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# Solubility Study of Lignin Monomeric Compounds in Deep Eutectic Solvents for Biomass Waste Pre-treatment

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# ABSTRACT

Lignin is a complex polymer class formed from the cell wall, it is an organic polymer with a variety of biological aspects and industrial applications. Deep eutectic solvent (DES) has been introduced as a green solvent to dissolve lignin from lignocellulosic biomass. DESs typically have low vapor pressure, high heat stability, low toxicity and biodegradation which are the ideal features for lignocellulosic biomass pre-treatment. In this work, Conductor-like Screening Model for Real Solvents (COSMO-RS) was used to determine the suitable DESs for lignin degradation. The performance of the selected DESs was tested on lignin monomeric compounds, commercial lignin and the actual biomass of oil palm empty fruit bunch (OPEFB). Three DESs were used to test its lignin dissolution capability, i.e. choline chloride:urea (ChCl:Ur) (1:2), choline chloride:glycerol (ChCl:Gly) (1:2) and choline chloride:glucose (ChCl:Glu) (1:1). The saturation points of dissolving each lignin type were determined for each DES. It was experimentally found that ChCl:Ur (1:2) could dissolve more lignin than ChCl:Gly (1:2) and ChCl:Glu (1:1). This work shows the possibility of using DES to dissolve lignin structures for biomass pretreatment and utilization.

# INTRODUCTION

Hardwood-based lignocellulose includes 40–60 percent cellulose, 24–40 percent hemicellulose, and 10–25 percent lignin, while softwood-based lignocellulose contains 45–50 percent cellulose, 25–35 percent hemicellulose, and 25–35 percent lignin [1]. Lignin is synthesized from oxidative coupling of the alcohol monomer *p*-hydroxycinnamyl and related compounds. This polymer occurs mainly in the second thickened plant cell wall. Lignin is covalently bonded to hemicellulose and provides the cell wall with strength and rigidity, allowing plants to grow higher. Lignin also offers the hydrophobicity that circulatory systems require for the movement of water and dissolved materials [2].

Lignin can be produced from the pre-treatment of biomass waste as in sugar production from oil empty palm fruit bunch [3]. All throughout, lignin has the long-term goal of advancing scientific and industry discourse on the permeating impacts of hydrolyzatesoluble lignin on biorefinery processing, whether as coproducts that can be valued or as inhibitors of biotransformation is still underused. Lignin is also often considered as waste by-products and is typically burned for heat and power supplies only [4].

The use of ionic liquids (ILs) in organic synthesis, catalysis, biocatalysts. extraction. dissolution. nanomaterials. polymerization, and electrochemical reactions has been reported [5]. ILs have been known for the past 20 years as solvents for extraction. Due to limitations of ILs such as high toxicity and cost, deep eutectic solvents (DESs) may be regarded as a useful alternative. Because of its similar traits and qualities with ILs, DESs are now largely recognised as the analogue of ILs. Despite the fact that DESs and ILs are two different types of solvents, the words have been used interchangeably in the literature [6,7]. DES is typically prepared by mixing hydrogen bond acceptor (HBA) compound with a hydrogen bond donor (HBD). The hydrogen bond networks caused the formed mixture to have a melting point much lower than that of the individual species. Thus, it can be expected that different HBA:HBD ratio will produce a eutectic solvent with different extend of hydrogen bonding networks, thus affect the lignin dissolution capacity.

In this study, COSMO RS was used to screen the solubility of four lignin monomeric compounds in 9 DESs. The lignin monomeric compounds were vanillic acid, ferulic acid, syringic acid and syringaldehyde, while the DESs were (choline chloride:glucose, choline chloride:glycerol, choline chloride:urea, choline chloride:1,6- hexanediol, choline chloride:maleic acid, choline chloride:formic acid, maleic acid:betaine, urea:propionic acid, tetramethylammonium chloride:glycerol). The performance of DESs was then validated with experimental solubility study, where the DESs with the highest solubility was used to dissolve commercial lignin and actual biomass sample, i.e. oil palm empty fruit bunch (OPEFB) in lab.

## MATERIALS AND METHODS

### **COSMO-RS** program

COSMO RS program version 19 was used to quantitatively predict the solubility of lignin monomeric compounds in the selected DESs. The solubility screening was predicted using 'multiple solvents' mode in the COSMO-RS program. Lignin monomeric compounds were set as the solutes and its respective solubility in DES was calculated at 25 °C and 1 atm via the relative solvent screening. The result is expressed as a relative molar solubility ranking, where the values differ from absolute values by a simple shift. Although the results are not the absolute solubility values, the qualitative trend and the relevant information about solute-solvent interactions are valid. As a benchmark, the solubility of lignin monomeric compounds in conventional solvents were also predicted and compared.

### **Materials and Chemicals**

Ferulic acid powder 20 g (purity >98%) used to test on the lignin solubility was purchased from IKO nature Sdn Bhd. Ferulic acid was chosen as the representative of lignin monomeric compounds due to chemical availability. Commercial lignin 10g and OPEFB 5g used to test on the lignin solubility. Choline chloride (ChCl) 50 g, urea (Ur) 30 g, glycerol (Gly) 30 mL, glucose (Glu) 30 g, hot plate, filter paper, beaker 50 mL.

### **COSMO RS Screening**

The COSMO-RS screening was performed with 9 DESs (**Table 1**), 4 lignin monomeric model (vanillic acid, ferulic acid, syringic acid, syringaldehydes). After the screening was complete, the solubility data was analyzed in Microsoft Excel.

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DESs	HBA:HBD ratio	Abbreviation	
Choline cloride:Glucose	1:1	ChCl:Glu (1:1)	
Choline cloride:Glycerol	1:2	ChCl:Gly (1:2)	
Choline cloride:Urea	1:2	ChCl:Ur (1:2)	
Choline cloride:1,6 hexanediol	1:3	ChCl:HD (1:3)	
Choline cloride: Maleic acid	1:1	ChCl:MA (1:1)	
Maleic acid:Betaine	3:1	MA:Bet (3:1)	
Choline cloride:Formic acid	1:2	ChCl:FA (1:2)	
Urea: Propionic acid	1:2	Ur:PA (1:2)	
Teatraetyhlammonium chloride: Ethylene glycol	1:2	TEACI:EG (1:2)	

### **Preparation of DESs**

Based on the screening results, three DESs were selected for experimental validation, i.e. ChCl:Ur (1:2), ChCl:Gly (1:2) and ChCl:Glu (1:1). For the first DES, individual compounds were

mixed and heated at 80°c with stiring for 60 minutes [7]. For ChCl:Gly (1:2), the mixture was heated at 80°c until homogenous liquid was formed [8]. Finally, for ChCl:Glu (1:1), the mixture was heated at 60°c until the clear liquid was formed [9]. After all the DESs were homogenous, the DES was kept in dry containers.

# Solubility Testing on Lignin Monomeric and Commercial Lignin

Ferulic acid was selected to represent the lignin monomeric compound in experimental solubility test. 0.1 g of ferulic acid was added into a beaker containing 10g of DES. The mixture was heated on a hot plate at 40°C until there were no solid particles left. Then, 0.1 g of lignin was continuously added until the solubility saturation point was achieved, where DES can no longer dissolve the lignin at 40 °C. The amount of lignin was recorded to calculate the saturation point. Then, the heating temperature was increased to 60 °C and the saturation point was recorded. These steps were repeated for 40°C, 60°C and 80°C. If solid particles remain, the lignin is considered insoluble in the DES. When solid particles were not identified in the samples, the lignin is regarded as soluble in the DES [10].

### Solubility of OPEFB in DESs

DES. Then, the mixture was heated on a hot plate at 80 °C with continuous stirring for 2 h. The filter paper was weighed before filtering the solution. The solution was filtered using filter paper. The filter paper was left inside oven overnight at 100 °C. The weight of the filter paper was recorded after the drying process and the increasing weight of filter paper indicates the solid content that DES cannot dissolve [11].

# **RESULTS AND DISCUSSION**

### **COSMO-RS** Screening

During the screening, nine DESs were selected into COSMO-RS program, and the relative dissolution performance was predicted with respect to four lignin monomeric compounds. The screening results are expressed as the relative lignin solubility, as shown in **Fig. 1**.



Fig. 1. Relative solubility of lignin monomeric compounds in DESs.

#### **Lignin Solubility**

From the nine DESs, three DESs were synthesized for experimental solubility determination, i.e. ChCl:Ur (1:2) ChCl:Gly (1:2) and ChCl:Glu (1:1). Fig. 2 shows the physical appearance of the mixture when lignin is completely dissolved in each DES. It was noteworthy that ChCl:Glu produced a darker solution. In addition, upon increasing the temperature, a

higher amount of lignin could be dissolved in the DESs. This can be expected as the solubility increased proportionally to the temperature [3].



Fig. 2. Dissolution of ferulic acid in DES; a) ChCl:Ur (1:2), b) ChCl:Gly (1:2), and c) ChCl:Glu (1:1).

### **Saturation Point**

When the amount of ferulic acid was added stepwise, it was observed that at the saturation point, no more ferulic acid can be dissolved in ChCl:Gly (1:2) (**Fig. 3(a**)) and ChCl:Glu (1:1) (**Fig. 3(b**)). As a result, the ferulic acid appears in the DES as undissolved solid where the solution becomes saturated. It is known that solvation involves bond formation, hydrogen bonding, and van der Waals forces [4]. During this dissolution, the interaction of ferulic acid with the DES leads to stabilization of ferulic acid in the solution. This process keeps ongoing until the DES no longer has sufficient solvation energy to interact with or dissolve the ferulic acid., i.e., saturation point [9].



Fig. 3. DES at its saturation point of dissolving ferulic acid; (a) ChCl:Ur (1:2), (b) ChCl:Glu (1:1).

### Validation of COSMO-RS screening

COSMO RS can be used to estimate the relative solubility of lignin monomeric compounds in DES. However, COSMO RS is unable to predict the solubility of lignin compounds because the unavailability and complexity of lignin structure to be imported in COSMOtherm. With this limitation, the experimental solubility of lignin monomeric compound (ferulic acid) and commercial lignin in DES may not sufficiently validate the computational screening [3]. Nonetheless, it is observed that ChCl:Ur (1:2) remains as a DES with the highest lignin dissolution capacity compared to ChCl:Gly (1:2) and ChCl:Glu (1:1). The solubilities of a lignin monomeric compound (ferulic acid) and commercial lignin in each DES are depicted in Fig. 4 and Fig. 5, respectively.



Fig. 4. Experimental solubility of ferulic acid in DESs.



Fig. 5. Experimental solubility of commercial lignin in DESs

# **Biomass Solubility**

After the DES was filtered on filter paper and left overnight at 50°C, the amount of OPEFB on the dried filter paper can be recorded to calculate the solubility. This is obtained by the following equation.

Lignin dissolved = (weight of lignin + initial weight of filter paper) - weight of dried filter paper

It was observed that ChCl:Ur (1:2) dissolved higher amount of lignin than those observed in other DESs. This is consistent with the COSMO-RS screening on the relative solubility. It can be assumed that ChCl:Ur (1:2) has stronger intermolecular interaction with OPEFB which helps increase the solubility [8]. In addition, since ChCl:Ur (1:2) was physically less viscous than other DESs, it can be deduced that higher fluid mobility and mass transfer contributes to the higher solubility. The solubility of OPEFB in the three DESs is summarized in **Table 2**.

DES	Lignin weight (g)	Filter paper weight before (g)	Filter paper weight after (g)	Dissolve lignin (g)
ChCl:Ur (1:2)	0.1013	0.8087	0.8892	0.0805
ChCl:Gly (1:2)	0.1033	0.7905	0.8295	0.0275
ChCl:Glu (1:1)	0.1006	0.7851	0.8140	0.0717

Table 2. Solubility of OPEFB in different DESs.

### CONCLUSION

In this work, COSMO-RS was used to screen 9 DESs as a solvent to dissolve lignin monomeric compound, commercial lignin and actual biomass. Three of the top screened DES were selected for experimental validation. As a result, ChCl:Ur (1:2) was identified as the best solvent candidate with and order of ChCl:Ur (1:2) > ChCl:Gly (1:2) > ChCl:Glu) (1:1). The results revealed that at higher temperature, stronger intermolecular interaction and viscosity contribute to a higher dissolution capacity of lignin. The experimental result also confirmed that COSMO-RS is a reliable tool to qualitatively screen the performance of DES for the dissolution of lignin.

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