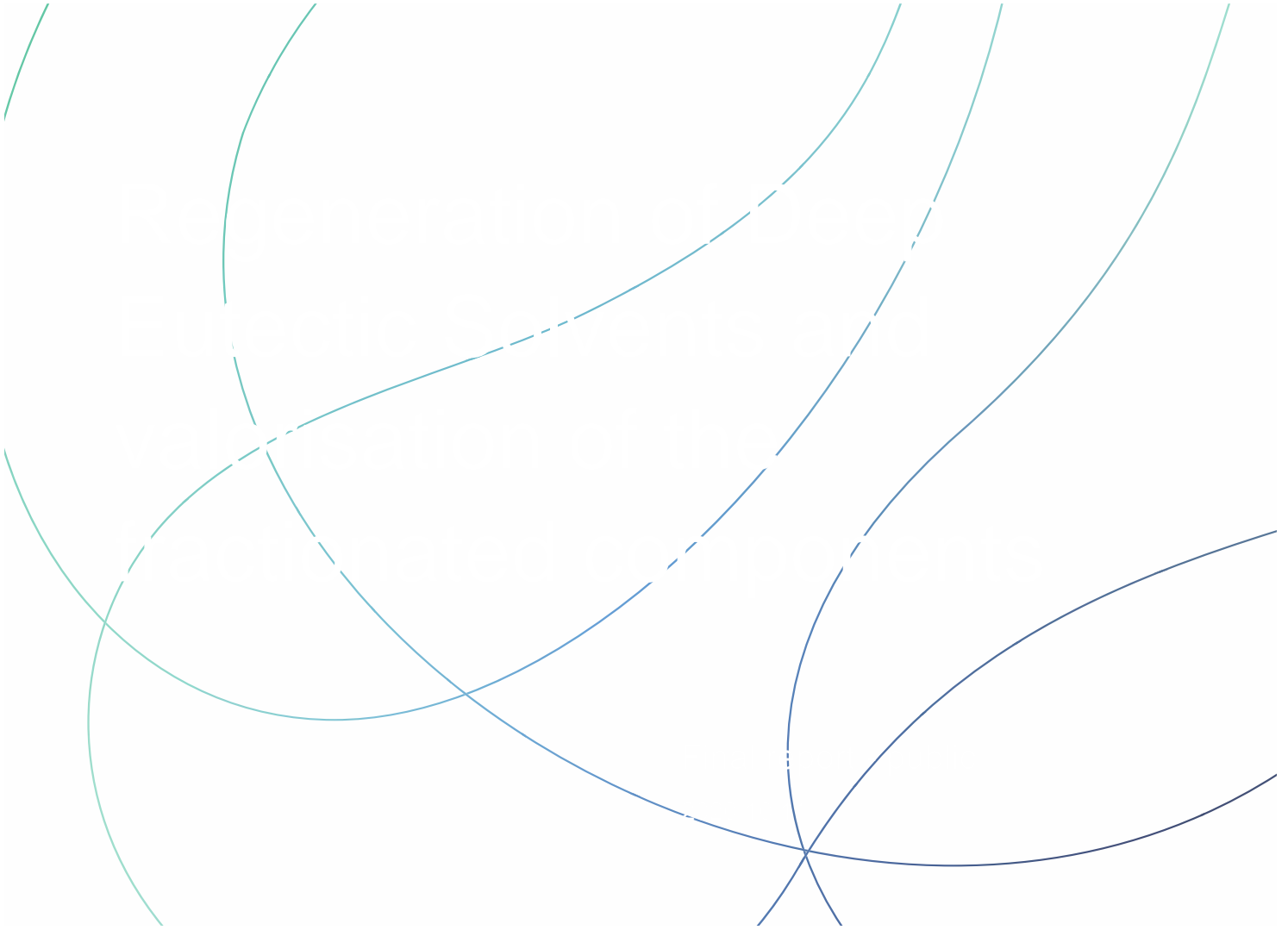


TKI ENERGIE EN INDUSTRIE
Topsector Energie



**Institute for
Sustainable
Process Technology**



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Sustainable
Process Technology**



Final report (public version)

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Public end report

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Summary

This project was about the regeneration of Deep Eutectic Solvent (DES) used in the pulping of wood. After such pulping, the wood pulp containing the fibers for paper making are separated from the DES dark liquor by filtration. The DES dark liquor contains all chemicals released from the wood and which dissolved or stabilized in the DES phase. Before sending the DES back to pulping new wood, it is key to remove lignin and other chemicals. To what extent regeneration is necessary is not known yet, but aspect of ongoing research.

Initial situation

At the beginning of this project, we knew from our previous project on the pulping of wood with DES (PROVIDES), that from the wood about 50% can be obtained as fibers, comparable as in kraft pulping, the industrial standard. We did not know much about the quality of the fibers, but had done a paper making test, which looked promising. We also developed a lignin recovery strategy based on liquid-liquid extraction (LLX), which appears suitable for lignin recovery. However, no solution yet was found for recovery of small molecule sugars (monomeric and oligomeric) and for that we proposed to work on a membrane-approach, or alternatively to convert these sugars *in situ* to extractable species that can be co-extracted with lignin or in a separate stage.

Targets

Develop sugar recovery approaches to valorize also the sugars in the DES dark liquor. For this, we aimed at:

- 1) A membrane-based approach where the sugars should be retained.
- 2) An *in-situ* conversion approach to convert the sugars into furans or possibly even carboxylic acids such as levulinic acid.

Next to the recovery of sugars from DES, also the recovery of lignin should be studied on larger scale in order to be able to isolate it. The larger scale lignin recovery studies have been done together with Suster BV. It was the aim to obtain various lignins and characterize them.

Discussion

In this discussion section, we discuss the results from DES regeneration studies, and the results from lignin production and characterization.

DES regeneration strategies

Considering that the pulped wood contains three main polymers: cellulose, hemicellulose and lignin, and that the main constituent of the fibers for paper making is cellulose, then based on a straight forward mass balance analysis, it follows that the DES dark liquor should contain most of the lignin and also hemicellulose and/or derivatives thereof. Based on earlier work in the PROVIDES consortium, it was known that lignin can be removed by liquid-liquid extraction (LLX) with the biobased solvent 2-methyl tetrahydrofuran (2-MTHF). Where this was done on very small scale obtaining milligram amounts of lignin during the PROVIDES project, part of the studies here described include scaling up the lignin recovery to multigram amounts so that the lignin can be more extensively analyzed.



The lignin recovery by LLX is based on the more apolar character of the lignin, through which it prefers the apolar 2-MTHF phase over the polar DES phase. Sugars in contrary are highly polar themselves, and have not been detected in 2-MTHF. Thus, if these compounds are present in the DES, they are not extracted, and when not attempting any other separation, are sent back to the pulping stage. In this project, we have investigated two options, that is to use membranes for separation of the sugars from the DES, and as an alternative approach, to use *in situ* conversion of sugars into furans or derivatives thereof. Since furans are molecularly similar to 2-MTHF, it is expected that these molecules are extracted, and can be recovered from the extract.

Regeneration studies for removal of sugars using membranes

For removal of sugars from DES, we have studied several membrane-based approaches.

Nanofiltration membranes

In the first approach, we have attempted to separate model sugars from the lactic acid (LA) and choline chloride (ChCl) DES using an Inopor inorganic nanofiltration membrane (Inopor TiO₂ membranes with MWCO 450). However, with this approach we could not find any separation factor between monomeric sugars and lactic acid or choline chloride. Therefore, we have moved towards reverse osmosis membranes.

Reverse osmosis membranes

The reverse osmosis (RO) membranes investigated in this study are given in Table 1, and the studied mixtures in Table 2. In Table 2 the concentrations are given in which the components are present in undiluted model DES dark liquors. In the RO experiments, the mother liquor was diluted in various solvents to study on the permeability of the components in the mixture. As measure for the separation of a component from the mixture, the rejection ratio is defined for component *i* according to equation 1:

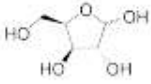
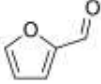
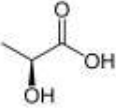
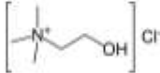
$$R_i = 1 - \frac{c_{i,p}}{c_{i,f}} \quad \text{Eq. 1}$$

Table 1. Reverse osmosis membrane characteristics

Membrane	Salt rejection performance	Operating condition limits
RO99	≥98 NaCl (2000ppm feed concentration, 16 bar, 25°C)	pH: 3-10 Temperature: 5-50°C Pressure: ≤ 55 bar
Alfa Laval NF	≥99 MgSO ₄ (2000ppm feed concentration, 9 bar, 25°C)	pH: 3-9 Temperature: 5-50°C Pressure: ≤ 55 bar



Table 2. Studied compositions

	Xylose (Xyl)	Furfural (Furf)	Lactic acid (LA)	Choline chloride (ChCl)
Molecular structure				
Molecular formula	C ₅ H ₁₀ O ₅	C ₅ H ₄ O ₂	C ₃ H ₆ O ₃	C ₅ H ₁₄ ClNO
Molecular weight [g mol⁻¹]	150.13	96.08	90.08	139.62
Stokes radius (r_S)[nm]	0.325	0.44	0.22	r _{S,Ch+} ≈ 0.315 [33], r _{S,Cl-} = 0.121
pKa	12.15	No dissociation	3.8	Strongest acidic: 13.97 Strongest basic: -3.2
log(K_{ow})	-1.98	0.41	-0.72 for ChCl-LA DES	
Concentration in undiluted model				
DES black liquor [mol L⁻¹]	0.16	0.16	7.0	3.5
(g L⁻¹)	(24.0)	(15.4)	(630.6)	(488.7)

In Eq. 1, the concentrations $C_{i,p}$ and $C_{i,f}$ refer to the concentrations of component i in the permeate and in the feed, respectively.

We found in our studies that xylose rejection by RO membranes is possible, while the LA by ChCl permeate concentration ratio should be close to that in the feed. Consequently, a solution flux corresponding to a dilution between 10x and 20x offers the most advantageous separation behavior among the tested dilution factors. An almost complete splitting of the incoming stream into a DES stream into a Xyl stream and a separate DES stream can be done if the final retentate stream is re-diluted and fed into another membrane separation stage using a concept similar to diafiltration.

A similar analysis was done for furfural, a typical breakdown product from hemicellulose. Opposite to the trend seen for xylose, furfural showed the lowest rejection ratio among the three components, showing RO membranes are not an interesting approach for separation of Furf from the DES. Nevertheless, furfural-like components may be separated by LLX with 2-MTHF.

With water as diluent, also the solute-DES interaction was studied. What can be concluded is that due to interaction of Xyl with LA and Furf with LA, rejection ratios can be increased.



Next to water as diluent, also aqueous ethanol, aqueous methanol and aqueous acetone were applied as diluents, and for aqueous acetone and aqueous methanol the separation for xylose was improved, while for furfural, none of the options improved the separation.

The requirement to dilute the DES appears undesired at first because additional water will be a burden for the energy requirement in the overall process. However, it should not be forgotten that during the filtration and washing of the pulp after the pulping stage, already a significant dilution takes place. Based on the work here reported, we propose to not use ethanol in the washing, but acetone.

Further studies with the membrane are ongoing in a separate project, and intended to form together with the here presented results a membrane-based separation opportunity to regenerate DES. Importantly, it should be added that concentrations of sugars have always been low in measurements we did on DES dark liquors, which we ascribe to conversion that is already happening during the pulping. To understand this, we have also carried out research on the alternative recovery option, via in-situ conversion. This is reported in the next section.

Conversion studies for *in situ* conversion of sugars followed by extraction

It is well-known that both cellulose and hemicellulose can degrade into their monomeric sugars, and that these are themselves not highly stable under pulping conditions (130 °C). The conversion via glucose and xylose into HMF and furfural, but eventually into humins is given in Figure 4.

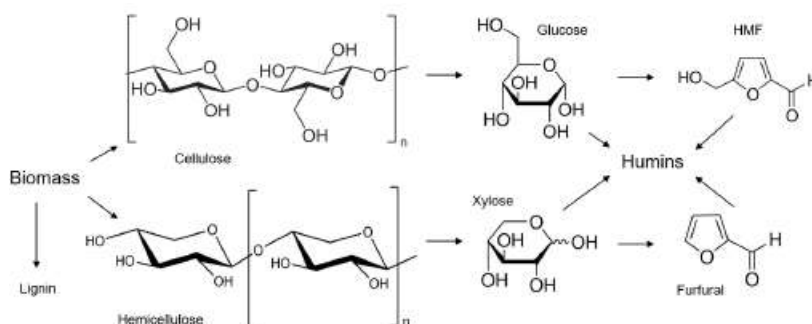


Figure 4. From biomass to humins {adapted from: Alice Mija, Jan C. van der Waal, Jean-Mathieu Pin, Nathanael Guigo, and Ed de Jong. Humins as promising material for producing sustainable carbohydrate-derived building materials. *Construction and Building Materials*, 139:594 - 601, 2017}.

From Figure 4 it follows that it is important to limit the conversions so that no or hardly any humins are formed, as they do not represent much value. Although much work has been reported on conversions of biomass and their sugars in aqueous environments, not much is known about the reactive pathways in DES. The conversion of glucose proceeds through isomerization into fructose, and therefore, we have studied conversion of fructose in a 1.5:1 LA: ChCl DES mixture.

Based on our results, we conclude that high fructose conversions can be achieved in short times, and that recovery of HMF as valuable byproduct is certainly possible.



Lignin production

The pulping method using Deep Eutectic Solvents (DESs) as developed in the PROVIDES consortium has been applied to produce lignin for further characterization. According to the procedure, 3 hours cooking at 130°C was applied. After the cooking, fibers were isolated by filtration, and the DES black liquor was collected as filtrate. The lignin was isolated from the DES black liquor by extraction with organic solvent 2-methyl tetrahydrofuran (2-MTHF), as explored at mg scale by the University of Twente within the PROVIDES consortium. Three types of lignin were produced, **(1)** from Spruce wood by pulping with [lactic acid – choline chloride] 10:1 molar ratio DES, **(2)** from Spruce wood by pulping with [malic acid – tetraethylammonium chloride] 2:1 molar ratio DES and **(3)** from Eucalyptus wood by pulping with [lactic acid – choline chloride] 10:1 molar ratio DES. After several experimental runs, a total of 35 g lignin from **(1)** was obtained, 10 g lignin from **(2)** and 12 g lignin from **(3)**.

Communication and Dissemination actions

Project webpagina: as part of the DES Cluster page <https://ispt.eu/projects/deep-eutectic-solvents/>

Presentation: 7th International Conference on Organic Solvent Nanofiltration (OSN), 28-30 October 2019, Enschede, The Netherlands. Presentation on *The recovery of DES by Nanofiltration using organic solvents*

Poster presentation: The Netherlands Process Technology Symposium (NPS16), 30-31 October 2019, Eindhoven, The Netherlands. Poster on *The recovery of DES by Nanofiltration using organic solvents* presented.

Scientific article: Smink, Dion, Sascha RA Kersten, and Boelo Schuur. "Recovery of lignin from deep eutectic solvents by liquid-liquid extraction." *Separation and purification technology* 235 (2020): 116127.

ISPT annual conference – yearly presence at the ISPT annual conference - November 2018 and 2019 at Prodentfabriek (20 Oude Fabriekstraat, Amersfoort Utrecht, Netherlands).

Newsitem and linkedin post announcing release of the final public report – planned for December 2020, will be available via: <https://ispt.eu/projects/deep-eutectic-solvents/>

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