



## Investigation of accessibility and reactivity of cellulose pretreated by ionic liquid at high loading



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### ABSTRACT

High loading of cellulose in ionic liquid (IL) pretreatment is potentially a key technique for cellulose conversion to glucose in biorefining. In this work, to expand the potential use of this high loading technique, the accessibility of microcrystalline cellulose pretreated with an IL across a wide cellulose loading range (5–50 mol%) and its relationship with the hydrolytic reactivity were comprehensively investigated. The results show that the estimated cellulose accessibility based on the crystallinity and specific surface area was notably higher in 25 mol% loading than that for a conventional loading of 5 mol%. Consistently, acid-catalyzed glucose conversion was faster at this high loading, showing that a higher cellulose loading improves the pretreatment efficiency. In contrast, enzymatic hydrolysis was not enhanced by a high cellulose loading. A key difference between the activities in these two hydrolytic reactions is the catalyst size.

### 1. Introduction

Cellulose hydrolysis to glucose is a key technique in biorefining. The glucose is then transformed to platform chemicals such as 5-hydroxymethyl-2-furfural and levulinic acid (Bozell & Petersen, 2010; Ragauskas et al., 2006). The main issue in this conversion is the extremely low reactivity of cellulose, stemming from its complex and rigid crystalline structure. Cellulose pretreatment is necessary, and various techniques for deconstruction of the recalcitrant (ligno)cellulose structure have been reported. Ionic liquid (IL) pretreatments are an emerging technique, and potential candidates for improving pretreatment of (ligno)cellulose (Brandt, Grasvik, Hallett, & Welton, 2013; Wang, Gurau, & Rogers, 2012). ILs are defined as salts that have melting points lower than 373 K (Wilkes, 2002). ILs are good solvents for (ligno)cellulose, can be designed for specific uses, and are practically non-flammable and non-volatile. However, despite these advantages, their industrial applications are limited by their high cost (Baral & Shah, 2016; Klein-Marcusamer, Simmons, & Blanch, 2011; Reddy, 2015; Sen, Binder, Raines, & Maravelias, 2012).

A direct method for reducing the cost is high loading (Klein-

Marcusamer et al., 2011; Modenbach & Nokes, 2012; Reddy, 2015), i.e., using a large amount of cellulose (or a low amount of IL) in the IL pretreatment process. This also reduces the amount of water needed for a given cellulose loading in subsequent washing processes. Conventionally, a (ligno)cellulose loading of around 5 wt% is used (Brandt et al., 2013). The potential use of higher loadings has been explored using various systems, for both cellulosic (Cheng et al., 2012; Dadi, Schall, & Varanasi, 2007; Guifen, Zijian, & Lixin, 2014; Kim et al., 2010) and lignocellulosic materials (Cruz et al., 2013; da Silva, Teixeira, Endo, Bon, & Lee, 2013; Haykir & Bakir, 2013; Li et al., 2013; Ninomiya, Soda, Ogino, Takahashi, & Shimizu, 2013; Qiu, Aita, & Mahalaxmi, 2014; Ren, Zong, Wu, & Li, 2016; Uju et al., 2013; Wang, You, Xu, Chen, & Yang, 2015; Wu et al., 2011; Zhang et al., 2014). Irrespective of the type of cellulose, IL, or pretreatment conditions, the results show that the hydrolytic reactivity is maintained up to a certain loading above 5 wt%.

Precise structural and morphological analyses of the pretreated cellulose and clarification of the relationship between the structure and the hydrolytic reactivity are needed to enable the development of high loading techniques using ILs. However, such information is limited at present for the following reasons. (1) In most previous studies, high

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temperatures were used to shorten the pretreatment time, which can cause undesirable degradation or depolymerization of cellulose (Ebner, Schiehsler, Potthast, & Rosenau, 2008; Michud, Hummel, Haward, & Sixta, 2015). (2) The results of studies on lignocellulose (Cruz et al., 2013; da Silva et al., 2013; Haykir & Bakir, 2013; Li et al., 2013; Ninomiya et al., 2013; Qiu et al., 2014; Ren et al., 2016; Uju et al., 2013; Wang et al., 2015; Wu et al., 2011; Zhang et al., 2014) are significantly affected by the presence and the chemical bonding states of hemicellulose and lignin. Studies of cellulose have been limited to loadings up to 30 wt% (Cheng et al., 2012; Dadi et al., 2007; Guifen et al., 2014; Kim et al., 2010), whereas our recent work showed that even ca. at a 40 wt% loading cellulose was completely deconstructed (Endo, Hosomi, Fujii, Ninomiya, & Takahashi, 2016). (3) Drying cellulose significantly changes its structure and morphology (Lovikka, Khanjani, Väisänen, Vuorinen, & Maloney, 2016; Zhao, Zhang, & Liu, 2012) while the accessibilities obtained to date have been elucidated for the dried state.

In this work, we aimed to expand the use of high loading techniques by resolving these issues. Microcrystalline cellulose (Avicel), which was used as a model cellulosic material, was pretreated with 1-ethyl-3-methylimidazolium acetate ([Emim][OAc]), which is the IL generally used for cellulose pretreatment. A wide loading range [5–50 mol%, where mol% = glucose moles/(glucose moles + IL moles); mol% can be approximated by wt% in the current system] and conditions that were mild enough to avoid undesirable chemical reactions of cellulose were used. Accessibilities were estimated for wet-state cellulose, except N<sub>2</sub> adsorption measurements, which were performed using carefully freeze-dried samples. The cellulose accessibility is governed by multiple factors. Here we employed some representative parameters, i.e., the crystallinity and specific surface area (SSA), in addition to pore volume and pore size. There are two major cellulose hydrolytic reactions, i.e., acid catalyzed and enzymatic. Conventionally, only one reaction, usually enzymatic hydrolysis, which is a more developed technique (Kumar, Barrett, Delwiche, & Stroeve, 2009), is used. However, progress in acid hydrolysis is being achieved, e.g., using solid acid catalysts (Huang & Fu, 2013; Kim et al., 2010). The mechanisms of the two types of reaction differ significantly. Both acid-catalyzed and enzymatic hydrolyses were therefore performed in this study. The reactivities are discussed in terms of the obtained cellulose accessibilities.

## 2. Experimental

### 2.1. Materials

Microcrystalline cellulose (Avicel PH-101) was purchased from Sigma-Aldrich, and [Emim][OAc] (> 95% purity) was purchased from IoLiTec. These samples were dried under vacuum with heating before use. The drying conditions were 343 K for 3 h for cellulose and 323 K for 1 day for [Emim][OAc] (Endo et al., 2016). Methylene blue was from Kanto Chemical Co., and cellulase from *Trichodema reesei* (ATCC 26921, ≥700 units/g) was from Sigma Aldrich.

### 2.2. Pretreatment of cellulose

Microcrystalline cellulose was pretreated with [Emim][OAc] in the range of 5–50 mol% of cellulose loading. The sample mixing procedure followed the previous report (Endo et al., 2016). Briefly, 0.1 g of dried cellulose and a certain amount of dried [Emim][OAc] were mixed at room temperature for ca. 5 min by a spatula to be visually homogeneous, and left for 2 days which is considered to reach a practical equilibrium state (Endo et al., 2016). The procedure was performed in an inert-atmosphere glove box where the water content was less than 10 ppm. Then the mixture was taken from the glove box, and the IL was removed by 5 times washing with water. The obtained pretreated cellulose in wet state was subjected to all the structural analyses (except N<sub>2</sub> adsorption experiments, vide infra) and hydrolytic reactions.

The pretreated samples were prepared for each experiment that was described below. It should be noted that with the current condition, we already confirmed occurrence of no detectable chemical reactions or degradations by the pretreatment (Endo et al., 2016). The sample appearances during and after the pretreatment are displayed in Fig. S1.

### 2.3. X-ray scattering

Wide angle X-ray scattering (WAXS) measurements were conducted with NANO-Viewer (IP system, Rigaku Co., Ltd, Japan) with a Cu K $\alpha$  radiation source ( $\lambda = 0.154$  nm) at an applied voltage of 40 kV and a filament current of 30 mA. The wet samples were packed into a Teflon cell having 1-mm thickness. The cell was sandwiched between two sheets of Kapton film. The samples were irradiated for 1 h. Scattering from water in the samples was subtracted from the original patterns whereas there remained unsubtracted scattering probably from bound water to cellulose.

To analyze cellulose crystalline structure, peak deconvolution (see Fig. S2) was conducted instead of the conventional Segal method (Segal, Creely, Martin, & Conrad, 1959). First, a WAXS pattern of untreated cellulose was simulated with 5 peaks, one of which represents amorphous cellulose positioning at  $2\theta = 21.1^\circ$ . Then, a WAXS pattern of cellulose pretreated at 5 mol% loading was simulated with 4 peaks. One of the peaks again represents amorphous cellulose, which was located at the same position with the same width as used for the untreated cellulose. These curve fitting procedures were done with the DMFit program (Massiot et al., 2002). To reproduce other pretreated cellulose, three X-ray patterns of untreated, pretreated with 5 mol% and amorphous (simulated) were used. The intensity of the three components was adjusted by eye to visually match the observed pattern with the simulated one.

### 2.4. Solid-state nuclear magnetic resonance

Solid-state NMR measurements were carried out on a JNM-ECX 500II (JEOL) spectrometer operating at resonance frequencies of 125.8 MHz and 500.2 MHz for <sup>13</sup>C and <sup>1</sup>H, respectively. The sample was taken in a 3.2 mm zirconia rotor (49  $\mu$ l) with sealing spacers (purchased from JEOL) to perform <sup>13</sup>C cross-polarization/magic angle spinning (CP/MAS) measurements. <sup>13</sup>C NMR spectra were collected with a  $\pi/2$  pulse (2.73  $\mu$ s) and high-power decoupling using a two-pulse phase-modulated decoupling (Bennett, Rienstra, Auger, Lakshmi, & Griffin, 1995) with a phase modulation angle of 15°. The <sup>1</sup>H decoupling frequency was 73.3 kHz. These spectra were collected using a contact time of 2 ms and a recycle delay of 3 s. A MAS speed of 5 kHz was employed for all samples. A <sup>1</sup>H spin-locking frequency of 91.6 kHz was used. Free induction decays of 8192–65536 were collected and averaged to obtain each <sup>13</sup>C spectrum. The <sup>13</sup>C chemical shifts were determined by referring to adamantane (29.5 ppm for CH).

Although <sup>13</sup>C CP techniques provide only semi-quantitative information in their intensity, they are widely used to estimate order/disorder fractions with the carbon at the 4-position (C4) (Horii, Hirai, & Kitamaru, 1982; Larsson, Wickholm, & Iversen, 1997), and tg/gt/gg fractions with the carbon at the C6 position (C6) (Fernandes et al., 2011; Horii, Hirai, & Kitamaru, 1983). The order fraction was estimated based on the areas of order (87.1–92.0 ppm) and disorder (81.0–87.1 ppm). Peak integration regions for tg, gt and gg were 64.3–67.6 ppm, 62.2–64.3 ppm and 60.3–62.2 ppm, respectively.

### 2.5. Specific surface area from methylene blue adsorption

The general procedure followed the previous work (Kaewprasisit, Hequet, Abidi, & Gourlot, 1998). The pretreated or untreated cellulose was soaked into methylene blue aqueous solution in a certain concentration. The mixture was centrifuged after 1 day stirring. Adsorbed methylene blue amount per unit weight of cellulose at equilibrium ( $q_e$

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