



Research Article

Bioethanol production from corn straw pretreated with deep eutectic solvents



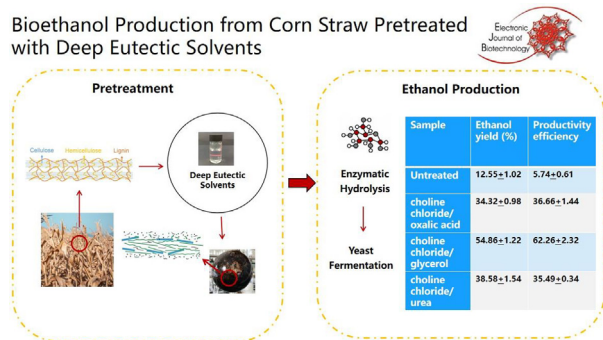
Jing Liu^a, Changmei Wang^a, Xingling Zhao^a, Fang Yin^{a,b}, Hong Yang^a, Kai Wu^a, Chengyue Liang^a, Bin Yang^a, Wudi Zhang^{a,b,*}

^aSchool of Energy and Environmental Science, Yunnan Normal University, Kunming 650500, PR China

^bEducation Ministry Key Laboratory of Advanced Technology and Preparation for Renewable Energy Materials, Yunnan Normal University, Kunming 650500, PR China

GRAPHICAL ABSTRACT

Bioethanol Production from Corn Straw Pretreated with Deep Eutectic Solvents



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ABSTRACT

Background: Deep eutectic solvents (DESs) have gained increasing attention as alternative solvents of environmental unfriendly solvents for biomass pretreatment.

Results: In this study, bioethanol production from DES-pretreated corn straw was investigated. The results revealed effective lignin removal from corn straw after pretreatment with choline chloride/oxalic acid (C:O), choline chloride/glycerol (C:G), or choline chloride/urea (C:U) DESs. After pretreatment with DESs, cellulose conversion significantly increased to 96.51% from 44.35% in the case of untreated corn straw. The best performance was obtained after the pretreatment of corn straw with C:O with a mass ratio of 1:15 at 120°C for 6 h, and this was mainly attributed to high lignin removal (60.60%). Another experiment showed that corn straw pretreated with C:G had a cellulose conversion of 86.82%, a glucose yield of 63.57%, and an ethanol yield of 54.86%.

Conclusions: Overall, this study demonstrated that the pretreatment of corn straw by a suitable DES can lead to efficient bioethanol production.

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* Corresponding author.

E-mail address: woutichang@163.com (W. Zhang).

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1. Introduction

Fossil fuels, such as oil, coal, and natural gas, play an important role in our daily activities including transportation, electricity

production, and many other uses. However, fossil fuels are examples of non-renewable energy resources, which means that they are limited in supply and cannot be used sustainably. With increasing energy demand and decreasing fossil fuel reserves, there is an unprecedented interest in renewable energy as a sustainable source of energy [1]. Biomass is a clean renewable energy resource, with its original energy coming from photosynthesis, which relies on readily available atmospheric carbon dioxide, water, and sunlight. Globally, 170 billion metric tons of biomass are produced annually [2].

Lignocellulosic biomass consists of three biopolymers: cellulose (35–50%), hemicellulose (20–35%), and lignin (10–25%) [3]. In China, more than 200 million tons of agricultural waste are produced annually, of which approximately 30% comes from lignocellulosic corn straw [4]. The amounts of cellulose, hemicellulose, and lignin in corn straws are 40–50%, 20–30%, and 10–15%, respectively [5]. Inedible corn straw has several advantages including its fast regeneration, abundance, and low cost. Consequently, it has attracted significant attention as a good source for the production of bioethanol, which is conducive to optimizing the energy matrix and improving the ecological environment. High-value utilization of corn straw will not only alleviate the shortage in fossil fuels but will also reduce environmental pollution caused by burning straw. In order to improve bioethanol production from corn straw, a pretreatment step prior to enzymatic hydrolysis is necessary to remove lignin and hemicellulose [6].

Ionic liquids (ILs) are considered promising green solvents for biomass pretreatment because of their low vapor pressure, high conductivity, and extensive designability. Importantly, deep eutectic solvents (DESs) have been identified as green and efficient alternatives to ILs for biomass pretreatment and conversion (Fig. 1) [7]. DESs have various advantages in addition to those of ILs, such as their simple and fast preparation, minimal purification, and low cost. DESs are mixtures of two or more components, namely, hydrogen-bond donors (HBDs) and hydrogen-bond acceptors (HBAs). The components of DESs form a uniform and stable solvent system through hydrogen-bond interaction. Francisco et al. [8] synthesized a variety of DESs using mixtures of organic acids and choline chloride (ChCl) and proved the ability of DESs to solubilize lignocellulosic biomass for the first time. Further, polyol-based DESs have shown high efficiency in improving enzyme

performance in hydrolysis [9,10], and acid-based DESs were found to be efficient in lignin extraction [11,12].

DES pretreatment process is a complex reaction system, and there are many parameters that affect the reaction process, such as DES properties and pretreatment condition. Massayev and Lee [13] investigated the variables for DES pretreatment with PCA and PLS analysis methods. The results revealed that the most significant variables were severity factor temperature, solvent resistance type, particle size, stirring intensity, and HBD type. Xu et al. [14] studied 54 important variables of the whole DES pretreatment process and found that the physic-chemical parameters of DES related to hydroxyl bond were beneficial to the removal of lignin and the recovery of glucan. Previous literature reports provided evidence supporting that different HBDs have different effects on DES pretreatment [15,16,17,18]. The acidity and alkalinity of DES are closely related to HBD [15], which also has a great impact on the effect of pretreatment.

In this study, three ChCl-based DESs were synthesized with three different HBDs: oxalic acid, glycerol, or urea. The obtained solvents were then used to pretreat corn straw for bioethanol production. Correlations were made between the pH, viscosity, extent of lignin removal, and cellulose digestibility during the enzymatic hydrolysis of corn straw residues to understand the pretreatment mechanism of these DESs. Most importantly, our research has put forward the way of corn straw recycling and efficient utilization, and used energy conversion efficiency to evaluate the process, which can provide guidance for the processing of other types of lignocellulose.

2. Material and methods

2.1. Materials

The corn straw used in this study was composed of cellulose, hemicellulose, and lignin contents of 35.8%, 22.3%, and 18.1%, respectively, and was obtained from Xuanwei, Yunnan Province. Cellulase (CAS: 9012–54–8) was purchased from Feijing Biotechnology Co. Ltd. ChCl (C₅H₁₄ClNO) (AR grade, 98%) was purchased from Aladdin Reagent Co., Ltd. Oxalic acid and urea were purchased

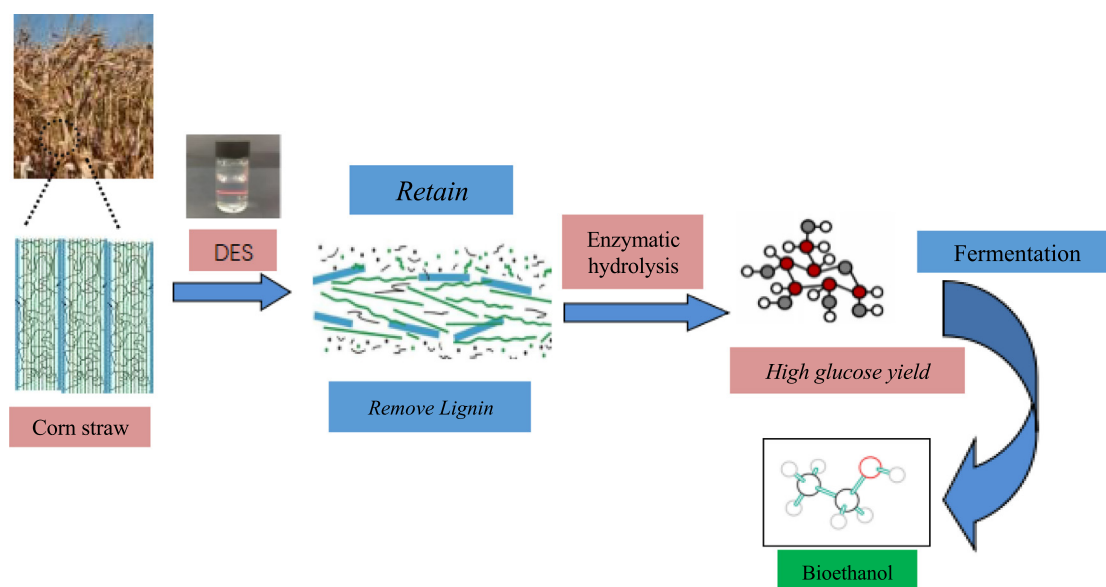


Fig. 1. Schematic diagram of the production of bioethanol via the enzymatic hydrolysis of corn straw with a pretreatment with deep eutectic solvents.

from Zhiyuan Chemical Reagent Co., Ltd. (Tianjin, China). Glycerol was purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. Synthesis of DESs

DESs were obtained by mixing HBAs and HBDs at different molar ratios and stirred at 90°C until the mixture became homogeneous, clear, and colorless. The compositions of DESs used in this study and their properties are listed in Table 1.

2.3. Corn straw pretreatment

Corn straw samples, pretreated with DES at different mass ratios of 1:10, 1:12.5, or 1:15, were placed in round-bottom flasks and set in an oil bath at 120°C for 6 h. After pretreatment, the obtained residues were washed with hot water and filtered until the supernatant became colorless in order to remove the DES completely. The residues were then lyophilized and stored at 4°C [21].

2.4. Compositional analysis

The compositional analysis of corn straw samples before and after pretreatment was performed according to the standard National Renewable Energy Laboratory (NREL) method [22]. Corn straw was extracted with ethanol using the Soxhlet method, air dried, and then transferred into a centrifuge tube to which sulfuric acid (72%) was added. The tube was placed in a water bath at 30°C for 1 h; the solution was diluted with sulfuric acid (4%), hydrolyzed at 121°C for 45 min, and then filtered with a sand core funnel G3. NaOH (8%) was used to adjust the pH of the filtrate to 2. The monosaccharide content was determined using high-performance liquid chromatography (HPLC). The filtered residue was washed with distilled water until it was neutral, dried at 105°C, and then ashed at 550°C.

Dissolution rate, cellulose reservation, and lignin removal were calculated according to Equation 1 and Equation 3 [23], respectively:

$$\text{Dissolution rate} = \left(1 - \frac{m_1}{m_0}\right) \times 100\% \quad \text{Equation 1}$$

where m_0 is the mass of corn straw before pretreatment, m_1 is the mass of corn straw after pretreatment.

$$\text{Cellulose reservation} = \frac{\text{Residue recovery} \times \text{cellulose content in residue}}{\text{Native cellulose content}} \quad \text{Equation 2}$$

$$\text{Lignin removal} = 1 - \frac{\text{Residue recovery} \times \text{lignin content in residue}}{\text{Native lignin content}} \quad \text{Equation 3}$$

2.5. Enzymatic hydrolysis

Enzymatic hydrolysis was performed according to the following procedure: the pretreated corn straw residue (3 g) was placed in a conical flask with cellulase (50 U/g) and sodium citrate solution

buffer solution (pH 5, 50 mL). The flask was shaken well, and the reaction was performed at 50°C. After 48 h, the flask was placed in a boiling water bath for 5 min to quench the reaction, and centrifuged at 8000 rpm for 5 min. The supernatant was collected to measure the glucose level by the 3,5-dinitrosalicylic acid (DNS) method. The supernatant (1 mL) was placed with 1.5 mL DNS solution in a 25 mL glass colorimetric tube, which was then placed into a boiling water bath for 10 min before being quickly cooled. The sample volume was then increased to 25 mL with distilled water, and a colorimetric analysis was performed using a spectrophotometer (Model 721) at a wavelength of 540 nm to obtain a standard curve ($y = 0.989x - 0.0024$, $R^2 = 0.9941$).

Cellulose conversion and glucose yield were calculated according to Equation 4 and Equation 5, respectively:

$$\text{Cellulose conversion} = \frac{\text{glucose amount (mg)} \times 0.9}{\text{cellulose amount in pretreated corn straw (mg)}} \times 100\% \quad \text{Equation 4}$$

$$\text{Glucose yield} = \frac{\text{glucose amount (mg)} \times 0.9}{\text{cellulose amount in untreated corn straw (mg)}} \times 100\% \quad \text{Equation 5}$$

2.6. Ethanol fermentation

In the flask in which the enzymatic hydrolysis was performed, active dry yeast (0.5%) was added. After fermentation at 30°C for 72 h, the ethanol content was determined by potassium dichromate ($K_2Cr_2O_7$) colorimetry: the fermented liquid (1 mL) was placed with $K_2Cr_2O_7$ solution (5%, 2 mL) into a 10 mL glass colorimetric, which was then held in a boiling water bath for 10 min before being quickly cooled. The sample was diluted with deionized water to a volume of 10 mL, and a colorimetric analysis was performed using a spectrophotometer (Model 721) at a wavelength of 600 nm to obtain the absorbance values. The standard curve ($y = 8.9444x + 0.013$, $R^2 = 0.9906$) was used to determine the ethanol content, which was calculated according to Equation 6:

$$\text{Ethanol content} = \frac{\text{ethanol amount (g)}}{\text{untreated cornstraw (g)}} \times 100\% \quad \text{Equation 6}$$

2.7. X-ray diffraction analysis

The crystallinity index (CrI) of corn straw before and after DES pretreatment was analyzed by X-ray diffraction (XRD). Samples were scanned in the range of $2\theta = 5^\circ - 90^\circ$ at a rate of $5^\circ/\text{min}$, with a D8 ADVANCE diffractometer. The CrI was calculated according to Equation 7:

$$\text{CrI}(\%) = \frac{(I_{002} - I_{am})}{I_{002}} \times 100 \quad \text{Equation 7}$$

Table 1
Deep eutectic solvents used in this study.

Abbreviation	HBAs	HBDs	Molar ratio	T_m (°C)	T_f (°C)
C:O	ChCl	Oxalic acid	1:1	37.7	34 [19]
C:G	ChCl	Glycerol	1:2	18	-35 [20]
C:U	ChCl	Urea	1:2	133	12 [7]

T_m : Melting point of pure HBD.

T_f : Freezing point of the reported DESs.

where I_{002} is the intensity of the crystalline region at $2\theta = 22.5^\circ$, and I_{am} is the intensity of diffraction of amorphous cellulose, hemicelluloses, and lignin at $2\theta = 18.2^\circ$.

2.8. Energy conversion efficiency

The energy conversion efficiency (E) is the ratio between the useful output of energy and the input (raw material) as shown in Equation 8:

$$E = \frac{\text{ethanol amount} \times Q_e}{\text{untreated cornstraw} \times Q_{cs}} \times 100\% \quad \text{Equation 8}$$

where Q_e is the calorific value of ethanol in kJ/kg, and Q_{cs} is the calorific value of untreated corn straw in kJ/kg.

3. Results and discussion

3.1. Effect of DESs on pretreatment

In ChCl-DESs, the effect of pretreatment is largely related to the selection of HBD. Based on the DES system composed of polyols, the number of hydroxyl groups is related to the lignin removal capacity. The acidic DES system shows remarkable effect in removing xylan and lignin, and meanwhile, it can ensure the integrity of most cellulose [24]. Alkaline solvent is helpful to the cleavage of ether bond in lignin and ester bond between lignin and hemicellulose [25,26]. For that reason, three DESs with different HBDs were selected including hydroxyl, carboxyl, and acylamin groups, respectively, namely C:O, C:G, and C:U.

Table 2 and Fig. 2 show that lignin removal varied depending on the conditions used in the pretreatment step. Using C:O at varying solid/liquid (S/L) mass fractions (Table 2), lignin removal ranged from 43.41% to 60.60% and the reserved cellulose exceeded 80% in all cases. On the other hand, lignin removal using C:G was in the range of 44.72–49.30% and the cellulose reservation was greater than 97%. Using C:U as a solvent system, the lignin removal ranged from 33.70 to 44.56%, with a cellulose reservation of over 78%. Lignin removal and hemicellulose loss approached 60.60% and 43.01%, respectively, after pretreatment with C:O, whereas those values were 49.30% and 8.83% for C:G, and 44.56% and 18.03% for C:U, respectively, revealing that C:O was the most effective solvent system in terms of both lignin removal and hemicellulose loss. As shown in Fig. 2, the cellulose content of corn straws pretreated by the three DESs increased compared to that of the untreated corn straw. This can be attributed to the small effects of DESs on cellulose and significant effects on lignin.

The cellulose content of corn straws pretreated by the three DESs increased as compared to untreated samples (Fig. 2). This increase is thought to be caused by the small effect of DESs on

the total cellulose content and their significant effect on the total lignin content (Table 2). Fig. 2a shows that the cellulose content in DES-treated corn straw was between 41.74% and 54.94%, showing an increase of 17.22–54.33% compared to the cellulose content in untreated corn straw (35.83%). As the ratio of DESs to corn straw increased, the cellulose content increased gradually with C:O as a solvent, decreased in the case where C:G was used, and did not change significantly with C:U. Fig. 2b shows the change in hemicellulose content of corn straw before and after pretreatment. After pretreatment with C:O, C:G, or C:U, the hemicellulose content of corn straw was between 12.72% and 22.93%. The most significant decrease in hemicellulose was observed when C:O was used. The hemicellulose content was only 12.72% after treatment with C:O (mass ratio of 1:15) at 120°C, compared to a content of 22.32% in untreated corn straw. Fig. 2c shows the changes in lignin content of corn straw before and after pretreatment. After pretreatment with C:O, C:G, or C:U, the lignin content of corn straw was between 13.27% and 16.85%, which was 6.96%–26.73% lower than the content in untreated samples. The lignin content in the groups treated with C:O and C:U decreased when the relative amount of DES was increased, but lignin removal in the group treated with C:O was found to be the most significant. The possible reason is related to biomass loading. Higher biomass loading increases the concentration of the reaction system, deteriorates the fluidity, and reduces the overall dissolution of biomass. Low loading helps in increasing the amount of ionic liquid entering the pores of the biomass. A similar pattern was reported by Khan et al. [27].

3.2. Properties of C:O, C:G, and C:U

According to the founding of Hou et al. [25], the pretreatment of corn straw was related to some physical and chemical properties of the DES, which may vary due to different combinations of HBA and HBD. The pH, viscosity, conductivity, density, and other characteristics of the three DESs at 298 K were listed in Table 3. By comparing the physical and chemical properties of the solvents with the changes in the corn straw components before and after pretreatment (Table 2), it was found that lignin and hemicellulose solubility in acidic solvents were greater than its solubility in neutral and alkaline ones. Xu et al. [34] have reported acidic DESs exhibited good performance in corn stove pretreatment. Sert et al. [35] synthesized three different deep eutectic solvents (DESs) with choline chloride as the HBA and oxalic acid/citric acid/tartaric acid as the HBD. The most effective DES was formed from choline chloride and oxalic acid.

The C:G solvent system resulted in the best residue recovery, followed by C:U and finally C:O. The same pattern was observed in cellulose reservation, which was above 75% with all solvents used, indicating that all three DESs slightly dissolved cellulose.

Table 2

Corn straw pretreatment using different deep eutectic solvents. (The number in the solvent system name corresponds to the solid/liquid mass fraction).

Solvent system	L/S mass ratio	Pretreatment (%)			
		Lignin removal	Hemicellulose removal	Cellulose reservation	Residue recovery
Untreated	/	/	/	/	/
C:O1	1:10	43.41 ± 0.57	18.53 ± 1.99	88.45 ± 2.96	62.65 ± 2.41
C:O2	1:12.5	51.75 ± 0.78	35.57 ± 1.78	84.81 ± 2.79	58.73 ± 1.79
C:O3	1:15	60.60 ± 0.33	42.45 ± 1.61	82.45 ± 3.02	53.77 ± 1.37
C:G1	1:10	44.72 ± 1.06	3.87 ± 0.46	97.25 ± 0.21	72.66 ± 1.26
C:G2	1:12.5	49.30 ± 1.10	4.17 ± 0.67	98.47 ± 0.19	73.65 ± 2.04
C:G3	1:15	48.53 ± 2.10	7.25 ± 0.97	98.46 ± 1.87	73.22 ± 1.15
C:U1	1:10	33.703 ± 0.39	7.07 ± 1.04	87.53 ± 0.58	71.89 ± 1.19
C:U2	1:12.5	36.25 ± 0.84	12.84 ± 0.91	85.67 ± 1.22	71.60 ± 1.83
C:U3	1:15	44.56 ± 0.89	14.47 ± 1.34	78.42 ± 2.16	69.90 ± 1.47

Pretreatment conditions: 120°C for 6 h.

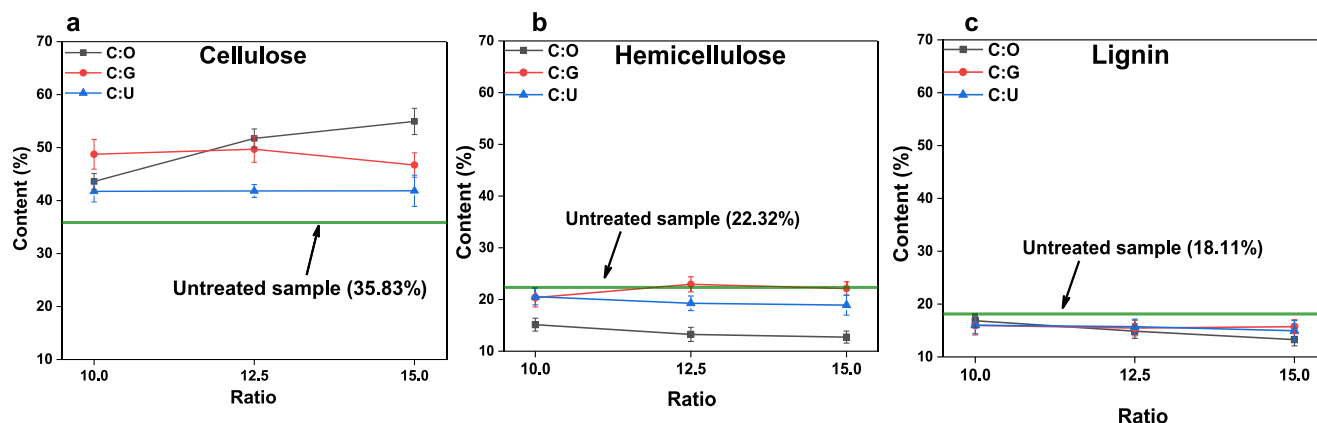


Fig. 2. Composition of corn straws before and after pretreatment with various deep eutectic solvents: (a) cellulose, (b) hemicellulose, and (c) lignin.

Table 3
Physicochemical properties of DES at 298 K, as reported in the literature.

DESs		HBA:HBD molar ratio	Density/g·cm ⁻³	pH	Conductivity /mS·cm ⁻¹	Viscosity mPa·S	References
HBA	HBD						
ChCl	Oxalic acid	1:1	1.15	1.22	0.38	597	[19,28,29]
ChCl	Glycerol	1:2	1.18	4.47	0.985	281	[29,30,31]
ChCl	Urea	1:2	1.21	10.07 (303 K)	2.31	750	[32,33]

Table 3 shows that the C:U solvents have highest pH values, but that the C:G solvent system was able to remove more lignin as compared to C:U (Table 2). Concerning the viscosity of the solvents (at 298 K), C:G was less viscous than C:U and the results revealed that solvents with lower viscosity improved the diffusion of solutes and thus promoted mass transfer between the solvent and corn straw. Viscosity and density were macroscopic performances of microscopic interactions among molecules inside the DES system [36]. The high viscosity of DES not only limits the solubility of biomass [37] but also hinders the heat and mass transfer during reaction [38]. Massayev and Lee [13] and Xu et al. [14] noted that DES with low viscosity has better quality conversion capacity and better delignification efficiency.

Density is an important physical parameter which reflects the activity and molecular mobility of solvents. The composition of DES and the molar ratio of HBA to HBD are related to the density of DES. Basaihgari et al. [39] reported that increasing the molar amount of HBD promotes the correlation between HBD molecules, and increased density. Furthermore, the density was affected by the temperature and decreases linearly with temperature increase [40]. The higher the liquid density, the higher the liquid viscosity, which may be related to the molecular void size of DES system [41]. In this study, the densities of C:O, C:G, and C:U have shown greater densities than water, but their densities were close. The influence of density on pretreatment effect was not obvious.

3.3. Dissolution of DES

The calculation of the dissolution rate in each DES can be used to evaluate the ability of DES to dissolve lignocellulose (Fig. 3). C:O3 showed the highest dissolution rate (up to 46.23%), while C:G showed the lowest rate. The influence of the DES on the dissolution can be explained by analyzing its components. DES is typically composed of an ammonium salt (cation and anion) and a hydrogen-bond donor (neutral component). In the pretreatment of lignocellulose, the anions interact with the hydroxyl groups in the cellulose resulting in hydrogen bonds [42]. The chloride ion (Cl) binds with the hydrogen-bond donor (e.g., glycerol) resulting

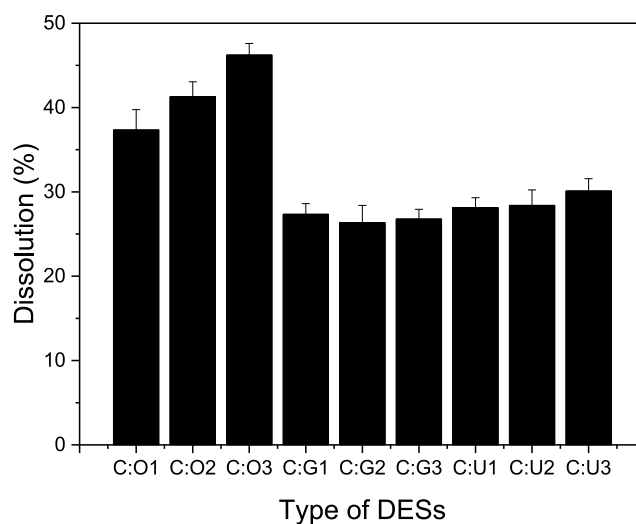


Fig. 3. Dissolution of corn straws in various deep eutectic solvents.

in a bulky HBD-Cl complex ion, and the cations can interact more easily with the lignocellulosic material compared to the anion [10,43].

The dissolution effect was related to the biomass loading. In the same pretreatment, as the biomass loading increased, the dissolution rate decreased. The higher dissolution rate observed at a lower loading can enhance the interaction between the DES and biomass samples. Unlike a lower biomass loading, a higher biomass loading can increase the viscosity in the reaction system, thus reducing the dispersion of particles and consequently the overall dissolution of the biomass. This was also reported by Jhansi et al. [43].

3.4. X-ray diffraction of corn straws

Fig. 4 shows the XRD spectra of corn straws before and after pretreatment by C:O, C:G, or C:U. The crystal structures of both

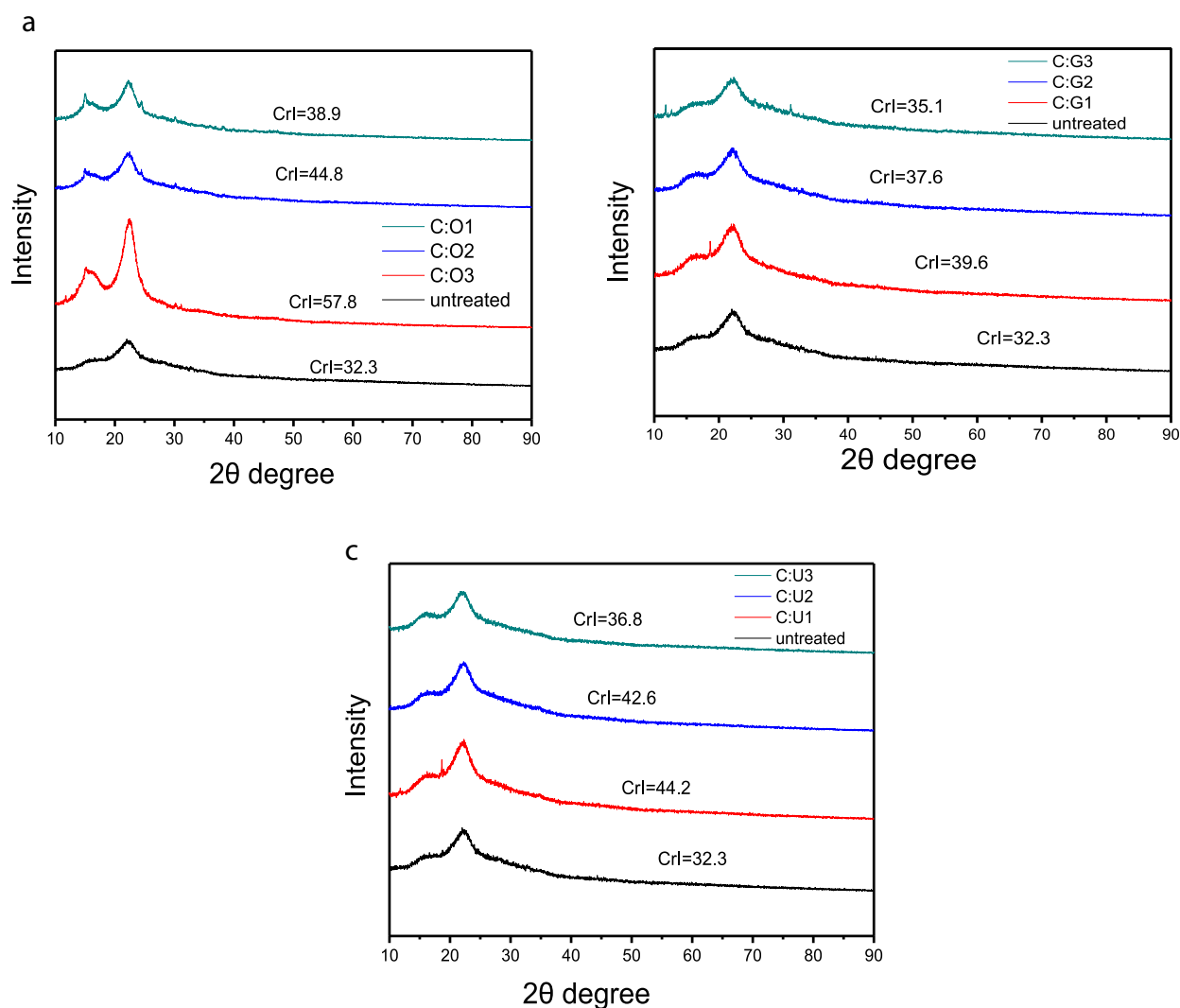


Fig. 4. XRD spectra of corn straws before and after treatment with various deep eutectic solvents with the following hydrogen-bond donors: (a) oxalic acid (C:O), (b) glycerol (C:G), and (c) urea (C:U).

untreated and treated corn straw samples were identical to that of cellulose I, especially the peak at $2\theta = 22.5^\circ$; consequently, the pretreatment step did not affect the crystal structure of cellulose. The crystallinity of the pretreated corn straws significantly increased as compared to the untreated straw, as revealed by the CrI values: 32.3 in the case of untreated straw, 57.8 after treatment with C:O3, 39.6 after treatment with C:G1, and 44.2 after treatment with C:U1. This can be explained by the removal of amorphous components such as lignin by pretreatment. In fact, two factors affected the measured CrI values: (1) the removal of disordered structures (such as lignin and xylan) in corn straw increased the fraction of crystalline cellulose, and (2) the destruction of the hydrogen bonding network structure in cellulose increased the disorder and decreased the crystallinity. These factors compete with each other [44]. All three DESs significantly removed lignin from corn straw after pretreatment at a temperature of 120°C for 6 h. Using C:O at an S/L ratio of 1:15 resulted in 60.60% lignin removal and preserved 82.45% of cellulose (Table 2, C:O3). The increase in the CrI value in this case demonstrated that the removal of disordered lignin or xylan was the dominating factor as compared to the destruction of the hydrogen bonding network structure. Comparing CrI values between straws treated by each of the three DESs, it was observed that the change in CrI after treatment with C:O was the

most obvious. CrI also increased as the amount of C:O used increased which was consistent with the trend observed in lignin removal [45,46,47].

3.5. Enzymatic hydrolysis and ethanol production

The enzymatic hydrolysis results are shown in Table 3 and reveal that as more lignin was removed, the hydrolysis effects improved. As the ratio of DES to straw increased, more lignin was removed and higher cellulose conversion was achieved. In accordance with the pretreatment results (Table 2), a pretreatment step with C:O resulted in better cellulose conversion as compared to the use of C:G and C:U. For example, after a pretreatment for 6 h at an S/L ratio of 1:15, the cellulose conversion approached 96.51% when C:O was used, while the conversion obtained with C:G and C:U under the same conditions was 86.82% and 73.72%, respectively. This might be explained by the fact that C:O displayed a higher efficiency in the removal of lignin from corn straw, which effectively reduced the adsorption of cellulase and increased its accessibility to cellulose. Consequently, the cellulose conversion improved [48].

After the enzymatic hydrolysis of corn straw samples, the fermentation of ethanol was studied (Table 4). The pretreatment step affected both the glucose yield and the ethanol yield. As more glu-

Table 4
Enzymatic hydrolysis and ethanol production of pretreated corn straw.

Solvent system	L/S mass ratio	Pretreatment (%)			Cellulose conversion (%)	Glucose yield (%)	Ethanol yield (%)
		Lignin removal	Cellulose reservation	Residues recovery			
Untreated		/	/	/	44.35 ± 0.86	25.62 ± 1.41	12.55 ± 1.02
C:O1	1:10	43.41 ± 0.57	88.45 ± 2.96	62.65 ± 2.41	88.56 ± 1.95	54.91 ± 2.11	27.81 ± 0.91
C:O2	1:12.5	51.75 ± 0.78	84.81 ± 2.79	58.73 ± 1.79	93.57 ± 2.78	58.01 ± 1.94	31.63 ± 0.76
C:O3	1:15	60.60 ± 0.33	82.45 ± 3.02	53.77 ± 1.37	96.51 ± 1.84	59.83 ± 1.12	34.32 ± 0.98
C:G1	1:10	44.72 ± 1.06	97.25 ± 0.21	72.66 ± 1.26	85.40 ± 1.70	62.25 ± 2.42	37.82 ± 1.05
C:G2	1:12.5	49.30 ± 1.10	98.47 ± 0.19	73.65 ± 2.04	85.77 ± 1.98	63.17 ± 0.33	49.38 ± 2.01
C:G3	1:15	48.53 ± 2.10	98.46 ± 1.87	73.22 ± 1.15	86.82 ± 2.32	63.57 ± 1.05	54.86 ± 1.22
C:U1	1:10	33.703 ± 0.39	87.53 ± 0.58	71.89 ± 1.19	64.78 ± 3.04	46.57 ± 2.70	23.23 ± 1.06
C:U2	1:12.5	36.25 ± 0.84	85.67 ± 1.22	71.60 ± 1.83	69.71 ± 2.76	49.91 ± 1.64	30.43 ± 0.85
C:U3	1:15	44.56 ± 0.89	78.42 ± 2.16	69.90 ± 1.47	73.72 ± 0.94	51.53 ± 3.02	38.58 ± 1.54

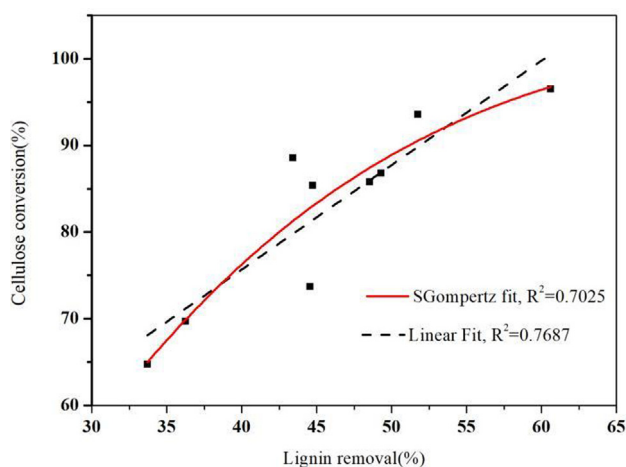


Fig. 5. Correlation between lignin removal and cellulose conversion.

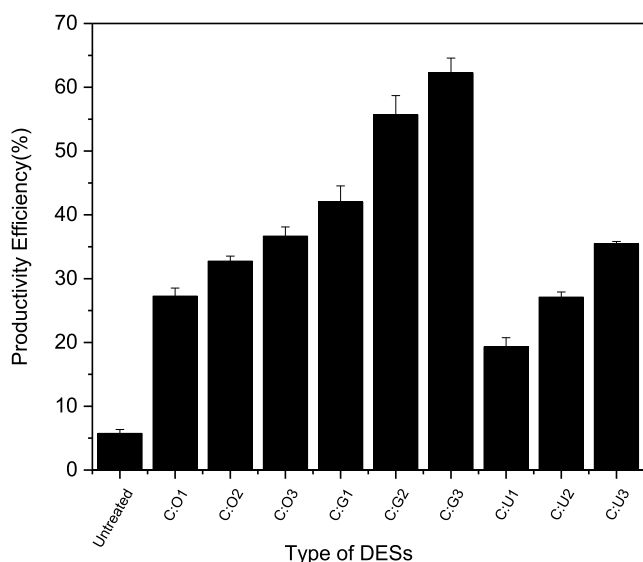


Fig. 6. Energy efficiency results.

cose was produced, the ethanol yield increased. Notably, although C:O showed a greater ability to remove lignin and hemicellulose and led to better cellulose conversion as compared to C:G, the glu-

cose yield and ethanol yield from C:O pretreatment residue were both lower than the case where C:G was used. For example, at a mass ratio of 1:15, the glucose and ethanol yields obtained using C:G were 63.57% and 54.86%, respectively, while these yields were 59.83% and 34.32%, respectively, after C:O pretreatment. This might be explained by the fact that the loss of xylan and cellulose led to a reduction in glucose production; upon a pretreatment for 6 h with an S/L ratio of 1:15, the cellulose reservation was 82.45% in the case of C:O and 97.26% in the case of C:G.

Cellulose conversion increased with an increase in lignin removal in corn straw (Fig. 5), as has been widely observed based on pretreatment results. There was a linear correlation between lignin removal and cellulose conversion; further, the correlation was in accordance with the Gompertz model. In this model, cellulose conversion was found to be more sensitive to lignin removal at lower levels. Overall, these results implied that the lignin removal was beneficial for cellulose conversion. For instance, a lignin removal of 44.72% led to a satisfactory cellulose conversion of 85.40%.

3.6. Productivity efficiency of different pretreatment

The energy efficiency results showed that an increase in ethanol production increased the efficiency (Fig. 6). C:G3 resulted in the highest efficiency (62.26%), which was nearly 10 times that of untreated corn straw. The productivity efficiency of corn straw pretreated with DESs was between 27.11% and 62.26%, which was higher than that of untreated corn straw. It can be seen that DES pretreatment not only improved the conversion efficiency of cellulose in raw materials but also solved the problem of resource utilization of straw.

4. Conclusions

This study showed that the synthesized C:O, C:G, and C:U DESs could efficiently remove lignin from corn straw. The properties such as pH and viscosity are related to pretreatment step, so three different DESs were compared. C:O showed the highest catalytic activity because of the acidity. Using C:O as pretreatment solvent, the removal rates of lignin and hemicellulose of corn straw were achieved 60.60% and 42.45%, respectively. Lower DES viscosity improved the pretreatment effect. Enzymatic hydrolysis of corn straw pretreated with DESs led to substantially higher glucose yields than that of untreated straw. The corn straw pretreated with C:G showed high glucose yield and resulted in high ethanol yield, which were 63.57% and 54.86%, respectively. Consequently, this study demonstrated the great potential for the use of C:O, C:G, and C:U DESs in corn straw pretreatment for efficient bioethanol production.

Author contributions

- Study conception and design: J Liu, W Zhang.
- Data collection: C Wang, X Zhao.
- Analysis and interpretation of results: J Liu, C Wang, F Yin, H Yang, K Wu, C Liang, B Yang.
- Draft manuscript preparation: J Liu, C Wang, W Zhang.
- Revision of the results and approval of the final version of the manuscript: J Liu, F Yin, B Yang, W Zhang.

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Conflict of interest

We declare that we have no financial and personal relationship with other people or organizations that can inappropriately influence our work. No potential conflict of interest was reported by the authors.

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