Carbohydrate Polymers 176 (2017) 307–314

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

# Physicochemical transformation of rice straw after pretreatment with a deep eutectic solvent of choline chloride/urea

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ARTICLE INFO

*Keywords:*
Rice straw
Choline chloride/urea
Pretreatment
Fractionation
Deep eutectic solvent

ABSTRACT

This study focused on the pretreatment with deep eutectic solvent of choline chloride (ChCl)/urea mixtures on rice straw and its chemical fractions of holocellulose, α-cellulose, and acid-insoluble-lignin (AIL). The pretreatment of ChCl/urea was significantly affected by the treated temperature prior to the treated time, and 130 °C and 4 h was an optimum condition for ChCl/urea pretreatment. The separation capacity of ChCl/urea on the chemical fractions was in an order of AIL (22.87%) > hemicellulose and amorphous cellulose (16.71%) > α-cellulose (9.60%). ChCl/urea had a higher selective solubility on lignin. The solubility of the whole fractionation of rice straw affected by ChCl/urea was a combination of solubilization on cellulose, hemicellulose and lignin. ChCl/urea pretreatment increased crystallinity index (*CrI*) of rice straw residue and α-cellulose, while had no obvious influence on *CrI* of holocellulose. The effect of structural properties of rice straw residue on enzymatic hydrolysis was also explored.

## 1. Introduction

Biomass fractionation has attracted tremendous attention in the past decades for utilizing lignocellulosic biomass as feedstock in biofuel and chemical production (Wahlström & Suurnäkki, 2015). Pretreatment of lignocellulosic material is a crucial step prior to its subsequent transformation because of the complex chemical cross-linking between chemical components. Ionic liquids (ILs) are considered as an attractive pretreatment on lignocellulosic materials due to its wide liquid range, negligible vapor pressure, non-flammability, higher thermal, and chemical stability (Wahlström & Suurnäkki, 2015; Wu, Wang, Jin, Matsumoto, & Zhai, 2014; Zhu et al., 2006). Amounts of studies show that lignocellulosic biomass are effectively pretreated with ILs, such as 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) (Ang, Ngoh, Chua, & Lee, 2012), 1-ethyl-3-methylimidazolium acetate ([Emim]Ac) (Weerachanchai, Leong, Chang, Ching, & Lee, 2012), 1-ethyl-3-methyl imidazolium diethyl phosphate ([Emim]DEP) (Li et al., 2009). ILs remove lignin and/or disordered crystalline structure of cellulose, which increases the accessibility and digestibility of enzymatic, and then, help promote enzymatic hydrolysis. However, the utilization of traditional ILs has been limited due to its expensive, highly toxic and poorly biodegradable (Hou, Li, & Zong, 2013). A more 'green' and much cheaper solvent has been prospective for separation or dissolution lignocellulosic biomass.

Recently, deep eutectic solvents (DES), which have similar characteristics with traditional ILs, but much cheaper, more biodegradable and environmental friendly, come up as a promising alternative solvent (Abbott, Capper, Davies, Rasheed, & Tambyrajah, 2003; Francisco, Van den Bruinhorst, & Kroon, 2012; Lian, Hong, Carranza, Mota-Morales, & Pojman, 2015; Zhang, De Oliveira Vigier, Royer & Jérôme, 2012). In generally, DES can be prepared by mixing suitable hydrogen bond donor (amino, lactic, malic, oxalic, or nicotinic acid) and hydrogen bond acceptor (alanine, betaine, choline chloride, cholinium, glycine, or proline) combinations with high melting points (Francisco et al., 2012; Zhang, Benoit, De Oliveira Vigier, Barrault, & Jérôme, 2012; Zhang, De Oliveira Vigier et al., 2012). The synthesized DES shows selectively deconstruct the lignocellulosic biomass structure. Francisco et al. (2012) reported that choline chloride/lactic acid (ChCl/LA) shows a high solubility for lignin, while cellulose is found to be immiscible. Malic acid/praline has a higher solubility for starch and cellulose. Zhang, Benoit et al., (2012) added 5–15 wt% of tributylmethylammonium chloride ([TBMA]Cl) to choline acetate ([Ch]OAc), and pointed that [Ch]OAc/[TBMA]Cl mixtures enable the complete dissolution of 2–6 wt% microcrystalline cellulose (MCC) within 5–10 min at 110 °C. After three cycles, [Ch]OAc/[TBMA]Cl mixture was still capable of dissolving 3 wt% of MCC. An, Zong, Wu, and Li (2015) found cholinium argininate ([Ch][Arg]) was an efficient delignification solvent for grass lignocellulose and > 69% of lignin in

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http://dx.doi.org/10.1016/j.carbpol.2017.08.088
Received 2 May 2017; Received in revised form 10 August 2017; Accepted 19 August 2017
Available online 24 August 2017
0144-8617/ 

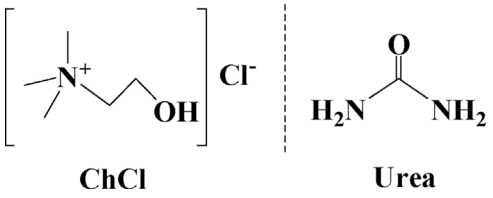


**Fig. 1.** Chemical structures of ChCl and urea.

these lignocelluloses was extracted. Kumar, Parikh, and Pravakar (2016) studied the pretreatment of rice straw using DES of ChCl/LA and it showed ChCl/LA at a molar ratio of 1:5 extracted maximum lignin of 68 ± 4 mg/g from rice straw.

DES consisting of ChCl/urea presented by Abbott et al. (2003) is also a widely investigated ChCl-derived DES. The chemical structure of ChCl and urea is shown in Fig. 1 and the freezing point of ChCl/urea at a molar ratio of 1:2 is 12 °C. ChCl/urea has been attractively investigated in catalysis (Zhang, Liu, Shang, Hu, & Zhang, 2017) and separation as a green solvent (Da Silva Lacerda et al., 2016), plasticizer of cellulose films (Wang et al., 2015), metal electrodeposition (Yang and Reddy, 2014), cationic fictionalization of cellulose (Abbott, Bell, Handa, & Stoddart, 2006), and synthesis of nanoparticles (Zeng et al., 2014; Zhang & Hua, 2014).

However, to our knowledge, there are few reports on separation of rice straw using DES of ChCl/urea. Herein, we have demonstrated ChCl/urea pretreatment on rice straw, which is abundant, renewable and available in the worldwide, particularly in China (Zhang, 2008). To better evaluate the transformation mechanism during ChCl/urea pretreatment on biomass fractionation of rice straw, subsequently, the chemical fractions of holocellulose, α-cellulose, and acid-insoluble-lignin (AIL) were isolated from rice straw. These isolated chemical fractions were further pretreated with ChCl/urea. The morphological and physicochemical properties of rice straw and the chemical fractions during ChCl/urea pretreatment were comprehensively compared with scanning electron microscope (SEM), Fourier transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD) techniques, respectively.

## 2. Materials and methods

### 2.1. Materials

Rice straws were collected from a suburb near Nanjing City, China. The samples were prepared with the screening system equipped with 40–60 mesh screens and were dried at 105 °C to constant weight. Holocellulose (60.80%), α-cellulose (34.15%), and AIL (11.10%) were isolated from rice straw according to the procedure as described in our previous study (Pan, Gan, Mei, & Liang, 2017). The isolated holocellulose, α-cellulose, and AIL were then dried at 105 °C to constant weight. Commercial urea (99%) and ChCl (98%) was purchased from Sinopharm Chemical Reagent Co., Ltd (China). In addition, all chemicals for biomass fractionation were purchased from Sinopharm Chemical Reagent Co., Ltd (China) and reagent grade. The cellulase (400 IU/mg-substrate) was bought from Yiji Co., Shanghai, China.

### 2.2. Preparation of ChCl/urea mixtures

DES of ChCl/urea mixtures was synthesized as our previous reported preparation procedure (Lian et al., 2015). ChCl and urea was dried under vacuum at 60 °C to constant weight. The eutectic mixtures was prepared by combining ChCl and urea at the molar ratio of 1:2 at 80 °C with a magnetic stirrer using an oil bath until a clear homogeneous, colorless and viscous solution was obtained.

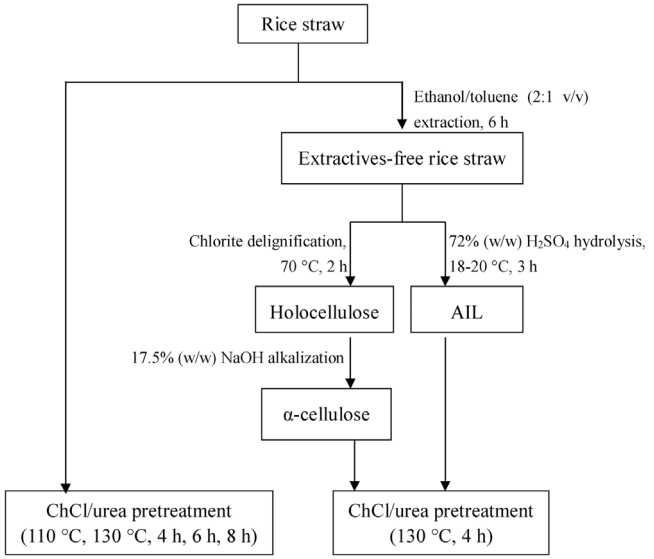


**Fig. 2.** The scheme of ChCl/urea pretreatment on rice straw and its chemical fractions.

### 2.3. Pretreatment of rice straw and its chemical fractions

About 10 g of the oven-dried rice straw mixed with 200 g ChCl/urea were put into in 500 mL erlenmeyer flasks, and then were stirred with a magnetic stirrer at 110 °C and 130 °C for 4 h, 6 h, and 8 h, respectively using an oil bath agitation with a rotator. Afterward, the reaction mixture was washed with the boiled deionized water to remove the DES completely, and the rice straw residues were separated by vacuum filtration, and then dried at 105 °C to a constant weight. For comparison, the oven-dried holocellulose, α-cellulose and AIL isolated from rice straw were also treated with ChCl/urea at 130 °C for 4 h. Fig. 2 illustrates the scheme of ChCl/urea pretreatment on rice straw and its chemical fractions. Solubilization rate (SR) of ChCl/urea on samples is calculated according to Eq. (1):

$$SR(\%) = \frac{m_0 - m_1}{m_0} \times 100 \quad (1)$$

where, $m_0$ is the oven-dried weight of samples, and $m_1$ is the oven-dried weight of the sample residues after pretreatment.

### 2.4. Characterization

#### 2.4.1. SEM analysis

A FEI company QUANTA 200 scanning electron microscope (SEM) was used to observe the surface morphology of the rice straw and chemical fractions with or without ChCl/urea pretreatments. The samples were coated with gold using an E1010 gold sputter (Hitachi, Japan) before examination.

#### 2.4.2. XRD investigation

X-ray diffraction (XRD) was performed with an ultima IV diffractometer (Rigaku, Japan) with Cu $K_\alpha$ radiation ($\lambda$ = 0.15406 nm), operating at 40 kV and 30 mA. The diffraction profile was detected using a locked couple 2$\theta$ scan from 5 to 50°. The samples were flatted into pellet form between two glass slides. The crystallinity index (*CrI*) of the samples is calculated according to Eq. (2):

$$CrI = \frac{I_{(002)} - I_{(am)}}{I_{(002)}} \times 100 \quad (2)$$

where, $I_{(002)}$ is the peak intensity at a plane (200) in the XRD profile, and $I_{(am)}$ is the minimum intensity at the valley between the plane (200) and (110) (Li & Renneckar, 2011).