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Contributed Paper

Laccase Pretreatment Enhancing Cellulose Extraction from Corn Straw with Deep Eutectic Solvent

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ABSTRACT

The aim of this study was to examine the effect of laccase pretreatment on the cellulose extraction of corn straw with deep eutectic solvent (DES). All pretreatments significantly differed in separation of hemicellulose and lignin, and further in extraction efficiency of cellulose. The overall performance of laccase/xylanase system (LXS) exhibited the highest level between various pretreatment processes, whereas the lowest had the absence of mediator to the pretreatment. The highest differences were observed in the extraction efficiency of cellulose. The viscosity-average molecular weight (M_v) of the obtained cellulose varied from 22678.5 of the control sample to 24871.6 of the LXS sample and the cellulose yield from 42.9% to 99.2%, in which the temperature required in DES-based extraction was only 90 °C, far lower than that commonly used in DES-based extraction of straws. The mechanism of pretreatment effect was explained according to the composition and texturality together with lignin substructures.

Keywords: corn straw, laccase, cellulose extraction, deep eutectic solvent.

1. INTRODUCTION

Cellulose is the most abundant natural polymer on the earth. It is a macromolecular polysaccharide with the formula $(C_{6H10O5})_n$ consisting of a linear chain of several hundred to many thousands of β(1→4) linked D-glucose units [1]. Due to the outstanding chemical activity, mechanical property, low cost and renewability, cellulose has been processed into various papers, membranes and textile materials. In recent years, with the gradually deepening understanding of the hierarchical structure and functionization of cellulose, cellulose products with new functionalities have been developing, and show great potential in applications such as biomaterials, pharmaceuticals, nanosynthesis, chemical calalysis, and energy storage [2,3]. Thus, great efforts have been committed in the extraction of cellulose from renewable lignocellulosic resources, mainly from agricultural residues and energy crops. Lignocellulosic feedstocks, such as corn straw mainly composed of cellulose (40−60%), hemicellulose (20−40%), and lignin (10−24%), provide low-cost and abundant resource for

cellulose extraction [4].

However, enhancing cellulose extraction from corn straw in high yield is still challenging. Therefore, improving cellulose extraction in a green and efficient way is an important stage during preparation of cellulose-based products, which allowing the extraction to end at a good property and a low yield losses. Although numerous green techniques for extracting cellulose have been explored in recent years, it still remains a serious challenge to break the biomass recalcitrance generally arising from the crosslinking of carbohydrate with lignin [5]. As such, besides the traditional methods involving physical, chemical, physicochemical and biological treatments [6], an efficient green extraction method should be developed to obtain high-quality cellulose from biomass. This allows us to hold that the combination of inexpensive green solvents and enzymatic assisted treatments instead of hazardous solvents is one of the most important considerations in green extraction.

Deep eutectic solvents (DESs) derived from natural and renewable components are generally composed of two or three compounds that include hydrogen bond donors (HBDs) and hydrogen bond acceptors (HBAs), respectively such as amide, sugars, organic acid, polyols, and choline chloride (ChCl), which are abundant in our daily life. The physicochemical properties of DES solvents are comparable to ionic liquids. Not only that, DESs are also excellent alternative media to organic hazardous solvents due to their biodegradability, low toxicity, easy preparation, and novel properties [7]. Currently, a series of DESs are applied on extraction media to extract active compounds from plants. Xu *et al.* [8] indicated that ChCl/formic acid was an excellent medium in the cellulose extraction from corn stover by removal of hemicellulose and lignin. Gedanken [9] found that ultrasound (US) could enhance the cellulose accessibility of lignocellulosic biomass by ultrasonic cavitation. Wei *et al.* [10] reported that a ChCl/lactic acid microwave (MW)-assisted extraction was promising for fast and green extraction of four main flavonoids in *Radix scutellariae*.

To a certain extent, although these US and/or MW assisted processes have improved the extraction efficiency of cellulose, they cannot meet the needs of the extraction selectivity and cost-effectiveness. Considering the biochemical properties of laccase in delignification [11], in this study, we attempted to apply laccase to DES-based treatment for highly efficient extraction of cellulose from corn straw. Furthermore, appropriate mediators are often used to give laccase/mediator system (LMS) in order to mediate the oxidation of refractory non-phenolic substructures [12]. For example, the mediator HBT (1-hydroxybenzotriazol) induced the side-chain oxidation of lignin and enhanced the oxidative delignification of biomass [13]. Laccase combining mediator is thus viewed as a green biocatalyst for biomass treatment. However, the usability of laccase is limited in improving cellulose extraction from biomass due to the presence of hemicellulose [14]. Therefore, the removal of hemicellulose should be considered for the overall performance of cellulose extraction from corn straw.

For this reason, addition of xylanase as a "mediator" is a preferred technology to form laccase/xylanase system (LXS) for maximization of the cellulose activity to reduce the operational costs of the DES processes. In principle, as a "mediator", xylanase may remove xylan from straw and increase the size of fiber pore [15]. Nevertheless, data regarding the laccase pretreatment using xylanase as a "mediator" for efficient cellulose extraction from corn straw with DES are limited. Hence, the influence of applying LXS to improve the fractionation of corn straw and fabricating high-quality cellulose are still mostly unknown. Detailed studies were comparatively performed to disclose these effects.

2. MATERIALS AND METHODS

2.1 Materials

Corn straw with no pith was obtained from a straw company (Yunnan Province, China). It was

adequately washed and air-dried, and then ground in a Wiley mill and sieved. The meal fraction that passed 80 mesh screen was collected and extracted with water for 24 h and with ethanol for 8 h to remove non-structural compounds. Finally, they were dried in a vacuum oven overnight at 40 °C and the resulting powders were stored at -4 °C in hermetically sealed bags until required.

2,2'-Azino-bis(3-ethylbenzothiazoline-6-sulfonic acid (ABTS) was commercially obtained from Sigma-Aldrich (Sigma-Aldrich (Shanghai) Trade Company, Shanghai, China). Laccase (1000 IU/g) and xylanase (25 IU/g) were purchased from Novozymes (Novozymes (China) Biotechnology Co., Ltd, Tianjin, China).

2.2 Preparation of DESs

All DESs used in this work were prepared by mixing ChCl with various HBDs (glucose, urea, glycerol, lactic acid and oxalic acid) under reduced pressure following the procedures as reported in the literature [16]. The preparation was allowed to perform using a molar ratio of 1:1 at 80 °C for 1 h until a homogenous and transparent liquid was obtained. DESs were used immediately once prepared. Kamlet-Taft solvatochromic parameters were determined with Shimadzu 2550 UV spectrophotometer (Japan) after treatment with Kamlet-Taft dyes [17].

2.3 Corn Straw Pretreatment with Laccase and Cellulose Extraction by DES

The pretreatment on corn straw (60 g, dry weight) was performed with laccase at 50 °C for 3 h. The straw concentration (6%) was adjusted with acetic acid-sodium acetate buffering solution (pH 5). In the course of the reaction, air was constantly and continuously bubbled through the mixture. Then the mixture was vacuum-filtered, thoroughly washed with Milli-Q water and vacuum-dried at 40 °C. After that, the straw meals commenced with a dewatering treatment by acetone exchange [18], and then mixed with DES under constant stirring. The resulting mixture was filtered and washed five times with an excess of anhydrous ethanol. The residual solid was then ultimately vacuum-dried at 40 °C and stored in desiccator before being used.

Replicates (at least 3 replicates) were carried out and better reproducibility was obtained, with a coefficient of variation less than 3% (significant power>90%).

2.4 Lignin Extraction

The straw meals before and after the pretreatment were ground with a Wiley mill and sieved. The lignin present in meals was then isolated using a method developed by Argyropoulos *et al.* [19].

The meals were hydrolyzed with cellulase (2267.5 U/g, Novozymes) in acetate buffer solution (pH 4.8) at 45 °C in order to minimize damage to the lignin structure during isolating process. The residues obtained from the enzymatic treatments were thoroughly washed with the buffer solution and water and then subjected to a mild acidolysis at a consistency of 4% with 0.05 M HCl solution in dioxane/water (85:15, v/v) under nitrogen positive pressure. The solution containing the dioxane extracts was acidified with 1 M HCl to pH 2.0, the lignin was then precipitated, centrifuged and thoroughly washed with 0.01 M HCl, and freeze-dried. Finally the lignin was extracted with dichloromethane to further remove accumulated extractives. Meanwhile, the yield and chemical composition of the lignin preparations were determined according to the National Renewable Energy Laboratory standard analytical method (NREL/TP-510-42618) [20].

The determination of the sugar content was carried out with ionic chromatograph (Metrohm ICS-883, Swiss) equipped with iColumn and iDetector. The yield, carbohydrate content, and protein content of the lignin samples were 60, 0.70 and 0.50%, respectively.

Correspondingly, the lignin samples extracted from the corn straw and pretreated straws were namely designated as CSL (corn straw lignin), CL (control puls lignin), LaL (laccase pretreatment plus

lignin), LaABTSL ((Laccase+ABTS) pretreatment plus lignin), and LaXL ((Laccase+xylanase) pretreatment plus lignin), respectively.

In addition, lignin samples were acetylated with acetic anhydride in pyridine for GPC (gel permeation chromatography) analysis [21].

2.5 GPC Analysis

The molecular weights of lignin preparations were analyzed with GPC (Agilent 1100, USA), which follow the procedures described in a previous study [22].

2.6 NMR Analysis

All the NMR analyses of the prepared lignin samples were performed in a a Bruker DRX 500-MHz NMR spectrometer. The lignin preparation (140 mg) was dissolved in DMSO-d_6 (0.50 mL). The 2D-HSQC NMR spectra were then recorded using the central solvent peak as an internal reference (δ_C 39.6/δ_H 2.48). In addition, the standard pulse program hsqcedetgpsisp2 was applied in the HSQC analysis of lignin [23]. Conditions for analysis were as follows: ^{13}C spectral width, 20,000 Hz; ^{1}H spectral width, 5000 Hz; temperature, 318 K; 90° pulse; acquisition time, 0.1 s; and 1.0 s acquisition delay (d_1). The main linkages in the obtained spectra were quantitatively assigned according to the reported literature [24−25].

2.7 Composition Analysis

The monosaccharide content of the samples was determined using hydrolysis method followed by HPLC chromatography. The analysis was done with a Dionex ICS-5000 HPAEC-PAD equipped with CarboPac PA20 column. The content of cellulose and hemicellulose in sample was thus calculated on the basis of the quantity of glucose, and xylose, arabinose, galactose and mannose, respectively [26]. The lignin content including Klason lignin and acid-soluble lignin was determined by acid hydrolysis according to NREL procedure [20].

The cellulose yield, hemicellulose removal rate and lignin removal rate were calculated based on the mass of cellulose, hemicellulose and lignin in raw corn straw, respectively.

2.8 Determination of Molecular Weight

The viscosity-average molecular weight (M_v) of cellulose was determined by copper ethylenediamine method [27].

2.9 Textural Characterization of Straw Samples

The textural characteristics of straw samples were measured by adsorption and desorption of nitrogen at the temperature of liquid nitrogen (77 K) on volumetric adsorption set-up (Micromeritics ASAP-2020, USA) [28].

2.10 Sample Characterization by X-ray Diffraction (XRD)

XRD spectra of the samples were recorded with a Rigaku Dmax X-ray diffractometer (Ni-filtered, CuKa radiation) [29].

3. Results and Discussion

3.1 DESs Extractability and Laccase Pretreatments Towards Cellulose

Cellulose extraction from corn straw with various methods in the absence of pretreatment was depicted in Figure 1. Results showed that different extraction methods led to variations in cellulose yield, removal rate of lignin and hemicellulose, and cellulose crystallinity. The DESs, including ChCl/glucose, ChCl/urea, ChCl/glycerol, ChCl/lactic acid, ChCl/oxalic acid, displayed the advantages for chemically delignification and hemicellulose removal, and they thus gave high cellulose yield and crystallinity compared to the peroxyformic acid (HCOOOH) and NaOH processes.

The extraction efficiency of the five DESs upon cellulose from corn straw was further compared under the same conditions: mole ratio of ChCl-HBD (1:1), extraction temperature (90 °C), extraction time (4 h), and ratio of liquid to solid (20:1). As shown in Figure 1, the cellulose yield obtained with these DESs was in accordance with

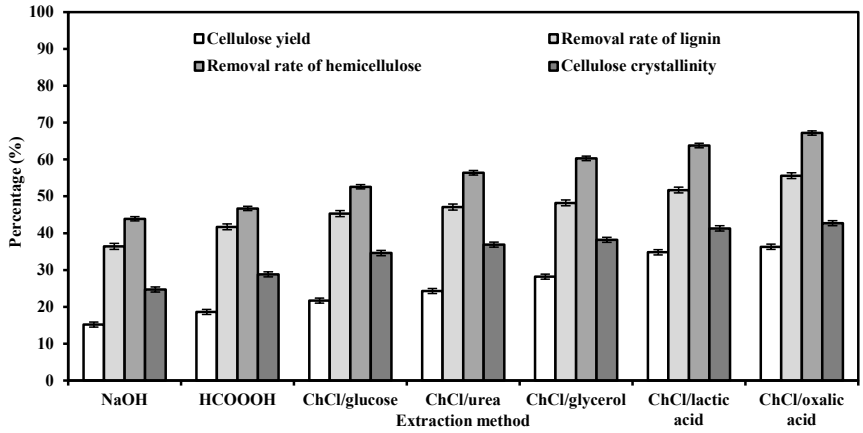

Figure 1. Efficiency of various extraction methods for extracting cellulose from corn straw. NaOH: mass fraction of NaOH, 4%; extraction temperature, 90 °C; extraction time, 4 h; ratio of liquid to solid, 20:1. HCOOOH: mass fraction of HCOOOH, 4%; extraction temperature, 35 °C; extraction time, 8 h; ratio of liquid to solid, 20:1.

the following order: ChCl/oxalic acid (36.3%) > ChCl/lactic acid (34.8%) > ChCl/glycerol (28.2%) > ChCl/urea (24.3%) > ChCl/glucose (21.7%). The maximum extraction yield was 36.3% using the ChCl/oxalic acid-based DES, which is slightly higher than that extracted by ChCl/lactic acid, and much higher than those extracted by ChCl/glycerol, ChCl/urea and ChCl/glucose systems. Furthermore, applying ChCl/oxalic acid to treat the straw afforded the most significant effect of using this chemical related to the increase of lignin and hemicellulose removal and cellulose crystallinity (Figure 1). These results indicated that the oxalic acid-based DES treatment contributed a significant efficiency to cellulose extraction. As shown by the determination with Kamlet-Taft solvatochromic method, the hydrogen-bond acidity (α) of ChCl/oxalic acid (1.73) was greater than those of DESs using glycerol (α 1.15), lactic acid (α 1.58), urea (α 0.87) and glucose (α 0.66) as HBDs, which may be responsible for the higher cleavage efficiency of lignin-carbohydrate complexes (LCCs) [29]. In addition, oxalic acid has a relative short molecular chain, which may led to a significant improvement in the accessibility of corn straw [30].

However, it can be considered that the obtained extraction yields of cellulose by these DESs were very low when the pretreatment was not carried out. Given the above test results, the ChCl/oxalic acid extraction towards corn straw was further enhanced by using the laccase pretreatment in order to improve the yield and quality of cellulose. The pretreatment with different laccase dosages (based on straw) was evaluated in the absence of mediator for the extraction of the target cellulose. As shown in Figure 2a, the removal rate of lignin and hemicellulose changed significantly when the laccase dosage increased from 0% to 1.0%. Furthermore, on the basis of comparison, the removal rate of lignin (10.6%) and hemicellulose (4.5%) obtained with 1.0% dosage of laccase was considered to be maximal, and thus we chose this dosage for the trials upon mediators. Furthermore, Figure 2b and 2c revealed that an increasing mediator dosage benefited the separation of hemicellulose and lignin. Moreover, the laccase/xylanase system (LXS) exhibited a higher removal rate (Figure 2c) than the laccase/ABTS system (Figure 2b). For example, when the optimal dosage of ABTS (0.10%) and xylanase

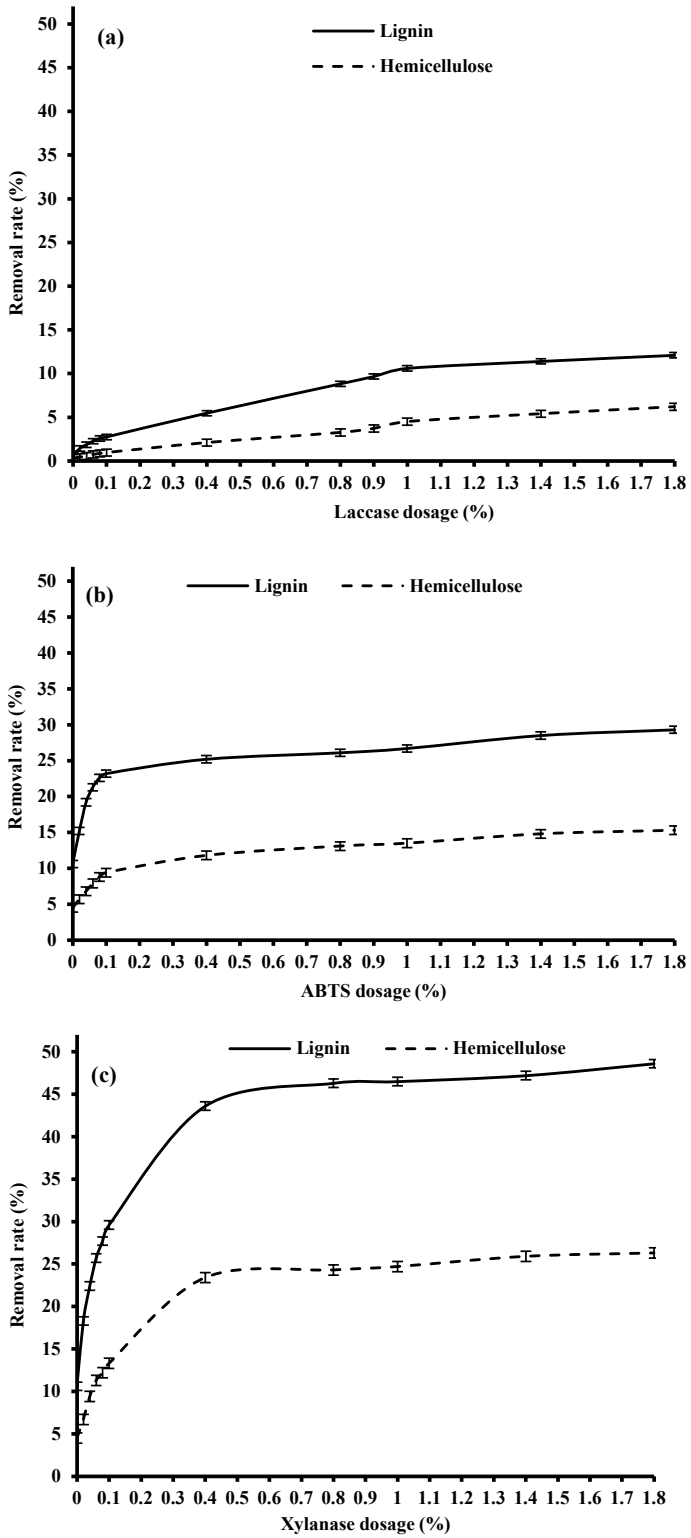

Figure 2. Pretreatment vs hemicellulose, and lignin removal rate.

(0.40%) was used, the former gave the removal rate of 9.4% hemicellulose and 23.2% lignin, while the latter gave that of 23.4% hemicellulose and 43.6% lignin.

Synchronously, the M_v and yield of the target cellulose increased with enhancing pretreatment, and they respectively reached 24871.6 and 99.2% when LXS was used as the pretreatment while those (M_v/yield) were 22678.5/42.9%, 23157.3/65.3% and 23638.2/77.4%, respectively for the control, laccase pretreatment and (laccase+ABTS) pretreatment followed by DES extraction. This suggested that the release of lignin and hemicellulose by the laccase pretreatment, especially the addition of xylanase as a mediator, was conductive to the improvement of the DP (degree of polymerization) and extraction of cellulose in the DES-based treatment. Besides the effect of laccase acting on lignin in straw, the xylanase removed xylan, and the combination of laccase and xylanase had positive synergy in LXS. These combined effects played a significant role in improving the extraction efficiency of cellulose [31].

In addition, although the xylanase dosage was higher than that of ABTS, it was more cost-effective [32]. Moreover, the pretreatment greatly reduced the temperature required in DES-based extraction, which was only 90 °C, far lower than that commonly used in DES-based extraction of straws [33−35]. Thus, it could be considered that the pretreatment with laccase plus xylanase instead of the expensive mediator provides a good basis for efficient cellulose extraction.

3.2 Mechanism of Pretreatment Effect Towards Lignin

The molecular weight of lignin is an important information for understanding the lignin depolymerization occurred in the pretreatment of the straw meals with laccase [36]. The weight-average (Mw) molecular weight, number-average (Mn) molecular weight and polydispersity (Mw/Mn) are thus summarized in Table1 for the prepared lignin samples. The Mn of CSL was 2883 g/mol, which was reduced by 1.28% to 2846 g/mol in CL, by 19.49% to 2321 g/mol in LaL, by 36.62% to 1827 g/mol in LaABTSL, and further by 58.51% to 1196 g/mol in LaXL. It can be concluded that the lignin present in corn straw was greatly degraded via the LXS process. Moreover, the polydispersity index (PDI) was found to decrease from 1.72 of CSL to 1.66 of CL, 1.43 of LaL, 1.21 of LaABTSL and 1.17 of LaXL, respectively, which suggested that some refractory lignin fragments of high molecular weights were decomposed in pretreatment. Therefore, the LaXL was expected to have most excellent solubility and degradability in DES due to its smallest molecular weight [37].

Table 1. Molecular weight and substructure of lignin.

Lignin	Molecular weight (GPC)			Substructure (/100Ar, HSQC NMR)					
	Mn (g/mol)	Mw (g/mol)	PDI (Mw/Mn)	β-O-4'	β-1'	β-β'	β-5'	5-5'	LCC
CSL	2883±6	4958±7	1.72±0.02	31.4±0.07	8.3±0.03	13.7±0.02	7.3±0.04	4.8±0.02	5.4±0.03
CL	2846±6	4724±7	1.66±0.03	30.3±0.05	7.9±0.04	13.2±0.02	6.8±0.02	4.6±0.03	5.2±0.02
LaL	2321±8	3319±5	1.43±0.04	26.7±0.03	5.7±0.03	10.6±0.04	5.2±0.03	2.2±0.02	4.4±0.03
LaABTSL	1827±10	2210±7	1.21±0.02	21.8±0.03	2.6±0.02	4.4±0.03	1.4±0.02	0.52±0.03	3.6±0.04
LaXL	1196±8	1399±7	1.17±0.03	17.6±0.02	2.4±0.03	3.8±0.02	1.3±0.02	0.46±0.03	0.13±0.03

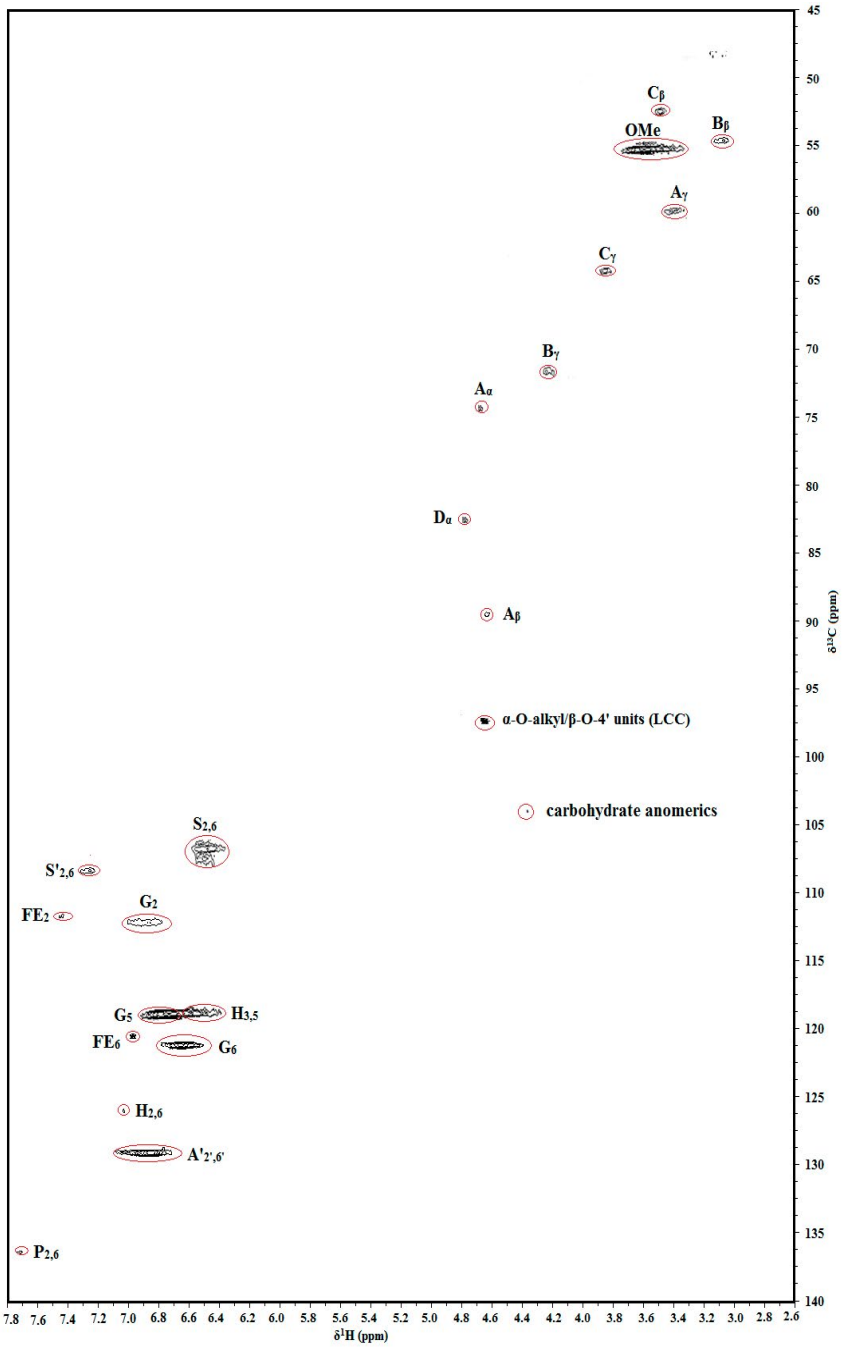

Figure 3. Typical 2D HSQC NMR spectrum of corn straw lignin. Main substructures of lignin: (A) β-O-4 linkages, (A´) β-O-4 linkages with a carbonyl group at C_α, (B) resinol structures formed by β-β´/α-O-γ/γ-O-α´ linkages, (C) phenylcoumaran structures formed by β-5´/α-O-4´ linkages, (D) spirdienone structures formed by β-1´/α-O-α´ linkages, (G) guaiacyl unit, (S) syringyl unit, (S´) oxidized syringyl unit with a carbonyl group at C_α, (S´´) oxidized syringyl unit with a carboxyl group at C_α, (H) p-hydroxyphenyl unit, (FE) esterified ferulic acid structure, (P) esterified p-acetoxy-benzoic acid structure.

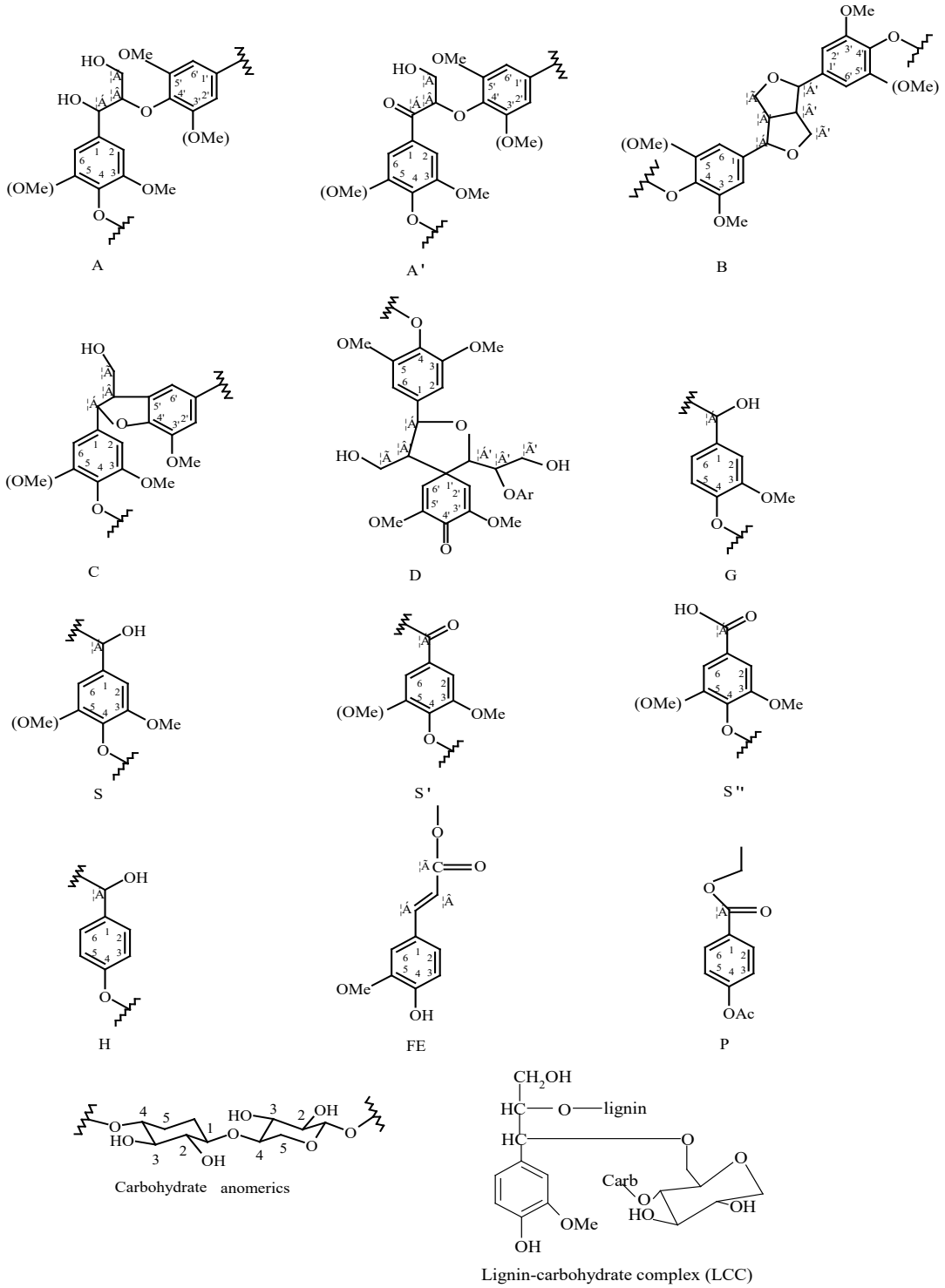

Figure 3. (Continued)

The changes in lignin molecular weight could be confirmed by the HSQC NMR characterization upon the substructures. A typical spectrum of the corn straw lignin was thus present in Figure 3. The content of substructure linkages was listed in Table 1, which was based on HSQC spectra. As shown in Table 1, the content of β-O-4 linkages in CSL was 31.4/100Ar, which decreased to 30.3/100Ar in CL, 26.7/100Ar in LaL, 21.8/100Ar in LaABTSL and 17.6/100Ar in LaXL, which suggested that the main lignin linkages were remarkably degraded in the laccase process. In contrast, the contents of C-C linkages including β-1›, β-β', β-5' and 5-5' in the corn straw lignin was evidently reduced in the pretreatment. Prominently, the LXS showed a superiority to the other processes in removing LCC moieties from the straw, which was due to the carbohydrate depolymerization by xylanase [38].

3.3 Mechanism of Pretreatment Effect Towards Textural Characteristics

In order to determine microstructure alterations occurred in different pretreatment processes, raw and pretreated corn straw samples were measured by method of adsorption and desorption of nitrogen. Changes in the textural characteristics were observed for straw samples in relation to the pretreatments, as shown in Table 2. Among the examined pretreatments, laccase imposed a slight effect on improving the textural property of corn straw in the case of no addition of mediator, and LXS pretreatment demonstrated the most positive effect on textural values, in which the specific surface area varied from 2.017 m^2/g to 5.014 m^2/g, total pore volume from 6.262 cm^3/mg to 7.884 cm^3/mg, and average pore from 5.217 nm to 8.512 nm. These results suggested that changes in textural performance index of corn straw corresponded closely to the M_v and yield of cellulose.

In addition, the XRD method provides useful information on the qualitative and quantitative changes in crystallography of the corn straw and cellulose samples. As indicated by the XRD spectra in Figure 4, there was no obvious change upon the crystalline structure, indicating little destruction of the pretreatment on the corn straw cellulose. Nevertheless, by calculation, a notable improvement was observed in the crystallinity with the pretreatment, and mediator could promote this evolvement, in which the pretreatment gradually increased the crystallinity of the samples from 42.7% of the straw to 43.3% of the control, 51.2% of the laccase pretreated, 62.8% of the (laccase+ABTS) pretreated, and to 77.2% of the (laccase+xylanase) pretreated.

The XRD characterization confirmed that the pretreatment factually improved the crystallography of corn straw cellulose. This may be explained by the removal of amorphous lignin from the straw

Table 2. Textural characteristics of pretreated straw samples, and DP and yield of cellulose obtained from pretreatment-ChCl/oxalic acid treatment.

Straw sample	Textural characteristics of pretreated straw samples		
	Specific surface area (m^2/g)	Total pore volume (cm^3/mg)	Average pore size (nm)
Straw	2.017±0.02	6.262±0.04	5.217±0.03
Control	2.057±0.03	6.328±0.03	5.409±0.04
Laccase	2.462±0.04	6.762±0.02	5.748±0.02
Laccase+ABTS	3.384±0.02	7.135±0.03	7.942±0.03
Laccase+xylanase	5.014±0.02	7.884±0.04	8.512±0.03

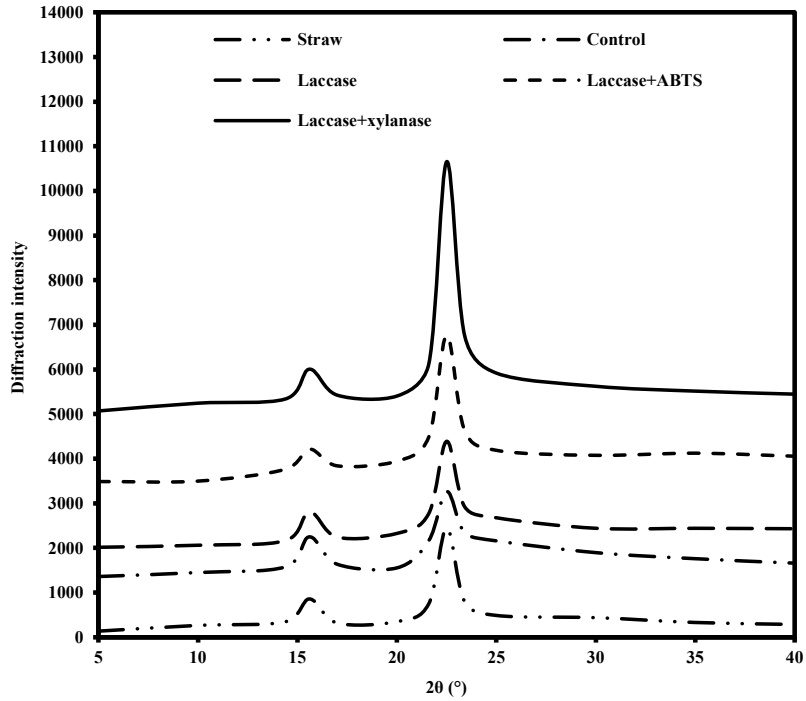

Figure 4. XRD spectra of straw and cellulose from pretreatment-ChCl/oxalic acid treatment.

due to the enzymolysis towards lignin [39, 40]. Furthermore, xylanase was another important positive factor by hydrolyzing carbohydrate (xylan) present in straw and LCC [41], in which it gave a much high removal of lignin and hemicellulose with good selectivity towards cellulose compared to ABTS (Figure 2). Also, the fact that the micropores of corn straw were enlarged by the pretreatment may be an important reason, which has been confirmed by the textural data (Table 2).

4. Conclusions

The pretreatment has been studied with different laccase processes, at 50 °C and in the presence of air bubbles in order to improve the cellulose extraction from corn straw with DES. All processes have shown improvement in release of lignin and hemicellulose, but higher level has been found for the pretreatment with LXS attending to the greater increase of M_v and yield of the extracted cellulose. Regarding the mechanism of pretreatment effect, more degradation of refractory lignin substructures and larger micropores of straw have been found in the case of LXS sample. This pretreatment also has been shown a higher crystallinity of cellulose.

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