

*Public summary of PhD-thesis of Carin Dietz*

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## **Biomass-based solvents for greener, lower-energy bioprocesses**

Our society still strongly depends on fossil fuels. If we care about our planet, we will have to find renewable resources, such as biomass, and use them as energy source and as feedstock for products. Biomass can be used to produce many platform chemicals, such as furfural (FF) and hydroxymethylfurfural (HMF). These are valuable intermediate products for pharmaceutical precursors, lubricants, adhesives, solvents (e.g. THF) and plastics.

Biomass-based furfural synthesis starts by transforming cellulose and hemicellulose from biomass into monosaccharides (pentose) through acid hydrolysis. These monosaccharides can then be converted into furfural. The resulting solution contains only a small fraction of furfural, so a separation step is required to obtain furfural in higher concentrations. Separation commonly uses distillation, which has a high energy consumption and uses organic solvents, which are volatile and toxic and pose risks for human health and the environment.

Deep eutectic solvents (DESs) are new bio-based designer solvents that can potentially replace organic solvents. They barely evaporate and are non-toxic and tunable. Since they are created by simply mixing substances, their easy preparation makes them relatively cheap. The focus of this thesis is to develop and test new bio-based solvents for extracting FF and HMF out of aqueous solutions.

A DES is a homogenous mixture of substances that, when put together in exactly the right ratio, melt or solidify at the same melting temperature, which is much lower than the melting temperatures of the individual substances. To investigate new hydrophobic DESs, we screened 507 combinations of plant-derived solids, resulting in 17 hydrophobic DESs. We then measured all their physicochemical properties. Their sustainability and applicability were assessed against four main criteria: the difference in density of the DES after it is mixed with water, the viscosity of the DES, the amount of DES that dissolves in water and the pH of the water upon mixing.

The total vapor pressure – a measure for volatility – of the new hydrophobic DESs was measured and it was confirmed that the total vapor pressures of the hydrophobic DESs are indeed very low in comparison to the vapor pressures of commonly used volatile organic solvents like toluene. We also managed to successfully predict the total vapor pressures of the hydrophobic DESs with Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT).

Hydrophobic DESs selectively extract FF and HMF from aqueous reaction solutions without extracting any of the monosaccharides that are also still present in the reaction mixture. This selective extraction is based on the DESs' diffusion coefficients, which we were also able to successfully predict with Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT). These predictions will help save a lot of time in future projects to develop DESs.

After a DES is used to extract a platform chemical from solution, it needs to be regenerated for reuse by breaking the bond between the DES and the furfural. To decrease the energy required for the regeneration of DESs, we incorporated the DESs into a polymeric membrane support. The FF/HMF synthesis reaction takes place on one side of the membrane. As the FF/HMF is formed, it adheres to the DES in the membrane. At the other side of the membrane, a stripping gas removes the FF and

HMF from the DES, thereby both isolating the reaction products and regenerating the DES without the use of a vacuum distillation step. The use of the liquid-supported membrane is very interesting for low-energy in situ isolation of FF and HMF from aqueous solutions.

Overall, the new bio-based solvents are a good alternative to organic solvents. They are tunable, more sustainable, less volatile and cheaper to produce. In addition, they decrease furfural degradation in the process and increase the production yield.

*Title of PhD-thesis: Solvent development for recovery of furfural and hydroxymethylfurfural from aqueous biorefinery solutions. Supervisors: Fausto Gallucci and Martin van Sint Annaland, both Eindhoven University of Technology. Co-supervisor: Maaike Kroon (Khalifa University).*

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