The overlooked interaction between cellulose and CO2(g) in NaOH(aq) turned into the potential for cellulose technology and carbon dioxide

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The overlooked mechanism of interaction between cellulose and $CO_{2(g)}$ in $NaOH_{(aq)}$ turned into the potential in cellulose technology and carbon dioxide capture.

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ABSTRACT

Cellulose gets a lot of spotlight in the world striving for eco-friendly and sustainable solutions. The obstacle on a way to cellulose processability is the low degradation temperature (degrades faster than melts) of the polymer which makes dissolution an attractive, if not only, option for the reshaping purposes. Dissolution of cellulose in aqueous NaOH is an attractive perspective from the industrial point of view. However, the multiple conditions need to be fixed in a narrow range for a successful process. On top of that, the recent studies carried out in our group pointed out on interaction between the dissolved cellulose and environmental $CO_{2\,(g)}$. This study aimed to further investigate the effect of $CO_{2\,(g)}$ on cellulose in $NaOH_{\,(aq)}$. Therefore, the CO_2 gas delivery was carried in a controlled manner into the polymer-solvent system with the *in-situ* observation of reaction, pH and temperature changes. Here, we present the recent understanding of the interaction between cellulose and delivered $CO_{2\,(g)}$ that resulted in the coagulation of polymer from $NaOH_{\,(aq)}$. We point out the potential of our findings in cellulose technology and discuss further research perspectives.

Keywords: *cellulose dissolution, $NaOH_{(aq)}$, $CO_{2(g)}$, coagulation*

INTRODUCTION

In nature, cellulose is a fundamental component of plant cell walls that supports the structure of plants and as such, it is exceptionally stable. As the world finally turned towards sustainable and environment-friendly solutions cellulose could play one of the first fiddles. Its hierarchical structure, being the result of multi-level assembly is an asset that makes cellulose a versatile platform biomaterial for multiple industrial applications. However, this peculiar morphology (with its robustness) stands in a way for some industrial applications.

Due to low degradation temperature (in relation to melting temperature), the range of processing methods to access industrially attractive cellulose is limited to dissolution. Amongst many studied cellulose solvents, the aqueous NaOH, even if restricted in terms of concentration and temperature, is a great perspective. The NaOH (aq) is cheap, vastly available and carries a real green potential. The concentration/temperature limitations of NaOH(aq) to dissolve cellulose have been continuously studied. On the other hand, the natural, well-established ability of cellulose/NaOH(aq) to bind environmental CO_2 (g) has been consistently omitted. The results of the initial analysis carried out in our group demonstrated the pitfalls of such a proceeding. It was shown that cellulose exhibit a strong affinity for alkali-dissolved CO_2 (g) that could lead to the formation of carbonate intermediates.[1,2]

In follow up to the previous analysis, here we took the control over the gas delivery and conclusively studied the effect of CO_2 (g) upon cellulose in NaOH(aq). We present the results of our complex approach based on in-situ studies of reaction between cellulose/NaOH(aq) and CO_2 (g), in terms of carbonation, pH and temperature changes in the system.[4] Furthermore, we introduce the potential of CO_2 (g) to regenerate cellulose from alkaline solution; subsequently, the carbonation of polymer is discussed in terms of mechanism, reversibility and its effect on the cellulose crystal structure. Our findings are presented with the implication for cellulose processability in the context of cellulose derivatives and regenerated fibres production.

EXPERIMENTAL

To assure fast, consistent, and complete dissolution of cellulose in $NaOH_{(aq)}$ the Avicel PH-101 microcrystalline cellulose (MCC, dp. ~230) was used. The final concentration of the studied solution was 2.0 % MCC in 2.0 M $NaOH_{(aq)}$.

The illustrative scheme of the experimental set-up, including in-situ measuring probes, is presented in **Fig. 1**. The studies of the interaction between $CO_{2\ (g)}$ and aqueous solutions of NaOH and MCC-NaOH were carried out at 5 °C and 25 °C in a reaction vessel connected to a pressurized gas tank *via* a valve-controlled flowmeter and solution-immersed glass inlet. The pH and inner temperature of solutions were in-situ measured during the CO_2 delivery (every 10 s) with a combination electrode connected to a laboratory multi-meter. The IR spectra were in-situ collected (every 10 s) with an ATR probe connected to an FTIR spectrometer.

The coagulated cellulose gels (5 °C and 25 °C) were collected and washed to neutral pH. The thoroughly dried samples were subject to XRD and FTIR-ATR analysis in reference to cellulose dissolved in NaOH (aq) and regenerated *via* EtOH quenching.

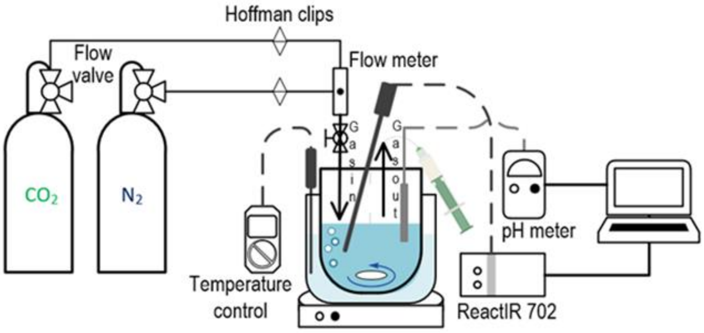

Fig. 1. The set-up was applied in the CO_2-chemisorption experiment.

RESULTS AND DISCUSSION

The delivery of $CO_{2(g)}$ to cellulose-$NaOH_{(aq)}$ resulted in the vast precipitation of gel-like material, as presented in **Fig 2.**, both at 25 °C and 5 °C.

The in-situ measurements of carbonated species, pH and temperature change provided inside the coagulation process of $NaOH_{(aq)}$ dissolved cellulose during the $CO_{2(g)}$ delivery. As presented in **Fig 3.**, the profiles collected for 25 °C (**a**) and 5 °C (**b**) differ.

At 25 °C (**Fig 3a.**), three sections were distinguished. The fast production of CO_3^{2-} in section 1 resulted in pH drop and temperature jump ($CO_{2(g)} \rightarrow CO_3^{2-}{}_{(aq)}$ is an exothermic change). Once the concentration of carbonate reached semi-plateau (end of section 1), the reaction vessel was filled with cellulose coagulants. Interestingly, after the precipitation, the ongoing reaction between hydroxide groups of alkali solvent and continuously delivered $CO_{2(g)}$ led to further pH drop (section 2), and finally $CO_3^{2-}{}_{(aq)} \rightarrow HCO_3^{-}{}_{(g)}$ exchange (section 3). The saturation with inorganic species led to salting out, clearly visible on the gel surface in **Fig 2**.

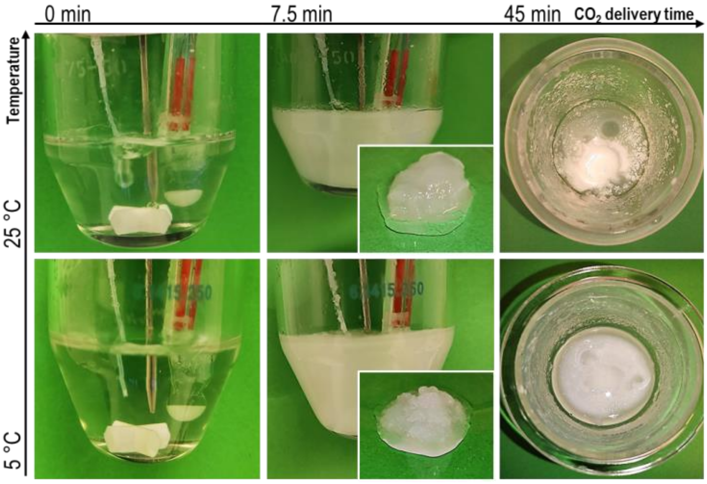

Fig 2. Pictures of reaction vessels before, during and at the end of the reaction between $CO_{2(g)}$ and MCC-NaOH solution (2% in 2.0M, respectively) at 25 °C and 5 °C.

The processat 5 °C (**Fig 3b.**) was divided into two sections. In section 1, although very moderate, the pH drop was observed upon the consumption of hydroxide group in $CO_{2(g)} \rightarrow CO_3^{2-}{}_{(aq)}$ exchange, accompanied by temperature increase. Similarly to 25 °C, cellulose precipitated at the end of section 1. However, in contrast to the previous process, both concentration of $CO_3^{2-}{}_{(aq)}$ and pH of the system after the coagulation remained stable (section 2), despite continuous gas delivery. There was also no salting-out observed.

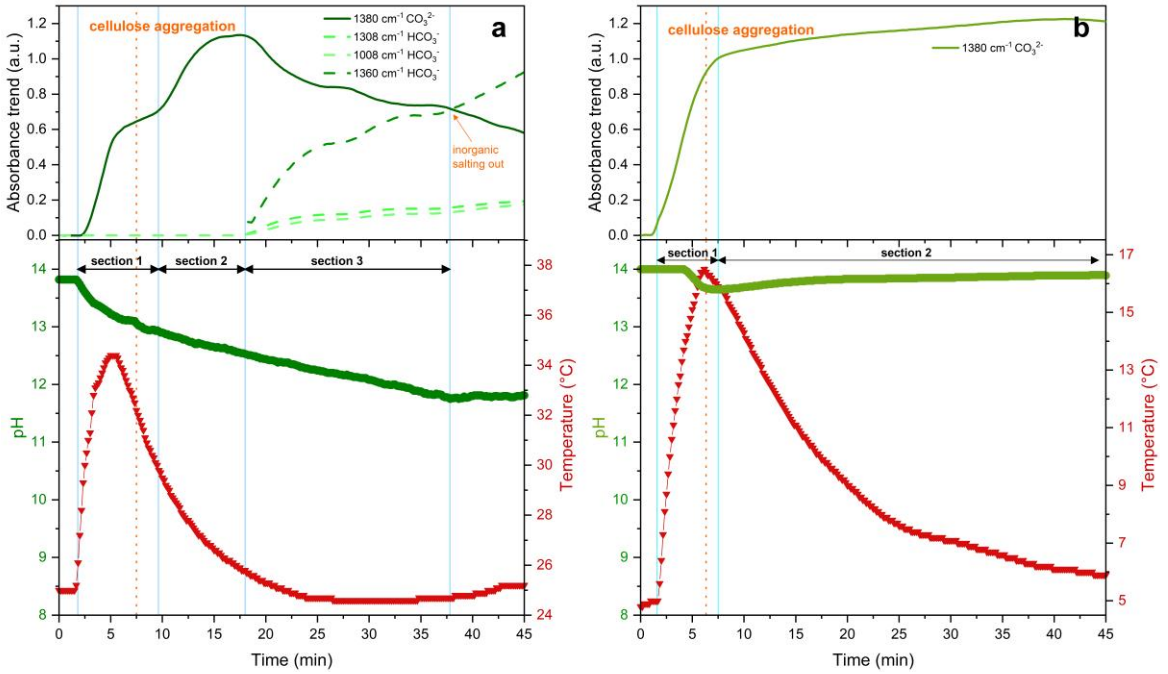

Fig 3. The absorbance trend of carbonated ions, change of pH and temperature, observed during the sparging of $CO_{2(g)}$ over the cellulose/ $NaOH_{(aq)}$ at **a)** 25 °C and **b)** 5 °C, as a function of reaction time. Aggregation of cellulose and inorganic salting-out were marked with orange.

The differences between the response of cellulose-NaOH$_{(aq)}$ systems to CO$_{2(g)}$ delivery at 25 °C and 5 °C could be the consequences of many overlapping variables. For example, decreased stability and 'simultaneous' precipitation of NaOH-dissolved cellulose upon increasing temperature (that would limit polymer availability for delivered gas),[3] temperature as a driving precipitation factor (especially after initial self-aggregation)[4], cellulose deprotonation (more probable at higher pH) and interaction with different carbonated species (CO_2 or CO_3^{2-}), or temperature-dependent dissolution of inorganic ions. All are valid when considering inconsistencies between the studied system.

Due to the efficiency of observed coagulation, the precipitated samples were examined from the perspective of polymer regeneration. The FTIR and XRD analysis of water-washed and dried samples demonstrated a lack of substantial deviation between CO_2-recovered materials and cellulose regenerated *via* EtOH quenching, as summarized in **Fig 4**.

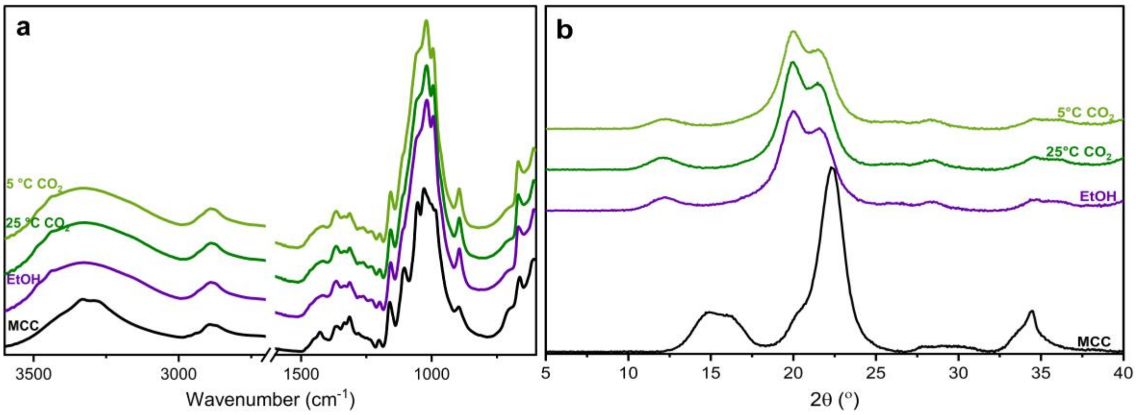

Fig. 4. a) The FTIR spectra in the range of 3600 – 600 cm^{-1} for and **b)** the XRD patterns of MCC standard, EtOH regenerate and CO_2 precipitates at 25 °C and 5 °C.

CONCLUSIONS

We have demonstrated that CO_2 (g) can be adapted as a cellulose coagulant from the NaOH(aq). The process is temperature-dependent and most likely relies on the interaction between dissolved cellulose and CO_2 (g); the cellulose dissolution status is also a decisive factor. The CO_2-coagulation of cellulose is a sustainable alternative to polymer regeneration that utilises one of the most available and cheap gases, the application of which would be also beneficial from the ecological point of view. On top of that, the minimum alkalinity loss opens for easier recycling of the coagulation bath.

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