



## 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),  $685.7 \text{ g h}^{-1} \text{ kg}^{-1}$  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.

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### 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  $18.8 \text{ g h}^{-1} \text{ kg}^{-1}$  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  $150^\circ\text{C}$ , yielding 74.5% glucose at a productivity of  $34.5 \text{ g h}^{-1} \text{ kg}^{-1}$  catalyst. At nearly similar conditions, Van de Vyver et al. [18] reported 50% glucose yield over sulfonated silica/carbon at a glucose productivity of  $23.2 \text{ g h}^{-1} \text{ kg}^{-1}$  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  $\beta$ -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  $\alpha$ -cellulose in [bmim]Cl using Amberlyst™ 15Dry. Rather than complete saccharification they stopped the reaction at the celooligomer 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  $\text{H}_3\text{O}^+$  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,  $88.9 \text{ g h}^{-1} \text{ kg}^{-1}$  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  $21.6 \text{ g h}^{-1} \text{ kg}^{-1}$  at 150 °C and  $150.3 \text{ g h}^{-1} \text{ kg}^{-1}$  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  $\sim 50 \mu\text{m}$ ,  $DP_w$  200–240 AGU), the ionic liquid used was 1-butyl-3-methylimidazolium chloride (Basionic ST 70, purity  $\geq 95\%$ ). 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 Albe-marle, 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 ( $>80 \text{ }^\circ\text{C}$ ). 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 ( $>80 \text{ }^\circ\text{C}$ ) 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.

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