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Evaluation of fractionation and delignification efficiencies of deep eutectic solvents on oil palm empty fruit bunch

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ABSTRACT

Deep eutectic solvent (DES) has been introduced as a new generation green solvent for lignocellulosic biomass pretreatment in recent years. In the current study, six DES varying from acidic to basic nature were synthesized and applied on oil palm empty fruit bunch (EFB) in a single step fractionation and delignification process. The effect of the properties of DES on its fractionation performance was assessed. Mass balance performed on the pretreatment process reveals that pH of DES has a significant impact on biopolymer fractionation efficiency. The dissolution trend of acidic and basic DES resembles those in the conventional acid and alkaline pretreatments. The pretreatment energy requirement for the DES used ranged from 2087 to 2451 J/g. The acidic choline chloride:lactic acid DES succeeded in achieving 100% hemicellulose extraction, 88% delignification and 50% lignin pellet extraction from EFB. Thus, it is feasible for acidic DES to be considered in a biorefinery scheme for biomass fractionation.

1. Introduction

Oil palm empty fruit bunch (EFB) is generated from mill processing after the stripping of fruits from fresh fruit bunch. It is a fibrous biomass waste rich in cellulose, hemicellulose and lignin which represents the most generated solid waste from oil palm industry (Sohni et al., 2018). Traditionally, EFB was incinerated and the ash was recycled as fertilizer. However, incineration of EFB has been discouraged due to air pollution. The flourish of oil palm industry has perpetually exerted pressure on the need to seek for alternative application of the EFB waste produced.

According to American National Renewable Energy Laboratory (NREL), biorefinery is an integration of facilities, equipment and biomass conversion processes to produce fuels, power and chemicals from biomass. Agricultural biomass waste, such as EFB, is a potential feedstock replacement for non-renewable fossil fuels to produce a variety of bio-based products (Procentese et al., 2017a; Raman and Gnansounou, 2015). A pretreatment step prior to product conversion process is essential to facilitate the dissociation and fractionation of biomass structure. The fractionation of biomass components is of major importance to exploit the distinctive biopolymers to their full potential. The major difficulty in an efficient fractionation process lies in the recalcitrant structure of lignin-carbohydrate complex (LCC) which is formed through the intermolecular bonding between lignin and hemicellulose (Liu et al., 2017).

Conventional chemical pretreatment, which involves the use of acid or alkali, has many limitations in hindering the process from being commercialized. For example, despite being commonly used, mineral acids are less desirable in this green technology advocated era as they are corrosive and toxic. While organic acids, on the other hand, are not efficient in biomass pretreatment (Zhao et al., 2009). Apart from that, alkali pretreatment is also less effective in pretreating biomass with high lignin content (Agbor et al., 2011). Thus, conventional pretreatment methods are still incapable of achieving the desired biomass components fractionation.

In view of the constraints imposed by conventional chemical solvents, green solvents have been introduced in biomass processing field. As proposed in Durand et al. (2016), low vapor pressure, thermal stability and non-flammability are among the important characteristics of a green solvent in the implementation of sustainable technologies. Green solvent such as ionic liquid (IL) which prevailed in the last decades has paved the pathway for other green solvents. ILs have proven their effectiveness in promoting saccharification of carbohydrate-rich biomass (Lee et al., 2015) and extracting lignin from lignocellulosic biomass (Rashid et al., 2018). New type of synthetic green solvent, deep eutectic solvents (DES) had been introduced by Abbott et al. (2003) as an alternative for ILs and first applied in biomass processing by Francisco et al. (2012). DES is formed by two or more components capable of associating with each through hydrogen bonding. The most prominent characteristic of DES is the significant

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depression of freezing point due to hydrogen bonding network between hydrogen bond acceptor (HBA) and hydrogen bond donor (HBD), which enables DES to be used as liquid under ambient condition (Abbott et al., 2003; Dai et al., 2013). Unlike ILs, DES synthesis involves a simple mixing process which can be easily carried out in large amount.

Effectiveness in fractionating biomass components implies a big advancement to the accomplishment of biorefinery. DES have nearly absolute selectivity of lignin and low to negligible solubility of cellulose (Francisco et al., 2012; Kumar et al., 2016; Yiin et al., 2016). Regardless of the poor performance in polysaccharides solubilization, DES pretreatment has been proven effective to increase the enzymatic saccharification efficiency of biomass for reducing sugar production (Gunny et al., 2015; Procentese et al., 2018; Zulkefli et al., 2017). The most commonly studied DES include choline chloride:polyalcohol and choline chloride:carboxylic acid. Other than reducing sugar, lignin was also released from the biomass matrix after DES pretreatment. Alvarez-Vasco et al. (2016) extracted 78% lignin pellet from poplar wood using choline chloride:lactic acid DES while choline chloride:glycerol DES was ineffective in biomass dissolution nor lignin extraction.

Thus far, little is being studied on the biopolymer compositional changes in the entire pretreatment system and their variation under different DES pretreatments. Performing study on mass balance and energy requirement are essential for a closed-system pretreatment to promote the understanding of DES biomass pretreatment process. Therefore, this study is aimed to assess the fractionation and delignification efficiency of DES with variation in pH and functional groups. The relationship between the solvent properties and the fractionation efficiency was investigated. Also, mass balance recovery and energy requirement studies were carried out to facilitate the selection of suitable DES for EFB fractionation and delignification.

2. Materials and methods

2.1. Materials preparation

Oil palm empty fruit bunch (EFB) was collected from a local plantation in Bera, Pahang Malaysia. After rinsing with reverse osmosis water and dried in oven at 40 °C, the EFB stalks were disintegrated into individual fibres using granulator (Rapid, Sweden) and sieved to mesh size between 0.250 mm and 0.707 mm, then stored in drying cabinet prior to DES pretreatment. Chemicals choline chloride, urea and alkali lignin were purchased from Sigma-Aldrich; D(+)-glucose from Merck; lactic acid, glycerol and potassium carbonate from R&M Malaysia.

2.2. DES synthesis and properties measurement

Different types of DES were synthesized from starting materials with various functional groups based on reported stable DES system (Abbott et al., 2003, 2011; Dai et al., 2013; Francisco et al., 2012; Mjalli et al., 2014). DES were prepared according to molar ratios listed in Table 1 at 80 °C in a water bath. The HBD and HBA mixture was magnetically stirred until homogeneous liquid was obtained. DES were used in the neat state except for viscous CCGLUC whereby 10 wt% of water was added to reduce its viscosity. All DES were kept overnight under ambient room condition before use.

Viscosities of the solvents were measured using Brookfield LV viscometer and HAAKE VT550 for $[K_2CO_3]$GLY at ambient temperature (27 °C). The pH value of the solvents was determined using Metrohm pH meter and Merck pH indicator strips. Heat capacity, C_p, measurement was performed with differential scanning calorimeter (Mettler Toledo, DSC1, USA) using the standard sapphire method. Around 10 mg of DES was crimped in a hermetic aluminium sample pan (ME-27331) and analysed under nitrogen atmosphere. The measurement began with a 5-min isothermal period at 20 °C, followed by dynamic ramp to 90 °C at 5 °C/min heating rate, and ended with 5-min isothermal period at 90 °C. Heat flow curve of sample and standard sapphire were blank-corrected and the sample curve was compared against sapphire curve to determine the C_p.

2.3. Biomass pretreatment

Fractionation and delignification of oil palm empty fruit bunch (EFB) were carried out in a single step pretreatment using DES. EFB was first extracted with water and followed by ethanol for 24 h according to NREL protocol for extractives removal (Sluiter et al., 2005). Extractive-free EFB (0.45 g) was mixed thoroughly with DES (4.5 g) at 10 wt% solid loading and then incubated in oil bath at 120 °C for 8 h. The pretreated biomass solid fraction (SF) and the liquid fraction (LF) were separated using Advantec 4 A Hardened filter paper. The SF was rinsed with ethanol until the washing liquid was no longer turbid. The ethanol washing liquid was mixed with LF to form the mixture LF1.

2.4. Biopolymer compositional analysis

2.4.1. Raw biomass and pretreated biomass solid fraction (SF)

Compositional analysis of raw EFB biomass was performed using standard NREL protocol. Two consecutive 24-h solvent extractions using water followed by ethanol were performed on EFB. The extractive-free EFB was then subjected to two-stage acid hydrolysis (Sluiter et al., 2008). Acid-hydrolysed filtrate and solid residue were separated using vacuum filtration. The carbohydrate content of the filtrate was measured using high performance liquid chromatography (Waters, USA) equipped with refractive index detectors and a Hi-Plex H column (Agilent, USA). Ultrapure water with 18.2 MΩ conductivity was used as mobile phase at the flow rate of 0.6 mL/min. Acid soluble lignin was measured using UV-spectrophotometer at the wavelength of 320 nm with absorptivity of 30 L/g cm (Raman and Gnansounou, 2015). Meanwhile, the solid residue collected was dried at 103 °C, ashed at 550 °C and measured as acid insoluble residue and ash, respectively; the difference between the two was calculated as acid insoluble lignin (Sluiter et al., 2008).

The pretreated biomass solid fraction (SF) collected was dried overnight in oven at 40 °C and the recovery percentage was determined according to Eq. (1a and 1b). Lignin, cellulose, hemicellulose and ash content in SF were characterized using the same NREL protocol used for raw EFB with the exception of extractives removal procedure.

$$\text{Pretreated biomass solid recovery (\%)} = \frac{\text{weight}_{SF}}{\text{weight}_{\text{raw EFB}}} \times 100\% \quad (1a)$$

Table 1
Deep eutectic solvents synthesized according to chemical classes and molar ratios.

HBA	HBD	DES Combinations (HBA:HBD)	Nomenclature	Molar ratio
ammonium salt	carboxylic acid	choline chloride : lactic acid	CCLA	1 : 5
sugar	carboxylic acid	D(+)-glucose : lactic acid	GLUCLA	1 : 5
ammonium salt	sugar	choline chloride : D(+)-glucose	CCGLUC	1 : 1
ammonium salt	polyol	choline chloride : glycerol	CCGLY	1 : 2
ammonium salt	amide	choline chloride : urea	CCUREA	1 : 2
inorganic carbonate salt	polyol	potasssium carbonate : glycerol	$[K_2CO_3]$GLY	1 : 6

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