Cellulose Isolation from Corn Stalk Treated by Alkaline Biochars in Solvent Systems

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Three kinds of biochars were prepared using corn stalk as the raw material. Corn stalk degradation was achieved in solvents by treatment with prepared biochars for 5 h at 170 °C. The solvent systems contained ionic liquid and water components, which presented synergistic effects on lignocellulosic degradation. The oxidized alkaline biochar (B_2) was most effective for the lignin degradation in corn stalk, which promoted corn stalk dissolution into the reaction system. For treated corn stalk, both the lignin and hemicellulose were degraded during the reaction under the combined effects of biochars and nucleophilic components in solvents, and cellulose dissolution was enhanced. Dissolved cellulose was regenerated by mixing ethyl acetate and water gradually.

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INTRODUCTION

Plants produce more than 100 billion tonnes of cellulose annually through photosynthesis; thus, cellulose is regarded as a renewable resource (Zhang *et al.* 2011; Andanson *et al.* 2014). Biomass conversion into materials has attracted increased attention in recent years. However, biomass materials are resistant to natural conversion, due to the chemical and physical factors including cellulose crystallinity and covalent linkages connecting hemicellulose to lignin (Tuck *et al.* 2012; Xu *et al.* 2013).

Various biomass waste treatments and extraction technologies have been analyzed for lignocellulosic biomass utilization. Many types of solid alkalis have been investigated in lignocellulosic materials treatment. Pang *et al.* (2012) introduced a novel method of cooking corn stalk with solid alkali and active oxygen for pulp production. Studies also reported that solid alkali was used as a catalyst for lignin degradation and polyurethane synthesis (Li *et al.* 2010). Ionic liquids, known as low-temperature molten salts or designable solvents, have been widely used in biomass extraction and separation, materials preparation, and other fields (Sun *et al.* 2010; Casas *et al.* 2013). In 2002, Swatloski and co-authors first reported the solubility of natural cellulose in a series of ionic liquids such as 1-butyl-3-methylimidazolium chloride (BMIMCl) (Swatloski *et al.* 2002). However, these techniques always result in environmental pollution. In the process of biomass treatments, some by-products will be produced. For example, the degradation of lignocellulose can produce benzene and the chelate pollutant. In addition, the improper use of catalyst can lead to the release of heavy metals and the discharge of some functional organics, resulting in pollution. In recent studies, biochar catalysts have attracted attention for biomass waste disposal (Sun *et al.* 2010; Casas *et al.* 2013; Wu *et al.* 2013). In particular, researchers have attempted to use magnesium (Mg)-based

biochars to develop a novel delignification system (Sun *et al.* 2010; Casas *et al.* 2013; Olsson *et al.* 2014).

In this study, several biochars were prepared and characterized. Corn stalk degradation was achieved in the prepared solvents *via* treatment with biochars at 170 °C for 5 h. Furthermore, the effects of biochars dosage and solvent systems on the degradation of corn stalk were examined. To characterize corn stalk degradation products and regenerated cellulose, gas chromatography–mass spectrometry (Shimadzu Corporation, Tokyo, Japan) and X-ray diffraction (XRD) were applied. The findings of this study provide a necessary theoretical basis for biochars application and biomass feedstock utilization.

EXPERIMENTAL

Corn stalk was collected from the Experimental Forest Farm in Tianjin, in northern China. Corn stalk samples were dried at 60 °C for 16 h, and then ground to approximately 0.7 mm in size. According to the Van Soest method (Liu *et al.* 2014), lignocellulosic components in the corn stalk were analyzed using a fully automated fiber analysis system (Fibertec 2010, FOSS Company, Shanghai, China), which showed the following composition: cellulose 40.86%, lignin 13.87%, and hemicellulose 28.01%.

Methods

Preparation of alkaline biochars

The powdered corn stalk was placed in a reaction kettle under an N_2 atmosphere. The corn stalk pyrolysis temperature was set at 500 °C for 2 h. The biochar produced was denoted as B_o. Likewise, magnesium oxide (MgO) powder and powdered corn stalk biomass were mixed in a aqueous solvent at a ratio of 1:10 (Liu *et al.* 2014). Subsequently, the mixture was dried at 105 °C for 5 h, and pyrolyzed under the above-mentioned conditions. The alkaline biochar produced was denoted as B_1. The obtained B_1 was oxidized using 30% hydrogen peroxide (H_2O_2) at 30 °C for 6 h at a solid/liquid ratio of 1:10 (w/v) and denoted as B_2.

Solvent system preparation

Two kinds of ionic liquids were added into water to prepare the solvent systems, which were used for corn stalk dissolution. The solvent system containing AMIMCl (1-allyl-3-methylimidazolium chloride, made in the authors' laboratory) was denoted as S_1, while that containing AMIMOAc (1-allyl-3-methylimidazolium acetate, made in the authors' laboratory) was indicated as S_2.

Corn stalk treatment

The sample was placed in a steel reactor. The reaction system contained 20 mL of the solvent. 5 g of corn stalk was treated by biochars at 170 °C for 5 h. Subsequently, the reaction products were filtered to collect the treated corn stalk. The corn stalk treated by different biochars were denoted as follows: C_1 (treated by biochar B_o in solvent S_1), C_2 (treated by biochar B_1 in solvent S_1), C_3 (treated by B_2 in solvent S_1), C_4 (treated without biochar in solvent S_1), C_1' (treated by B_o in solvent S_2), C_2' (treated by B_1 in solvent S_2),

C$_3$' (treated by B$_2$ in solvent S$_2$), and C$_4$' (treated without biochar in solvent S$_2$). The residual rate was counted according to Eq. 1 (Liu *et al.* 2013),

$$R_{s,i} = \frac{M_{r,i}}{M_{o,i}}$$ (1)

where *i* represents the lignin, cellulose, or hemicellulose, $R_{s,i}$ is the residual rate, $M_{r,i}$ is the residual mass (g) of the above contents in corn stalk after treatment, $M_{o,i}$ is the mass (g) of above contents in the raw corn stalk samples.

Separated filtrate was used for cellulose regeneration. Corn stalk solubility in the solvent system was calculated according to Eq. 2 (Liu *et al.* 2013),

$$R_d = 1 - \frac{M_r}{M_o}$$ (2)

where R_d is the corn stalk solubility in the solvent, M_r is the mass of residual sample after treatment (g), and M_o is the original corn stalk mass (g).

Regeneration of cellulose

For the filtrate, the components were separated by adding ethyl acetate with continuous stirring. The separated components were the corn stalk degradation products, and denoted as following: DCS$_1$ (components from C$_1$), DCS$_2$ (components from C$_2$), DCS$_3$ (components from C$_3$), DCS$_4$ (components from C$_4$), DCS$_1$' (components from C$_1$'), DCS$_2$' (components from C$_2$'), DCS$_3$' (components from C$_3$'), and DCS$_4$' (components from C$_4$').

After separation by adding ethyl acetate, this filtrate was mixed with water for cellulose regeneration. The rate of cellulose regeneration was calculated according to Eq. 3 (Liu *et al.* 2013),

$$R_r = \frac{M_{r-cel}}{M_{o-cel}}$$ (3)

where R_r is the rate of cellulose regeneration, M_{r-cel} is the regenerated cellulose mass (g), and M_{o-cel} is the cellulose mass in raw corn stalk (g).
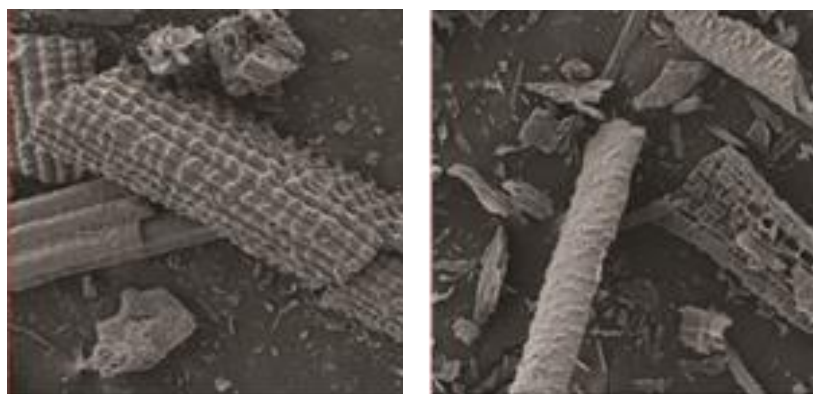
Characterization

Elemental analyses were conducted using an elemental analyzer (Vario El Cube, Thermo Scientific, Boston, MA, USA). The oxygen content was examined using mass balance. The O/C atomic ratio was correlated with biochars aromaticity and polarity. Higher O/C atomic ratio means the higher biochars polarity, while lower O/C atomic ratio means the higher biochars aromaticity. The elemental analysis was operated using a scanning electron microscope with NiCrAl sputter coating (S-3500N, Hitachi, Ltd., Tokyo, Japan) and Energy Dispersive Spectrometer (1791-N-016-000, Thermo Scientific, Boston, USA) at the same surface locations. The specific surface area and porosity of the biochars were determined based on N$_2$ adsorption isotherms by the Brunauer–Emmett–Teller (BET) method using a surface area analyzer (Tristar 3000, Thermo Scientific, Boston, MA, USA). The regenerated cellulose structure was examined by a XRD analyzer (Rigaku D/max-III X-ray diffractometer, (Rigaka, Ltd., Tokyo, Japan). The X-ray intensities were recorded at 2θ, which ranged between 3° and 60°. The surface structure of corn stalk was observed with an S-3700N SEM (Hitachi, Ltd., Tokyo, Japan). The DCS samples were determined by gas chromatography–mass spectrometry with a SHRXI-5 MS column (Shimadzu Corporation, Tokyo, Japan). The column temperature

was set at 50 °C to 280 °C (10 °C/min, hold for 20 min) (Tuck *et al.* 2012; Xu *et al.* 2013).

RESULTS AND DISCUSSION

Characteristics of the Biochars

As shown in Fig. 1A, the structure of the biochars was almost a fibrous tube of 1 micron. The composition and structural characteristics of the biochars are shown in Table 1. The C and O contents of the biochars were within 55.32% to 63.21% and 19.15% to 29.35%, respectively. The O/C ratio of B_2 was higher, illustrating that a large amount of oxygen-containing groups were located on B_2 with its surface remaining hydrophilic, which are beneficial for the sorption of lignin degradation products (Liu *et al.* 2013). The surface area of all the materials examined in the present study ranged from 10.38 m^2/g to 11.22 m^2/g. The pore diameters of all the materials were almost 2 nm. Meanwhile, the surface area of B_o was larger, which indicated that abundant MgO may have been located on the surface of B_1 and B_2. The load of MgO will occupy the pore structure on biochar surface, making a smaller surface area. In addition, both B_1 and B_2 presented a higher amount of alkaline components (Mg^{2+} ions), approximately 10 times higher than that noted in B_o, and exhibited higher alkalinity.
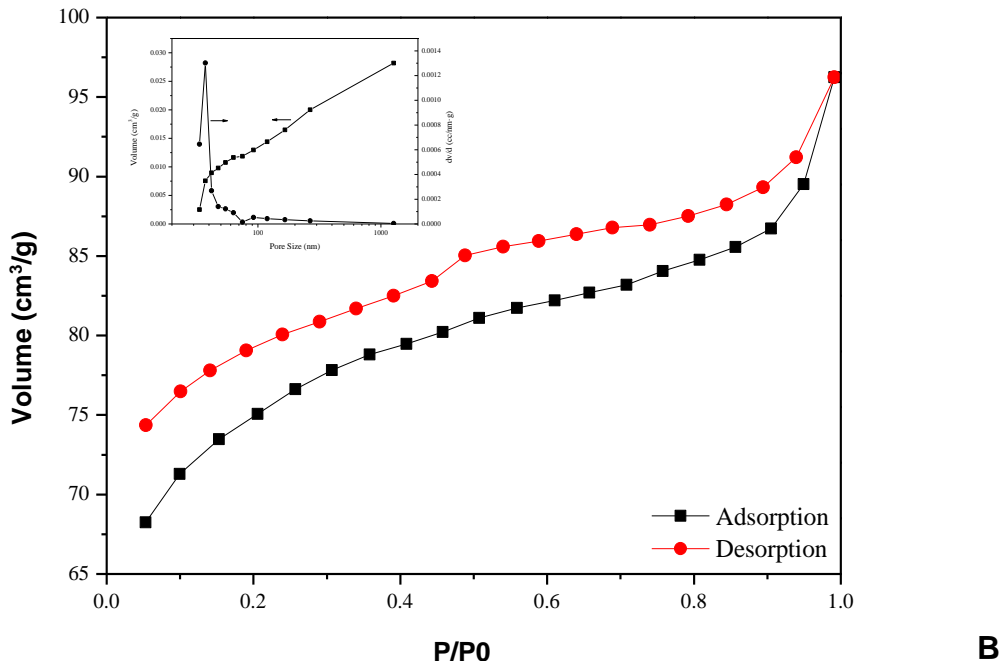

A

Fig. 1. Structures of original biochars (A), and N_2 adsorption-desorption curve of biochar B_2 (B)

Table 1. Biochars Composition and Structural Characteristics

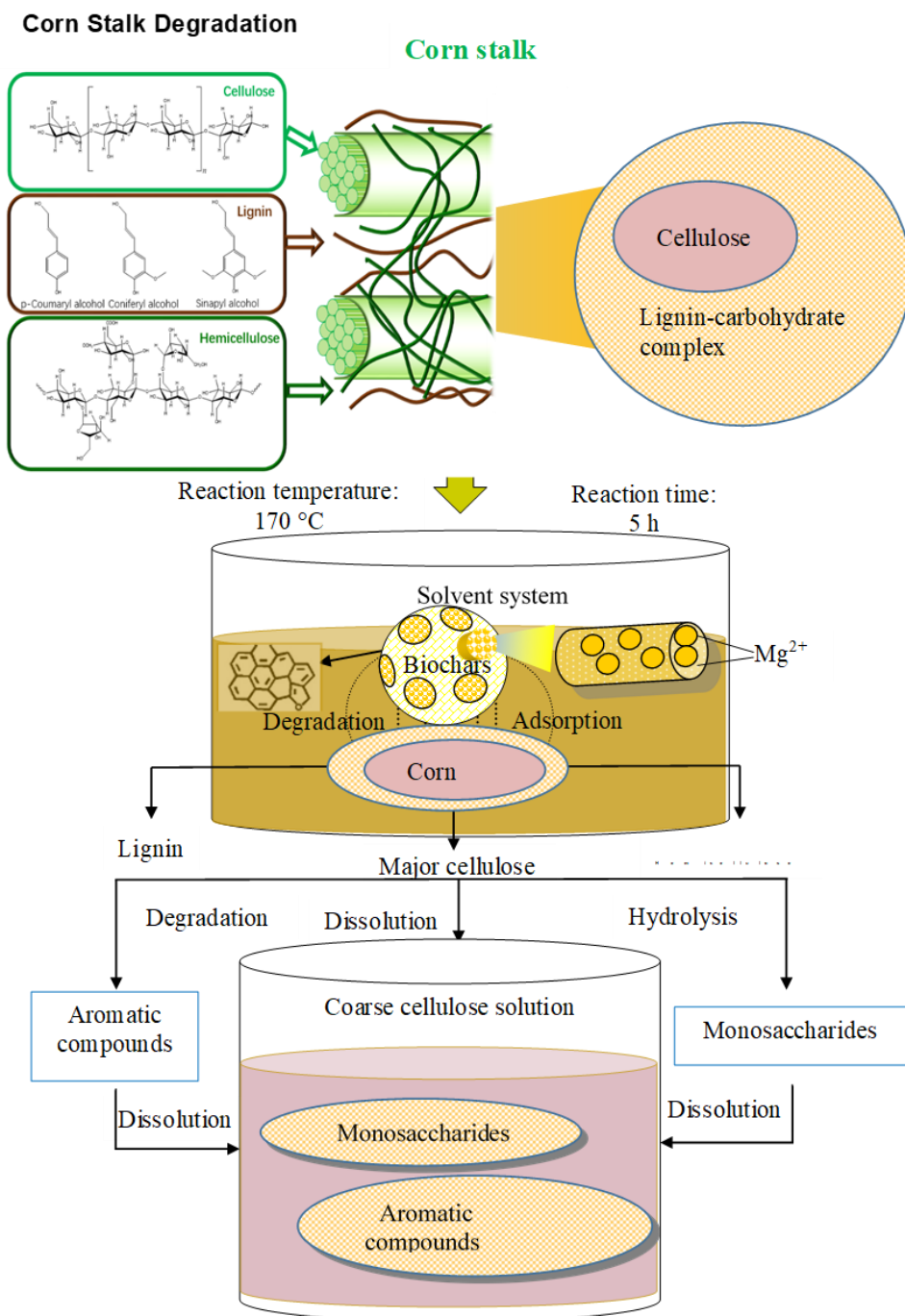| Sample	Component (%)				Ratio O/C	SA (Surface Area) (m^2/g)	PD (Pore Diameter (nm)	Concentration (mg/g)		
	C	H	N	O				Ca^{2+}	Mg^{2+}	Na^+
B_0	63.21	3.53	1.02	19.15	0.30	11.22	1.82	5.62	5.21	3.11
B_1	61.56	3.32	0.93	21.23	0.34	10.38	1.79	5.12	52.35	3.08
B_2	55.32	3.03	0.96	29.35	0.53	10.85	1.80	5.09	51.21	3.00

Fig. 2. Mechanism of corn stalk degradation by biochar catalysis in solvent systems

The corn stalk structures were observed under SEM to analyze the process of corn stalk degradation. Figure 3 shows that the corn stalk was destroyed after treatment by biochars, which resulted in a rougher surface. Furthermore, the treated corn stalk exhibited higher pore volume compared with the original corn stalk. Moreover, the pretreatment of corn stalk with biochars loosened lignocellulosic organization.
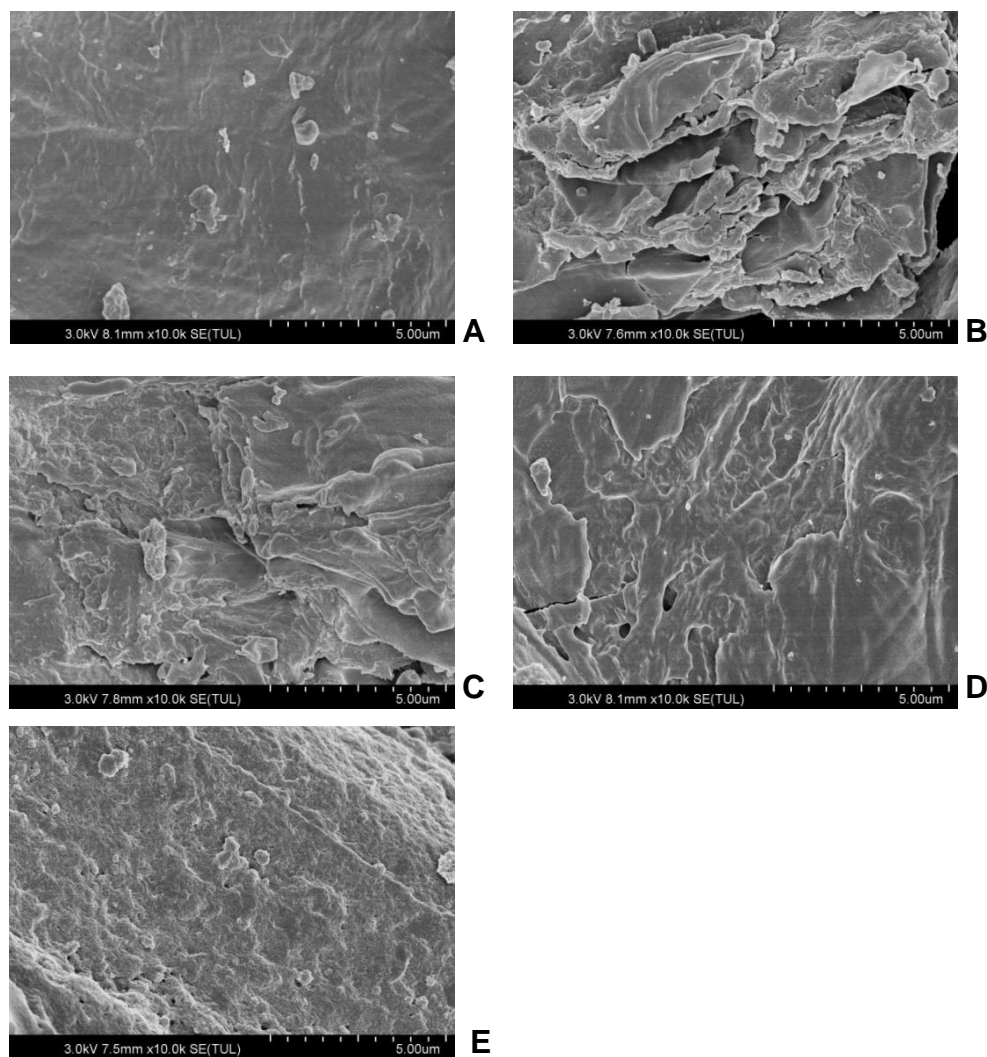
Fig. 3. Structures of original corn stalk (A), treated sample C_1 (B), treated sample C_2 (C), treated sample C_3 (D), and treated sample C_4 (E)

As shown in Table 2, C_3 and C_2 presented lower cellulose, hemicellulose, and lignin residual rates. It must be noted that different biochars have varied effects on corn stalk degradation, resulting in various lignocellulose degradation degrees during the process (Clements 2003). The alkaline biochars B_2 and B_1 possessed appropriate alkaline components (Mg^{2+} ions), which can effectively promote the degradation of lignin macromolecules (Gadenne *et al.* 2004; Zhang and Lynd 2004). Due to complete lignin degradation, the corn stalk was efficiently dissolved into the prepared solvent system in the treatment (Leclercq *et al.* 2001).

All of the cellulose contents of treated corn stalk were less than 18%. With the increasing amount of applied alkaline biochars, the alkalinity of the treatment system increased (Ebiura *et al.* 2005; Zhang *et al.* 2011). The cellulose content in the treated samples was not remarkably reduced, suggesting that an alkalinity increase was not a key factor on cellulose degradation (Li *et al.* 2010).

Table 2. Cellulose Residual Rate, Hemicellulose Residual Rate, and Lignin Residual Rate in Corn Stalk Cooked with Different Dosage of Biochars at 170 °C for 5 h in a Stainless Reactor Charged with Solvent System S_1

Samples	Biochars Dosage (%)	Cellulose Residual Rate (%)	Hemicellulose Residual Rate (%)	Lignin Residual Rate (%)
C_3	2	14.3 ± 0.7	21.1 ± 0.4	16.53 ± 0.5
C_3	4	14.6 ± 0.7	20.9 ± 0.2	15.60 ± 0.3
C_3	6	14.0 ± 0.7	20.0 ± 0.2	15.50 ± 0.2
C_3	8	13.9 ± 0.7	19.6 ± 0.2	14.25 ± 0.2
C_3	10	13.1 ± 0.7	18.8 ± 0.1	13.25 ± 0.2
C_3	12	13.6 ± 0.7	16.5 ± 0.1	12.10 ± 0.1
C_3	14	13.1 ± 0.7	15.0 ± 0.1	10.30 ± 0.1
C_2	2	15.5 ± 0.8	22.3 ± 0.4	21.99 ± 0.5
C_2	4	15.6 ± 0.8	21.8 ± 0.3	21.03 ± 0.4
C_2	6	15.1 ± 0.8	22.2 ± 0.3	20.62 ± 0.3
C_2	8	14.2 ± 0.8	20.9 ± 0.2	19.20 ± 0.2
C_2	10	14.1 ± 0.7	20.8 ± 0.2	18.10 ± 0.2
C_2	12	14.2 ± 0.7	19.9 ± 0.1	17.81 ± 0.2
C_2	14	14.7 ± 0.7	19.3 ± 0.1	16.58 ± 0.2
C_1	2	17.9 ± 0.8	25.2 ± 0.4	25.55 ± 0.5
C_1	4	17.5 ± 0.8	24.5 ± 0.3	25.21 ± 0.4
C_1	6	16.5 ± 0.8	24.2 ± 0.3	22.21 ± 0.3
C_1	8	15.1 ± 0.8	23.1 ± 0.2	21.53 ± 0.2
C_1	10	15.7 ± 0.7	22.8 ± 0.2	20.11 ± 0.2
C_1	12	16.2 ± 0.7	21.9 ± 0.1	17.12 ± 0.2
C_1	14	15.0 ± 0.7	20.9 ± 0.1	16.72 ± 0.2

The comparison of treatment by various biochars revealed that the lignin residual rate of C_3 was barely lower than that of C_2. With increased biochar dosages, the lignin content in the corn stalk gradually decreased and finally reached a stable level. In addition, the hemicellulose content in the corn stalk maintained a low level. It must be noted that lignin and hemicellulose are connected by glucosidic bonds (Ebiura *et al.* 2005; Sun *et al.* 2010), and hence, the bonds between hemicellulose and lignin were hydrolyzed with the increased dosages of biochars, resulting in decreased lignin content and affecting the hemicellulose hydrolysis (Zhang *et al.* 2011). The result demonstrated that the treatment on corn stalk with biochars made lignocellulose degrade effectively.

As shown in Table 3, the corn stalk treated in S_1 presented a lower cellulose residual rate than that treated in S_2, and this could be due to the different property of these two applied ionic liquids. With regard to AMIMCl, the anions and cations are involved in corn stalk dissolution (Fu and Mazza 2011), which particularly affects cellulose dissolution from corn stalk. The hydrogen and oxygen atoms in cellulose could form electron acceptor and electron donor complexes with the above ionic liquids. The AMIMCl cations could bind to oxygen *via* intramolecular and intermolecular linkages in cellulose chains. Similarly, chloride anions could also bind to hydrogen atoms in cellulose. For AMIMOAc, comprising of a huge amount of acetate anion, it presented greater steric hindrance, which is not efficient for the contact to the hydrogen atoms, resulting in lower solubility of cellulose into AMIMOAc (Liu *et al.* 2012).

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Table 3. Cellulose Residual Rate, Hemicellulose Residual Rate, and Lignin Residual Rate in Corn Stalk Cooked at 170°C for 5 h in a Stainless Reactor Charged with Different Solvent Systems

Samples	Solvent Systems	Ionic Liquids Ratio (%)	Cellulose Residual Rate (%)	Hemicellulose Residual Rate (%)	Lignin Residual Rate (%)
C_3	S_1	80	12.3 ± 0.5	18.06 ± 0.3	7.55 ± 0.1
C_3'	S_2	80	17.6 ± 0.7	23.89 ± 0.3	13.36 ± 0.2
C_4	S_1	80	21.1 ± 0.5	31.98 ± 0.4	23.57 ± 0.2
C_4'	S_2	80	23.9 ± 0.6	35.61 ± 0.3	26.15 ± 0.3
C_3	S_1	70	13.6 ± 0.1	20.79 ± 0.2	12.03 ± 0.2
C_3	S_1	75	13.1 ± 0.1	19.20 ± 0.3	9.62 ± 0.1
C_3	S_1	85	13.5 ± 0.2	19.83 ± 0.2	10.10 ± 0.1
C_3	S_1	90	14.1 ± 0.1	20.38 ± 0.2	12.81 ± 0.1
C_3	S_1	95	14.4 ± 0.1	20.82 ± 0.2	20.58 ± 0.2
C_3	S_1	100	15.9 ± 0.2	21.23 ± 0.3	23.55 ± 0.2

The presence of alkaline biochars in the solvents enhanced the nucleophilic reaction capacity, improving the hydrolytic and solvolytic effect on lignin degradation (Zhu *et al.* 2006; Li *et al.* 2010; Zhang *et al.* 2011). As shown in Table 3, C_3 presented a lower lignin residual rate, because the addition of alkaline biochar into the solvents considerably accelerated lignin degradation, while the reaction system without biochars did not exhibit complete lignin degradation and required a higher amount of water to achieve total corn stalk degradation.

The water in the solvents had a key function in lignocellulosic degradation (Sun *et al.* 2010), which was effective for promoting the polar reactions and free-radical reactions (Gadenne *et al.* 2004; Zhang and Lynd 2004). As presented in Table 3, when the ionic liquid ratio reached 80%, the lignin residual rate of C_3 decreased to 7.55%, which suggested the synergistic effects of water and ionic liquid on corn stalk degradation. It has been reported that the use of an appropriate water–ionic liquid ratio could enhance the delignification capacity of the solvent system, retaining the solubility of the biomass (Wang *et al.* 2011; Zhang *et al.* 2011). For biomass degradation, the reaction system should have nucleophilic components to enhance lignin degradation, as well as dissolution ability for lignocellulosic degradation products (Cantrell *et al.* 2005; Xie *et al.* 2006).

Characterization of the DCS Samples

As illustrated in Fig. 4A, for DCS_3 treated by biochar, the major identified products were aromatic compounds, including 2-methoxy-4-methyl-phenol, 2,4-bis(1,1-dimethyl-ethyl)-phenol, and 2,6-dimethoxy-phenol. The products primarily resulted from the cleavage of the *α-O*-4 and *β-O*-4 linkages in corn stalk lignin (Tang *et al.* 2005; Pinkert *et al.* 2009). While for DCS_4, the main constituents were degraded carbohydrate, including acetic acid and formic acid.
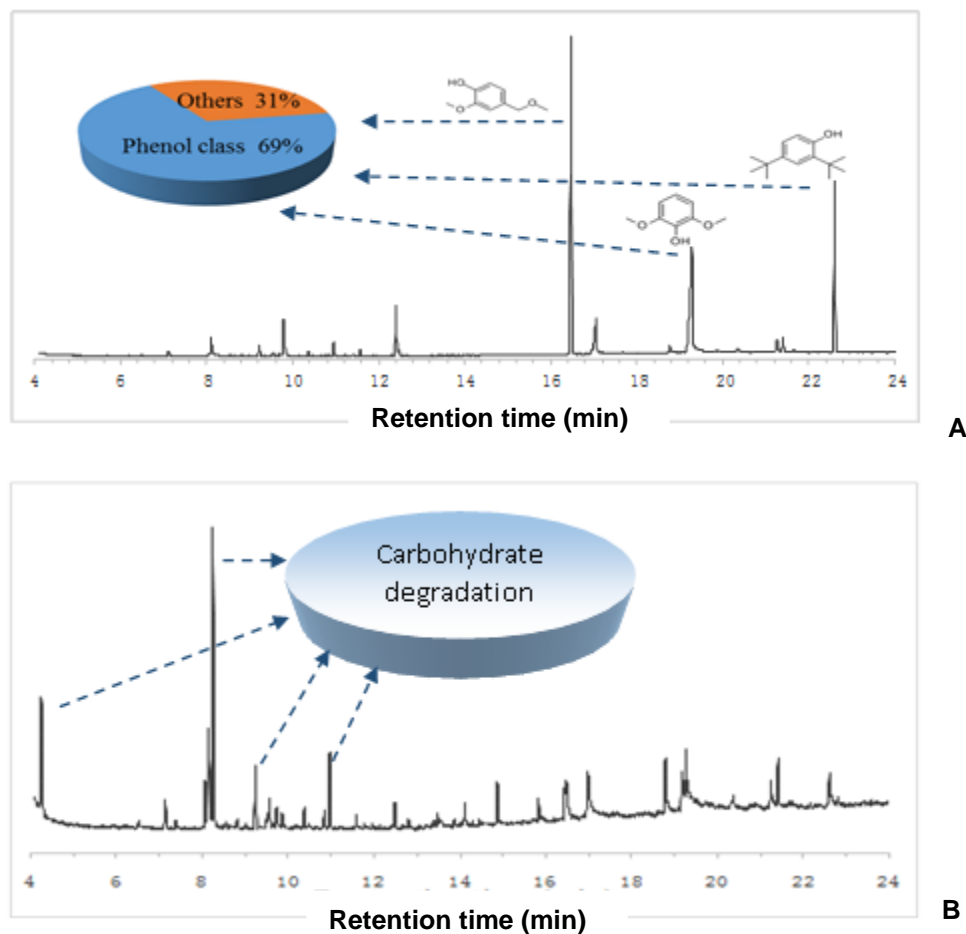
Fig. 4. Major compounds detected from corn stalk degradation products DCS$_3$ (A) and DCS$_4$ (B)

These results showed that alkaline biochars had noticeable effects on lignin degradation in corn stalk. The oxygen atom in MgO, as a key content of alkaline biochars, has a lone electron pair, which can form chemical bonds with other atoms in the biomass degradation reaction (Liu *et al.* 2014). With an appropriate increase of solid alkali, the reaction system alkalinity could be enhanced, facilitating the ether cleavage in lignin structure (Lee *et al.* 2009; Fu and Mazza 2011). Moreover, trace amounts of cellulose-degraded products were found, including levulinic acid and 5-hydroxymethylfurfural.

Cellulose can be regenerated from these reaction systems by treatment using biochars. Analyses were employed to compare the structure of regenerated cellulose and microcrystalline cellulose. As shown in Fig. 5, the intensity of microcrystalline cellulose at the 2θ value was higher compared with regenerated cellulose. The peaks of regenerated cellulose at 15.1°, 16.3°, 20.8°, and 35.1° nearly disappeared, which could be due to the crystallinity reduction in this reaction (Zhang *et al.* 2005; Li *et al.* 2010; Liu et al. 2015).
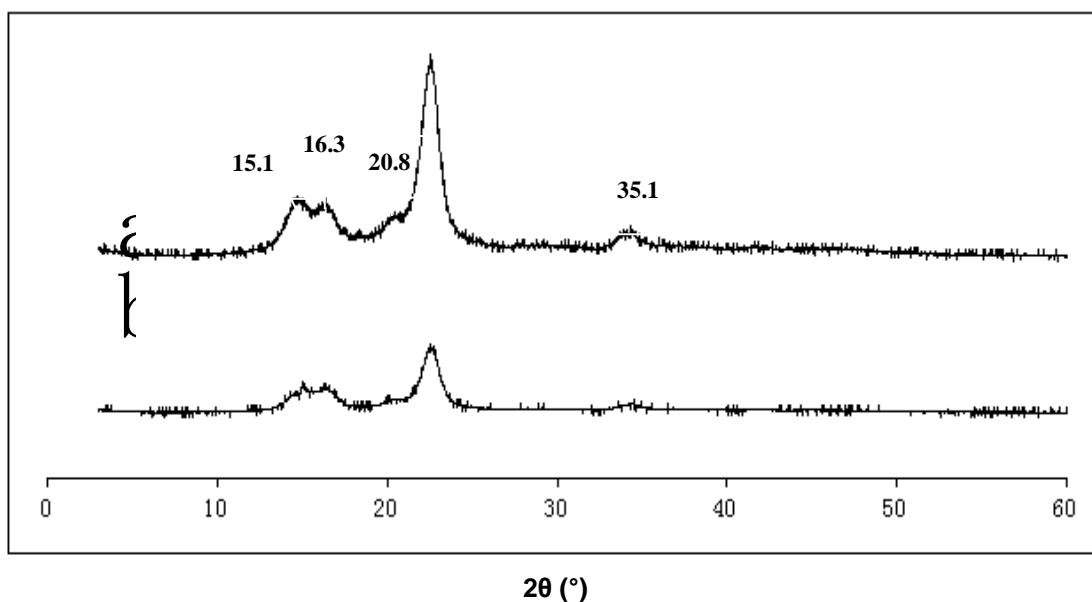
Fig. 5. XRD curves of microcrystalline cellulose (a), and cellulose regenerated from corn stalk (b)

Degradation Mechanisms

As shown in Fig. 2, the chemical linkages of the lignocellulosic components in corn stalk were gradually cracked due to the combined effects of biochars and nucleophilic contents in the solvents, which resulted in the reduced molecular weights (Lee *et al.* 2009; Fu and Mazza 2011). The lignin degradation products were dissolved in the solvent system, and a large amount of degraded lignin fragments were adsorbed onto the biochar surface, forming strong surface complexes with oxygen-containing groups through polar bonds. Furthermore, the glucosidic bonds connecting lignin to hemicellulose were disrupted during the treatment process, and the original hemicellulose was degraded to smaller monosaccharides (Li *et al.* 2010). Moreover, the lignin–carbohydrate complexes were degraded, which were the protective layer wrapped around cellulose, directly exposing cellulose into the reaction solvent. Cellulose swelling disrupted its crystalline state (Gadenne *et al.* 2004), and macromolecular cellulose was hydrolyzed to smaller molecules, which could dissolve in the solvent system (Swatloski *et al.* 2002; Ren *et al.* 2003; Oh *et al.* 2005).

CONCLUSIONS

Corn stalk degradation was achieved in solvents by treatment with prepared biochars for 5 h at 170 °C. Three kinds of biochars were prepared using corn stalk as the raw material. The solvent systems contained ionic liquid and water components, which presented synergistic effects on lignocellulosic degradation. The oxidized alkaline biochar (B_2) was most effective for the lignin degradation in corn stalk, which promoted corn stalk dissolution into the reaction system. For treated corn stalk, both the lignin and hemicellulose were degraded during the reaction under the combined effects of biochars and nucleophilic components in solvents, and cellulose dissolution was effectively enhanced.

ACKNOWLEDGMENTS

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Erratum (January 27, 2020): 1.) Figure 3 has been corrected with different corn stalk images. The correction does not affect the original discussion of corn stalk structure, which shows that the corn stalk was destroyed after treatment by biochars, resulting in a rougher surface. 2.) In the third paragraph of 'Characterization of the DCS Samples', some viewpoints of another paper were cited to explain the structure difference between microcrystalline cellulose and cellulose in corn stalk. Therefore, the following reference has been added:

Liu, L., Ju, M., Li, W., Liu, Y., and Huang X. (2015). "Influence of solid alkali application on corn stalk dissolution and degradation in solvent systems," *Polymer Degradation and Stability*, 120, 98-106. DOI: 10.1016/j.polymdegradstab.2015.06.010