**Recovery of lignin from deep eutectic solvents by liquid-liquid extraction**

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**Highlights**

* Lignin was recovered from DES by liquid-liquid extraction
* 2-MTHF is a suitable, bio-based extractant for lignin
* Addition of water greatly enhances lignin extraction by 2-MTHF

**1. Introduction**

Deep eutectic solvents (DES) are composite solvents that exhibit deep eutectic behavior upon mixing, and are often biocompatible, biodegradable and have a low toxicity.[1] Regeneration of deep eutectic solvents is most often performed by precipitation of either the solute or solvent in an anti-solvent. Especially in biomass fractionation, large amounts of water are required as anti-solvent for the precipitation of lignin.[2] We propose liquid-liquid extraction as an alternative method for the recovery of lignin from DES.

 **2. Methods**

DES, solvent and any lignin were equilibrated in a shaking bath at overnight. The phases were separated and the concentrations of the DES constituents and solvent analyzed by high pressure liquid chromatography (HPLC). The lignin concentrations were analyzed as function of the molar weight by gel permeation chromatography (GPC). The lignin distribution coefficient was calculated as follows:

$$D=\frac{\left[lignin\right]\_{Solvent}}{\left[lignin\right]\_{DES}}$$

**3. Results and discussion**

The equilibria between the lactic acid - choline chloride DES and 2-MTHF were determined at three different temperatures. The phase equilibria are shown in figure 1. From this figure it can be seen that the temperature dependence of the equilibria is very small. Also, high amounts of choline chloride are required to create a phase split. All DES phases contained more than 27 wt.% choline chloride, but no choline chloride was found in the DES phases.

The lignin distributions between the 1.7:1 lactic acid - choline chloride DES and 2-MTHF were determined at 50 °C. Since water has a great influence on the lignin solubility in both DES[3] and low-hydrogen bond accepting solvents -such as 2-MTHF-, its influence on the lignin distribution was studied. It was found that the distribution coefficient increases with increasing amounts of water. Also, the effect of water is greater on the extraction of the higher molar weight fractions of the lignin. The results are shown in figure 2.

  

**Figure 1.** Phase diagram with liquid-liquid equilibrium data between choline chloride, lactic acid and 2-MTHF at 25, 50 and 75 °C. The axis show the mass fractions of the constituents.



**Figure 1.** Distribution of lignin between DES and 2-MTHF at 50 °C. Various amounts of water were added to the DES: 50% (green-solid), 25% (yellow-dashed), 10% (blue-dotted), 5% (red-dash-dotted) and dry (black-dot-dot-dashed). For the parts of the green line that are out of the graph, no lignin fractions were found in the DES phase, and thus the distribution coefficient is infinite.

**4. Conclusions**

2-MHTF is a suitable extractant for lignin from DES. Addition of choline chloride to the DES is required to form two liquid phases and addition of more choline chloride decreased leaching of lactic acid to the 2-MTHF phase. The extraction lignin was studied and increases with increasing amounts of water.

**References**

1. Macário, I.P.E.; Jesus, F.; Pereira, J.L.; Ventura, S.P.M.; Gonçalves, A.M.M.; Coutinho, J.A.P.; Gonçalves, F.J.M., Chemosphere 212 (2018) 890-897
2. Alvarez-Vasco, C.; Ma, R.; Quintero, M.; Guo, M.; Geleynse, S.; Ramasamy, K.K.; Wolcott, M.; Zhang, X., Green Chem. 18 (2016) 5133–5141
3. Soares, B.; Tavares, D.J.P.; Amaral, J.L.; Silvestre, A.J.D.; Freire, C.S.R.; Coutinho, J.A.P., ACS Sustain. Chem. Eng. 5 (2017) 4056–4065