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Effect of Temperature in Deep Eutectic Solvent on Chemical Composition and Structure of Lignocellulose from Corncob

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ABSTRACT. Agricultural waste biomass has significant potential and can be processed into high-value materials. Corncobs are a biomass source with high cellulose content. Processing lignocellulosic biomass is challenging due to the complex molecular structure of the bonds. Deep Eutectic Solvents (DES) are used to break the lignin bonds of corncob lignocellulose. The delignification process using ChCl-urea at temperatures of 80 °C, 95 °C, and 110 °C for 6 hours was carried out to determine the chemical composition of corncobs before and after pre-treatment. The highest cellulose content of 59.85% was obtained at 110 °C. The kinetic energy of molecules increases with higher temperatures, leading to more effective collisions. FTIR indicates reduction of lignin-associated peaks and changes consistent with the removal of hemicellulose/lignin. XRD analysis shows that the crystallinity of corncobs increases after DES pre-treatment. In short, this study provides a simple and green method to prepare cellulose and an efficient utilization route of corncob.

1. INTRODUCTION

Lignocellulosic biomass as a sustainable and renewable raw material has been utilized for biofuels, biochemicals, and valuable materials [1]. Corncob is an abundant biomass, rich in cellulose, hemicellulose, and lignin, making it a promising raw material for valorization and biorefinery applications. Cellulose can be converted into biodegradable composites, biofuels, and biofilms. Hemicellulose, due to its amorphous and heteropolymeric nature, can be transformed into xylitol, furfural, and xylooligosaccharides for chemical and food applications. Meanwhile, lignin is utilized as a renewable aromatic resource for the production of phenolic resins, polymer additives, carbon materials, and bio-based chemicals. However, the intrinsic recalcitrant structure of lignocellulose, due to the complexation of cellulose microfibrils with hemicellulose and lignin, imposes a significant limitation on its application [2].

Deep eutectic solvent (DES) is an environmentally friendly solvent consisting of a stable and recyclable eutectic mixture [3]. DES is easy to produce, has low costs, and has a low melting point compared to ionic liquids [4]. These solvents are synthesized by combining hydrogen bond acceptors (HBAs) and hydrogen bond donors (HBDs) [5]. Choline chloride (ChCl) is commonly used as the HBA [6], while HBDs include acids, polyols, and amines [7]. Based on reported studies, DES can separate lignin and cellulose by breaking the ether bonds in carbohydrate complexes, thereby efficiently deconstructing plant cell walls. ChCl–lactic acid at 145°C for 6 hours removed 78% of lignin and 70% of hemicellulose from poplar wood [8]. Zhou et al investigated the effect of temperature on lignin reduction in corn cobs using ChCl-ethanolamine, observing a decrease in lignin content from 13.91% to 1% as the temperature increased from 30°C to 110°C [9]. A binary DES combining ChCl – formic acid was developed for bagasse pre-treatment at 90–120°C with various times (30–120 min). The results showed that the maximum lignin and hemicellulose removal were 74.3% and 96.4%, respectively [10]. Tan et al utilized the DES combination for the pre-treatment of empty oil palm fruit bunches (EFB). The results showed that after pre-treatment at 120°C for 8 hours, approximately 34% of lignin was removed [11].

Yanak and Buyukkileci (2024) conducted the treatment of corncobs with three different DESs: ChCl-lactic acid, ChCl-acetic acid, and ChCl-urea, to produce xylooligosaccharides (XOS) from xylan. The ChCl-urea treatment at 130°C resulted in the highest XOS production of 4.36 g/L. Further temperature increases negatively affected XOS production by enhancing xylan hydrolysis [12]. Research study by Procentese et al. (2015) processed corn cobs with ChCl urea at 80 °C and 115 °C. The results at 115 °C produced a higher CrI of 36.54. The increase in the rate and extent of saccharification can be attributed to changes in the crystal structure seen in the CrI measurements with XRD [13]. Structural characterization of treated corncob was studied using FTIR.

Considering that temperature affects the pre-treatment process of lignocellulosic biomass with DES, in this study, ChCl-urea was prepared to analyze the chemical composition of corncobs. Structural changes were observed before and after pre-treatment for further application.

2. MATERIALS AND METHODS

2.1 Materials

Corncob was sourced from Yogyakarta (Indonesia). Corncob was reduced to 120 mesh, then washed and dried at 105°C until the moisture content was under 10%. Corncob powder was stored at room temperature for further use. Choline chloride ($C_5H_{14}ClNO$) > 99.0% purity was obtained from Himedia (India), and urea ($CO(NH_2)_2$) $\geq$ 98% purity was obtained from Sigma – Aldrich (China).

2.2 Pre-treatment corn cob using DES

DES was synthesized by combining choline chloride with urea in a 1:2 mass ratio. The mixture was placed in a flask and heated at 80 °C with stirring for 2 hours, resulting in a transparent liquid. DES was placed in a three-necked flask and combined with corncob powder at a 1:20 biomass/DES ratio [14]. The mixture was heated at 80, 95, and 110 °C with stirring for 6 hours. Optimum delignification conditions were achieved at 6 hours [15]. The solid was separated by vacuum filtration, washed to neutral pH, homogenized by ultrasonication for 15 minutes, and dried for 24 hours. The solid was analyzed for cellulose, hemicellulose, and lignin content using the Chesson Method [16].

2.3 Characterization

An infrared spectrophotometer with a diamond Attenuated Total Reflectance (ATR) was used to record FTIR spectra that can analyze various functional groups in samples. The investigations were carried out in transmittance mode, with 32 scans per sample over the 500-4,000 cm^{-1} range.

The XRD patterns were obtained with Cu Kα radiation ($\lambda = 0.154$ nm) at 40 kV and 30 mA. The scanning rate was 2° min^{-1}, and data were collected from $2\theta = 5-50°$. The relative crystallinity index (CrI) was calculated using the Segal method as follows:

$$CrI\ (\%) = (I_{200} - I_{am})/I_{200}\ x\ 100\%$$

Where I_{200} is the peak intensity, which represents both the crystalline and the amorphous region ($2\theta \approx 22.8°$), I_{am} is the diffraction intensity of the amorphous fraction ($2\theta \approx 15.6°$).

3. RESULTS AND DISCUSSION

The effect of temperature on the chemical composition and structural properties of lignocellulose in corn cobs was investigated using a deep eutectic solvent (DES). The content of cellulose, hemicellulose, and lignin for raw and DES-treated corncob was quantitatively determined. Structural changes were evaluated using Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) analysis.

3.1 Effect of Pre-treatment Temperature on Chemical Composition of Corncob Lignocellulose

DES pre-treatment resulted in a significant increase in cellulose content, accompanied by the removal of hemicellulose and lignin as the pre-treatment temperature increased, indicating the temperature-dependent efficiency of DES in lignocellulose fractionation.

Table 1 shows the changes in the chemical composition of raw and treated corncob. Lignin content decreased significantly from 10.58% to 4.10–4.61%, accompanied by a consistent increase in cellulose (46.95% to 53.88–59.85%). This trend indicates that DES can effectively disrupt the lignocellulosic matrix and fractionate some non-cellulosic components, consistent with its well-established role as a tunable hydrogen-bonding solvent system for biomass deconstruction and fractionation [17].

Cellulose content increased from 46.95% to 59.85% at increasing temperature (80°C to 110°C). This increase was due to the dissolution/removal of the amorphous fraction (hemicellulose and lignin). DES performance improves at higher temperatures because viscosity is reduced, mass transfer is increased, thereby accelerating the breakdown of unstable bonds in the lignin-carbohydrate complex [18]. This temperature-driven improvement has been widely reported for DES pre-treatment systems, where higher temperatures often lead to greater delignification and improved accessibility of the carbohydrate-rich solid fraction [19].

Table 1. Chemical composition of corncob using DES

Corn Cob	Chemical composition	Content (%)		
		80°C	95°C	110°C
Treated corncob	Hemicellulose	39.96 ± 0.23	35.31 ± 0.16	33.01 ± 0.09
	Cellulose	53.88 ± 0.03	57.67 ± 0.38	59.85 ± 0.09
	Lignin	4.20 ± 0.19	4.61 ± 0.01	4.10 ± 0.01
Raw corncob	Hemicellulose	41.24 ± 0.02		
	Cellulose	46.95 ± 0.07		
	Lignin	10.58 ± 0.06		

Hemicellulose decreased from 41.24% to 33.01% at 110 °C (Figure 1), indicating that hemicellulose is more sensitive to temperature under ChCl–urea DES conditions. Hemicellulose is more amorphous and less resistant to degradation than cellulose, and it can be partially dissolved through strong DES–hydroxyl interactions and temperature-enhanced diffusion into the cell wall matrix. Consequently, increasing the average temperature results in a decrease in the measured hemicellulose content in the pretreated solids due to deacetylation-related changes [20].

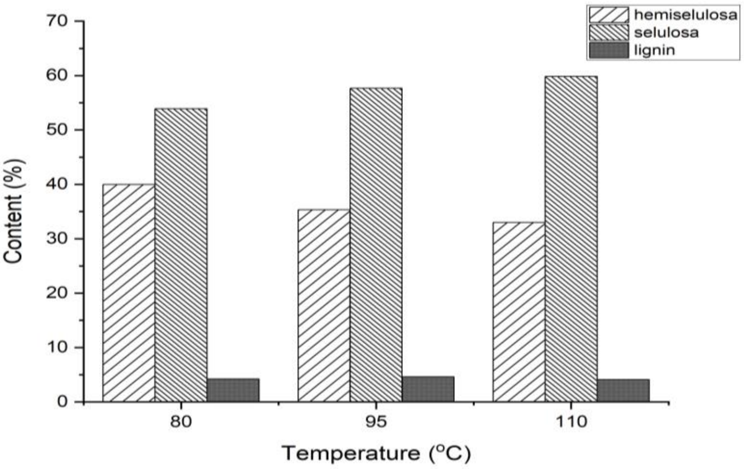


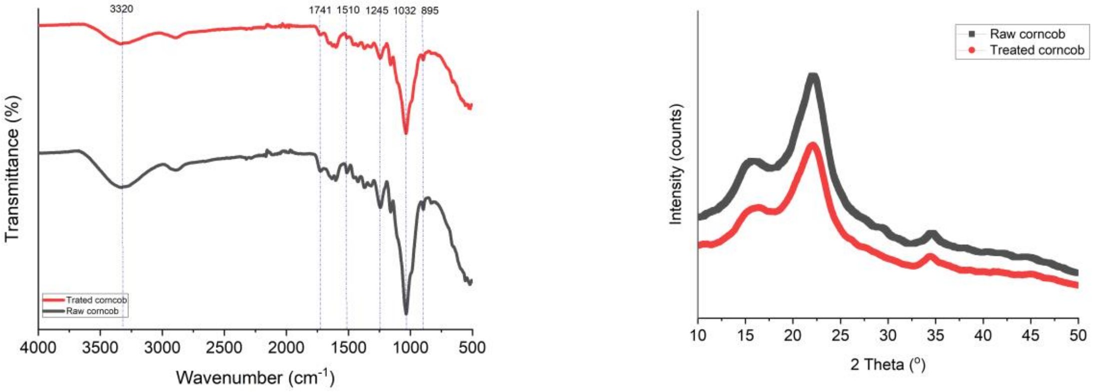
Figure 1. Effect of temperature pre-treatment on corncob

In this study, lignin content decreased from raw corn cobs by 10.58% to 4.1% after pre-treatment with DES. ChCl-urea is highly effective at solubilizing lignin in biomass. Li *et al.* found that ChCl–urea–based DES preferentially removes lignin over hemicellulose during biomass pre-treatment, selectively extracting lignin, leaving the cellulose fraction intact [21]. Similarly, Costa-Trigo *et al.* reported ~39.7% delignification of chestnut burrs (agro-waste rich in hemicellulose and lignin) by 1:2 ChCl-urea pre-treatment (with 40% water) at 100°C for 8–16 h [22]. These results illustrate that even under mild conditions, ChCl-urea can remove a substantial portion of biomass lignin.

Pre-treatment temperature affects lignin extraction efficiency. Higher temperatures increase lignin removal. Temperature pre-treatment from 80°C to 110°C significantly enhanced the delignification of corncob. Although increasing pre-treatment temperature generally enhances lignin removal, the lignin content of the DES-treated corncob did not decrease monotonically with temperature. Lignin content decreases with higher temperatures. However, at 95°C, lignin content increased from 4.2% to 4.61%. This phenomenon can be attributed to the formation of pseudo-lignin from carbohydrate degradation products and to the reprecipitation of dissolved lignin onto the surface of corncob solids treated with DES [23]. Recondensation of these fragments resulted in higher measured lignin content. Further temperature to 110°C resulted in increased mass transfer, which suppressed lignin reprecipitation. At the end of the pre-treatment process, lignin solubility increased again, reducing the solid lignin content to 4.1% [24].

3.2 Effect of Pre-treatment DES on Lignocellulose Structure

The sample with the highest cellulose content at 110°C was then analyzed using FTIR and XRD. Figure 2a shows the FTIR spectra of corncob before and after ChCl–urea pre-treatment. The FTIR spectrum shows the difference between untreated corncobs and those treated with DES. The 3320 cm^{-1} spectrum shows O – H stretching, which can be attributed to the formation of intramolecular hydrogen bonds in cellulose. The 1741 cm^{-1} spectrum shows C – O stretching associated with ester groups in hemicellulose. Corncobs after DES treatment show a reduction in the 1510 cm^{-1} spectrum, which is related to the aromatic band during delignification. The C – O band at the 1245 cm^{-1} peak in treated corncob was much lower than that of raw corn cob due to the dissolution of partial lignin and hemicellulose. Simultaneously, the 1032 cm^{-1} band associated with carbohydrates and the 895 cm^{-1} glycosidic band become relatively increased, in accordance with the increasing cellulose content [25].



(a) (b)

Figure 2 (a) FTIR Spectra; (b) XRD spectra of treated and raw corncob

XRD diffractogram (Figure 2b) showing cellulose peaks at 15.6° and 22.8°, representing the crystalline and amorphous regions. The crystallinity index of treated corncob increased from 35.75% to 37.25% after DES pre-treatment. ChCl-urea can remove hemicellulose and amorphous cellulose. The mechanism is through N–H--Cl, the formation of hydrogen bond complexes between chloride and choline of ChCl with hydrogen and oxygen atoms in the hydroxyl group of cellulose, respectively, along with the urea linking to chloride [26]. Based on FTIR and XRD analysis, the pre-treatment process with DES was shown to affect the structures of raw and treated corncob, with higher cellulose crystallinity.

4. CONCLUSION

Corncob was treated with DES of ChCl-urea mixtures in this study. The chemical composition of cellulose, hemicellulose, and lignin was studied due to the influence of temperature variations used during DES pre-treatment. The results showed that at 110 °C, the treated corncob had the highest cellulose content of 59.85%, lignin and hemicellulose content decreased by 4.1% and 33.01%, respectively. These results are consistent with the 1245 cm^{-1} peak in the FTIR, which indicates lignin bond cleavage. XRD analysis showed that the treated corncob had a higher crystallinity of 37.25% after pre-treatment.

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