



## Effective separation, recovery and recycling of deep eutectic solvent after biomass fractionation with membrane-based methodology

Xiaocong Liang, Yan Fu, Jie Chang\*

The Key Lab of Enhanced Heat Transfer and Energy Conservation, Ministry of Education, School of Chemistry and Chemical Engineering, South China University of Technology, No. 381, Wushan Road, Guangzhou 510640, China



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### ABSTRACT

Robust membrane-based methodology with ultrafiltration and electrodialysis was employed to separate and recover the deep eutectic solvent constituents (formed with choline chloride-ChCl and ethylene glycol-EG) after biomass fractionation using hydrothermal and DES treatment. Ultrafiltration was designed for the profound removal of lignin in DES solution. Concentration of degradation products was less than 0.1 g/L when the resulting DES solution was diluted to 40 g/L of ChCl after ultrafiltration. Electrodialysis was proven effective to separate and recovery of ChCl and EG with ChCl transferred and EG retained. Recovery ratio of ChCl and EG approached 92% and 96% and purities reached 98–99% after electrodialysis treatment. Insight gained from this study suggests a green methodology for the recovery of DES constituents after biomass fractionation as well as the foundation for large-scale DES-based bio-refineries.

### 1. Introduction

Lignocellulosic biomass has been widely studied for energy application and chemical fabrication due to the exhaustion of fossil resource [1,2]. Biomass pretreatment has been extensively studied and been considered as the essential process for bio-refinery [3,4]. The fractionated components by pretreatment such as lignin, monosaccharide and polysaccharide could be materials for producing chemicals and energy conversion [5]. Besides, pretreatment products could also be fine starting-material to produce high-value chemicals and fuels by the pretreatment method of pyrolysis and following separation [6,7].

As the recent representative family of ionic liquids, deep eutectic solvents (DES) have gained more and more concern on its application for biomass pretreatment [8,9] and other bio-finery processes [10,11]. DES is a eutectic mixture generally formed by the heating of hydrogen-bond donator and hydrogen-bond acceptor with final melting point significantly lower than each component. And DES usually comprises choline and carboxylic acids or polyol [12,13]. With the traditional superiority of ionic liquids such as non-volatile and devisable, DES also displays significant advantages over traditional ionic liquids when further considering the cost and toxicity as well as the adaptability for enzyme activity in following saccharification [14]. However, application of DES in large-scale bio-refinery is still in its infancy and a lot work needs to be performed [15]. One of the significant issues for DES-

based bio-refinery is the recovery and recycling of DES after pretreatment [16].

For the purpose of large-scale operation, membrane-based methodologies should be considered for such recovery task due to their robust and low-cost features. Electrodialysis (ED) has been used in industrial fields for the oriented transfer and concentration of electrolyte chemicals [7]. Electrodialysis module works based on the selective migration of anions and cations through the regularly displayed ion-exchange membranes after voltage being applied. Research on the ED-assisted ionic liquid recovery has been reported by researchers [17–19]. Considering the presence of salt constituents within DES, electrodialysis is a considerable option for DES recovery after such biomass fractionation process according to the working principle of electrodialysis. The electrolyte constituent in DES such as choline chloride could be transferred through ion-exchange membranes, while other constituent of DES such as polyol would remain in original section due to its non-electrolyte nature. Nevertheless, DES recovery using electrodialysis has not been reported as far as we can search. At present, recovery and recycling of DES has been proven technically feasible in the extracting process of certain natural products such as polyphenols [10], flavonoids [2] and so on. While the recovery and recycling of DES involved with biomass pretreatment has been rarely studied according to the best of our retrieval, and research on this topic was mainly focused on the pretreatment effect of DES [20–22]. Besides, the potential of

\* Corresponding author.

E-mail address: [changjie@scut.edu.cn](mailto:changjie@scut.edu.cn) (J. Chang).

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electrodialysis for such recovery task also needs sufficient test and proof by repeating experiments.

Generally, DES-based biomass fractionation involves with: (i) pretreatment to dissolve specific component (ii) liquid-solid separation (iii) regeneration of the dissolved component by adding anti-solvent (iv) separation of the precipitated component [20]. Thus DES recovery after biomass fractionation was mainly influenced by the dissolution-regeneration of biomass component and the use of anti-solvents. Water has been proven effective and was frequently-used in the regeneration of lignin after DES pretreatment [23]. Obviously, the recovery of DES from the resulting aqueous solution after biomass fractionation will be the task of current research. Common strategy for DES recovery mainly focused on the direct removal of water by evaporation from the aqueous solution by biomass fractionation [24]. As the accumulation of degradation products, pretreatment efficiency of the recovered DES would get noteworthy reduction. Besides, degradation products would also result in the fouling of ion-exchange membranes and affect the ED process [25]. Deeper filtration treatment is required to remove the degradation products generated during biomass pretreatment before DES recovery. Recently, effective methods for degradation products separation including molecular distillation [26] and multi-step acid-base treatment [27] have been reported by researchers to sequentially remove lignin derivatives from bio-oil resulted by biomass pyrolysis. The use of membrane-based method in lignin-removal process would meet with the purpose of large-scale operation. Considering the molecule-weight distribution characteristics of lignin products after biomass pretreatment (generally more than 1000 g/mol), ultrafiltration treatment with the molecule-weight interception of 650 g/mol (0.65 kDa) and 1000 g/mol (1 kDa) were used for the deeper filtration treatment for resulting solutions after DES treatment.

In this study, biomass fractionation was performed with hydrothermal treatment and DES treatment to sequentially separate hemicellulose and lignin fractions from eucalyptus globulus wood. The DES was formed with choline chloride-ChCl and ethylene glycol-EG. The resulting solution after DES treatment was used for DES constituents recovery by ultrafiltration and electro dialysis

## 2. Experiments section

### 2.1. Materials and biomass pretreatment

40–60 mesh dewaxed eucalyptus globulus wood was used for pretreatment. Reagent-grade choline chloride (ChCl, 99% purity) and ethylene glycol (EG, 99.8% purity) were purchased from Sigma-Aldrich. Hydrothermal treatment for wood sample and following DES treatment for the residue obtained by hydrothermal treatment was executed for the sequential fractionation of hemicellulose and lignin [20,28]. The measurement of cellulose, hemicellulose and lignin in wood sample and residue was executed following a NREL laboratory protocol [29]. Eucalyptus globulus wood and water was mixed with the liquid to solid ratio of 8 g/g and reacted in hydrothermal reactor at 170 °C for 4 h. After hydrothermal experiment, the residue was washed with hot

ethanol and water. Abluent hydrothermal residue was oven-dried before DES treatment. DES solvent was prepared by mixing EG and ChCl with the mole ratio of 2:1 at 90 °C. 1 g hydrothermal residue was added into 20 g DES solvent and stirred at 90 °C for 24 h (see Fig. 1). The resulting mixture was filtrated by Buchner funnel and washed with distilled water. The washing liquor was also collected into the Buchner funnel filtrate. Afterwards, fixed amount of distilled water was added to precipitate lignin.

### 2.2. Preparation of standardized DES solution for DES recovery

Precipitated lignin was removed by Buchner funnel filtration or ultrafiltration. Minimate OAPMP-220 ultra (UF) membrane modules (Pall Corporation, USA) was used for ultrafiltration experiments and operated in the following conditions: 400 kPa of TMP,  $2.4 \text{ ms}^{-1}$  of cross-flow velocity and  $25 \pm 2^\circ \text{C}$  of temperature. Molecular weight cut-off of ultrafiltration experiments was 0.65 kDa and 1 kDa. The resulting filtrate was collected and defined as original filtrate. Afterwards, original filtrate was further diluted to get ChCl concentration to 40 g/L and the resulting solution was used as the standardized DES solution for DES recovery. Concentration of ChCl in aqueous solutions was measured with  $\text{Ch}^+$  using Ion Chromatograph (Dionex, DX-120). Content of ethylene glycol was determined by GC-MS (Shimadzu QP 2010 Plus, RXI-5 column) after water evaporation. In addition, concentration of biomass derivatives such as neutral sugars, uronic acids and lignin in the filtrate were determined using HPAEC and UV-VIS chromatography according to previous study [18,19].

### 2.3. Deep eutectic solvent recovery

A commercial ED stack module containing 40 pairs of heterogeneous ion-exchange membranes (AEM/CEM, with resins and divinylbenzene as the base matrix) with an effective membrane area of  $620 \text{ cm}^2$  was used in this step (IONLYZER-40-2040, IONTECH Company, China).  $\text{Na}_2\text{SO}_4$  solution of 5% wt. was used as electrode rinsing solution. The diluting, concentrating and electrode rinsing solutions of ED module flowed with identical flow rate and fixed volume of 2.0 L. ED experiments were carried out at room temperature and started with distilled water as the initial solution in concentrate side and standardized DES solution as the initial solution for diluting section. Single recovery process and semi-continuous recovery process were employed to figure out the efficient method for DES recovery by ED treatment (see Fig. 2). Single recovery process was ended when the variation of ChCl concentration in concentrate section was less than 5 mg/L within 2 min. The solution in dilute section and concentrate section was collected and evaporated to get EG and ChCl. For semi-continuous process, ED experiment was paused when ChCl concentration in concentrate section arrived at 20 g/L and solution in concentrate section was collected and evaporated to get ChCl. Simultaneously, the solution in dilute section was mixed with aqueous DES solution after ultrafiltration treatment with 0.65 kDa as the molecular weight cut-off. The mixture was diluted to get ChCl concentration to 40 g/L and used

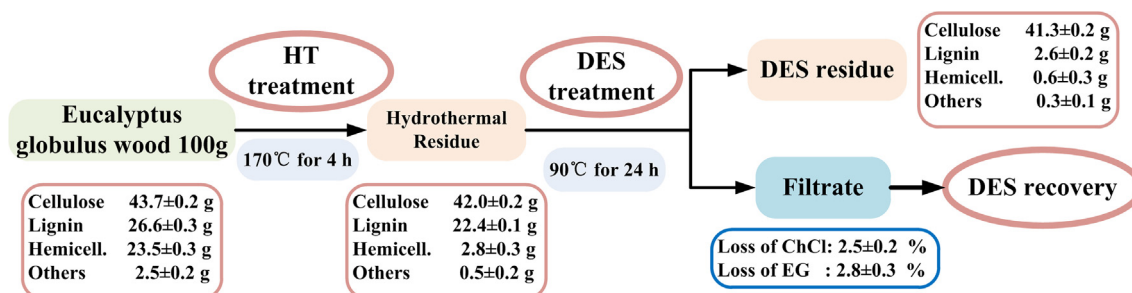


Fig. 1. A summary of mass balance for major components during pretreatment.

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