Institute for Sustainable Process Technology

Screening of Deep Eutectic Solvents (DES) for the fractionation/delignification

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Summary

The aim of this project was to develop a fast screening process to study the delignification capability of novel Deep Eutectic Solvents. Although acidic, basic and neutral conditions were studied, the focus was especially on neutral and alkaline systems. Fast screening was done using a heat block system and different analytical methods to determine the lignin content were studied.

Not all studied solvents did stand alkaline conditions (as imposed by adding alkaline additives) and degradation was observed. The best method to determine the lignin content was conventional composition analysis which is rather time consuming analysis. A lot faster method, UV-Vis spectroscopy at 280 nm, resulted in too high yields for soluble lignin. It is assumed that the degradation products are interfering the absorption.

The tested alkaline systems were able to dissolve up to 25 % of original lignin based on conventional composition analysis of the undissolved wood meal. Although solvent systems were able to delignify to some extent, the delignification degree was not enough to produce separated fibres. The solvent systems were not particularly selective towards lignin (also hemicellulose was dissolved). To continue with alkaline systems, the solvent system is advised to:

- Have good delignification ability,
- Be selective for lignin,
- tolerate alkaline conditions.

Introduction

The aim of the ISPT DES cluster was to develop an innovative lignocellulose pulping process based on Deep Eutectic Solvents. The overall objective of the ISPT DES cluster is (2030):

- Total process concept producing high quality cellulose that has a 40% lower energy intensity and a 80% lower CO2 footprint compared to the combined conventional kraft process and fossil based chemicals production;
- Business case of the total concept that proves running costs that are lower than the conventional kraft process. Capital investments should be significantly lower at similar mill size.

One of the key parameters is to isolating high quality cellulose fibres comparable to kraft fibres in strength and bleachability. While good progress is made in energy efficiency and recovery, the isolated cellulose fibres so far seem inferior in quality. Recently it was suggested that the DESs that were selected and used so far to get high delignification rates at low energy consumption will not be able to delignify without cellulose degradation. It is therefore proposed that new DESs are to be found.

In order not to further delay the follow-up research, a fast screening and selection of DESs is needed. That is the subject of the underlying project.

Discussion

a. Results

The first tested DES systems were composed of choline chloride (ChCl) and ethylene glycol (EG) in the molar ratio of 1:1 with different acidic additives. These acidic systems were found to delignify wood meal (Heptane Soxhlet-extracted Wiley-milled spruce). It was decided not to continue with acidic systems as they are known to degrade cellulose and by-products like furfurals are formed.

The extensive screening was then carried out for neutral and alkaline systems. All the experiments were carried out at 130 °C for 3 h.

- When ChCl:EG was tested with NaOH addition it was found that ChCl did not tolerate alkaline addition and the DES systems itself degraded. Thus, only EG was tested with various alkaline additions such as NaOH, Na2CO3, KOH and K2CO3.
- Besides EG, also 1,6-hexanediol and glycerol were tested. However, with 1,6-hexanediol phase separation was observed while systems with glycerol formed foams.
- Also different DES systems like EG:NaCl, EG:urea, EG:N-Benzylaniline, EG: 1,4-diaminobutane and EG: DL-1-phenylethylamine were tested. However, these systems were not more effective than EG with alkaline additives or phase separation was observed.

The conventional composition analysis of the extraction residue was found to be the most reliable method to determine the dissolved lignin content.

- In general, it was found that higher alkali charge dissolved more wood meal. Different alkaline additives did not differ much from each other. It was noted that 0.025 wt% of basic additive was not enough to neutralize the acetyl groups and alkali binding groups in wood, and therefore the filtrate was acidic. The highest amount of dissolved lignin in alkaline conditions (2.5 wt% alkaline addition) was 25 % of the original lignin. Thus, no significant delignification was observed and the delignification degree was not enough to produce separated fibres.
- Based on the composition analysis, the solvent systems were not selective towards lignin. Solvents removed lignin together with hemicellulose.,Especially the content of mannose and galactose decreased from the wood meal residue. The yield of undissolved wood meal was 75 %.

b. Bottlenecks

Acidic mixtures lead to the formation of degradation products, such as furfurals, as side reaction. These products overlap at 280 nm in UV-Vis spectrum making the detection of lignin challenging.

Also in the alkaline mixtures some overlapping absorbance at 280 nm was observed.

It was also observed that precipitation of lignin from the filtrate is not a reliable method to determine the lignin content at small scale experiments. From the methods tested, it seems that the conventional composition analysis is the most reliable method to determine the lignin content. Unfortunately, this method is too time-consuming and thus not suitable for fast screening.

There were some technical issues arising during the development and execution of fast screening. First of all, it was observed that the systems with ChCl did not stand too alkaline systems, and therefore these systems clearly degraded (observed as smell, darkening of the solutions and by UV-Vis spectroscopy). It was also observed that some solvent systems even without ChCl degraded during the cooking, i.e. EG color change was detected with 2.5 wt% NaOH and KOH addition indicating degradation. In UV-Vis spectroscopy method, the absorbance of solvent degradation at 280 nm could be taken into account with baseline correction. However, despite the baseline correction, it was observed that UV-Vis spectroscopy method was not reliable when the results were compared to the conventional composition analysis. Finally, some of the tested amine samples i.e N-benzylaniline formed two phases with EG.

There was also an issue with amines being too explosive and toxic. Moreover, due to the small scale, the analytical error is relatively high.

It was also learned that low alkaline addition was not able to keep the pH at alkaline level. Thus higher alkalinity was applied..

c. Application perspective

d. Alkaline systems and pulping are known to be a potential approach to produce high quality cellulosic fibres without extensive degradation. Possible spin-off

To continue the research with alkaline DES systems, the solvent systems should ensure:

- Good delignification ability,
- Selectivity,
- Tolerance of alkaline conditions.

Fit with TKI program:

Programmalijn 1: CO2 neutral industrial heat system. The DES delignification should become far more energy-efficient compared to the current kraft pulping proceses as to enable lignin to be utilized for other purposes (either allowing other industrial heat systems to become CO2 neutral or as a valuable biobased feedstock for chemicals to replace fossil feedstock)

Efficient process technology. Separation technology and process intensification. The DES based delignification is an advanced separation technology with designer solvents. The aim is to isolate in a much faster and less energy-intensive way, as to significantly reduce the energy consumption.

Communication / dissemination

Communication /dissemination of this project is a part of the DES Cluster communication/dissemination and the following activities :

- Poster at the ISPT Annual Conference on the 14th of November 2019
- News item announcing the final public report of the project (pending)
- This final public report will be available on the DES project webpage at the ISPT webpage: https://ispt.eu/clusters/deep-eutectic-solvents/
- https://ispt.eu/clusters/deep-eutectic-solvents/ - webpage with the general description of the research in the cluster, news on upcoming events and public reports/publications of the project.

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