

Derivation of cellulose in novel switchable ionic liquid system

TanDem Forest Value research project between Laboratory of Industrial Chemistry and Reaction Engineering at Åbo Akademi and Technical Chemistry at Umeå University was carried out under supervision of Project Leader Academy Professor Tapio Salmi and Cooperation partner Professor Jyri-Pekka Mikkola. Dr. Pasi Virtanen was hired as a researcher for the project. The project was accomplished during period of 31.12.2018-31.10.2021. The time of the project was extended because of COVID-19 restrictions, leave of absence of the main researcher and moving of the laboratory of Industrial Chemistry and Reaction Engineering to a new building. The collaboration between the laboratories have also included research work by other people in both laboratories, such as Ramakrishna Jogi and Päivi Mäki-Arvela in Åbo Akademi as well as Ajaikumar Samikannu, Santosh Khokarale and Chandrakanth Mukesh in Umeå University.

Description of the research

The aim of the research was to develop a method to produce cellulose derivatives in a simple and cost-efficient manner. Different cellulose derivatives such as cellulose acetate, cellulose propionate, hydroxyethyl cellulose and hydroxypropyl cellulose are utilized in pharmaceuticals, membranes, textile fibres, coatings and paints. Traditionally, *e.g.* cellulose acetate, is prepared in solid-liquid reaction between cellulose acetic acid, acetic anhydride and catalyst, typically sulfuric acid. The mixture is let to react for 20 h and cellulose acetate is purified from the mixture by dissolving it to acetone, filtrating unreacted reactants and finally spinning the solution in a column of warm air to remove the solvent.

The research work included building up the experimental reactor set-up to study cellulose dissolution in novel switchable ionic liquid systems. The plan was to dissolve cellulose into dimethyl sulfoxide (DMSO) by reacting hydroxyl-groups of cellulose with CO₂ or SO₂ and superbase pentaethylenhexamine (PEHA) or 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU) in

order to form a cellulose carbonate which should be soluble to DMSO or other similar solvents (Fig. 1).

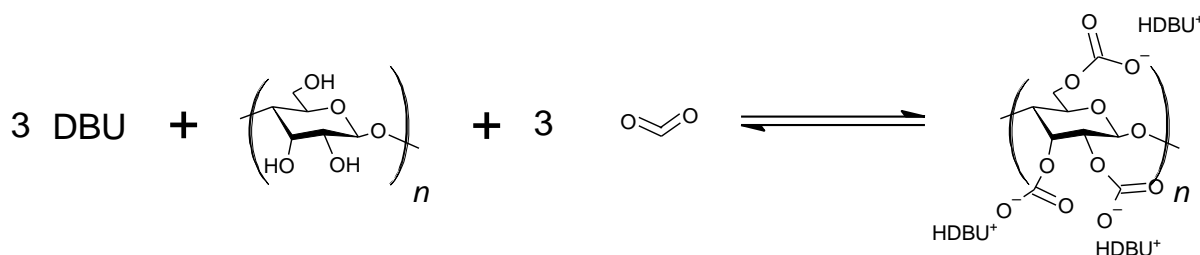


Figure 1. Formation cellulose carbonate HDBU in a reaction between DBU, cellulose and CO₂.

The dissolution of cellulose was studied with above mentioned combinations in DMSO, dimethylformamide (DMF), dimethylacetamide (DMA). These solvents were chosen since DMSO was known to work in similar systems and DMF as well as DMA having similar properties as DMSO. For the experiment 2 g of cellulose was mixed with 80 ml of solvent. Acid gas was bubbled through the mixture, so that the unreacted CO₂ was led away from the reactor. Also heating of the system was studied in the temperature range between 30-80 °C. Unfortunately, any of the systems were not able to make cellulose soluble in the beginning. The experiments ended up like in Fig. 2. One could clearly see that the reaction took place since the colour changed from white to yellow, however, the product was not completely soluble.



Figure 2. Cellulose dissolution experiment with PEHA and CO₂ in DMSO. On the left before bubbling of CO₂ and heating. On the right after the reaction.

Finally, the answer to the dissolution problem for one combination was figured out and it was so simple that all the components and the solvent must be completely dry. Therefore, the solvents and superbases were dried by heating them to 80 °C under vacuum (~50 mbar) for 4 h and stored over molecular sieve. Still the dissolution was not successful with the systems with PEHA. However, dissolution was eventually possible in DMSO with DBU and CO₂ as can be seen in Fig. 3. The reaction was completed in 4 h at room temperature.



Figure 3. Dissolution of cellulose in DMSO with DBU and CO₂. On the left before bubbling of CO₂, in the middle after 30 min and on the right after 4 h, when the reaction was complete.

The achieved cellulose solution was further utilized in derivation of cellulose with different acid anhydrides to produce cellulose acetate, cellulose propionate and cellulose butyrate according to Fig. 4.

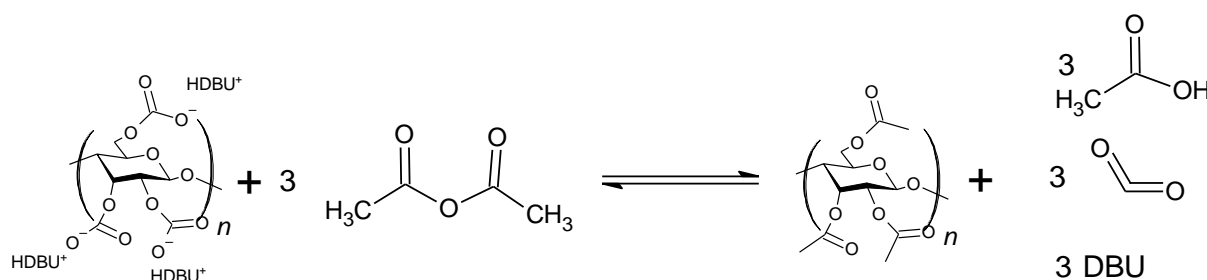


Figure 4. Formation of cellulose acetate from cellulose carbonate DBU and acetic anhydride.

For the derivation experiments, 20 ml of prepared cellulose solution was diluted with 30 ml of DMSO and over 3 equivolar, compared to amount of hydroxyl groups in cellulose, of acid anhydride was added to the stirred solution and let to react for 30 min. One could observe the

reaction taking place by gas (CO_2) bubbles formed. Solution was poured into 300 ml of water to precipitate the product and the product was filtrated. In order to clean the product, it was dissolved again into DMSO and precipitated again in water and filtrated and washed with water. The product was then dried in oven at 70°C overnight. The products were qualitatively analysed by ATR-IR to identify formed compounds (Fig. 5).

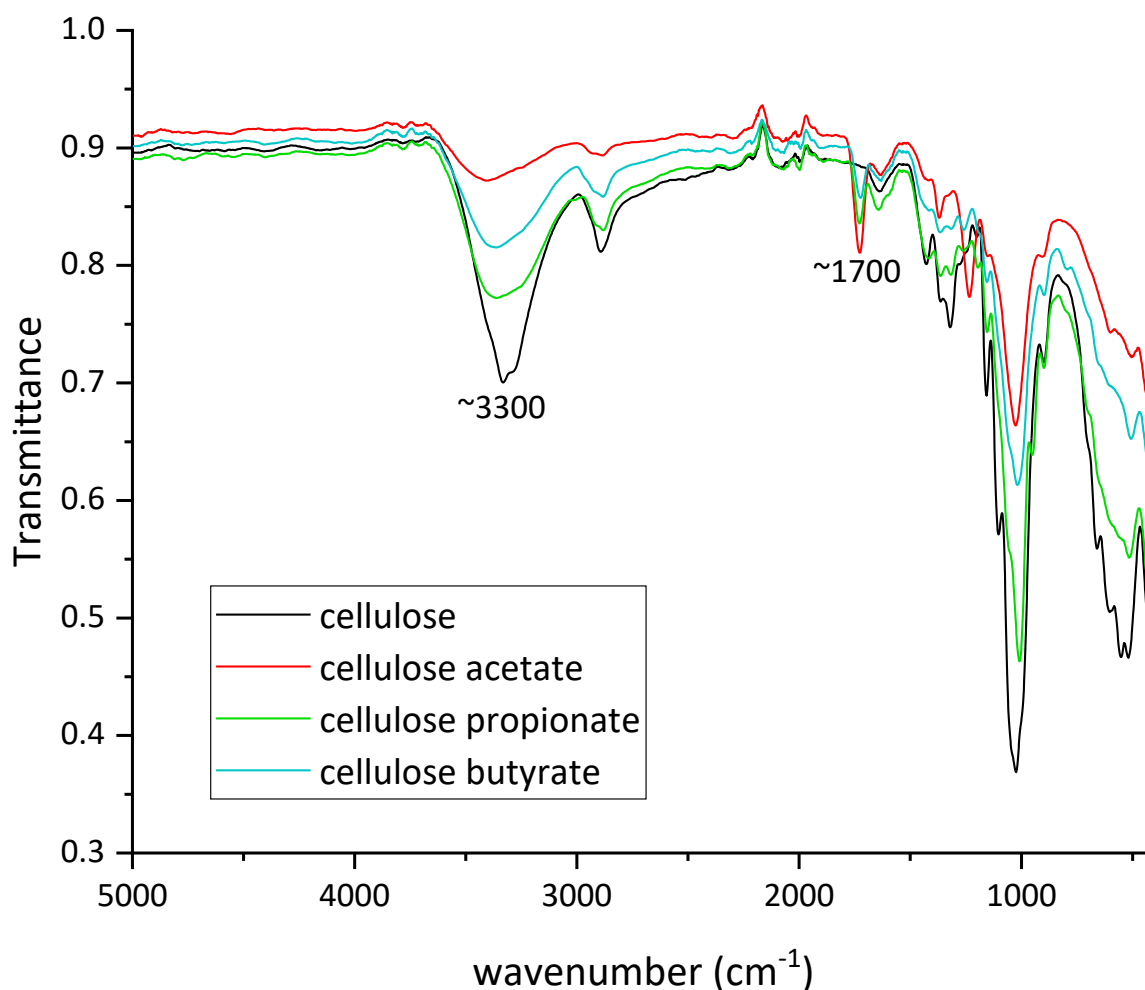


Figure 5. IR spectra of cellulose and cellulose derivatives.

From the IR spectra of cellulose and the products, it can be observed that the peak at approx. 3300 cm^{-1} caused by OH-vibration is strongest with pure cellulose and is faded away with the products, since acids have formed ester bonds with hydroxyl groups. Another indication of the product formation can be observed from the peak at approx. 1700 cm^{-1} . This peak is caused by C=O-vibration from acid that has been attached to the hydroxyl group. In the spectrum of pure cellulose, the peak does not exist, but in the spectra of the products, it can be clearly

observed. The original plan was to quantitatively analyse the products by NMR, in order to determine the degree of substitution of cellulose, *i.e.* determine exactly the portion of the hydroxyl groups in cellulose have reacted. This was planned to be done during research visits to Umeå during 2020. Unfortunately, because of current situation in the world the visits were cancelled. The idea is that this could be done in the future.

Since the main research plan was not working as expected in the beginning the main researcher participated also other projects which also considered utilisation of biomass or CO₂ same way as in this project and were collaborations between same laboratories in Åbo and Umeå.

The first project considered development polyamine-based deep eutectic solvents and tetraethylenepentamine anion based ionic liquids for CO₂ capture technology. During the study, polyamine based ionic liquids and deep eutectic solvents were successfully synthesized for reversible chemisorption of CO₂ under ambient conditions. The mechanistic CO₂ absorption was established via carbamate salt formation in the presence of ethylene glycol in deep eutectic solvent which turned out to be beneficial, resulting in decreased viscosity, enhanced CO₂ diffusion and improved absorption capacity. The high uptake of CO₂ and robust desorption in deep eutectic solvents at low temperatures and atmospheric pressure makes the media a suitable absorbent. Low temperature (70 and 80 °C) desorption of CO₂ is also feasible and enables the utilization of low value heat from industrial outputs. The excellent reversible CO₂ capture performance was demonstrated in 4 consecutive cycles at 100 °C with only ~1% lower absorption capacity after consecutive cycles. The proposed deep eutectic solvent media exhibit a high thermal stability, low solvent loss, high CO₂ uptake and robust desorption efficiency in comparison to conventional scrubbing processes. The project was mainly performed in Umeå University and some analytics was made in Åbo Akademi.

Two other projects targeted to production of renewable jet-fuel from bio-based materials. In the other one a highly active mesoporous Brønsted acidic catalysts NbOPO₄/SBA-15, Pd/NbOPO₄/SBA-15 and Pd/Nb₂O₅/SBA-15 were developed and characterised. The catalysts were applied in C-C coupling of 2-methyl furan with carbonyl compounds and palladium containing catalysts as bifunctional catalysts upon subsequent hydrodeoxygenation of C-C coupling products. This project was mainly done in Umeå University and part of the catalyst characterisations were carried out in Åbo Akademi. In the other project hydrothermal

liquefaction of wood in supercritical ethanol over acidic catalyst Pd/NbOPO₄ first to produce bio-crude and further bio-jet fuel was studied. An efficient method to extract lignin monomers from birch was developed. Phenolic monomers were extracted from the achieved bio-crude by Deep eutectic solvents for hydrodeoxygenation process in order to produce jet fuel. This project was mainly carried out in Åbo Akademi, but the catalyst preparation and characterisation were mainly made in Umeå University.

Collaboration

Bilateral collaboration between two laboratories has worked well and researchers in both laboratories have worked together shared knowledge and discussed with each other in person and via email. Also, different samples and analysis results have been travelled between the two laboratories. As a result of this collaboration, three international journal articles have already been published, and one article submitted to international journal is under review at the moment.

The collaboration has created competence in both laboratories by increasing knowledge in wood treatment, utilisation biomass derived components, catalyst preparation and characterisation as well as in development and utilisation of deep eutectic solvents and ionic liquids. The collaboration has been beneficial to both laboratories, since different characterisation and analytical methods have fulfilled each other and helped both laboratories to get better results as well as understand more of different phenomena in research projects. This fruitful collaboration will definitely continue, since it is beneficial to both laboratories. In general, it can be said that the collaboration has strengthened many research areas in both laboratories. Cellulose derivation was developed towards new direction, new kind of catalysts were developed and characterised as well as utilised in liquefaction of biomass and in reaction of biomass derived components, knowledge in utilisation of deep eutectic solvents was widened in extraction and CO₂ capture.

Impact for society

These research projects have created knowledge that can be utilised *e.g.* in designing product portfolio and processes of modern biorefineries both in Finland and Sweden. The results have already been made available for everybody in the area of research by publishing them in well-known scientific journals. Hopefully, after world returns back to normal, these results can also be presented in scientific conferences, so that even wider audience can find them

Publications

Mukesh C., Khokarale S., Virtanen P., Mikkola J.-P., Rapid desorption of CO₂ from deep eutectic solvents based on polyamines at lower temperatures: An alternative technology with industrial potential, *Sustainable energy & Fuels*, **2019**, 3, 2125-2134

Samikannu A., Konwar L., Rajendran K., Lee C. C., Shchukarev A., Virtanen P., Mikkola J.-P., Highly dispersed NbOPO₄/SBA-15 as a versatile acid catalyst upon production of renewable jet-fuel from bio-based furanics via hydroxyalkylation-alkylation (HAA) and hydrodeoxygenation (HDO) reactions, *Applied Catalysis B: Environmental*, **2020**, 272, 118987, DOI: 10.1016/j.apcatb.2020.118987

Jogi R., Mäki-Arvela P., Virtanen P., Kumar N., Hemming J., Russo V., Ajaikumar S., Lestander T., Mikkola J.-P., Understanding the formation of phenolic monomers during fractionation of birch wood under supercritical ethanol over iron based catalysts, *Journal of the Energy Institute*, **2020**, 93, 2055-2062, DOI: 10.1016/j.joei.2020.05.001

Jogi, R., Samikannu, A., Mäki-Arvela, P., Virtanen, P., Hemming, J., Mukesh, C., Lestander, T. A., Xu, C., and Mikkola, J.-P. Liquefaction of lignocellulosic biomass into phenolic monomers over multifunctional Pd/NbOPO₄ catalyst, *ACS Sustainable Chemistry & Engineering Manuscript*, **submitted**

Financial accounting

Financial accounting is presented in the table below.

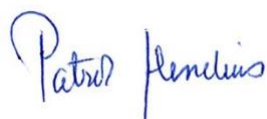
						Utfall 001.2019 - 012.2020
Projektdefinition		Projektelement		Kostnadsslag		EUR
28002013	Cellulose/TANDEM	28002013F1	Cellulose/TANDEM KSLA int	301300	Int samfin verksamh	85.250,68
				303701	Övriga intäkter per	11.132,96
				Resultat		96.383,64
		28002013K1	Cellulose/TANDEM KSLA kostn	431350	Laboratorietillbehör	-314,27
				436600	Dagtr o måltidsers	-177,00
				941200	AK-tillägg, univers	-27.397,83
				970100	Allokerade löner	-45.969,49
				970110	Allok lönebikostn	-8.807,28
				970120	Kalk lönebikostn	-13.717,77
				Resultat		-96.383,64
Resultat		0,00				
28002225	Cellulose/TANDEM	28002225F1	Cellulose/TANDEM KSLA int	301300	Int samfin verksamh	84.286,24
				303701	Övriga intäkter per	-11.132,96
				Resultat		73.153,28
		28002225K1	Cellulose/TANDEM KSLA kostn	941200	AK-tillägg, univers	-26.289,50
				970100	Allokerade löner	-44.109,84
				970110	Allok lönebikostn	-8.759,34
				970120	Kalk lönebikostn	-12.854,50
				Resultat		-92.013,18
		Resultat		-18.859,90		
		Totalt resultat				

Signatures



Åbo 15.11.2021

Project Leader, Academy Professor Tapio Salmi



Åbo 15.11.2021

Principal Investigator, Professor Patrik Henelius, Dean