyst, mainly due to the long processing time.

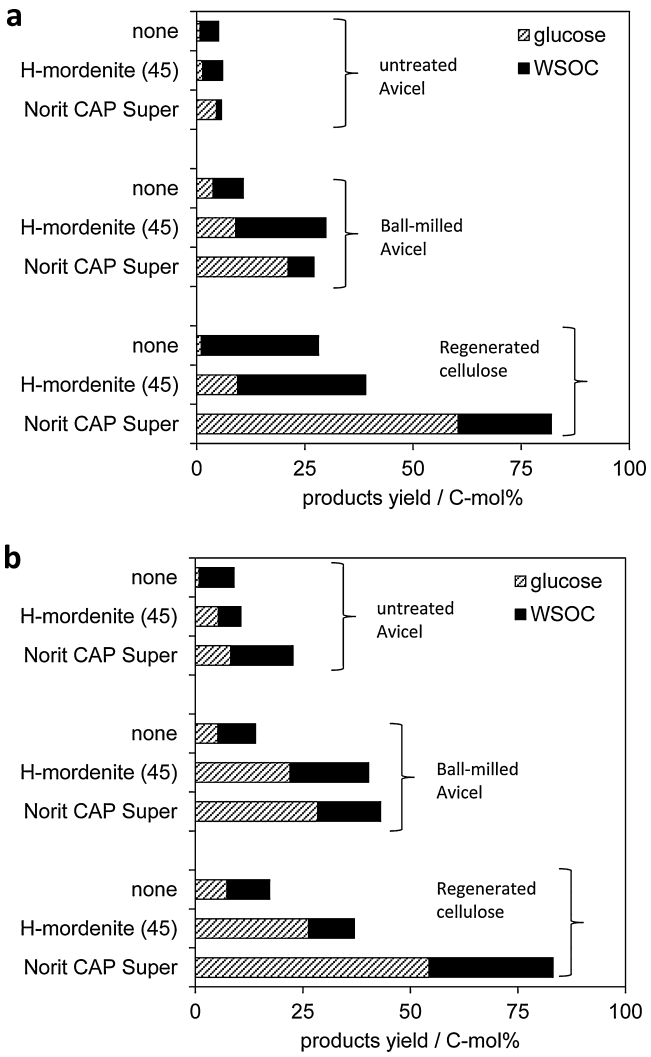


**Fig. 2.** Effect of pretreatment on the hydrolysis of cellulose over H-mordenite (45) and Norit CAP super (NCS): cellulose 1.0 g, catalyst 1.0 g, demineralised water 25 mL. Cellulose solubilisation and glucose yield after (a) 24 h at 150 °C, and (b) 4 h at 180 °C.

A similar comparison was performed for a 4 h process at 180 °C (Fig. 2b). Overall, similar trends were found, but both the degree of substrate solubilisation and the glucose yield were increased as compared to the 24 h process at 150 °C. The yield increase was largest in the case of mordenite (45) and smallest for NCS. The highest glucose yield was 54.3 C-mol% in the case of regenerated cellulose with NCS, corresponding to a productivity of 153.7 g $h^{-1}$ $kg^{-1}$ catalyst. The increase in productivity originates mainly from the shorter reaction time. Remarkably, the higher process temperature did not lower the selectivity towards glucose much.

The observed behaviour is consistent with the hypothesis that the first step in saccharification of cellulose is the formation of water soluble cellooligomers, and that subsequent hydrolysis of the solubilised fractions to glucose is accelerated in the presence of a solid catalyst. Herein, NCS is more effective as compared to H-mordenite (45). The amount of substrate that is solubilised depends on the process time and temperature, but mostly on the substrate pretreatment. The enhanced cellulose conversion after pretreatment is explained by an increased accessibility and the lower crystallinity of the substrate, shifting the solubilisation limits.

Various hydrolysates were subjected to a post-hydrolysis step (2 h, 100 °C, 1 M $H_2SO_4$) in order to determine the amount of soluble cellooligomers originally present in the hydrolysate from the increase of glucose concentration after post-hydrolysis. An increase in concentration was indeed found, however, quantitative analysis was not possible due to simultaneous glucose degradation reactions. Besides glucose and cellooligomers, also other water-soluble organic compounds (WSOC) were identified, such as HMF, furfural, formic and levulinic acid, as well as traces acetic acid. After processing at 150 °C the combined yield of these compounds was 1–2 C-mol% for all catalysts and all substrates, indicative of limited glucose degradation under these conditions. After processing regenerated cellulose at 180 °C, an increased HMF yield was found for the none-catalysed reaction, viz. 1.1 C-mol%. For the reaction catalysed by H-mordenite (45) increased levels of formic and levulinic acid were observed, respectively 0.9 and 2.1 C-mol%. Despite of the considerably higher activity, the yields of HMF (0.1 C-mol%), formic acid (0.5 C-mol%) and levulinic acid (0.3 C-mol%) were significantly lower when NCS was used as the catalyst. The lower yields are thought to be related to the adsorption capability of NCS.

### 3.4. Optimising glucose productivity

In situ spectroscopic results [19] suggest that preventing degradation of glucose to products, such as HMF, cannot be avoided completely but the formation of acids can be reduced by operating at shorter contact times. In addition, shorter reaction times are interesting from the point of view of productivity, as it is defined as yield per hour. An extensive study has been carried out to optimise the glucose productivity from [bmim]Cl regenerated cellulose in which the reaction time, temperature, substrate and catalyst concentration were varied. The main results are listed in Table 2.

Productivity numbers for saccharification of cellulose at 150 °C were limited by the long process times required for substantial conversions, typically 24 h (Table 2, Entry 1–4). Cellulose pretreatment in [bmim]Cl led to some improved productivity due to higher conversion rates, especially with NCS (Table 2, Entry 4). The productivity was increased to maximum 34.9 g $h^{-1}$ $kg^{-1}$ catalyst by shortening the process from 24 to 16 h, however, at the cost of conversion (Table 2, Entry 5). Further decreasing the process time does not seem functional without simultaneously increasing the temperature to compensate for the observed loss of activity. At a 4 h process a temperature raise to 180 °C more than makes up for the shorter reaction time in terms of conversion, while the selectivity to glucose increased for H-mordenite (45) (Table 2, Entry 7–8). The selectivity for the NCS catalysed reaction decreased to some extent, however still overall resulting in a 6–8 times higher productivity (Table 2, Entry 10–11).

Reducing the substrate concentration at fixed substrate to catalyst ratio led to a slight improvement in the glucose productivity over NCS from 153.7 to 172.9 g $h^{-1}$ $kg^{-1}$ catalyst (Table 2, Entry 11–14). The improvement may be correlated to slower glucose degradation reactions as a result of the lower glucose concentration. This is in agreement with the higher selectivity found for the lower concentrations. Quite the opposite was found for H-mordenite (45), in which higher substrate ratios were preferred (Table 2, Entry 8, 15–17). The improved productivity is directly related to an enhanced selectivity. The degree of cellulose solubilisation is similar for all cases. Using H-mordenite (45) at low

**Table 2**
Cellulose saccharification over solid acids. Reaction conditions: catalyst 50% (w/w, based on total dry weight), demineralised water 25 mL.

| Entry | Catalyst | Temperature (°C) | Time (h) | Substrate (g)[a] | Solubilisation (%, w/w)[b] | Yield (C-mol%) | Selectivity (C-mol%) | Productivity (g $h^{-1}$ $kg^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| 1[c] | H-mordenite (45) | 150 | 24 | 0.96 | 29.9 | 9.0 | 30.1 | 4.0 |
| 2 | H-mordenite (45) | 150 | 24 | 0.25 | 39.1 | 9.5 | 24.2 | 4.4 |
| 3[c] | Norit CAP Super | 150 | 24 | 1.00 | 27.1 | 21.1 | 77.8 | 9.7 |
| 4 | Norit CAP Super | 150 | 24 | 0.50 | 76.5 | 53.9 | 70.5 | 25.1 |
| 5 | Norit CAP Super | 150 | 16 | 0.50 | 66.6 | 50.1 | 75.2 | 34.9 |
| 6[d] | H-mordenite (45) | 180 | 4 | 1.00 | 10.6 | 5.4 | 50.4 | 15.0 |
| 7[c] | H-mordenite (45) | 180 | 4 | 1.00 | 40.3 | 22.0 | 54.6 | 61.1 |
| 8 | H-mordenite (45) | 180 | 4 | 1.00 | 37.0 | 26.3 | 71.1 | 72.5 |
| 9[d] | Norit CAP Super | 180 | 4 | 1.00 | 22.7 | 8.2 | 36.2 | 23.1 |
| 10[c] | Norit CAP Super | 180 | 4 | 1.00 | 43.1 | 28.4 | 65.9 | 78.8 |
| 11 | Norit CAP Super | 180 | 4 | 1.02 | 83.2 | 54.3 | 65.3 | 153.7 |
| 12 | Norit CAP Super | 180 | 4 | 0.75 | 87.0 | 55.8 | 64.2 | 155.5 |
| 13 | Norit CAP Super | 180 | 4 | 0.50 | 88.1 | 61.1 | 69.4 | 169.4 |
| 14 | Norit CAP Super | 180 | 4 | 0.25 | 83.9 | 62.2 | 74.2 | 172.9 |
| 15 | H-mordenite (45) | 180 | 4 | 0.25 | 40.9 | 18.8 | 45.8 | 52.3 |
| 16 | H-mordenite (45) | 180 | 4 | 0.50 | 37.8 | 22.2 | 58.9 | 61.4 |
| 17 | H-mordenite (45) | 180 | 4 | 0.75 | 36.3 | 24.1 | 66.2 | 67.2 |
| 18[e] | Norit CAP Super | 180 | 4 | 1.02 | 82.7 | 61.3 | 74.0 | 346.8 |
| 19[f] | Norit CAP Super | 180 | 4 | 1.00 | 83.0 | 61.2 | 73.8 | 685.7 |
| 20[f] | Norit CAP Super | 180 | 3 | 1.00 | 68.5 | 45.4 | 66.3 | 674.4 |
| 21[f] | Norit CAP Super | 180 | 6 | 1.00 | 88.7 | 63.0 | 71.0 | 468.5 |
| 22[f] | Norit CAP Super | 170 | 4 | 1.01 | 64.6 | 43.0 | 66.6 | 481.9 |
| 23[f] | Norit CAP Super | 170 | 6 | 1.00 | 76.9 | 54.3 | 70.5 | 390.5 |
| 24[f] | Norit CAP Super | 170 | 8 | 1.00 | 85.1 | 60.8 | 71.5 | 340.3 |

[a] Dry weight.
[b] Solid mass loss not including catalyst weight.
[c] Regenerated cellulose substituted with ball-milled cellulose.
[d] Regenerated cellulose substituted with Avicel cellulose.
[e] Catalyst loading 33% (w/w) based on total dry weight.
[f] Catalyst loading 25% (w/w) based on total dry weight.

substrate loadings, it is thought that after reaction still a significant amount of cellulose resides in the hydrolysate as incompletely hydrolysed, soluble cellooligomers. At higher substrate loadings it may be expected that the concentration of those soluble cellooligomers in the hydrolysate is higher and, hence, there will be a higher probability for soluble cellooligomers to (successfully) interact with the catalyst yielding glucose in more concentrated suspensions [16,39]. If so, regarding the unselective nature of this catalyst, also higher yields of glucose degradation products may be expected. Indeed, an increased levulinic acid yield was observed when increasing from 0.8 to 2.1 C-mol% in the more concentrated suspensions. The yields of HMF and formic acid, were stable around 0.1 and 0.9 C-mol%, respectively. The highest glucose productivity obtained with H-mordenite was 72.5 g $h^{-1}$ $kg^{-1}$ catalyst (Table 2, Entry 8), roughly half the amount obtained with NCS at similar conditions. Further optimisation was limited to NCS catalysed reactions, only.

Reducing the NCS catalyst loading to 33% and 25% (w/w, dry weight) resulted in similar conversions at an improved glucose selectivity (Table 2, 18–19) as compared to a similar experiment with 50% catalyst loading (Table 2, Entry 11). Apparently, the catalyst concentration is not limiting at loadings above 25% (w/w, dry weight). As a result of the improved performance and the lower amount of catalyst required, the glucose productivity added up to 685.7 g $h^{-1}$ $kg^{-1}$ catalyst at a glucose selectivity of 73.8 C-mol%. Subsequent alterations in time (Table 2, Entry 20–21) and temperature (Table 2, Entry 22–24) did not result in further improvements, due to lower glucose yields per hour of reaction.

### 3.5. Catalyst stability

To test the robustness of the catalyst, NCS was heated in demineralised water for 4 h at 200 °C and autogenous pressure. The sample was centrifuged and the supernatant was separated by decantation and stored. The solid was washed and dried in vacuum at 50 °C. This procedure was repeated on a portion of the resulting treated material. Hydrolysis of ball-milled cellulose was performed on once and twice treated NCS, as well as in the supernatant resulting from the first treatment. The results were compared to hydrolysis using fresh NCS.

With subsequent heat treatments, the activity of the NCS catalyst reduced significantly (Table 3). In addition, the liquor originating from the first hydrothermal treatment was active in cellulose hydrolysis, indicative of leaching of catalytic active species into the liquid phase upon hydrothermal treatment. Indeed, $PO_4^{3-}$ was found in the hydrolysates and the leaching of acidity was confirmed by the acidic character of the liquors (pH 2.2). The phosphate content was quantified by standard Ion Chromatography (IC) analysis with conductivity detection (Dionex DS3 conductivity analyser). The error in measured concentration is <0.1 mmol/L. As expected, the amount of phosphate detected in the hydrolysate became smaller with subsequent hydrothermal treatments.

Remarkable is the relative high glucose selectivity when NCS is present, irrespective of the activity. Apparently, close contact is beneficial for high glucose selectivity. The highest selectivity, 94.5 C-mol%, was obtained after co-milling cellulose with (fresh) NCS in a ball-mill in a 1:1 weight ratio. The higher observed selectivity is expected to originate from adsorption of glucose degradation products, such as HMF and derivatives immediately upon their formation. Since the selectivity is expressed as the quotient of the amount of carbon in glucose over the amount of carbon in all solubilised species, adsorption of non-glucose species leads to a higher apparent glucose selectivity. Nonetheless, the corresponding glucose productivity was 108.1 g $h^{-1}$ $kg^{-1}$ catalyst.

### 3.6. Sorption enhanced saccharification of cellulose

To evaluate the true effects of NCS as a solid catalyst, hydrolysis of regenerated cellulose was performed with $H_3PO_4$ in the absence and presence of NCS. The $H_3PO_4$ concentration chosen was based on the concentration of phosphate found in the hydrolysate after hydrolysis with fresh NCS. Special attention was given to the detection of HMF and levulinic acid, the key by-products in acid catalysed hydrolysis of cellulose.

Under the applied conditions, dilute $H_3PO_4$ was catalytically active yielding glucose with 66.3% selectivity. The major by-product identified was HMF. Also small quantities of levulinic acid, formic acid, and 2-furaldehyde and traces acetic acid were found. At a nearly similar yield, H-mordenite (45) performed slightly better with 71.9% selectivity towards glucose. The amount of HMF found,

**Table 3**
Hydrolysis of ball-milled cellulose. Reaction conditions unless noted otherwise: 1.00 g cellulose (dry weight), 1.00 g NCS, 25 mL $H_2O$, $T$ = 180 °C at autogenous pressure and $t$ = 4 h.

| Catalyst | Cellulose dissolved (%, w/w) | Glucose yield (C-mol%) | Glucose selectivity (C-mol%) | $PO_4^{3-}$ (mmol/L) |
|---|---|---|---|---|
| – | 14.0 | 5.2 | 37.5 | –[e] |
| –[a] | 32.1 | 12.6 | 39.3 | 14.6 |
| NCS | 43.1 | 28.4 | 65.9 | 10.6 |
| NCS[b] | 32.1 | 16.6 | 51.6 | 1.8 |
| NCS[c] | 22.0 | 14.5 | 65.9 | 0.3 |
| NCS[d] | 41.1 | 38.9 | 94.5 | –[e] |

[a] Water replaced by liquor resulting from first hydrothermal treatment.
[b] Hydrothermally treated at 200 °C, 4 h.
[c] Twice hydrothermally treated.
[d] Co-milled with cellulose.
[e] Not measured.

**Table 4**
Hydrolysis of regenerated cellulose. Reaction conditions: unless noted otherwise: 1.00 g cellulose (dry weight), 1.00 g catalyst (dry weight), 25 mL $H_2O$, $T$ = 180 °C at autogenous pressure and $t$ = 4 h.

| Catalyst | Glucose yield (C-mol%) | HMF yield (C-mol%) | Levulinic acid yield (C-mol%) | Formic acid yield (C-mol%) |
|---|---|---|---|---|
| – | 7.5 | 0.9 | 0.0 | 0.2 |
| –[a] | 25.2 | 2.3 | 0.6 | 0.5 |
| MOR (45) | 26.3 | 0.1 | 2.1 | 0.9 |
| NCS | 54.3 | 0.2 | 0.1 | 0.1 |
| NCS[a] | 54.6 | 0.3 | 0.2 | 0.1 |

[a] Added $H_3PO_4$ (10.8 mmol/L).

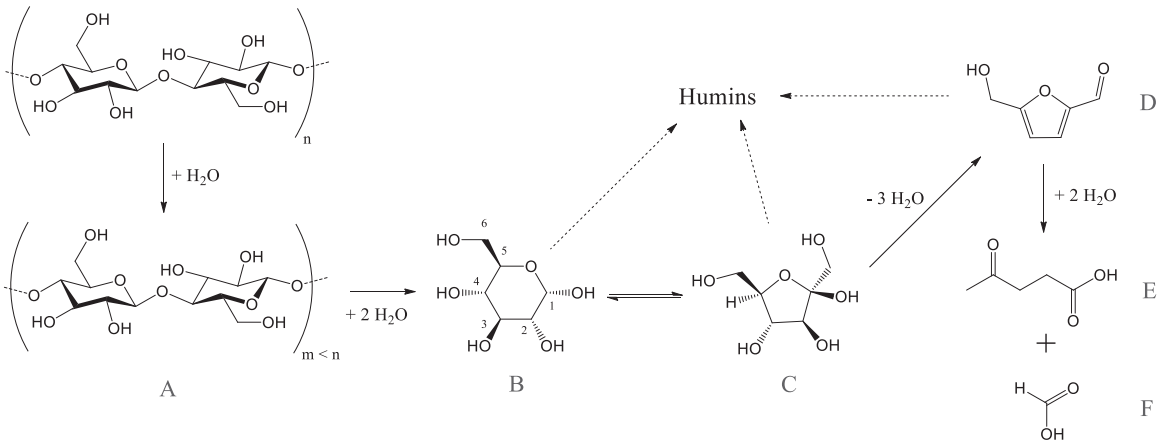


**Fig. 3.** Proposed reaction pathway for cellulose hydrolysis.

Adapted from Ref. [19].

however, was low. The amounts of levulinic and formic acid, on the other hand, were higher, indicative of enhanced decomposition of HMF over this catalyst. Using NCS, the glucose selectivity was 65.3%, but due to the superior solubilisation activity, still higher glucose yields were obtained (Table 4). Despite of the higher activity, the amount of typical by-products found was limited. The specific selectivity, as well as the high activity, was maintained upon addition of $H_3PO_4$ to the NCS; in the NCS/$H_3PO_4$ mixture, NCS dominated the results. It was noted that all NCS containing hydrolysates were colourless.

Clearly, NCS is not stable under typical reaction conditions, in a sense that phosphoric acid groups leach into the solution. Undoubtedly, these species will take part in the hydrolysis of cellulose. However, when comparing the results of NCS and $H_3PO_4$ catalysed hydrolysis (at equal final $PO_4^{3-}$ concentration) some differences can be observed. First, for both ball-milled and regenerated cellulose, the carbon catalyst results in a higher degree of solubilisation. Apparently, the leached phosphorous species are not the only species active in the depolymerisation of cellulose. Second, in the presence of NCS the concentrations of by-products, in particular glucose degradation products, such as HMF, levulinic acid and formic acid, are much lower. We explain this by assuming that carbons like NCS act as scavengers for HMF (derivatives), intermediate(s) in the formation of formic and levulinic acid. In addition, HMF is an important species in the formation of humins (Fig. 3).

Once formed, organic acids, such as formic and levulinic acid, catalyse their own formation, a process in which glucose is consumed. In situ removal of HMF (D) suppresses the subsequent formation of levulinic acid (E) and formic acid (F), thus inhibiting the auto-catalysed glucose degradation. In addition, due to removal of species reactive in humins formation, the actual loss of glucose (B) by condensation will also be reduced. Both features lead to increased observed glucose selectivity. These effects will be most pronounced at high product concentrations, and thus, in the case of highly reactive [bmim]Cl regenerated cellulose. Upon adsorption, the weight of the carbon catalyst, and thus of the solid residue, must increase. Indeed, a slight increase in solid-weight was observed by screening experiments with glucose and NCS.

Current study illustrates that adding a scavenger is beneficial for the (selective) production of glucose from cellulose by (solid) acid catalysed hydrolysis. Further research should focus on the development of a more hydrothermally stable catalyst with intrinsic selective sorption capacity for glucose degradation products, or a catalytic system consisting of a (solid) acid catalyst and an optimised (sacrificial) scavenger.

## 4. Conclusions

A limited part of microcrystalline cellulose can be hydrolysed under relatively mild conditions to form soluble cellooligomers and glucose, without the formation of large amounts of degradation products. A catalyst is not required per se, but the presence of an acid accelerates the depolymerisation and may steer the reaction further towards the desired product. However, the glucose productivity is limited.

To improve the productivity, microcrystalline cellulose must first be pretreated to enhance its reactivity. Ball-milling or dissolution/regeneration from an ionic liquid, such as [bmim]Cl results in more reactive celluloses. In particular, regenerated cellulose can be converted to glucose at high yields and high selectivity using (solid) acids. Herein, proper selection of pretreatment conditions is important to prevent gelling and substrate loses.

Regenerated cellulose can be converted into glucose with high selectivity over microporous zeolites, in which mildly acidic zeolites with larger pores are preferred. The glucose production over zeolites is limited by restricted cellulose solubilisation under mild conditions and by progressive glucose degradation reactions at more severe conditions. Highest yields were obtained with H-mordenite (Si/Al = 45), producing glucose at a rate of 72.5 g $h^{-1}$ $kg^{-1}$ catalyst with 71.1% selectivity.

Considerably higher glucose productivities are obtained with Norit CAP Super (NCS), 685.7 g $h^{-1}$ $kg^{-1}$ catalyst at 73.8% selectivity. The high productivity results from a high solubilisation activity at low catalyst loadings and short processing time at elevated temperatures, without losing much of the selectivity. NCS is not hydrothermally stable and loses activity due to leaching of phosphate moieties. These leached species aid in solubilising the substrate. Still, NCS retains some intrinsic activity and outperforms phosphoric acid in terms of selectivity. We hypothesise that NCS, and related carbon species, is able to promote higher glucose yield and selectivity due to in situ scavenging of HMF and derivatives thereof, thus preventing the formation of organic acids and soluble humins that otherwise trap and convert glucose.

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