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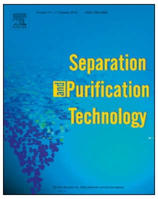

Recovery of lignin from deep eutectic solvents by liquid-liquid extraction

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ABSTRACT

After biomass fractionation using deep eutectic solvents (DESs), solvent recovery is an essential step. Laboratory routine is to precipitate lignin using cold water, however large amounts of water are required, resulting in energy intensive operations. Therefore, we propose liquid-liquid extraction as alternative method for industrial applications, and have studied this to recover lignin from a DES consisting of lactic acid and choline chloride, which we applied in various ratios. In this study six solvents were investigated for this purpose, from which 2-methyl tetrahydrofuran (2-MTHF) was selected for further studies. The phase equilibria between the DES and 2-MTHF were determined at 25, 50 and 75 °C. At least 30 wt% choline chloride in the DES was required to form two phases. Addition of more choline chloride decreases the mutual solubility of 2-MTHF and lactic acid. The overall equilibrium lignin distribution between DES and solvent did not change much with varying DES compositions, but the distribution was dependent on the molar mass of lignin. The low molar weight fractions showed a distribution coefficient around 1, while for the heavy fractions the distribution coefficient was below 0.1. Addition of water changes the system greatly, and high molar mass lignin extraction is tremendously enhanced. At 25 wt% water in the DES, the minimum distribution coefficient was 4, allowing effective extraction of lignin from DES by 2-MTHF.

1. Introduction

DESs are composite solvents that exhibit deep eutectic behavior upon mixing the constituents, meaning the melting points of these mixtures is reduced considerably more (> 50 °C) than would be the case for ideal mixtures [1,2]. These solvents can easily be prepared in numerous ways by combining a hydrogen bond donor and acceptor [3] and are often biocompatible, biodegradable [4] and can have a low toxicity [5].

Lignocellulose can be converted into cellulose fibers and lignin by delignification technologies. The obtained cellulose pulp can be used for paper production, production of other materials, or can be converted to bio-ethanol or other platform chemicals [6–8]. Lignin is an aromatic biopolymer with advocated potential for the chemical industry and current research is focusing on lignin valorization [9]. The traditional pulp mills used in the paper making industry make use of kraft pulping, in which the extracted lignin is burnt in the solvent recovery boilers [10]. The kraft mills are highly integrated and energy effective plants [11]. Nevertheless, over the past decades continued scientific efforts have been made to develop alternative pulp mills, in which lignin could be obtained as byproduct of the cellulose fibers [12–14]. Recently, DESs have often been used for biomass delignification [15–21]. DES based processes offer many advantages over the traditional kraft or organosolv processes. The major disadvantage of kraft pulping is that the produced lignin contains sulfur, which makes valorization difficult, while organosolv processes requires high amounts of organic solvents, which are often volatile and flammable [22].

Regeneration of DESs is most often performed by precipitation of either the solute [23] or solvent [24–25] in an anti-solvent. Especially in biomass fractionation, large amounts of water are required as anti-solvent for the precipitation of lignin [16]. To recover the DES, these anti-solvents forming a homogeneous mixture with the DES must be evaporated from the DES, which is very energy intensive. Therefore, alternative separation techniques are desired, and will aid industrial applicability of DESs. Yoo et al. recovered phenolic compounds from DES using resins [26], but required large solvent volumes to elute the extractants from these resins. Tian et al. recovered flavonoids from DESs by sorption, but this required high dilutions of DES in water [27]. Liang et al. used electrodialysis membranes to recover DESs after biomass fractionation [28], but needed high dilutions of DES in water to achieve this.

Liquid-liquid extraction is a separation technique that can be energy efficient [29], and has been reported for biorefineries, e.g. for lipid

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extraction from microalgae [30,31] and fractionation of pyrolytic bio-oils [32,33]. Stiefel et al. investigated equilibria of lignin between 2-methyl tetrahydrofuran (2-MTHF) and alkali solutions [34] and showed that lignin can be recovered by liquid-liquid extraction (LLX). Hu converted fructose to 5-HMF in DES and showed the product can be recovered later on by LLX with ethyl acetate [35]. In line with these promising results with LLX, we investigated the possibilities to recover lignin from DESs by LLX.

In this study we performed a solvent screening to find suitable solvents for extraction of lignin from a DES comprised of L-lactic acid (LA) and choline chloride (ChCl). Of primary importance for LLX is that the solvents are not miscible with the DES, or at least show limited mutual miscibility. Then, a high lignin distribution to afford a low solvent to feed ratio is beneficial for the required energy improving the sustainability. Because a low environmental footprint and low toxicity is highly desired, also the (eco)toxicity was evaluated. In the screening procedure two phase formation was investigated first, just as the sustainability and finally the lignin extractability of the suitable solvents. For the selected DES - solvent combination, the phase behavior was studied and further studies were performed on the lignin distribution between the solvent and DES.

2. Experimental Section

2.1. Materials

Lactic acid (> 85%), choline chloride (> 98%), 1,4-dioxane (99.8%), 2-MTHF(> 99%, 250 ppm BHT), γ-valerolactone (GVL, 99%), Guaiacol (natural, > 99%), cyclopentyl methyl ether (CPME, > 99.9%, 50 ppm BHT) and Cyrene (99%) were purchased from Sigma-Aldrich. Crystalline L-lactic acid was kindly donated by Corbion. Eucalyptus globulus wood chips were kindly supplied by The Navigator Company.

2.2. Solvent screening

Screening of solvents for liquid-liquid extraction of lignin from DES requires a lignin-loaded DES, which was accomplished by using DES comprised of ChCl and LA in a 1:10 M ratio that was previously used in pulping experiments [15]. In these pulping experiments, 50 g of eucalyptus chips were treated by 1 kg DES for 8 h at 120 °C. Afterwards, the DES with dissolved lignin was filtered from the cellulose fibers over a 50 µm steel mesh. In the LLX solvent screening experiments, 5 mL solvent was added to 2.5 mL DES obtained from pulping. The vials were shaken at room temperature over-night at 200 rpm in a Julabo SW22 shaking bath. Two phase formation was determined visually. When two phases were observed, an estimate of the lignin distribution over the phases was made using UV–vis absorption spectrometry (aromatics from lignin show much stronger UV absorbance than the solvents). To facilitate this, the settled phases were separated and diluted in ethanol. The lignin concentrations were estimated by UV–VIS absorption at 320 nm using a Hach Lange DR5000 spectrophotometer. The overall average distribution coefficients of lignin species measured at 320 nm were calculated by dividing the concentration in the solvent phase by the concentration in the DES phase. Next to the averaged distribution as determined for the solvent screening experiments, for the selected solvent also the lignin molar weight distribution was determined in both the original DES and in the organic solvents after extraction were determined by gel permeation chromatography (GPC). The lignin molar weight distribution in the DES raffinates could not be determined since they were not fully soluble in the GPC eluent resulting in solids deposition on the column.

2.3. 2-MTHF-DES phase equilibria

3 g 2-MTHF and 3 g DES composed of crystalline LA and ChCl were added to a glass vial. This vial was shaken at 200 rpm at over night at 25, 50 or 75 °C in a Julabo SW22 shaking bath. The two phases were allowed to settle and were separated. Concentrations of ChCl, LA and 2-MTHF were analyzed by high performance liquid chromatography (HPLC). An Agilent 1200 system was equipped with a Hi-Plex-H column operated at 60 °C and a refractive index detector at 55 °C. 5 mM sulfuric acid in water was used as mobile phase with a flowrate of 0.6 mL/min.

2.4. Lignin extraction experiments

Lignin extraction experiments were performed using lignin that was previously recovered from the DES by precipitation. Precipitation was done by addition of three g water per g DES. The lignin was separated by centrifugation, washed twice with water and dried in vacuum. Crystalline lactic acid, choline chloride and 2-MTHF were added to a flask to form 3 g of DES comprising of ChCl:LA ratios between 1:1.1 and 1:2.4, and 3 g solvent phase at equilibrium. 50 mg lignin that was previously obtained by cold water precipitation from another portion of DES after the same pulping procedure was added per vial. For the experiments with varying water contents a 1:1.7 ChCl:LA DES at equilibrium was used. 0.15–3 g water was added to the vials to create water contents varying from 5 to 50 wt% based on the DES. These vials were shaken at 200 rpm at 50 °C over night in a Julabo SW22 shaking bath. The phases were separated and analyzed by GPC.

2.5. GPC analysis

For GPC, an Agilent 1200 series was used with a refractive index detector and a UV detector operating at 254 nm using 3 GPC PLgel 3 µm MIXED-E columns in series. The column was operated at 40 °C and a 95:5 (v:v) tetrahydrofuran and water mixture was the solvent at a flowrate of 1 mL/min. Molecular weight distributions were calibrated using polystyrene solutions having molecular weights ranging from 162 to 27,810 Da. The product of the UV absorbance and the dilution factor were used as measure for the lignin concentrations in both the DES and 2-MTHF phase. The distribution coefficients were calculated by dividing this product for the 2-MTHF phase by the product for the DES phase. More information on the method and reproducibility can be found in the supplementary data.

2.6. Karl-Fischer titration

The water content of the DES used in the pulping experiment was determined by Karl-Fischer titration using a Metrohm 787 KF Titrino. Hydranal composite 5 (5 mg water/mL) was titrated from a 20 mL burette in a 3:1 (v:v) mixture of methanol and dichloromethane. The sample was measured in duplo with a relative error < 1%.

3. Results and discussion

3.1. Solvent screening

The first requirement for a suitable LLX solvent is the formation of two phases. Considering the high polarity of the DES phase, organic solvents that have an apolar character should be accessed. For lignin extraction from DES, in order to make a real benign process, it would be preferable if the solvent could be bio-based. Six solvents were selected for this screening that all have limited polarity. The first solvent investigated is dioxane, which is not bio-based, but serves as benchmark, since this cyclic ether is commonly used as a solvent for dissolving lignin [36,37]. Although the acute toxicity of dioxane is relatively low (5170 mg/kg is lethal for rats) and it is bio-degradable [38], because dioxane is produced from petrochemicals [39], another cyclic ether was also investigated, namely 2-MTHF [40]. This solvent is produced from pentosan [41], does not seem to be genotoxic or mutagenic [42,43], and is used in the OrganoCat process to extract lignin [34]. Also, the ether CPME was accessed, as it has been suggested that this solvent can

Table 1
Overview of solvent screening with 6 solvents for liquid-liquid extraction with lactic acid choline chloride DES. Miscibility with DES, solubility of lignin and bio-based origin are shown.

Solvent	2 phase formation	Bio-based	Distribution coefficient (–)
1,4-Dioxane	Yes	No	0.46
2-MTHF	Yes	Yes	0.31
GVL	No	Yes	–
Guaiacol	No	Possibly	–
CPME	Yes	Possibly	0.11
Cyrene	No	Yes	–

be produced from biological sources [44,45], and its higher boiling point and greater stability and narrow explosion range make a greener and safer alternative to dioxane [46]. Guaiacol was selected as an aromatic solvent, which may be produced by hydrocracking of lignin [47], or from pyrolytic bio-oils [48]. GVL [49] and cyrene [50] were also selected as bio-based ketone solvents, which are produced from hemicellulose and cellulose.

The selected solvents were equilibrated with ChCl – LA (1:10) DES and two phase formation was determined visually. GVL, guaiacol and cyrene turned out to be miscible with the DES, and are therefore not suitable for liquid-liquid extraction using this DES. For the solvents that did form a biphasic system, the overall distribution coefficient of the lignin over the solvent phase and the DES phase (total lignin in solvent over total lignin in DES) was estimated by UV–VIS spectroscopy, see Table 1. The highest distribution coefficient was found for dioxane, followed by 2-MTHF and CPME showed the lowest overall average lignin distribution coefficient.

To get further insight in the lignin distribution, the molar weight distribution of the extracted lignins was compared to the molar weight distribution of the original lignin in DES. The molar weight distributions are plotted in Fig. 1, from which it was found that both dioxane and 2-MTHF could extract lignin with a broad range of molar weight fractions from the DES, while CPME could only extract the lower molar weight fractions. Presumably, the lower polarity of CPME compared to dioxane and 2-MTHF reduces its ability to extract these lignin fractions. Although this behavior may be useful in the fractionation of lignin when low molar weight fractions are desired in further applications, it is in the current study left out of consideration since the objective of this study was to find a solvent that can recover as much lignin from the DES as possible. Considering the bio-based nature of 2-MTHF, in combination with the reasonable lignin distribution, it was decided to investigate the lignin extraction in more detail for 2-MTHF.

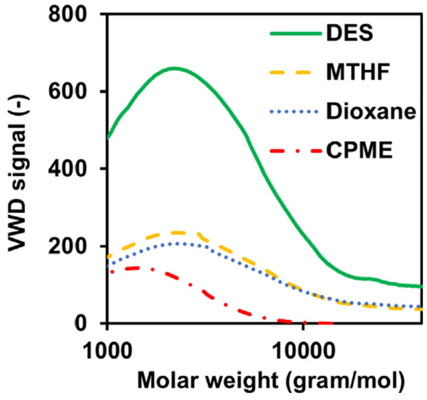

Fig. 1. Molar weight distributions of the lignin originally dissolved in the DES and the lignin extracted by the solvents. Raw variable wave detector (VWD) signals are shown. The solid green line shows the molar weight distribution of lignin in the original DES and the dashed yellow, the dotted blue, and dash-dotted red lines the molar weight distributions of lignin in 2-MTHF, Dioxane and CPME after extraction. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.2. Phase behavior studies for 2-MTHF with ChCl and LA

Before the extraction of lignin was studied further, the phase behavior between DES and 2-MTHF was studied further since the constituents of the DES may have a different partitioning between the DES and solvent [51]. Therefore, the partitioning of the DES constituents and the solvent were determined at three temperatures. The phase equilibrium results are shown in Fig. 2. From this figure it follows that the temperature dependence of the equilibria is very small, because the tie lines are similar at the different temperature measurements. Furthermore, lactic acid concentrations in the 2-MTHF phase after equilibration are significant with fractions from 12 to 36 wt%. Where the lactic acid showed significant partitioning into the 2-MTHF phase, choline chloride hardly transferred, and as a result all DES phases contained more than 30 wt% choline chloride, but no choline chloride was found in the 2-MTHF phases. A mixture comprised of 14 wt% choline chloride, 36 wt% 2-MTHF and 50 wt% lactic acid formed a homogeneous liquid. From a process point of view, the LA that leached to the 2-MTHF must be washed from the produced lignin when the 2-MTHF is evaporated. The amount of LA leached to the 2-MTHF decreased with increasing amounts of ChCl. During pulping, the ChCl concentration is an important factor in the delignification rate [15], and addition of more ChCl to a 10:1 LA to ChCl DES decreases the delignification rate. Therefore, the optimal amount of choline chloride -from a process point of view- will be a trade-off between the delignification rate and the amount of lactic acid leaching to the solvent phase.

3.3. Influence of DES composition on lignin extraction

Since the DES composition is an important factor in the process design, the distribution of lignin between the DES and solvent was investigated for 4 different DES compositions varying in ChCl to LA molar ratio from 1:1.1 to 1:2.4. The results for these trials are shown in Fig. 3. For every DES composition, the distribution coefficient of low molecular weight fractions is higher than the high molecular weight fractions, but does not seem to be influenced much by the DES composition. It is remarkable that all distribution coefficients are lower than the distribution coefficient obtained from the initial screening. The initial screening was performed using a DES that was directly obtained from a biomass fraction experiment, while the experiments in this series to investigate on the effect of the DES composition were performed using lignin precipitated from this biomass fractionation experiment. The lower distribution compared to the distribution obtained with the DES directly from the pulping experiment is possibly caused by a difference in nature of the UV absorbing species present in the DES, and the lignin that did precipitate. During pulping, (hemi)cellulose from the wood matrix can be hydrolyzed to form glucose and xylose, which may react further to (hydroxymethyl)furfural and humin, which are also UV responsive. Analysis by HPLC showed that (hydroxymethyl)furfural was extracted by 2-MTHF, while glucose and xylose remained in the DES. These compounds may likely not precipitate from the DES, and are thus not present in the further studies using redissolved lignin that was first precipitated. These components will thus interfere with the results of the initial screening, but not with the further studies using precipitated lignin [35]. Also, the DES used in the solvent screening experiments after fractionation contained 12.8 ± 0.1 wt% water (as determined by Karl-Fischer titration), while the DESs used in these lignin extraction experiments were ambient dry. The presence of water in the system may also have a strong influence on the lignin distribution.

3.4. Influence of water

The lignin distribution was determined at 5 different water concentrations in the DES and the results are shown in Fig. 4. The lignin

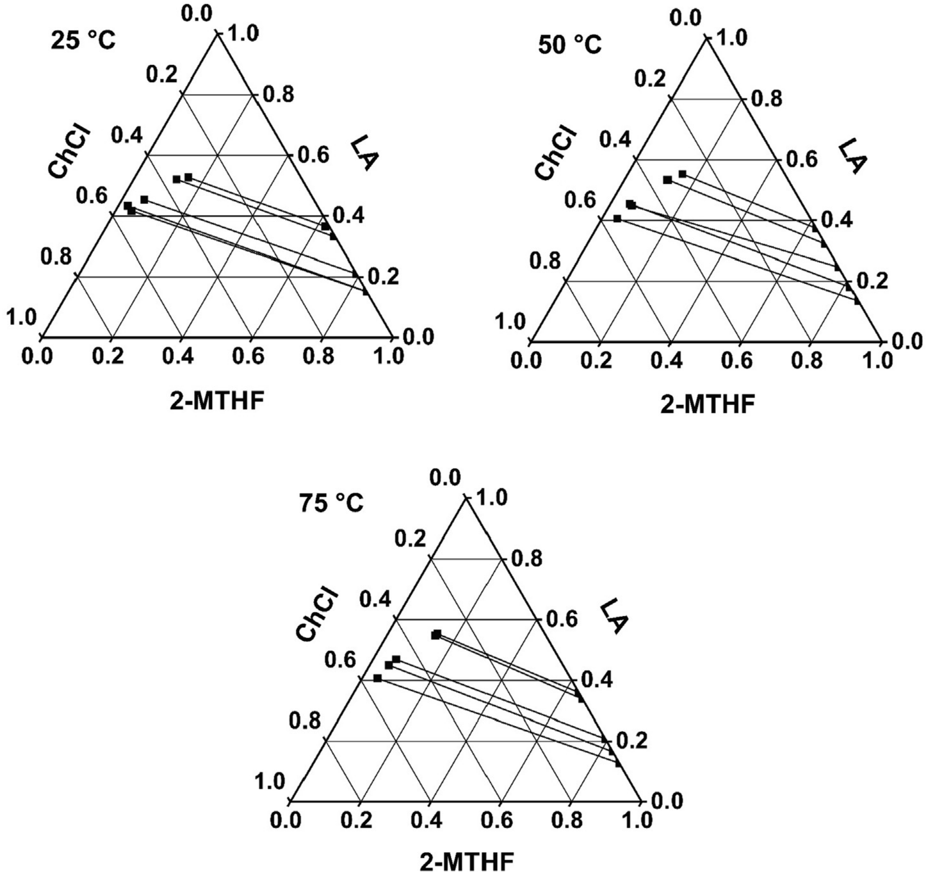

Fig. 2. Phase diagram with liquid-liquid equilibrium data between choline chloride, lactic acid and 2-MTHF at 25, 50 and 75 °C. The axis show the mass fractions of the constituents.

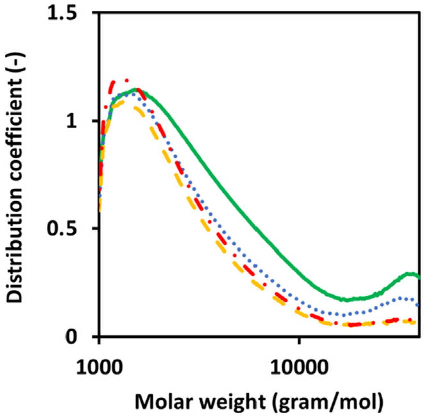

Fig. 3. Distribution of lignin between DES and 2-MTHF at 50 °C. Choline chloride to lactic acid equilibrium molar ratios: 1:2.4 (green-solid), 1:1.7 (blue-dotted), 1:1.4 (yellow-dashed) and 1:1.1 (red-dash-dotted). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

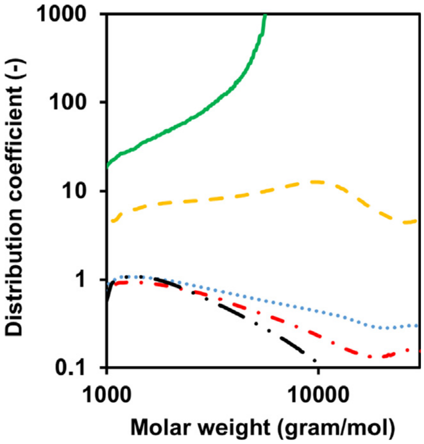

Fig. 4. Distribution of lignin between DES and 2-MTHF at 50 °C. Various amounts of water were added to the DES: 50% (green-solid), 25% (yellow-dashed), 10% (blue-dotted), 5% (red-dash-dotted) and dry (black-dot-dot-dashed). For the parts of the green line that are out of the graph, no lignin fractions were found in the DES phase, and thus the distribution coefficient is infinite. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

extraction by 2-MTHF is greatly enhanced by the addition of water. Especially the extraction of the higher molar weight fractions improves more upon the addition of water than the extraction of the lower molar weight fractions. At 25 wt% water in the DES, the minimum distribution coefficient was 4, allowing effective extraction of lignin from DES by 2-MTHF using a countercurrent LLX method.

Soares et al. determined the solubility of organosolv and kraft lignin in the propionic acid – Urea DES and found the highest lignin solubility at 50% DES in water [52]. Also the lignin solubility in low hydrogen-bonding capacity solvents -such as 2-MTHF- is greatly enhanced when a little water is added to them. The presence of water thus seems to both limit the solubility of lignin in DES by interfering with the hydrogen bonds between lignin and DES, while at the same time also facilitating hydrogen bonding connections for solvents that are only hydrogen bond acceptors.

3.5. Industrial applicability

In this article we describe an alternative method for the recovery of lignin from DES by LLX. However, the addition of an extra solvent inherently increases the complexity and thus the costs of the process. Therefore, the energy saving should be significant to justify the increased complexity. For this reason, we elaborate on the potential energy savings that can be achieved by replacing cold water precipitation by LLX.

The water content is an important factor in both the pulping and the recovery stage. For example, Kumar et al. [18] found that lignin removal from rice straw increased upon the addition of small amounts of water to DES. Furthermore, many authors [15,20,21] use lactic acid syrup for the preparation of DES used for biomass fractionation, which contains around 15 wt% water. Also, wood is a hygroscopic material, meaning it will naturally contain significant amounts of water. It thus seems reasonable that the DES after pulping can contain around 25 wt% water, which allows for successful extraction using 2-MTHF without adding additional water.

Soares et al. studied the solubility of two technical lignin in mixtures comprised of water and various DES [53]. They found that the lignin solubility in a DES comprised of lactic acid and choline chloride decreased by a factor 7 when the water content was shifted from 25 to 75 wt%, which seems sufficient for industrial application. In order to achieve this shift, 2 kg of water must be added to 1 kg of pulping liquid (containing 25% water), which must subsequently be removed by evaporation. The heat of evaporation of water is 2.3 kJ/kg, meaning 4.6 kJ is required for the recovery of 1 kg pulping liquid using cold water precipitation.

In Section 3.4 we showed that the distribution coefficient of lignin is > 4 for all molar weight fraction when the DES contains 25 wt% water. This means that the minimum solvent to feed ratio is $1/4 = 0.25$. However, the lignin distribution coefficient may change during multistage extractions. Therefore, we assume a conservative solvent to feed ratio of 0.5. This means that for the regeneration of 1 kg pulping liquid, 0.5 kg 2-MTHF must be removed from the extracted lignin, for example by evaporation. The heat of evaporation of 2-MTHF is only 0.40 kJ/kg [54], meaning the heat required to regenerate 1 kg DES used for pulping is only 0.20 kJ, and since no water evaporation is necessary in this approach, a saving of over 95% compared to cold water precipitation can be achieved. Although these calculations are still preliminary, the potential savings justify further studies on recovery of lignin from DES by more complicated LLX.

4. Conclusions

2-MHTF was found as a suitable extractant for lignin recovery from a DES comprised of choline chloride and L-lactic acid. In biphasic systems with 2-MTHF, at least 30 wt% choline chloride in the DES was found because of large amounts of lactic acid being transferred to the 2-MTHF phase. The more choline chloride in the system, the lower the leaching of lactic acid to the 2-MTHF phase. The distribution of lower molar weight fractions was higher than the high molar weight fractions, and did not seem to depend on the DES composition. Also, the influence of water on lignin extraction was studied and the lignin extraction improved upon addition of water. At 25 wt% water, the lignin distribution was larger than 4 for all lignin molar weights, showing that all lignin can be recovered by LLX with a few countercurrent stages. It can thus be concluded that LLX with 2-MTHF is an industrially applicable method for the recovery of lignin from DES. For the design of a DES based biomass fractionation process all components from biomass must be recovered from the DES. For the fractionation trial described in this paper, 55% of the initial biomass is recovered as solid material by filtration and 20% of the initial biomass consists of lignin. The rest of the biomass consists of predominantly (hemi)cellulose breakdown products, which may be separated from the DES by membranes [28] or converted in-situ [35]. More research on the identification and recovery of these components is required to design a process for biomass fractionation using DES.

Declaration of Competing Interest

Herewith, all authors, including Boelo Schuur, Dion Smink and Sascha RA Kersten, state that they do not have a conflict of interest.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.seppur.2019.116127.

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