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Published in: Carbohydrate Polymers

DOI: 10.1016/j.carbpol.2022.120388

Published: 15/02/2023

Document Version Publisher's PDF, also known as Version of record

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Please cite the original version:

Wang, Y., Pääkkönen, T., Miikki, K., Maina, N. H., Nieminen, K., Zitting, A., Penttilä, P., Tao, H., & Kontturi, E. (2023). Degradation of cellulose polymorphs into glucose by HCl gas with simultaneous suppression of oxidative discoloration. *Carbohydrate Polymers*, *302*, Article 120388. https://doi.org/10.1016/j.carbpol.2022.120388

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Contents lists available at ScienceDirect

### **Carbohydrate Polymers**

journal homepage: www.elsevier.com/locate/carbpol

### Degradation of cellulose polymorphs into glucose by HCl gas with simultaneous suppression of oxidative discoloration

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#### ARTICLE INFO

Keywords: Acid hydrolysis Biomass conversion Cellulose crystal Cellulose microfibril Gas-solid reactions Humins

#### ABSTRACT

As cellulose is the main polysaccharide in biomass, its degradation into glucose is a major undertaking in research concerning biofuels and bio-based platform chemicals. Here, we show that pressurized HCl gas is able to efficiently hydrolyze fibers of different crystalline forms (polymorphs) of cellulose when the water content of the fibers is increased to 30–50 wt%. Simultaneously, the harmful formation of strongly chromophoric humins can be suppressed by a simple addition of chlorite into the reaction system. 50–70 % glucose yields were obtained from cellulose I and II polymorphs while >90 % monosaccharide conversion was acquired from cellulose III<sub>II</sub> after a mild post-hydrolysis step. Purification of the products is relatively unproblematic from a gas-solid mixture, and a gaseous catalyst is easier to recycle than the aqueous counterpart. The results lay down a basis for future practical solutions in cellulose hydrolysis where side reactions are controlled, conversion rates are efficient, and the recovery of products and reagents is effortless.

#### 1. Introduction

Biomass, rich in polysaccharides, provides an attractive alternative to fossil-based sources on the route to carbon neutrality (Alonso, Wettstein, & Dumesic, 2012; Climate strategies and targets-2050 long-term strategy, 2020). Cellulose, the main structural ingredient of all green plants, has been a particularly popular subject to studies on biomass conversion. A green, cost-efficient, and facile process to degrade the polymer cellulose into its monomeric constituent, glucose, would unleash an unprecedented potential concerning the production of biofuels and platform chemicals (Corma, Iborra, & Velty, 2007; Huber, Chheda, Barrett, & Dumesic, 2005; Lin & Tanaka, 2006; Mascal, 2015; Zabed, Sahu, Suely, Boyce, & Faruq, 2017). Unfortunately, however, the structural role of cellulose renders it recalcitrant and prone to sidereactions in the hierarchical assembly of the plant fiber (Fig. 1), and a viable degradation method is still pending broader approval (Naik, Goud, Rout, & Dalai, 2010). The purpose of this study is to introduce an effortless and scalable platform technology for cellulose degradation, utilizing a solid/gas acid hydrolysis system that manages simultaneously to tackle problems of catalyst recycling and suppress unwanted side-

#### reactions.

Enzymatic hydrolysis has been the most widely studied degradation method for cellulose in the recent decades. Yet the requirements for dilute suspensions, long reaction times, and costly downstream purification, together with the high price of enzymes are complications that inevitably have a negative impact on the market competitiveness of the target products (da Silva et al., 2020; Padella, O'Connell, & Prussi, 2019; Rosales-Calderon & Arantes, 2019). As a result, multitudes of more esoteric alternatives to enzymatic hydrolysis have been proposed, including hydrolysis assisted by microwaves (Fan et al., 2013), supercritical water (Buffiere, Ahvenainen, Borrega, Svedström, & Sixta, 2016; Kumar & Gupta, 2008), or high frequency ultrasound (Haouache et al., 2020). While scientifically interesting, all these processes bear significant pragmatic obstacles, such as impractical reaction conditions or infrastructural demands. Thermal conversion of cellulose, on the other hand, generally requires multistep processes and involves generation of undesired by-products (Lin, Cho, Tompsett, Westmoreland, & Huber, 2009).

Aside all these efforts, acid-catalyzed hydrolysis in a solid(fibers)/ liquid(acid) system has been the most traditional approach to cellulose

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https://doi.org/10.1016/j.carbpol.2022.120388

Received 28 September 2022; Received in revised form 15 November 2022; Accepted 18 November 2022 Available online 25 November 2022 0144-8617/© 2022 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).







Fig. 1. Schematics of the hierarchical structure of plant fibers.

degradation but somewhat out of fashion in modern biorefinery research except for its possible use as a pre-treatment step with mild acid concentrations (Rinaldi & Schüth, 2009; You, Shao, Wang, Zhang, & Xu, 2016; Zhou, Liu, & Zhao, 2021). The main challenges with acid hydrolysis are related to the harsh concentrations of aqueous acid required for a meaningful conversion of cellulose to glucose, for example, 72 wt% for sulfuric acid or 42 wt% for HCl (Kong-Win Chang, Duret, Berberi, Zahedi-Niaki, & Lavoie, 2018). Purification of the products and recycling of the acid is cumbersome from such reaction mixtures. To this end, solid acid catalysts have been widely explored in cellulose hydrolysis, but the required ratio of catalyst/substrate can be as high as 1:1, which is not industrially feasible (Shrotri, Kobayashi, & Fukuoka, 2018). Unrealistic practicalities concerning scale-up are also problematic in more specific solutions with acid hydrolysis, such as mechanochemical routes (Käldström, Meine, Farès, Schüth, & Rinaldi, 2014) or using hyperbranched polymers (Woodward, Kessler, Lima, & Rinaldi, 2018) to improve the recyclability.

Another severe drawback of acid hydrolysis is the production of humins as an unwanted side-reaction to glucose conversion (Tsilomelekis et al., 2016; Zandvoort et al., 2015). Monosaccharides like glucose are prone to undergo further acid-catalyzed dehydration to furfurals and further into larger structures and even macromolecules (Fig. 2). These structures are enormously chromophoric, resulting in strongly discolored hydrolysis products even at trace concentrations. The proposed ways to overcome humin formation – such as flowthrough pretreatments (Jung et al., 2018), continuous extraction by an organic solvent (Wettstein, Alonso, Gürbüz, & Dumesic, 2012), or selective adsorption by metal-organic frameworks (Yabushita et al., 2016) – also suffer from the lack of scalability.

Altogether, very few techniques have targeted both conceptual disadvantages in acid hydrolysis of cellulose: the difficulty to separate the substances from the reaction mixture (acid recycling and product purification), and discoloration by humin formation (Rinaldi & Schüth, 2009; Tsilomelekis et al., 2016; Zandvoort et al., 2015). In this paper, we show how a simple polymorphic transition of crystalline cellulose prior to the hydrolysis can increase the monosaccharide yield from cellulosic fibers up to 90 % in a solid(fibers)/gas(HCl) system (Kontturi et al., 2016; Lorenz, Sattler, Reza, Bismarck, & Kontturi, 2017; Pääkkönen et al., 2018; Pääkkönen et al., 2019) when accompanied by a mild posthydrolysis step. Product purification and acid recycling are far easier to perform in a solid/gas system. Earlier, we have demonstrated that HCl (g) hydrolysis is able degrade the crystal of cellulose if the water content of the fibers was increased to 30-50 wt% (Pääkkönen et al., 2018). Unfortunately, however, the formation of humins started to interfere with the hydrolysis at such conditions. Here, we demonstrate that the addition of sodium chlorite (NaClO<sub>2</sub>) - a widely applied industrial chemical - is able to suppress the humin formation under elevated HCl gas pressures.

#### 1.1. Hypothesis

HCl gas can hydrolyze cellulose to glucose in high yields if the water content of the fibers is 30–50 wt%, while simultaneously the addition of chlorite suppresses the formation of harmful humins.

#### 2. Experimental

#### 2.1. Materials

Birch dissolving pulp (predominantly cellulose  $I_\beta$ , hereafter cellulose I) was obtained from a pulp mill in Eastern Finland, and it contains 94 % cellulose and 6 % xylan (Table 1). HCl gas (99.8 %, 10 dm<sup>3</sup>, 6 kg) was purchased from AGA (Sweden). Ethylene diamine ( $\geq$  99 %, 0.896–0.898 g/cm<sup>3</sup>, Merck (Germany)) and methanol (VWR Chemicals (France)) were used with cellulose polymorph production. NaClO<sub>2</sub> (Sigma Aldrich (Germany)) was mixed with cellulose prior to the hydrolysis. 50 wt% aqueous NaOH, which was diluted and used to neutralize acid gas residues, was purchased from AKA Chemicals, Finland.

#### Table 1

The DP and the mass fractions of glucose and xylose in the raw materials (Cellulose I, Cellulose II, Cellulose III $_{\rm II}$  and Cellulose III $_{\rm II}$ ).

se



Fig. 2. Typical reaction scheme with humins formation.

#### 2.2. Preparation of cellulose polymorphs

Different cellulose polymorphs were prepared from birch dissolving pulp (cellulose I) according to Fig. 3. Cellulose II was produced with mercerization. First, small pieces of dissolving pulp were immersed into 22 % NaOH solution overnight. Subsequently, cellulose was washed with distilled water until the pH of the solution was neutral. Finally, the mercerized pulp was collected and stored in moist conditions (Kolpak & Blackwell, 1978; Kolpak, Weih, & Blackwell, 1978).

Raw materials of cellulose III<sub>I</sub> and cellulose III<sub>II</sub> were dissolving pulp (cellulose I) and mercerized pulp (cellulose II), respectively (Fig. 3). First, the cellulosic material was dissolved in 75 % ethylenediamine (EDA) solution for 5 h with 35 °C temperature, the whole process was under constant stirring during the treatment. Subsequently, EDA was extracted through a wire cloth by squeezing the fiber material with pressure. Purification with squeezing was conducted three times with anhydrous methanol. Finally, the fibers were air dried overnight. The whole procedure with EDA was repeated three times for each sample (Niinivaara, Arshath, Nieminen, Bismarck, & Kontturi, 2018).

The relevant glucose/xylose ratio, relating to the cellulose/hemicellulose ratio can be seen from Table 1. The mercerization process from cellulose I to cellulose II removed most of the xylan, whereupon the ratio increased from 15.8 to 91.8 in cellulose II. Also, the EDA process continued removing the xylan, so the glucose/xylose ratio upon cellulose I to III<sub>I</sub> conversion increased from 15.8 to 19.7. Moreover, the glucose/xylose ratio when converting cellulose II to cellulose III<sub>II</sub> increased from 91.8 to 125.4 (Table 1). The DP values stay more or less intact during the polymorphic conversion steps. A slight increase in average DP is observed with cellulose II and cellulose III<sub>I</sub> because of the removal of low DP xylan in the process.

The polymorph conversion was certified successful with X-ray diffraction on the account of cellulose II and cellulose III<sub>I</sub> (see, Table 2). With cellulose III<sub>II</sub>, the conversion was partial with 55.5 % pertaining to cellulose III<sub>II</sub> and 44.5 % remaining as cellulose II (see, Table 2). The polymorphs were also analyzed by FTIR spectroscopy (Fig. S1 in Supplementary Material).

#### 2.3. Acid hydrolysis with NaClO2 and pressurized HCl gas

Cellulose was mixed with 0–6 wt% NaClO<sub>2</sub> - water solution. Solution was mixed thoroughly overnight. Later, the mixture was percolated through 10 µm cloth with Büchner filtration system and the dry matter content was adjusted to a certain value between 30 and 50 % with the most common condition being 50 %. The carefully mixed cellulosic sample was transferred to the glass reactor system as described previously (Pääkkönen et al., 2018) Pressurized HCl gas was added to the reactor (1 bar pressure). HCl gas was added few times to the reactor to compensate HCl which was adsorbed to the pulp matrix. Reaction time of hydrolysis was within the range of 0.5 h – 14 days. The reaction bottle

#### Table 2

The crystallinity indices of cellulose polymorphs with different hydrolysis times, as deduced from diffractograms in Fig. S4 (Supplementary Material). See Tables S1 and S2 in the Supplementary Material for a more complete analysis of XRD data.

Hydrolysis time (h)	Polymorph	Crystallinity index (%)
0	$I_{\beta}$	44
0	п	29
0	III <sub>I</sub>	25
0	$\mathrm{III}_\mathrm{II}$ (56 %) + II (44 %)	25
18	$I_{\beta}$	53
18	П	65
18	${ m III}_{ m I}$ (31 %) + ${ m I}_{ m eta}$ (69 %)	33
18	$\mathrm{III}_\mathrm{II}$ (0 %) + II (100 %)	63

was flushed with compressed air after reaction time prior to the washing of hydrolyzed cellulose through 10  $\mu$ m cloth with Büchner filtration system and pure water (2  $\times$  2000 ml H<sub>2</sub>O).

#### 2.4. Experimental design

The full flow of the process is described here with the relevant characterization steps. Prior to the acid hydrolysis, the cellulose polymorphs (cellulose I, II, III<sub>I</sub>, III<sub>I</sub>) were pretreated with a NaClO<sub>2</sub> solution. Later, the cellulosic samples were filtrated and adjusted to a certain dry matter content. The prepared samples were then hydrolyzed in a solid/gas system based on the use of pressurized HCl gas (Pääkkönen et al., 2018), based on the earlier studies with HCl vapor and gas (Kontturi et al., 2016; Lorenz et al., 2017; Niinivaara et al., 2018).

After the acid hydrolysis reaction was completed, the products were transferred to the Büchner filtration system equipped with 10  $\mu$ m cloth (Fig. 4). Washing of the hydrolyzed cellulosic sample with 2 dm<sup>3</sup> of pure water was repeated twice. Subsequently, the products were divided in two parts: the upper layer is referred to as the solid residues and the lower layer is referred to as the filtrates. The gravimetric yield analysis and degree of polymerization analysis based on the limiting viscosity number in dilute cupriethylenediamine (CED) solution were conducted with solid products. The filtrates, containing dissolved and colloidal cellulosic material able to penetrate 10  $\mu$ m cloth, were analyzed with a series of liquid chromatographic methods. Colloidal carbohydrate fraction was calculated based on the assumption that the rest of carbohydrates are distributed in 4 categories: solid residue, dissolved monosaccharides, and dissolved cello-oligosaccharides (see the equation at the bottom of Fig. 4).

#### 2.5. Degree of polymerization (DP)

The limiting viscosity of cellulose dissolved in cupriethylenediamine solution (CED) was determined according to the



Fig. 3. Polymorphic transformation of cellulose into different polymorphs.



Colloidal carbohydrate fraction (%) = 100 % - Solid residues (%) - Dissolved monosaccharides (%) - Dissolved cello-oligosaccharides (%)

**Fig. 4.** Flow chart of experiment. Time-lapse videos were conducted with NaClO<sub>2</sub> treated samples hydrolyzed with HCl gas hydrolysis (several days reaction time). Filtration before and after acid hydrolysis was conducted with Büchner system and 10 µm cloth. The carbohydrate chromatographic analyses of filtrates were conducted with 3 categories: (1) Dissolved carbohydrates, (2) Dissolved monosaccharides and (3) Dissolved cello-oligosaccharides.

standard ISO 5351:2004. The limiting viscosity ( $\eta$ ) was converted to  $DP_v$  with the Mark-Houwink equation ( $\eta = Q'DP_v^{\alpha}$  where  $Q^{\circ} = 2.28$  and  $\alpha = 0.76$  when DP > 950, and  $Q^{\circ} = 0.42$  and  $\alpha = 1$  when DP < 950).

# 2.6. Carbohydrate analysis of dissolved carbohydrates (including monosaccharides) with high performance anion exchange chromatography (HPAEC)

After  $HCl/NaClO_2$  acid hydrolysis and washing, the solid samples and filtrates were collected. Dissolved monosaccharides (2, Fig. 4) were analyzed without post-hydrolysis. Dissolved carbohydrates (1, Fig. 4) were cleaved into monosaccharides with 72 %  $H_2SO_4$  (post-hydrolysis). Monosaccharides, cello-oligosaccharides, and colloidal carbohydrates were processed with post-hydrolysis conditions (4 % sulfuric acid, 121 °C temperature and 1 h reaction time). Finally, all samples were analyzed with HPAEC (ICS-3000, Dionex with CarboPac PA20 column and pulse amperometric detector), as described in detail by Sluiter et al. (2012). Water was used as an eluent and NaOH was added upon reaching the detector.

# 2.7. Carbohydrate analysis of dissolved cello-oligosaccharides with HPAEC-PAD (pulsed amperometric detector)

The cello-oligosaccharide content (3, Fig. 4) of acid hydrolysis filtrates was analyzed with HPAEC-PAD. This system consists of a Carbo Pac PA100 column (Dionex, Sunnyvale, CA) and a Waters 2465 pulsed amperometric detector (Waters, USA). The gradient elution solvents were 100 mM NaOH and 1 M NaOAc in 100 mM NaOH (Rantanen et al., 2007). The total test time of each sample was 50 min, and the sample volume was 10  $\mu$ l. Xylotriose was added to all samples as an internal standard, and besides the internal standard and H<sub>2</sub>O, different concentrations of cellobiose, cellotriose, cellotetraose, cellopentaose and cellohexaose were also added into that 6-standard series (Megazyme, Wicklow, Ireland).

#### 2.8. Scanning electron microscopy (SEM)

JEOL JSM-7500F FEG (Japan) was used for SEM imaging of the filter paper samples, with an acceleration voltage of 1-5 kV, varied depending on the sample. All samples were coated with an Au—Pd mixture for preventing the surface charging effect.

# 2.9. Time-lapse video and color analysis of acid hydrolysis cellulose with pressurized HCl and chlorite

A camera system based on Raspberry Pi was used to record the color change of the hydrolyzed cellulose as a function of the reaction time and

#### NaClO<sub>2</sub> concentration during the experiment (Miikki et al., 2021).

The glass reactor system containing the sample was placed in an environment where the ambient light was completely eliminated. The light illuminating the container came from a flicker-free LED lamp (Clas Ohlson 36–6325 10.5 W 2800 K). The total shooting time for each sample was 1–2 weeks and the basic exposure time was 5 ms or 10 ms. After the shooting, the average value of red, green, and blue (RGB) was calculated from the whole image area to obtain the color change as a function of the reaction time. The related time-lapse video was a cropped image and created with the glvideo.py script.

#### 2.10. X-ray diffraction measurement (XRD)

X-ray scattering from unhydrolyzed and hydrolyzed samples was measured using the Xenocs Xeuss 3.0 SAXS/WAXS device with a GeniX 3D Cu-source (wavelength  $\lambda = 1.542$  Å) and EIGER2 R 1M-detector, with the sample-to-detector distance being 50 mm. Samples were placed within a sample holder covered by a Kapton tape, trying to avoid any preferred orientation. Background (empty sample holder with the tape) and each sample was measured for 20 min. Background was then subtracted from each sample. The 2D scattering images were integrated to get the 1D scattering intensity as a function of the scattering angle 20. Gaussian peaks were fitted on the 20-angle range of 10-26 degrees. Peak locations were used to calculate d-spacings of the cellulose crystal lattice and to identify the cellulose polymorph(s). Peak widths were used to calculate crystal size using Scherrer equation with shape factor K = 0.9. Crystallinity index was determined by using the fraction of crystalline peak area and the total (crystalline + amorphous) peak area on angles 10-26 degrees. The proportions of different polymorphs were determined by the relative fraction of the area of the most prominent diffraction peaks. Due to overlap between peaks, especially for the mixture of II and III<sub>II</sub>, reliable determination of the relative fraction was difficult. However, the results should still be accurate within 5-10 percentage points.

#### 3. Results and discussion

## 3.1. Time-lapse video and color analysis results of acid hydrolysis cellulose with pressurized HCl and chlorite

Although NaClO<sub>2</sub> is known to react copiously with aldehydes (Dalcanale & Montanari, 1986), its applicability in blocking humin formation by reacting with furfurals during cellulose hydrolysis (Fig. 2) has never been investigated. To this end, cellulose hydrolysis in a HCl/ NaClO<sub>2</sub> system was investigated by photometric analysis which reveals the formation of strongly chromophoric humins. Fig. 5a shows how 2 wt % and 3 wt% NaClO<sub>2</sub> addition managed to prevent the discoloration for several days by contrast to the control reference (0 wt% addition) where the discoloration commenced immediately with cellulose II samples. Fig. 5b further demonstrates the efficiency of 2 wt% NaClO<sub>2</sub> addition on suppressing the discoloration of humin with all investigated cellulose polymorphs. The period at which the samples become completely black due to humin formation appears in the order: cellulose I (2.5 days), cellulose II (3 days), cellulose III<sub>I</sub> (7 days), and cellulose III<sub>II</sub> (11 days). The accelerated videos used as raw data for the photometric analysis are available as Supplementary Material (Videos S1-S3).

The sheer complexity of the humin formation hampers an exhaustive kinetic description of the resulting discoloration. Therefore, we limit the kinetic simulation to a potential explanation of a singular effect observed in Fig. 5. The effect in question involves the rate at which the darkening occurs for different levels of NaClO2 present. The interesting phenomenon is that delaying the darkening by adding NaClO<sub>2</sub> results in the darkening being faster than in the case with no added NaClO<sub>2</sub>, when it finally commences after the consumption of all NaClO<sub>2</sub>. We must consider here that the furfurals – and further, the humins – emerge from monosaccharides (Fig. 2), and the glucose from cellulose is generally thought to be peeled off from the chain ends in the leveling-off degree of polymerization (LODP) stage (Sharples, 1957). This means that the formation of new monomers is proportional to the number of end groups. If we assume that the cellulose degrades only through endwise peeling of the crystallites, it is difficult to explain the rapid discoloration by humin formation in Fig. 5 because then the number of end groups would remain constant as the peeling proceeds. Allowing scissions at interior bonds of the polymer chains in the simulation, however, offers a mechanism to increase the number of end groups with time as the scissions take place even when the NaClO<sub>2</sub> remains. (These scissions could be due to the yet unknown microfibrillar morphology of cellulose II and III and/or the presence of oligosaccharides.) When the formation of humins starts after the consumption of the NaClO<sub>2</sub> there are more end groups available leading to faster darkening.

Fig. 6 shows a simulation case employing a simple interior scission model (see the Supplementary Material for the mathematical treatise). We note that, according to the simulation, for the number of end groups there is an initial rapid increase followed by a slow decrease. This reflects the darkening pattern shown in Fig. 7, as a high number of end groups indicates the rapid formation of monomers and further humins, thus accelerating the darkening.

### 3.2. Degree of polymerization (DP) of cellulose and monosaccharides of filtrates

The effect of  $NaClO_2$  on the degradation of cellulose per se was also investigated. Fig. 7a shows how the addition of  $NaClO_2$  influenced the reduction in DP of various cellulose polymorphs after 0.5 h exposure to 1 bar HCl (g) at 50 % moisture content. The initial DP for all polymorphs



**Fig. 6.** An example of simulated time development of cellulose II ( $2 \text{ \% NaClO}_2$ ) chain properties during gaseous HCl catalyzed hydrolysis assuming scissions in the interior of the chains. Selected rate constant for the scission 0.52 (day<sup>-1</sup>) and assumed initial chain length 1000 elements. A full mathematical description of the model is featured in the Supplementary Material.

was ca. 1000. It is evident that the DP reduction was impeded by NaClO<sub>2</sub> addition with unquestionably the strongest effect on cellulose III<sub>II</sub> under high NaClO<sub>2</sub> (>2 wt%) dosages. This correlates with the photometric results (Fig. 5b) which suggest that NaClO<sub>2</sub> remains active with cellulose III<sub>II</sub> for the longest period. Similar trend was observed also for mono-saccharide (glucose and xylose) generation in 0.5 h hydrolysis with 1 bar HCl (g) (Fig. 7b). The impediment of NaClO<sub>2</sub> on cellulose hydrolysis is likely due to unstable chlorine intermediates that react with chlorite and HCl to a varying extent and have been shown to influence the reaction efficacy of NaClO<sub>2</sub> with model substances (Launer & Tomimatsu, 1959). Because 2 wt% appeared to be the threshold value for NaClO<sub>2</sub> addition to significantly interfere with the hydrolysis, yet it managed to suppress the humin formation for several days on end (Fig. 5), we opted for utilizing a 2 wt% NaClO<sub>2</sub> concentration in the more extended set of experiments.

Fig. 8a illustrates the development of cellulose DP of the different polymorphs under 1 bar HCl (g) at 50 % moisture content and 2 wt% NaClO<sub>2</sub> addition (room temperature). The decrease in DP is initially very rapid, after which it settles to a temporally stable value. This development is well-established in acid hydrolysis of cellulose: first, the chain cleavage occurs at the disordered segments of cellulose microfibrils, after which the recalcitrant crystallites are left with little further



**Fig. 5.** a) Black/white color analysis  $NaClO_2/HCl$  hydrolyzed mercerized cellulose. (Cellulose II) samples with different  $NaClO_2$  additions (0 %, 2 % and 3 %). b) Black/white color analysis  $NaClO_2/HCl$  hydrolyzed between different Cellulose polymorphs with 2 %  $NaClO_2$ . Color analysis is based on the video files collected. Hydrolysis reaction was monitored with time-lapse video system. Videos are available as Supplementary Material (Videos S1-S3).



**Fig. 7.** a) Degree of polymerization of acid hydrolyzed cellulose polymorphs as a function of NaClO<sub>2</sub> additions (0.5 h acid hydrolysis time, 50 % moisture content of cellulose). b) Monosaccharides measured with post-hydrolyzed cellulose polymorphs as a function of NaClO<sub>2</sub> additions (0.5 h acid hydrolysis time, 50 % moisture content of cellulose.



**Fig. 8.** a) Degree of polymerization of acid hydrolyzed cellulose polymorphs as a function of time (2 % NaClO<sub>2</sub> addition, 50 % moisture content of cellulose). b) Monosaccharides measured with post-hydrolyzed cellulose polymorphs (the hydrolysis time for each sample was 6 h, 18 h and 2 weeks); samples from left to right in groups of three bars: cellulose I, II, III<sub>I</sub>, and III<sub>I</sub>.

degradation to the LODP stage (Fig. 9) (Battista, Coppick, Howsmon, Morehead, & Sisson, 1956). Interestingly, cellulose I and cellulose III<sub>I</sub> polymorphs undergo extended degradation below the LODP under prolonged (335 h, that is, 2 week) hydrolysis periods. The LODP values in Fig. 8a are somewhat lower than – but close to – the literature values of wood-based cellulose polymorphs (Yachi, Hayashi, Takai, & Shimizu, 1983; Analytical methods in cellulose chemistry: Section 3.1, 1998, with one notable exception: cellulose II is immediately degraded to a DP of ca. 30 which is well below the reported value of 75 for mercerized pulp (Yachi et al., 1983).

The efficiency of pressurized HCl (g) on cellulose fibers with 50 % moisture content becomes increasingly apparent when they are subjected to a mild post-hydrolysis step at 4 wt%  $H_2SO_4$  after the gas hydrolysis (see process schematics in Fig. 4). Monosaccharide yields after the post-hydrolysis were analyzed by HPLC and figures of >50 % were routinely detected (Fig. 8b). The monosaccharides consist of glucose



Fig. 9. Schematics of solid-gas acid hydrolysis of cellulose. High-pressure HCl gas is very easy to enter and cleaved the disordered segments of cellulose, thus the crystallites have a greater chance of contacting with each other. With prolonged exposure time to HCl gas, the crystallites are finally decomposed into dissolved and colloidal material, monosaccharides, and cello-oligosaccharides.

from cellulose and small amounts of xylose from xylan (Fig. S3 in Supplementary Material). In the case of cellulose III<sub>II</sub>, a staggering 91.8 % monosaccharide yield was observed after 6 h hydrolysis at 1 bar HCl (g) and subsequent post-hydrolysis. Such high yields generally require harsh acid pretreatments either in terms of high concentration (Kong-Win Chang et al., 2018) or elevated temperatures (You et al., 2016). Evidently, extended hydrolysis times appear to have an adverse effect on the monosaccharide yields of cellulose III<sub>I</sub> and cellulose III<sub>II</sub> substrates, which can be reasonably attributed to extended furfural generation from glucose and xylose (Fig. 2). It is noteworthy that subjecting cellulose polymorphs under ambient conditions (moisture content ~5 %) to HCl vapor (pressure ~ 8 kPa) was not sufficient for appreciable monosaccharide conversion (Niinivaara et al., 2018).

When comparing the monosaccharide yields with the enzymatic hydrolysis, the reported values fall between 50 and 75 % for native cellulose I (da Silva et al., 2020). For cellulose II and cellulose III<sub>I</sub>, our monosaccharide yields at ca. 50–70 % are relatively similar or somewhat higher than those reported for enzymatic hydrolysis of the same polymorphs (Chundawat et al., 2011).

#### 3.3. Degradation products of different cellulose polymorphs

To shed light on the circumstances surrounding the high monosaccharide yields after post-hydrolysis, the hydrolysate after HCl (g) hydrolysis, but before post-hydrolysis, was investigated in detail (see process schematics in Fig. 4). Dissolved cello-oligosaccharides up to the water-soluble DP of 6 were analyzed from the hydrolysis filtrates (Fig. 10). Cello-oligosaccharides easily decompose to glucose during the post-hydrolysis conditions (Tolonen et al., 2015), but the relatively low yields (0–15 %) indicated that they were only a partial reason behind the high monosaccharide yields. The amount of cello-oligosaccharides decreased after 6 h hydrolysis, signaling their decomposition to monosaccharides already at the gas hydrolysis stage. Before the 6 h mark, the amounts with cellulose I and cellulose III<sub>I</sub> gradually increased while with cellulose II and cellulose III<sub>II</sub> they decreased at the early stages, i.e., <4 h hydrolysis time.

As the oligosaccharide composition was not fit to explain the high monosaccharide yields after post-hydrolysis, HCl (g) hydrolysis products were divided into four distinct components after filtration with a cloth of 10  $\mu$ m pore size: monosaccharides, cello-oligosaccharides and a colloidal carbohydrate fraction (all in the filtrate), and a solid residue



remaining after filtration (Fig. 4). Fig. 11 shows the shares of each component with each cellulose polymorph. Typically - and logically the amounts of monosaccharides and cello-oligosaccharides are negatively correlated, that is, the amount of monosaccharides increases as that of cello-oligosaccharides decreases. Likewise, the colloidal fraction increases as the solid residue decreases over time. Solid residue corresponds to the remnants of fibers which are - over the course of hydrolysis - being disfigured into smaller and smaller pieces and ultimately into the colloidal particles ( $<10 \ \mu m$ ) that make up the colloidal fraction. The SEM images in Fig. 12 demonstrate the partitioning and gradual disappearance of the fibers and fiber fragments with mercerized cellulose II fibers. Already after 2 h hydrolysis by HCl (g), the fibers already appear similar to fragments typically found in microcrystalline cellulose (Spiliopoulos et al., 2021), and the colloidal fraction ( $\sim$ 30 %) is close to the solid fraction ( $\sim$ 45 %) (Fig. 11b). After longer periods of hydrolysis (>24 h), the amount of colloidal fraction has grown to such extent that the SEM images are showing merely a flocculated, featureless sheet of the material dried for SEM analysis (Fig. S2).

The development of larger fiber fragments (solid fraction) and, in particular, the increasing colloidal fraction during extended (>6 h) HCl (g) hydrolysis (Fig. 11) is key to understanding the phenomena leading to high monosaccharide yield after post-hydrolysis. The formation of sticky humin-containing material hampered the filtration of degradation products, which caused a drop in the monosugar yields with the cellulose III<sub>II</sub> sample at reaction times of >6 h (Fig. 11d). As the average DP in the solid fraction does not appear to decrease during the 2 h - 18 h interval (Fig. 7a), the changes in reactivity are likely of morphological origin in the fiber fragments. 50 % moisture content within the fibers allows for a better accessibility of the reagents when compared to previously tested fibers with only 3-5 % moisture content (Pääkkönen et al., 2018). However, the increased accessibility of water does not generally lead to significantly increased susceptibility to degradation within cellulosic fibers (Thybring, Thygesen, & Burgert, 2017). The crystallinity of the solid fraction, as determined by XRD, follows an expected trend: the crystallinity index increases on the course of the hydrolysis (Table 2). This is generally interpreted as being due to the removal of disordered segments in cellulose microfibrils (Fig. 9). The effects of decisive alterations in the texture of the fibers (Fig. 12) on the diffraction were minimized by random orientation of the samples. What is interesting here is the behavior of cellulose III samples (Table 2). Cellulose III<sub>I</sub> was converted partially back to cellulose  $I_{\beta}$  – a phenomenon which is well established upon hydrothermal treatment of cellulose IIII (Wada, 2001) but apparent also here when treating the fibers with HCl gas. Meanwhile, the cellulose  $III_{II}$  sample was completely rid of cellulose  $III_{II}$ upon 18 h hydrolysis, although roughly half of the initial (unhydrolyzed) sample consisted of cellulose  $III_{II}$  (Table 2). There can be three reasons for such behavior: (i) the cellulose chains in cellulose IIIII crystallites get fully hydrolyzed with a preference over cellulose II, (ii) the cellulose III<sub>II</sub> crystallites are converted to cellulose II, or (iii) both cellulose II and III<sub>II</sub> are partially being hydrolyzed and the remaining unhydrolyzed cellulose III<sub>II</sub> crystallites are converted to cellulose II. Whatever the underlying phenomena, it is clear that HCl gas manages to increase the amount of colloidal material in the filtrate with all polymorph samples (Fig. 11) but the cellulose within the colloidal particles is clearly more susceptible to hydrolysis to glucose with cellulose III samples, particularly with cellulose  $III_{II}$  (Fig. 8). The presence of chlorite may play a role in this as chlorite has been shown to quantitatively affect the reactivity of cellulose (Hubbell & Ragauskas, 2010; Javed & Germgard, 2011) with many side reactions in acidic environment, resulting in, e.g., chlorine dioxide formation (Lehtimaa, Kuitunen, Tarvo, & Vuorinen, 2010). Full treatise of the role of different chlorine-containing species in the system is, however, beyond the scope of this initial study.

#### 4. Conclusions

The study on different cellulose polymorphs showed that, when



Fig. 11. Effect of long exposure times to degradation products: a) The degradation products of Cellulose I. b) The degradation products of Cellulose II. c) The degradation products of Cellulose III<sub>1</sub>. (2 % NaClO<sub>2</sub> addition, 50 % moisture content of cellulose).



Fig. 12. SEM images of fibers with the morphology slowly vanishing to non-existence during long exposure times (0 h, 1 h, 2 h and 4 h) HCl (g) and NaClO<sub>2</sub>. The inset in each SEM image is a photograph of the solid residue sample. (2 % NaClO<sub>2</sub> addition, 50 % moisture content of cellulose).

coupled with a mild post-hydrolysis step, HCl (g) can efficiently degrade cellulose into glucose when the moisture content of cellulosic fibers has been set to 50 %. Simultaneously, the addition of chlorite in the system prevents the formation of humins which otherwise cause problems in extended acid hydrolysis of cellulose by strong discoloration. The conversion of cellulose to glucose was comparable with the state-of-the-art results on enzymatic hydrolysis of cellulose. Although the high conversion rates in this system require industrially impractical actions, such as polymorphic transition, these results are an important step forward in understanding how extensive saccharification of cellulose proceeds in a gas/solid system while the formation of harmful humins has been chemically blocked. Ultimately, we have shown that the gas/solid system in acid hydrolysis is a basis for future practical solutions in cellulose degradation where side reactions are controlled, conversion rates are efficient, and the recovery of products and reagents is effortless.

Supplementary data to this article can be found online at https://doi.org/10.1016/j.carbpol.2022.120388.

#### CRediT authorship contribution statement

Yingfeng Wang: Methodology, Verification, Formal Analysis, Investigation, Writing – Original Draft, Visualization; Timo Pääkkönen: Conceptualization, Methodology, Validation, Formal Analysis, Investigation, Writing – Original Draft, Writing – Review and Editing, Supervision; Kim Miikki: Software, Formal Analysis, Writing – Review & Editing, Visualization; Ndegwa H. Maina: Methodology, Validation, Formal Analysis, Investigation, Writing – Review & Editing; Kaarlo Nieminen: Software, Formal Analysis, Writing – Review & Editing, Visualization; Aleksi Zitting: Investigation, Validation, Formal Analysis, Writing – Review & Editing, Visualization; Paavo Penttilä: Methodology, Formal Analysis, Supervision, Funding Acquisition, Writing – Review & Editing; Han Tao: Investigation, Visualization, Writing – Review & Editing; Eero Kontturi: Conceptualization, Methodology, Resources, Writing – Original Draft, Writing – Review & Editing, Supervision, Project Administration, Funding Acquisition

#### Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

This work was supported by Academy of Finland (grant numbers No. 318890 and 318891), Kaute foundation, and Business Finland (R2B project: Gas-driven technology for cost-efficient production of cellulose nanocrystals 42472/31/2020).

#### Data availability

Data will be made available on request.

#### Acknowledgements

This work was supported by Academy of Finland (grant numbers Nos. 318890, 318891 and 338804) and Kaute foundation. The research is part of FinnCERES Materials Bioeconomy ecosystem. TP acknowledges the funding from Business Finland (R2B project: Gas-driven technology for cost-efficient production of cellulose nanocrystals 42472/31/2020).

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