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Rice straw pretreatment using deep eutectic solvents with different constituents molar ratios: Biomass fractionation, polysaccharides enzymatic digestion and solvent reuse

Ao-Lin Li, Xue-Dan Hou,* Kai-Peng Lin, Xuan Zhang, and Ming-Hui Fu

School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou 510006, China

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Lignocellulosic biomass pretreatment with deep eutectic solvents (DESs) is a promising and challenging process for production of biofuels and valuable platform chemicals. In this work, rice straw was mainly fractionated into carbohydrate-rich materials (CRMs) and lignin-rich materials (LRMs) by 90% lactic acid/choline chloride (LC)-water solution with different molar ratio of hydrogen bond donor (HBD, lactic acid) and hydrogen bond acceptor (HBA, choline chloride). It was found that high HBD/HBA molar ratio of DESs was favorable for achieving CRMs and LRMs with high purity, and both HBD and HBA were responsible for effective biomass fractionation possibly due to their synergistic effect on highly efficient breakage of the linkage between hemicellulose and lignin and thus lignin extraction. About 30%–35% of lignin in native rice straw was fractionated as LRMs, and exceeding 70% of xylan were removed and fractionated into the liquid stream as forms of xylose, furfural and humins after pretreatment using aqueous LC (3:1, 5:1) solution. Consequently, polysaccharides enzymatic hydrolysis of the CRMs were significantly enhanced. Moreover, all the DESs could be recovered with high yields of around 90%, and 69% of the LC (3:1) was recovered after 5 cycles reuse at 90 °C. Besides, the recycled DES maintained a good pretreatment ability, and glucose yields of 60–70% were achieved in the enzymatic hydrolysis of CRMs obtained in each cycle. The facile process established in present work is promising for large scale production of fermentable sugars and other chemicals.

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[**Keywords:** Deep eutectic solvents; Biomass fractionation; Cellulose enzymatic hydrolysis; Lignin recovery; Hemicellulose hydrolysis; Deep eutectic solvents reuse]

Lignocellulosic biomass from agriculture is considered as a promising feed stock in future large-scale, sustainable production of liquid biofuels and chemicals (1). The three main components of lignocellulosic biomass namely cellulose, hemicellulose and lignin could be converted to the corresponding chemicals (2). However, obtaining the main components with high purity is impeded by the complex structure of biomass (3). Moreover, it is desirable to fractionate the lignocellulosic biomass for comprehensive utilization of its main constituent molecules and avoid a great waste of resources. Therefore, an efficient and economic route for lignocellulosic biomass pretreatment and fractionation is generally necessary prior to its subsequent transformation (4).

In the past decade, ionic liquids (ILs) have been extensively explored in the field of biomass processing because of their many advantages over the traditional acid-, base- or organic solvent-based techniques (5). And efforts have been exerted to exploit renewable ILs with high lignin selectivity (6–8). Recently, deep eutectic solvents (DESs), being similar with ILs but more cheaper and atom economic, provide an alternative to ILs in biomass deconstruction (9). Some DESs have displayed unique ability to dissolve biomass components and pretreat various biomass, which is attracting a growing attention (10–14). Results from recent studies suggest that certain DESs, such as lactic acid/choline chloride (LC), have a good capability of improving cellulose enzymatic hydrolysis or extracting lignin with high purity from wood (10,15,16). Interestingly, water presence in DESs system could promote the lignin dissolution or extraction, which was confirmed in several works (10,17,18). Since the anhydrous starting materials are expensive and drying of the DESs or starting material is energy-consuming due to their strong hygroscopicity, it is sensible to use DES-water mixture as biomass pretreatment agent. Moreover, adding a small amount of water to the mixture could not only reduce the preparation time, temperature and viscosity (17,19), but also ensure a unique solvents system formed by water participated inter-molecular interactions (20). Therefore, water addition (10%) into the pretreatment mixture was employed during the DES mediated rice straw deconstruction processes. More importantly, hydrogen bond donor (HBD) amount of DES was claimed to be important for biomass pretreatment efficiency (15,18), however, detailed investigation on biomass fractionation with DESs of different constituents ratios is limited, particularly for the recovery of lignin and the conversion of hemicellulose components. Besides,

* Corresponding author. Tel./fax: +86 20 39322172.
E-mail address: houxd@gdut.edu.cn (X.-D. Hou).

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the intermolecular hydrogen-bonding strength in DESs was proved to be closely related with their mobility and biomass deconstruction power (19,21), and both HBDs and hydrogen bond acceptors (HBAs) exhibited non-negligible effect on the biomass dissolving (18) and pretreating efficiency of DESs (22). Hence, in present work, 90% LC- water solutions with different lactic acid (HBD) and choline chloride (HBA) molar ratios were applied for rice straw pretreatment; subsequently, the detailed distribution and conversion of lignin, xylan and cellulose components during the fractionation processes and the enzymatic hydrolysis of the carbohydrate-rich materials (CRMs) were studied and compared with the lactic acid-water solution pretreatment to unveil the potential role of HBD/HBA on rice straw fractionation. Additionally, the DESs recovery and reuse were carried out to establish a simple and cheap biomass pretreatment and fractionation process.

MATERIALS AND METHODS

Materials and reagents Cellulase/xylanase from *Trichoderma reesei* was purchased from Sigma–Aldrich (St. Louis, MO, USA) and used as received. Choline chloride (ChCl, 98%) and lactic acid (85wt% in water) were purchased from Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). Rice straw, obtained locally, was mechanically powdered to particle sizes of 250–600 μm. Other chemicals were of the highest purity commercially available.

DESs preparation ChCl and lactic acid were mixed in molar ratios of 1:1, 1:3 and 1:5, respectively, keeping 10 wt% water content by adding or evaporating water in the mixture. The mixture was heated and stirred at a certain temperature in a closed flask, and the homogenous colorless solution was formed quickly. Once the liquid was formed with no evidence of solid particles, the mixture was cooled down to room temperature to store in a sealed vial before use.

Rice straw pretreatment and fractionation using LC-water mixture Rice straw pretreatment was carried out as described recently (23), and the whole pretreatment and the subsequent fractionation procedures are depicted in Fig. S1. Briefly, the rice straw were mixed with aqueous LC solution with a biomass loading of 5 wt%, and the mixture was stirred and refluxed at a certain temperature for a specific time. Then, the mixture was thoroughly separated by centrifugation after pretreatment. The solid fraction 1 recovered as CRMs was washed with ethanol and then water until the washings was neutral, then lyophilized prior to compositional analysis and enzymatic hydrolysis. The washings was condensed by evaporation and combined with the remaining supernatant as supernatant 1. Two volumes of water was added into the supernatant 1, and the mixture was stored at 4 °C overnight to precipitate the dissolved lignin. After that, the precipitate 2 was collected by centrifugation, and then washed with water until the washings was neutral and lyophilized as lignin-rich materials (LRMs). The remaining supernatant together with condensed washings (supernatant 2) was adjusted to the pH value of 6.8 and precipitated with three volume of 96% ethanol under continuous stirring (24), then the precipitate 3 was obtained as hemicellulose-rich materials (HRMs) after centrifugation, washing with 96% ethanol and drying at 70 °C in Oven. The remaining supernatant combined with the condensed washings of HRMs was collected as supernatant 3, which was used for monosaccharides and furfural or 5-hydroxymethylfurfural (HMF) determination as well as DES recovery. All experiments were carried out at least in duplicate.

Composition analysis of -rice straw sample and - liquid stream Cellulose, xylan, and lignin contents of the rice straw samples were determined according to standard NREL analytical procedure including acid hydrolysis and subsequent HPLC and gravimetric analysis (25). Xylose, glucose, furfural and HMF in the liquid stream were also detected by HPLC. Sugars in the liquid stream were monitored using HPLC (Waters 2515, Waters Corporation, Milford, MA, USA) equipped with a Bio-Rad Aminex HPX-87H column (Bio Rad, Hercules, CA, USA) and a refractive index detector (Waters 2414). The mobile phase was a 5 mmol L^{-1} sulfuric acid aqueous solution, the flow rate was 0.5 mL min^{-1}, and the column and detector temperatures were 65 °C and 50 °C, respectively. Furfural and HMF in the liquid stream was detected using an HPLC (LC-20AT, Shimadzu, Kyoto, Japan) equipped with a C-18 column (Eclipse XDB-C18, Agilent Technologies Inc., Santa Clara, CA, USA) and a DAD detector at 280 nm (SPD-M20, Shimadzu). The mobile phase was acetonitrile/water (15/85, v/v), and the flow rate was 1 mL min^{-1}. The values were calculated as follows:

$$\text{Conversion(Xylose)}(\%) = \frac{\text{Xylose amount in liquid stream} \times 0.88}{\text{Total xylan amount in native biomass}} \times 100 \quad (1)$$

$$\text{Conversion (Furfural)}(\%) = \frac{\text{Furfural amount in liquid stream} \times 1.375}{\text{Total xylan and arabinan amount in native rice straw}} \times 100 \quad (2)$$

The value 1.375 is the ratio of molecular weight of $C_5H_8O_4$ over $C_5H_4O_2$ (26).

$$\text{Conversion (Glucose)}(\%) = \frac{\text{Glucose amount in liquid stream} \times 0.9}{\text{Total cellulose amount in native biomass}} \times 100 \quad (3)$$

$$\text{Conversion (HMF)}(\%) = \frac{\text{HMF amount in liquid stream} \times 1.286}{\text{Total cellulose amount in native rice straw}} \times 100 \quad (4)$$

The value 1.286 is the ratio of molecular weight of $C_6H_{10}O_5$ over $C_6H_6O_3$ (26).

$$\text{Residual Lignin}(\%) = \frac{\text{Lignin amount in CRMs or HRMs}}{\text{Lignin amount in native rice straw}} \times 100 \quad (5)$$

$$\text{Residual Xylan}(\%) = \frac{\text{Xylan amount in CRMs or LRMs}}{\text{Xylan amount in native rice straw}} \times 100 \quad (6)$$

$$\text{Residual Cellulose}(\%) = \frac{\text{Cellulose amount in LRMs or HRMs}}{\text{Cellulose amount in native rice straw}} \times 100 \quad (7)$$

$$\text{Cellulose recovery}(\%) = \frac{\text{Cellulose amount in CRMs}}{\text{Cellulose amount in native rice straw}} \times 100 \quad (8)$$

$$\text{Lignin recovery}(\%) = \frac{\text{Lignin amount in LRMs}}{\text{Lignin amount in native rice straw}} \times 100 \quad (9)$$

$$\text{Xylan recovery}(\%) = \frac{\text{Xylan amount in HRMs}}{\text{Xylan amount in native rice straw}} \times 100 \quad (10)$$

$$\text{Lignin or xylan removal}\ (\%) = 1 - \text{Residual lignin or xylan in CRMs}\ (\%) \quad (11)$$

$$\text{lignin loss}(\%) = 1 - \text{lignin recovery (LRMs)} - \text{residual lignin (CRMs)} - \text{residual lignin (HRMs)} \quad (12)$$

$$\text{xylan loss}(\%) = 1 - \text{xylan recovery (HRMs)} - \text{residual xylan (CRMs)} - \text{residual xylan (LRMs)} - \text{conversion (xylose)} - \text{conversion (furfural)} \quad (13)$$

$$\text{cellulose loss}\ (\%) = 1 - \text{cellulose recovery (CRMs)} - \text{residual cellulose (LRMs)} - \text{residual cellulose (HRMs)} - \text{conversion (glucose)} - \text{conversion (HMF)} \quad (14)$$

Enzymatic hydrolysis of rice straw residues Enzymatic hydrolysis of the sample was carried out according to our previous method (27). The polysaccharide digestibility were calculated as follows:

$$\text{Polysaccharide digestibility}(\%) = \frac{\text{Released sugar amount}}{\text{Theoretic sugar amount in the CRMs used for enzymatic hydrolysis}} \times 100 \quad (15)$$

$$\text{Sugar yield}(\%) = \frac{\text{Released sugar amount}}{\text{Theoretic sugar amount in native rice straw}} \times 100 \quad (16)$$

DES recovery and reuse DES recovery was achieved by removing ethanol and water from the supernatant 3 under vacuum evaporation. With respect to DES reuse, the supernatant 1 was directly used in the next cycle of pretreatment without further separation, purification and fresh DESs supplement between batches. Repeat these operations for five cycles. Small amount of supernatant 1 from each cycle was withdrawn for LMRs recovery and compositional analysis, and CRMs from each cycle was washed and dried for compositional analysis and the subsequent enzymatic hydrolysis.

NMR analysis of DESs structure ^1H NMR spectra of DESs (fresh and recovered) were recorded at 400 MHz by an NMR spectrometer (Bruker Avance Digital 400 MHz NMR, Bruker, Germany). About 5–10 mg of sample was dissolved in 0.5 mL of dimethyl sulfoxide-d_6. The relaxation delay was 1 s. The number of scans was 128 with an acquisition time of 3.98 s.

Statistical analysis All data recorded were the average values of duplicates. A 95% confidence interval ($p < 0.05$) was applied for statistical analysis of variance (ANOVA), performed with SPSS (19.0 version).

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