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Improvement of lignin yield and purity from corncob in the presence of steam explosion and liquid hot pressured alcohol

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Non-food biomass such as corncob is a very abundant and promising feedstock for sustainable energy production in China. Many studies have focused on overcoming the barrier of saccharification of corncob. However, lignin was not well exploited as the renewable aromatic resource in the nature since the simple single protocol usually cannot facilitated the bio-recalcitrance or advanced methods (ionic liquid etc.) hardly met the economic viability in plant scale. Here we provided a easy combined process which could reap pure, high-yield and low molecular weight lignin. Moreover, other components of corncob (cellulose and hemicellulose) were easy digested into value-added products (xylose and glucose).The lignin rich fraction (LRF) from corncob was identified by the heteronuclear single quantum correlation (HSQC) NMR, gel permeation chromatography (GPC) and Fourier transform infrared spectroscopy (FTIR) to illustrate structure characteristics. The cellulose rich fraction (CRF) was analyzed by X-Ray Diffraction (XRD) and experienced an enzymatic hydrolysis. The results showed that: (1) the LRF was pure and high-yield, main linkages was cleaved during the combined process; (2) hemicellulose was utterly removed and transformed into xylose; (3) the CRF was easy for enzymatic digestion and the glucose conversion was 95.7% of theoretical value.

1. Introduction

Corn yield (21.85 million tons) represented the greatest proportion of the total grain yield in 2013 in China[1]. Usually the rest corncob was burned and this treatment has negative effects on air environment, which is one of the reasons of smog[2]. Corncob is rich in lignocellulose which has huge potentials on producing glucose, xylose, and aromatic chemicals. Many technologies were studied on utilising the single component of corncob, such as using ionic liquid to enhance the enzymatic hydrolysis of cellulose[3]， microwave was employed to enhance conversion of hemicellulose into xylose[4]. Lignin is the second most abundant source of renewable carbon accounting for 15%-30% of dry weight of lignocellulose[5]. Abundant lignin in corncob was interlaced with carbohydrate complex but not well exploited. High quality lignin, as renewable material, has great potential to produce basic industrial aromatic chemicals[6]. Pulp and paper industries generate a great amount of lignin currently as by-product of delignification and biofuel refinery is expected to produce more lignin in the future [7]. However, this lignin could only be exploited in low valued application[8] and generate heat[9] nowadays. Consequently, to improve the added-value worth of lignin has been attracting more attention in the lignocellulose biorefinery[10].

It has been demonstrated that lignin constitutes the main barrier for the enzymatic hydrolysis of cellulose in lignocellulose and the removal of lignin could facilitate the enzymatic efficiency[11]. Up to now, the alkali treatment was the most extensive-used method for delignification. However, alkali delignification is considered to be environmental unfriendly, it produced a variety of pollutants, especially the inorganic salts, which were unable to be utilized by biodegradation[12]. Ionic liquid attracted attention as a green promising solvent for biomass pre-treatment[13]. Currently, 1-ethyl-3-methylimidazolium acetate ([Emim][CH3COO]) was considered to be the best solvent which could selectively extract lignin from lignocellulose. However, the lignin yield was low and the molecular weight was higher relatively[14].

In the 1990s, the ethanol delignification was developed and reached a pre-commercial stage as a green delignification method[15], which was characterized with the advantages of easy recovery of ethanol, less production of pollutants and elimination of the odour when compared to alkali delignifying methods.

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Moreover, organosolv lignin was considered to be high quality because of its high purity and primarily unaltered structure. It could be applied to the fields of adhesives[16], nanostructured films[17] and copolymers[18]. However, ethanol lignin could not meet the industrial requirements in comparison with the conventional kraft lignin in terms of economic performance because of low yield of lignin caused by the structure complexity of lignocellulose. A feasible solution for overcoming this was to modify this process to produce profitable products.

More recently, a clean process for xylose production in pilot scale by using screw-steam-explosive extruder was developed in our previous study. More than 90% of hemicellulose was degraded and converted into mono xylose, a high-valued fine chemicals[19]. In the present study, the ethanol solution was applied to extract organosolv lignin from the steam explosion residue (SER) and the higher yield and purity of organosolv ethanol lignin was obtained in the presence of diluted acid steam explosion (DASE) and liquid hot pressured alcohol delignification (LHPAD).

In order to improve the value-added worth of lignin, this study aimed to develop a clean, effective and economic process for organosolv ethanol lignin preparation in combination of steam explosion and ethanol delignifying process.

2. Experimental

2.1 Raw materials and the combined process of DASE and LHPAD

Dried untreated corncob (UC) was from Shandong province and chipped to a size of 2cm and stored at room temperature. Lignin was isolated by the procedure described at Fig 1. The sample was immersed in H_2SO_4 solution (0.5% w/w) overnight and drained by squeeze. It was treated by steam explosion in a screw-steam-explosive extruder at the optimal operating parameters (5min and 1.5MPa) and the component of elution was mono xylose as described in our previous work[19]. The dried SER was treated with ethanol aqueous (20/80 v/v) at 160^{o}C for 120min. The solid to liquid ratio was 1:10. This experiment was carried out in a 0.5L stainless steel high-pressure reactor. After alcohol delignification, the insoluble residue was filtered and washed with the same ethanol aqueous three times, which was rich in cellulose and named as cellulose rich fraction (CRF). The filtrate was collected and concentrated, 3 volumes of acid water (pH=2) were dropped to precipitate the lignin rich fraction (LRF), which was collected by centrifugation and air dried at 40^{o}C for 24 hours**.**

2.2 Chemical composition analysis

The cellulose, hemicellulose, lignin and ash were determined by the NREL method (Determination of Structural Carbohydrates and Lignin in Biomass)[20].Dried samples (300mg) was hydrolyzed using 3ml 72% H_2SO_4 for 60 min at 30^{o}C in a water bath with intermittent shocking every 5-10 minutes. Add 84ml water to dilute H_2SO_4 to 4% and hydrolyze at 121^{o}C for 60 min in an autoclave. The dried residue of hydrolysis was acid insoluble lignin (AIL). The hydrolysate was analyzed by UV spectrophotometer (Shimadzu UV2450) to determine acid soluble lignin (ASL) and carbohydrate was determined by High Performance Liquid Chromatography (Hitachi, Tokyo, Japan) equipped with a Sugar-pak 1 column (Waters, Milford, MA, USA). The AIL was placed in a muffle furnace at 575 ^{o}C to determine the ash content.

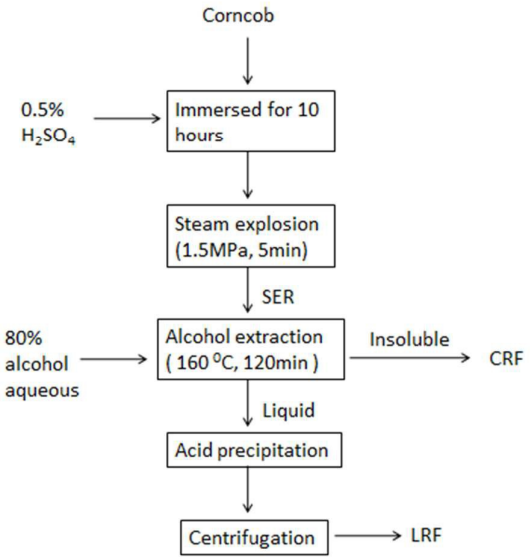

Fig.1 Lignin isolation procedure.

2.3 Fourier transform infrared spectroscopy

The FTIR spectrums of all samples were recorded in a Nicolet 6700 spectrophotometer in the scan range from 400 cm^{-1} to 4000 cm^{-1} with a resolution of 4 cm^{-1}. A 200mg KBr disc containing 1 mg sample was used in FTIR measurement.

2.4 X-ray differaction

XRD was carried out in a Rigaku D/Max 2500 VB2+/PC, with 5^{o}/min scan speed and 5-50^{o} scan scope. Copper radiation (k=0.154185nm) was generated at a voltage of 40 Kv. The crystal index was calculated by the following equation:

$$CrI=\frac{I_{total}-I_{am}}{I_{total}}*100$$

Where I_{total} is the scattered intensity at 2θ=22.1^{o}, and I_{am} is the scattered intensity at 2θ=16.0^{o}.

2.5 HSQC of LRF

Acetylation was frequently performed on lignin before NMR analysis (Support information). The HSQC spectrum of LRF was done by a Bruker AV 600 spectrometer. 100mg acetylated lignin was dissolved in 0.5 mL DMSO-d_6. The spectral widths were 7788 Hz and 27165 Hz for ^{1}H and ^{13}C dimensions respectively. The number of collected complex points was 2048 for ^{1}H dimension with a recycle

delay of 1.5s. The number of transients was 64 and 256 time increments were recorded in ^{13}C dimension. The $^{1}J_{CH}$ used was 145 Hz. Data was analyzed by Bruker Topspin software. The DMSO peak (δC/δH=39.5/2.49) was used as an internal chemical shift.

2.6 Gel permeation chromatograms

LRF sample was dissolved in 1ml 1% NaOH aqueous solution and then diluted to proper concentration with deionized water for GPC analysis. The Waters GPC system (Milford, Massachusetts, USA) equipped with UV detector was employed for molecular weight determination. The column was TSK G3000PWxl. The different molecular-weight (Mw=210, 4300, 6800, 10000, 17000, 32000, 150000) poly styrenesulfonic acid salt (purchased from Sigma-Aldrich) was hired as standards. The experiment was operated at room temperature and eluted with 0.1M $NaNO_3$ solution at a flow rate of 1ml/min and 50μl sample was injected into the GPC system.

2.7 Enzymatic hydrolysis of CRF

The enzymatic hydrolysis of UC, SER and CRF was carried out in 50mM citrate buffer (pH=4.8) with 5g substrates in 100ml buffer at 50°C, 150 rpm for 72h. The cellulase (Novozyme Cellic CTec2) activity was 206 FPU/ml and the enzyme loading was 18 FPU/g cellulose. The results of enzymatic hydrolysis were determined by HPLC described in 2.2.

3. Results and discussion

3.1 Chemical compositions of samples

Table 1 The chemical compositions (w/w, %) of UC, SER, LRF and CRF.

Sample	Cellulose	Hemicellulose	ASL[a]	AIL[b]	Ash
UC	34.24	29.27	17.98	11.33	2.46
SER	30.17	1.11	5.86	59.33	6.40
LRF	0.28	0.02	2.37	91.20	2.20
CRF	66.58	1.90	0.49	34.87	5.60

[a]ASL, acid soluble lignin.
[b]AIL, acid insoluble lignin.

The chemical compositions of each fraction were given in Table 1. The chemical compositions of UC were 34.24% cellulose, 29.27% hemicellulose, 17.98% acid soluble lignin and 11.33% acid insoluble lignin. Based on the chemical composition of LRF in Table 1, it indicated that purity of lignin was improved by the combination of DASE and LHPAD. The lignin purity reached 93.57%, which was primarily consisted of acid insoluble lignin. Acid soluble lignin was dissolved and could not be recovered by acid precipitate since the existence of diluted acid, as a catalyst, providing hydrion and cleaving the α- and β-aryl ether linkages of ASL during the DASE[21] .The lignin yield was improved from 6.81% to 40.94% (Fig. S1). It was higher than that from previous Alcell process significantly[22]. The hemicellulose composition after DASE was 1.11%, demonstrating that most hemicellulose was depolymerized and removed from the lignocellulose during the DASE via autohydrolysis reaction[23]. Therefore, the high lignin yield could attribute to the physical crushing ability of DASE, offering more accessible area for alcohol to enrich the lignin after removal of the hemicellulose component. The cellulose (66.58%) in CRF increased twofold after combined process, which indicated that most ASL and partial AIL was dissolved and removed from SER, while cellulose was retained in the solid phrase. Ethanol process with acid catalyst, such as H_2SO_4, HCl and phosphoric acid, was frequently used to extract lignin from different biomass. However, lignin purity from swithgrass was approximate 70-80% (with 0.9w/w% sulfuric acid) and this lignin was contaminated by carbohydrates[24]. Other organosolv lignin extraction after steam explosion was complex and it needed subsequent lignin purification process involved many operations and chemicals (acetic acid, dioxane, ethyl ether etc.)[25]. Lignin has complex and irregular structures crosslinking with carbohydrates by tight physical bonding and chemical linkages. Single process is too powerless to overcome lignin-carbohydrate recalcitrance, leading to low purity and low yield. For example, ionic liquid was considered to be the green solvent for lignin, however, only up to 20wt% lignin isolated from pine kraft pulp could dissolve in $[hmim][CF_3SO_3]$[26]. During the combined process of DASE and LHPAD, amorphous hemicellulose and part of cellulose was separated by DASE, which contributed to the higher lignin purity and yield than ethanol process with acid catalyst obviously.

3.2 FTIR analysis

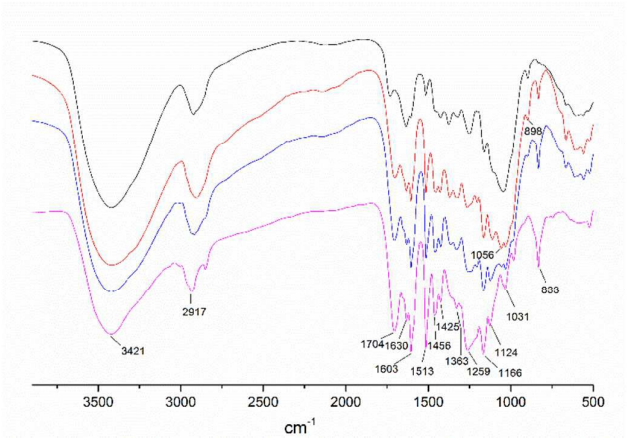

Fig.2 FTIR spectra of corncob (black), SER (red), CRF (blue) and LRF (pink).

Table 2. FTIR spectrum bands and corresponding assignments in corncob, SER, CRF and LRF.

Band (cm^{-1})	Assignment	UC	SER	CRF	LRF
3500-3300	O-H stretching	3421	3421	3421	3421
2918	Aliphatic	2891	2902	----	2917
2850-2830	C-H symmetric stretching in methyl and methylene group	----	----	2850	----
1720-1680	C=O stretching in unconjugated ketone ,carbonyl, and ester groups	----	1702	1704	1704
1660-1640	C=O stretching in conjugated p-substituted aryl ketones	1633	1631	1631	1630
1610-1590	Aromatic skeletal vibrations plus C=O stretching	1606	1604	1604	1604
1515-1505	Aromatic skeletal vibrations	1515	1513	1513	1513
1470-1460	C-H deformations (asymmetric in –CH3 and –CH2-)	----	1454	1460	1456
1420	Aromatic skeletal vibrations combined with C-H in plane deformations	1427	1429	1425	1425
1365-1370	Aliphatic C-H stretching in CH3 (not in OMe) and phenolic OH	1373	1371	1362	1363
1267	G unit breathing	----	1261	1263	1259
1166	HSG unit	----	1164	1168	1166
1161	Anti-symmetrical bridge C-O-C stretching	1160	-----	----	----
1130-1120	S unit	----	----	1126	1124
1056	C-O stretching	1054	1058	1056	----
1033	Aromatic C-H in plane deformation (G+S units)	----	1031	1033	1031
897	β-linkage of cellulose	898	898	898	----
833	C-H out of plane in positions 2, 5 and 6 (G+S unit)	833	833	833	833

FTIR spectroscopy was applied to compare the molecular conformation changes of samples after different treatments. All FTIR data was recorded in Fig.2 and corresponding band assignments were showed in Table 2. The bands at 3421 cm^{-1} and 2900 cm^{-1} were attributed to stretch of -OH groups and C-H stretching, which existed in cellulose, hemicelluloses and lignin. The signals at 1739cm^{-1}, 1705cm-^{1} and 1639cm^{-1} in UC were assigned to *p*-coumaryl ester group, which is the typical sign of the natural lignin. After combined treatments, carbonyl group was detected in the sample of SER, LRF and CRF, characterized with presence of signal peak at 1705cm^{-1} while absence of signal peaks at 1739 cm^{-1} and 1639 cm^{-1}.This change could be assigned to dehydration reaction of lignin during steam explosion, which generated ketone groups[27](Fig. S2). Obvious characteristic peaks of the aromatic skeletal vibrations at 1604 cm^{-1}, 1513 cm^{-1} and 1425 cm^{-1} were observed in all samples, which indicated the existence of lignin in them. The signal at 1166 cm^{-1} was the sign for H/S/G lignin and this signal in LRF was more intensive than that in other samples, which agreed with the chemical composition analysis of LRF, i.e. lignin in LRF with higher purity. Moreover, the FTIR data of LRF was in agreement with reported literatures that G unit and S unit usually were incorporated in herbaceous plants with significant amounts of H unit. According to F. Carrillo[28], the signals at 1161 cm^{-1} and 1056 cm^{-1} were assigned to the C-O anti-symmetrical bridge stretching and C-O-C pyranose ring skeletal vibration. The signals at 1161 cm^{-1} and 1056 cm^{-1} could be observed in UC and SER, while in CRF the signal at 1161 cm^{-1} was disappeared and the signal at 1056 cm^{-1} was weakened**.** Apparent peak was detected at 897 cm^{-1}, showing the glycosidic C_1- H deformation with ring vibration, which indicated the existence of β-glycosidic linkages in the UC, SER and CRF. The peak at 1105cm^{-1} was detected in UC while absent in other samples, indicating the change of cellulose structure caused by the combined process: the tendency of conformation change from cellulose Ⅰ in UC to cellulose Ⅱ in SER and CRF[29].

3.3 HSQC spectrum of LRF

Lignin has an immense potential to produce aromatic chemicals and meet energy fuel requirements. The specific utilization of lignin wa s depended on its unique structure. Consequently, LRF structure was characterized by HSQC. In the aromatic area (Fig. 3A), signals of syringyl (S), guaiacyl (G), *p*-hydroxyphenyl (H) units could be observed. The S unit showed signals for the $C_{2,6}$-$H_{2,6}$ correlation at δC/δH 104.1/6.67; the G unit showed signals for the C_2-H_2 correlation at δC/δH 111.3/7.02, C_5-H_5 correlation at δC/δH 115.4/6.69, C_6/H_6 correlation at δC/δH 119.0/6.79 and the oxidized G unit had signals for the C_6-H_6 correlation at δC/δH 123.3/7.60. The signals corresponding to $C_{2,6}$-$H_{2,6}$ correlation in H unit were observed at δC/δH 128.2/7.16. These results agreed with FTIR analysis indicating that H/S/G lignin was obtained after steam explosion and liquid hot alcohol delignification. In addition, the *p*-coumaroylated substructures could also be observed at δC/Δh 144.1/7.43, δC/δH 130.2/7.48 and δC/δH 115.4/6.78 for its C_7-H_7, $C_{2,6}$-$H_{2,6}$ and C_3-H_3, C_5-H_5 correlations, respectively. The S/G ratio of LRF was 1/72 according to their relative abundance in the HSQC spectrum. The S/G ratio in LRF was higher since the methoxyl group in S unit was removed by the acidic environment and leading to high G content.

In the side chain areas (Fig. 3B), methoxy group had an apparent signal for the C-H correlation at δC/δH 56.0/3.72; the cinnamyl alcohol end groups showed C_γ-H_γ correlation at δC/δH 61.4/4.05; signals represented the C_γ-H_γ in *γ*-acylated β-O-4 linkage showed

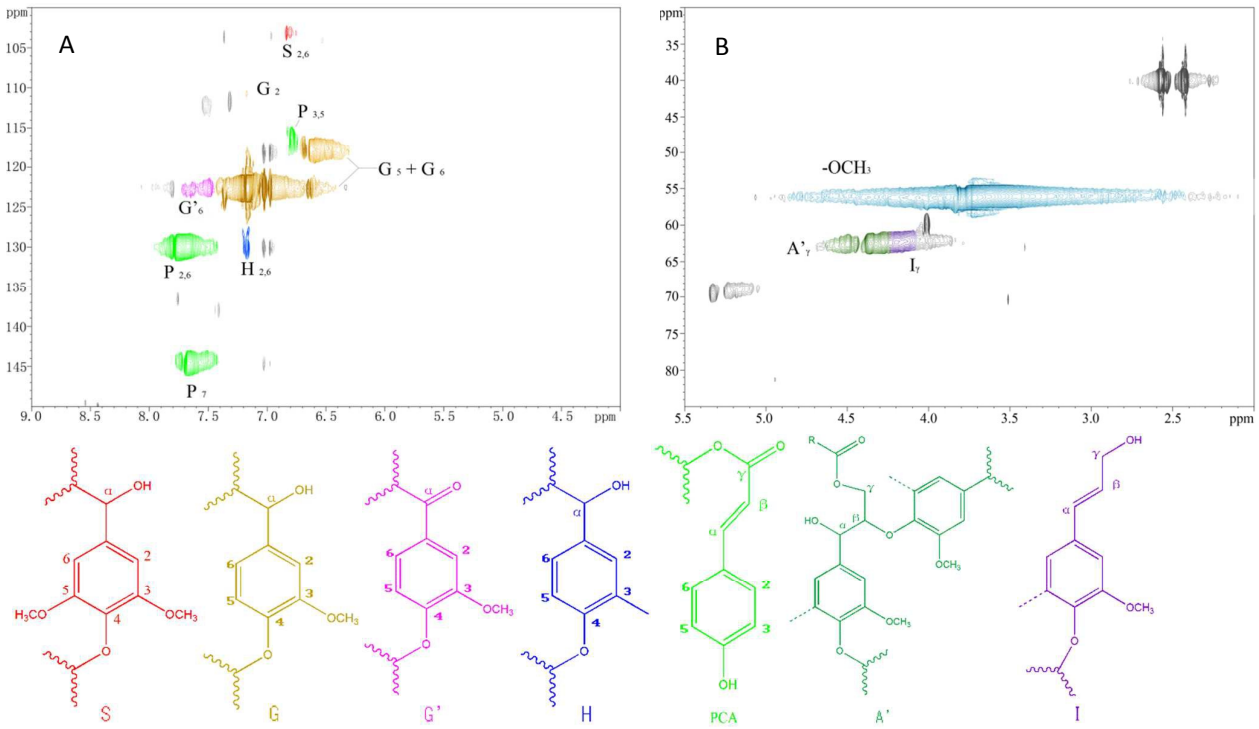

Fig.3 HSQC spectrum of main structures in the LRF: (A) aromatic area, (B) side chain area. The assignments of the 13C-1H cross signals were identified by published literatures XXX and showed in Table SXX. Lignin substructure: (S) syringyl unit; (G) guaiacyl unit; (G'): oxidized guaiacyl unit; (H) *p*- hydroxyphenyl unit; (PCA) *p*-coumarated unit; (I) cinnamyl alcohol ending grous; (A') acylated β-O-4 linkage.

correlation at δC/δH 62.7/42.8. Based on the HSQC, signal corresponding to β-O-4 linkages were not observed in LRF while acylated β-O-4 linkages were detected. The breakdown of interlinkages could be caused by the acidolysis and ethanolysis. Similarly, Hallac *et al.* reported the decreasing β-O-4 linkages in *B. davii* after ethanol pre-treatment, which was caused by the homolytic breakage of β-O-4 linkages[30]. Besides, El Hage *et al.* showed that organosolv pre-treatment would lead to a cleavage of β-O-4 linkages during the Miscanthus pre-treatment[31]. In our study, most β-O-4 linkages and C-C linkages were severely broken down during the combined process of DASE and LHPAD which essentially was the acidolysis plus ethanolysis.

The HSQC signals in LRF from the associated carbohydrate (β-D-xylopyranoside, β-D-glucopyranoside etc.) could not be detected, which agreed with chemical composition analysis in Table1 that LRF was pure. Assignments of ^{13}C-^{1}H correlation signals in the HSQC spectrum of the LRF were showed in Table S1.

3.4 GPC analysis of LRF

The molecular weight of LRF was showed in Table 3 and Fig. S3. The value was much lower than those obtained by other methods considerably. Lignin isolated from sugarcane bagasse by the phosphoric acid steam explosion and organosolv extraction had much higher molecular weight (Mw=3731g/mol with ethanol extraction and Mw=3176g/mol with dioxane extraction), In this study, acidolysis was used to cleave the aryl-ether bonds in heterogeneous system and steam explosion enhanced the process, which leading to the low molecular weight of LRF. In addition, ethanol was the most effective solvent and reactant for the degradation of lignin[32]. Ethanol hydrolysis of corncob lignin could contribute to the cleavage of α-aryl ester bonds and β-aryl ester bonds. GPC results well tallied with HSQC spectrum that most linkages in LRC was cleaved by the combined process.

Table 3. The data of LRF by aqueous phase GPC

	Mw(g/mol)	Mn(g/mol)	Polydispersity
LRF	683	504	1.36
Ethanol lignin[25]	3731	1811	2.1
Dioxane lignin[25]	3972	884	4.5

3.5 XRD analysis of UN, SER and CRF

X-ray diffraction (XRD) was frequently used to analyse the cellulose structure and crystallinity. Fig.4 showed the XRD spectrum of the UC, SER and CRF. There were two main peaks at 16.4° and 22.5° in the XRD spectrum of UC, which is the typical sign of cellulose Ⅰ[33]. However, in SER and CRF samples an additional small shoulder peak emerged at 21.8° besides the two main peaks at 16.4° and 22.5°. The emergence of small shoulder peak at 21.8° indicated the

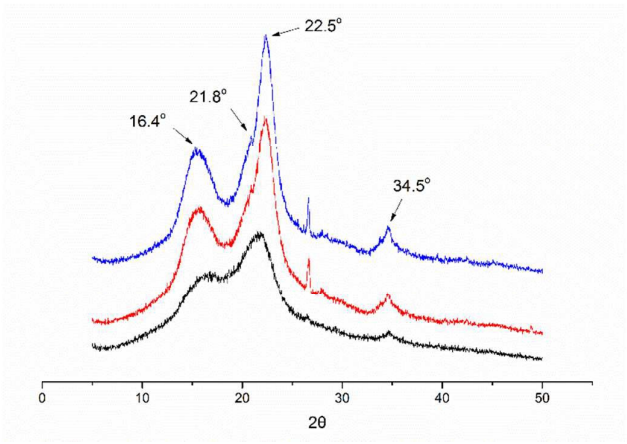

Fig. 4 Power XRD pattern of UC (black), SEP residue (red), CRF (blue).

expansion of the lattice[34], which was caused by the expansion of the cellulose matrix structure and the removal of hemicellulose during the process of steaming explosion[35].The small peak at 34.5° represented the quarter length of one cellobiose unit along the fibre direction. In general, the characteristics of XRD spectrum in SER and CRF were not changed significantly in comparison to that in UC (cellulose Ⅰ), although they preferred to forming cellulose Ⅱ,in well agreement with the data of FTIR analysis. The crystal index (CrI) of UC, SER, CRF were 26.45%, 37.33% and 45.02%, respectively. The increased CrI after DASE and LHPAD should arise from the removal of amorphous hemicellulose.

3.6 Effect of structural changes on the enzymatic hydrolysis

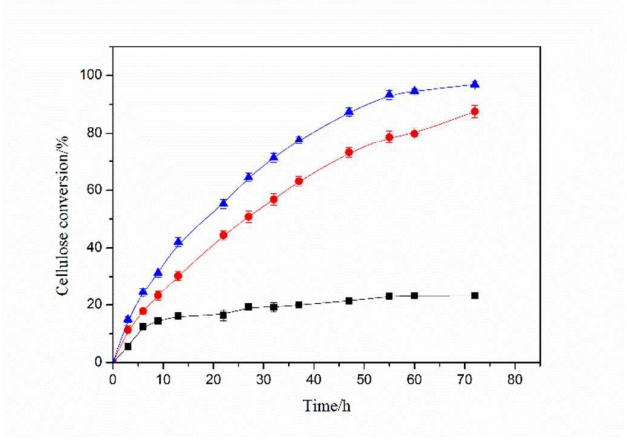

Fig. 5 The enzymatic hydrolysis of different fractions: UC (black), SE residue (red), CRF (blue).

The cellulose conversion of untreated corncob, SER and CRF were 22.8%, 86.5% and 95.7% respectively (Fig.5), indicating that the removal of hemicellulose and could facilitate the enzymatic hydrolysis of cellulose. However, the cellulose enzymatic hydrolysis rate was unsatisfactory and this was speculated that the cellulose structure was incompletely destroyed and small partial lignin in the CRF hindered the cellulose accessibility to cellulase[36]. In the combined process, xylose, the precursor of xylitol and also a fine chemical, was obtained by degradation of hemicellulose with steaming explosion[14].Subsequently, the organosolv lignin was prepared from the SER by ethanol delignification, which was characterize with higher purity, yield and low-molecule-weight (Mw=683g/mol, Fig. S3). It had applications in petroleum feedstock, aromatic platform chemicals and functional fine chemicals[37]. The similar process was used to extract lignin from corn stalk of which yield was close to our results, but the molecular weight of corn stalk lignin was much higher[38]. It indicated that the lignin obtained from different biomass by the similar process had different characteristics and this process had potential to be applied on other types of biomass. In addition, three advantages could benefit the industrial application of the combined process: (1) trace amounts of H_2SO_4 for hemicellulose degradation, (2) recyclable and renewable ethanol for organosolv lignin preparation, (3) complete utilization of the components in lignocellulose of corncob. Consequently, the proposal process was environment friendly and industrially feasible, and it could be applied to biofuel production in the future.

4. Conclusions

A cleaning, effective and economic process for lignin preparation from corncob was developed. In our work, diluted acid steam explosion (DASE) plus liquid hot pressured alcohol delignification (LHPAD) was applied on the production of lignin from corncob. DASE played an important role which could degrade the hemicellulose into xylose and remove it from the lignocellulose by wash. In addition, proper DASE give more accessible room for the next LHPAD, resulting in the high yield (41%) and high purity (94%). In addition, the cellulose rich fraction (LRF) after DASE and LHPAD was easy for enzymatic hydrolysis and the results showed that glucose conversion was close to 100%.

Abbreviations

UC: untreated corncob.
SER: steam explosion residue.
CRF: cellulose rich fraction.
LFR: lignin rich fraction.
DASE: diluted acid steam explosion.
LHPAD: liquid hot pressured alcohol delignification.

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