

**Projekt****Tailoring cellulose networks from sustainable NaOH(aq) solutions  
(ref. nr 19-726)****Background and goal**

The goal of this project has been to, based on the recently discovered CO<sub>2</sub>-chemistry of cellulose solutions in NaOH(aq), investigate the possibilities of governing cellulose re-association behavior by employing its interactions with CO<sub>2</sub>.

The CO<sub>2</sub> chemistry of cellulose/NaOH(aq) entails incorporation of CO<sub>2</sub>(g) in cellulose/NaOH(aq) through a specific reaction with partly deprotonated cellulose leading to formation of transient cellulose carbonate intermediate capable of affecting cellulose reassembly from the solution (as observed in the previous preliminary studies). The mechanism and conditions governing this reassembly are not resolved and have been in focus of this project.

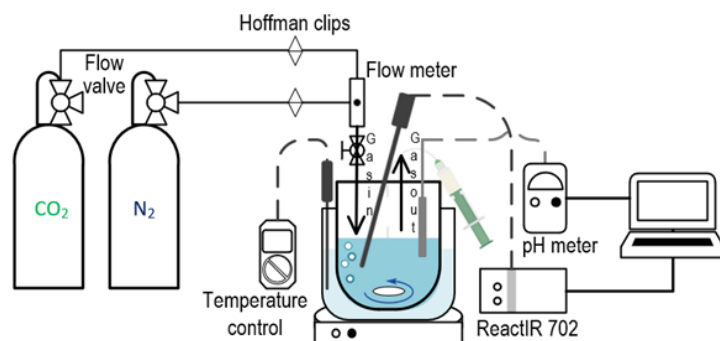
Our studies were conducted in two different directions:

- Elucidating conditions and mechanism governing CO<sub>2</sub>(g) coagulant (reassembly) action on cellulose in NaOH(aq).
- Elucidating structural characteristics of obtained coagulated materials (hydrogels, i.e. networks) as a function of employed coagulation conditions.

Post doc. Aleksandra Kozlowski was hired to the project and performed the main part of the experimental, evaluation and dissemination work under guidance of Merima Hasani and in collaboration with the team at Forest Products and Chemical Engineering and the community at Chalmers.

**Performance**

The experimental work was centered around the set up enabling rigorously control of temperature, gas supply (CO<sub>2</sub> or N<sub>2</sub>) and stirring during cellulose dissolution and coagulation from NaOH(aq) along with *in situ* monitoring of FTIR signals (capable of following conversions of carbonate species in solutions) as well as temperature and pH, illustrated in Figure 1. Reference solutions were sparged with N<sub>2</sub> to minimize the influence of CO<sub>2</sub> chemisorbed from the environment.



**Figure 1.** The experimental set-up applied in the dissolution/coagulation experiments employing CO<sub>2</sub>(g) as a coagulant.

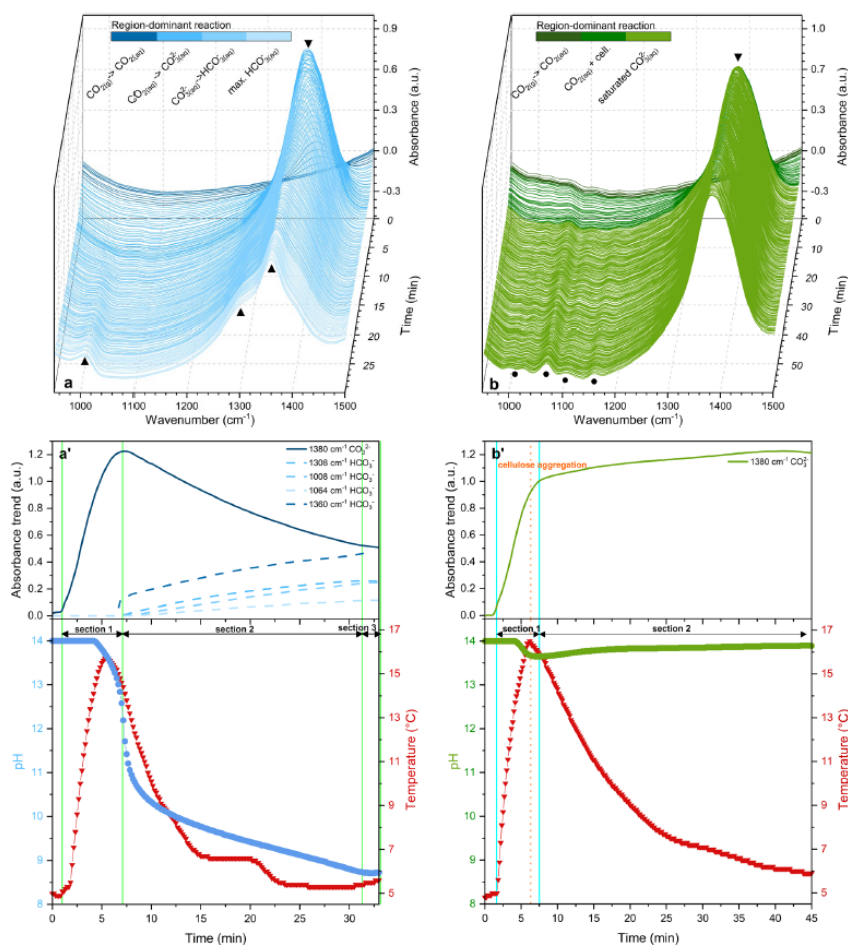
The generated cellulose hydrogels were neutralized and analyzed in terms of chemical structure (NMR, FTIR), crystallinity (XRD) and stabilizing intermolecular forces (XRD, FTIR) and

compared to the microcrystalline cellulose reference as well as cellulose hydrogels obtained by the commonly used ethanol coagulation.

## Findings

Our findings based on series of dissolution/coagulation studies conducted under varied conditions along with thorough characterization of the obtained materials can be summarized as follows:

- Incorporation of  $\text{CO}_2(\text{g})$  into cellulose/ $\text{NaOH}(\text{aq})$  as of decisive influence on properties of the dissolved state and solution stability
- $\text{CO}_2(\text{g})$  works as a highly efficient coagulant accomplishing a surprisingly quick formation and consolidation of a cellulose hydrogel (Figure 2 shows a typical coagulation point as a function of applied conditions).
- The  $\text{CO}_2(\text{g})$ -mediated coagulation is highly temperature dependent likely due to temperature influence on both dissolution state of cellulose and on  $\text{CO}_2(\text{g})$  solubility in the  $\text{NaOH}(\text{aq})$ ; coagulation at low temperature being more efficient due to favored  $\text{CO}_2(\text{g})$ -chemisorption by cellulose.
- The  $\text{CO}_2(\text{g})$ -mediated coagulation proceeds under surprisingly modest loss of alkalinity due to incorporation of the  $\text{CO}_2$  coagulant through cellulose-chemisorption opening up for a highly resource efficient recycling of the solvent/coagulation bath (see Figure 2, particularly the pH plot in the figure to the right).
- The recovered cellulose appeared competitive to EtOH recovery in terms of structure.



**Figure 2.** A typical finger print obtained for a coagulation procedure investigated showing here the absorbance trend of carbonated ions, change of pH and temperature, observed during the sparging of  $\text{CO}_2(\text{g})$  over the **a)** 2.0 M  $\text{NaOH}$  and **b)** cellulose/ 2.0 M  $\text{NaOH}$  at 5 °C as a function of reaction time. Aggregation of cellulose and inorganic salting-out were marked with orange. ▼ –  $\text{CO}_3^{2-}$  peaks; ▲ –  $\text{HCO}_3^-$  peaks; ● – cellulose peaks.

## Dissemination

- A manuscript entitled “Cellulose interactions with CO<sub>2</sub> in NaOH(aq): the (un)expected coagulation creates a potential in cellulose technology” has been submitted to *Carbohydrate Polymers*
- The work will be presented in an oral presentation at the 16<sup>th</sup> European Workshop on Lignocellulosics and Pulp, EWLP in Gothenburg 28/6-1/7 2022.
- A master thesis project has been initiated to further investigate on specific mechanisms of the CO<sub>2</sub>(g)-cellulose reactions observed in model reaction studies in this work but not further explored due to time constrains.
- Grant applications for continued investigations of the CO<sub>2</sub>(g)-mediated coagulation have been submitted to VR and Formas
- A collaboration on further development of the materials based on the obtained hydrogels (e.g. aerogels, all-cellulose composites, etc.) with MINES Paris Tech (Dr. Tatiana Budtova) has been established and joint grant applications are in preparation.

## References

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