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Physicochemical properties of corn stalk after treatment using steam explosion coupled with acid or alkali

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ABSTRACT

The aim of this study was to evaluate comparatively the effects of different pretreatments including steam explosion, acid, and alkali, alone or in combination, on the structural properties and thermal stability of corn stalk. All of the treated treatments decreased the contents of hemicellulose and lignin and thereby increased the content of cellulose in corn stalks. But the combined treatments with alkali and steam explosion under 0.4–0.6 MPa were better as compared with other treatments based on the removals of hemicellulose and lignin, and about 71.58–79.59% of hemicellulose and 64.32–71.83% of lignin were removed. Treatment with steam explosion coupled with acid or alkali changed the bonding distribution and surface morphology and increased the crystallinity and thermal stability of corn stalks, and the degradation temperature reached over 350 °C. These results suggest that steam explosion coupled with alkali is a better method for the depolymerization of corn stalk polymer.

1. Introduction

Lignocellulose mainly consists of cellulose, hemicelluloses and lignin which are bonded together by covalent bonding, various intermolecular bridges, and van der Waals forces forming a complex polymer (Bian, Peng, Xu, & Sun, 2010; Egüés, Sanchez, Mondragon, & Labidi, 2012). Therefore, for effective utilization of cellulose for conversion into high valued products, lignocellulose must be depolymerized to change or destroy the connection between constitutional units and thereby to increase the rate and conversion effect of enzymatic hydrolysis for subsequent preparation of cellulosic ethanol and other chemicals (Gullón, Romaní, Vila, Garrote, & Parajó, 2012; Ruiz, Rodríguez-Jasso, Fernandes, Vicente, & Teixeira, 2013). Recently, many pretreatment methods such as acid, alkali, steam explosion, liquid hot water, ammonia fiber explosion, and biological processes have been used for depolymerization of lignocellulose (Kaushik & Singh, 2011; Karagöz, Rocha, Özkan, & Angelidaki, 2012). But no single pretreatment method was found to meet these requirements. Among these pretreatment methods, steam explosion, dilute acid, dilute alkali, and oxidative agent have been widely employed (McIntosh & Vancov, 2011; Peng, Peng, Xu, & Sun, 2012). Steam explosion is characterized by little to no use of chemical reagents, efficient separation of cellulose, reduced environmental pollution, and relatively high energy consumption (Ranjan & Moholkar, 2013; Oliveira et al., 2013). Acid pretreatment is more efficient in hemicellulose solubilization but high temperature, equipment corrosion, and formation of many inhibiting by-products, whereas alkaline pretreatment is more effective in removal of lignin but high cost of alkali and environmental pollution (Talebnia, Karakashev, & Angelidaki, 2010). Based on the advantages and drawbacks of each pretreatment method, the use of two or more methods together may be a more effective alternative.

In this work, two different schemes were conducted to process corn stalks. (1) Corn stalks were pretreated by acid or alkali. (2) Corn stalks were pretreated by steam explosion under different pressure followed by acid or alkali. The change of structural feature and thermal stability of corn stalks before and after pretreatment were comparatively investigated using Fourier-transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), Scanning electron microscope (SEM), and Derivative thermo-gravimetric (DTG) analysis techniques. The data from this study may be used as the foundation to further optimize the method for straw pretreatment and to improve the efficiency of enzymatic hydrolysis.

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2. Materials and methods

2.1. Materials

The corn stalk sample used in this study was obtained from Yinchuan, China. The sample was harvested at the dough stage of maturity. The plant was separated into ears, leaves and stalks. The stalks were dried at 105 °C for 16 h, ground in a rotary mill and passed through of 80 mesh in size which was used as the raw material in this study.

2.2. Pretreatment

2.2.1. Steam explosion

The steam explosion was carried out in a zipper-clave autoclave. For pretreatment, 10 g of corn stalk with soaking in water at solid–liquid ratio of 1:20 (wt/vol) was introduced, which was then heated to targeted pressure (0.4 MPa, 0.6 MPa, and 0.8 MPa) using steam, respectively. Pretreatment time (1 h) started to count upon the desired pressure inside the zipper-clave autoclave was reached. After the pretreatment was completed, the steam was release suddenly, the pretreated sample was collected and cool down, it was dried at 105 °C for 16 h and the samples were screened into powders 80 mesh in size for further experiments (Chundawat, Venkatesh, & Dale, 2007; Pedersen & Meyer, 2009).

2.2.2. Acid and alkali

The raw material was treated with 5% (wt/wt) NaOH or 5% (wt/wt) H_2SO_4, The concentrations of NaOH and H_2SO_4 were determined according to the results from our previous study. (Sun, Ma, Ma, & Chang, 2013; Zhou, Ma, Xie, & Cai, 2011). The assays were performed on a rotary thermostat heating shaker series DHSZ-300 with an agitation of 150 rpm at 60 °C for 24 h. The solid–liquid ratio was 1:20 (wt/vol). After treatment, the mixture was filtrated by Buchner funnel and the solid product was washed to neutral by distilled water, and then stored in sealed plastic bags at 4 °C. The total sugar yield (TSY) in the liquid phase fraction was quantified by ultraviolet spectrophotometer (UVS) according to 3,5-dinitrosalicylic acid (DNS) colorimetric method (Qi, Gou, Han, & Yan, 2004).

The amounts of glucose, xylose, and arabinose in the liquid fraction were determined using a HPLC method with a refraction index detector (Shimadzu, Japan) and an Aminex® HPX-87H lon Exclusion column at 65 °C. Sulfuric acid (0.005 M) at flow rate of 0.6 mL/min was used as mobile phase, all samples were filtered through 0.22 μm filters prior to analysis, and then 20 μL of sample was injected. The complete sample elution was accomplished within 20 min. The concentrations of oligosaccharides were also obtained by HPLC determination of monosaccharides present in liquors previously subjected to quantitative post-hydrolysis. The increase in the concentrations of monosaccharides caused by post-hydrolysis provided a measure of the oligosaccharides concentration (Vegas, Alonso, Domínguez, & Parajó, 2004). The contents of degradation products [mainly furfural and 5-hydroxymethyl furfural (5-HMF)] and by-products of phenolic acid [mainly ferulic acid (FA) and *p*-coumaric acid (P-CA)] were determined by a HPLC method using a diode array detector (Shimadzu, Japan) and an InertSustain® C_{18} column at 40 °C. Acetic acid (0.5 wt%) and methanol ratio of 9:1 (vol/vol) at flow rate of 1 mL/min was used as mobile phase, the detection wavelength was 280 nm and the injection volume was 20 μL.

2.2.3. Combination of steam explosion and acid or alkali

The corn stalk sample was first treated with steam explosion and followed by 5% (wt/wt) NaOH or 5% (wt/wt) H_2SO_4. The treatment condition was the same as described above.

2.3. Enzymatic hydrolysis

The residue of pretreated corn stalk was enzymatically h ydrolyzed as follows. The reaction conditions were 50 °C, pH 4.8 (0.05 M sodium citrate buffer), 150 rpm in a shake flask. The solid-to-liquid ratio is 1:10. The commercial enzyme Celluclast 1.5 L with a filter paper activity of 74 FPU/mL and Novozym 188 with a β-glucosidase activity of 154 IU/g, were employed for the enzymatic hydrolysis experiments (Adney & Baker, 1996). The cellulase loading was set at 20 FPU/g dry matter of the Celluclast 1.5 L, which was supplemented with 15 IU/g of Novozym 188 β-glucosidase, the values were determined according to the results from the fundamental research. An aliquot of 0.5 mL hydrolyzate was taken at different time intervals (6 h, 12 h, 24 h, 36 h, 48 h, 60 h, 72 h) before the enzymatic hydrolysis test was completed. Upon completion, the entire enzymatic hydrolysis sample was ended by boiling the hydrolyzate for 10 min. After cooling with cold water the hydrolyzate was filtered through a 0.22 μm filter. The HPLC method was used for monosaccharide and oligomers determination. The 3,5-dinitrosalicylic acid (DNS) colorimetric method was used for total sugar determination.

2.4. Composition analysis of corn stalk

All the treated and untreated samples were milled into 0.2 mm (80 mesh) particles using the DFT-40 cutting mill. The contents of cellulose, hemicellulose, and lignin in the treated and untreated corn stalks were analyzed according to the procedures of the Van Soest method (Goering & Van Soest, 1970). The optimum pretreatment was determined based on the relatively high ratio of cellulose and lignin contents.

2.5. Derivative thermo-gravimetric analysis

The pyrolysis of biomass components was carried out in a Derivative Thermal Gravimetric (DTG) Analysis (Setaram, France). To mitigate the difference of heat and mass transfer, the sample weight was kept at ≈8 mg. The tested corn stalk was heated up to 600 °C at a constant heating rate of 5 °C/min. Purified nitrogen at a flow rate of 20 mL/min was used as the carrier gas to provide an inert atmosphere for pyrolysis.

2.6. FT-IR analysis

The corn stalk powder samples were prepared with potassium bromide (KBr) pellet method. Infrared spectra were measured with a FT-IR 8400S at room temperature. Each spectrum was collected with a resolution of 4 cm^{-1} with 32 scans from the 4000 to 500 cm^{-1} region. Three replicated spectra were collected for every sample. The background spectrum was obtained against the air.

2.7. X-ray diffraction and crystallinity measurement

The crystallinity of the untreated and treated samples was examined by XRD technique using Cu K_α radiation ($\lambda = 1.54$ Å), equipped with computerized data collection and analytical tools. The scattering angle range was 5–60° and a rate of 4° min^{-1}.

2.8. Surface morphology observation

Morphological characterization of corn stalk particles was performed on images acquired using a SEM method. The samples were coated with platinum or gold of 10 nm thicknesses to make the samples conductive.

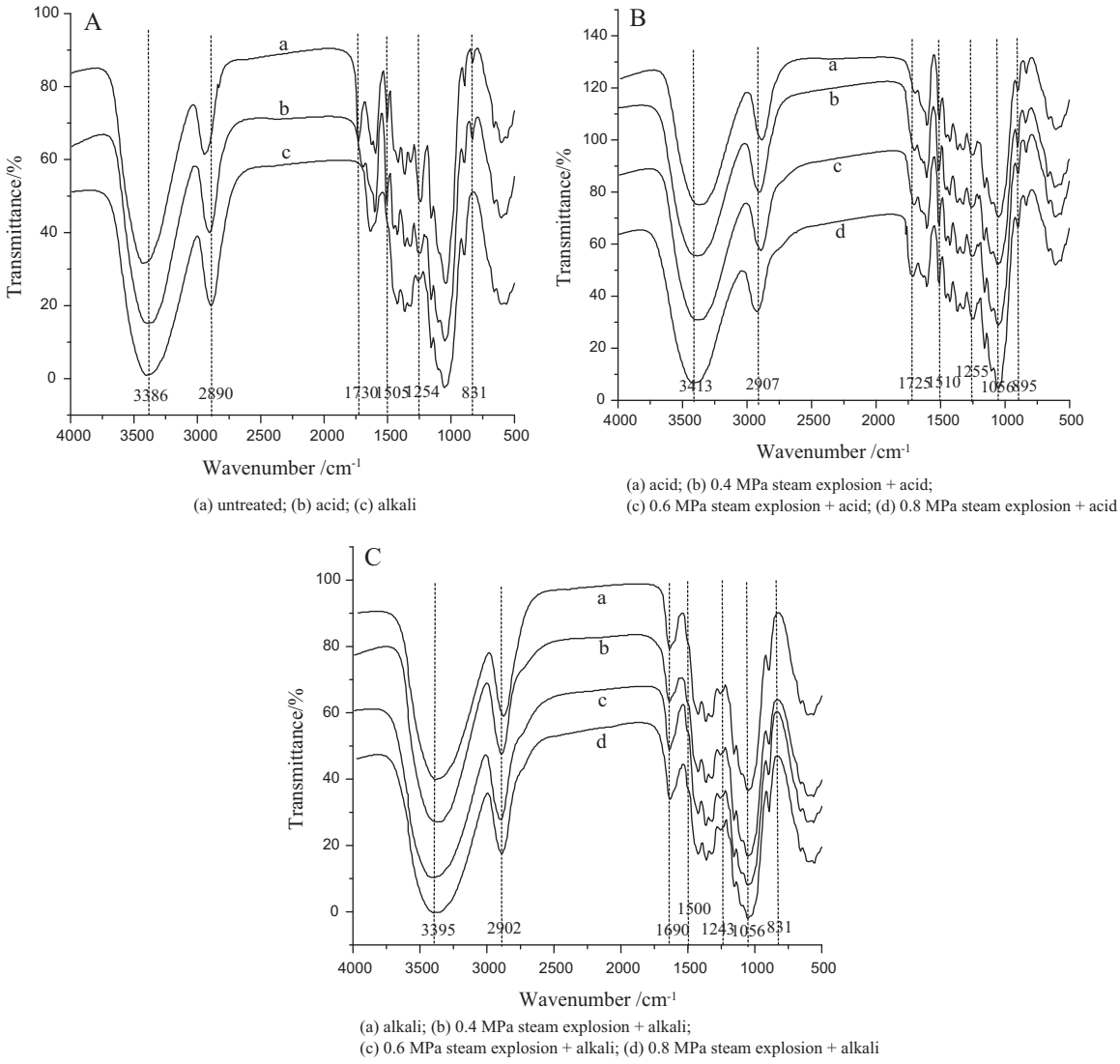


Fig. 1. Infrared spectra of corn stalk before and after treatment with different methods. (A) Acid and alkali; (B) steam explosion + acid; (C) steam explosion + alkali.

3. Results and discussion

3.1. FT-IR spectroscopic analysis

The distributions of functional group of corn stalk after treatment with steam explosion, acid, and alkaline, alone or in combination, are showed in Fig. 1. Absorption bands at 3360 cm^{-1} and 2890 cm^{-1} were attributed to —OH stretching of hydrogen bonds and C—H stretching within the methylene of cellulose, respectively. These absorption peaks in the untreated corn stalk were similar to that in the treated sample, indicating that most of the crystalline cellulose in corn stalk was not disrupted by the tested pretreatment. These results were in agreement with the investigations of Kumar and Wyman (2009) who reported that the crystalline cellulose in corn stover was not disrupted by acid hydrolysis. Furthermore, the prominent bands at 1250–900 cm^{-1} were typically related to the structural features of cellulose and hemicelluloses. The vibrations of these bands overlapped the C—O stretching vibrations at 1254 cm^{-1}, C—O—H stretching of primary and secondary alcohols at 1056 cm^{-1}, C—O—C glycosidic bond stretching and C—O—C ring skeletal vibration at 1160–1100 cm^{-1} (Moharram & Mahmoud, 2008), the adsorption peaks of these bands were enhanced after treatment with steam explosion, acid, and alkaline, alone or in combination. This suggested that the cellulose content in pretreated solid residue increased because the hemicelluloses fraction in corn stalk was removed by hydrolytic reaction. These results were in agreement with the changes of chemical composition of corn stalk after treatment (see Table 1). This was further supported by the fact that the adsorption peaks at 1730 and 1250 cm^{-1} were detectable in the untreated corn stalk and these have been proposed to be associated with the alkyl ester of the acetyl group in hemicelluloses. Furthermore, the ester linkage C=O with an absorption peak at 1720 cm^{-1} was usually defined as the acetyl group in hemicelluloses structure and/or the linkage between hemicelluloses and lignin (Chundawat et al., 2007). Both of these bands were absent in pretreated solid residue as a result of the removal of hemicelluloses from corn stalk. Interestingly, the band at 895–830 cm^{-1} was dominated by the β-(1 → 4)—glycosidic bond (C_1—O—C_4), which was cleaved by treatment with a combination of steam explosion and dilute acid or alkali-catalyzed reaction.

The distribution of lignin-associated bands was also investigated. The bands at 1600–1510 cm^{-1} belonged to aromatic skeletal stretching. The bands at 2852, 1460 and 1425 cm^{-1} were attributed to absorption of —C—H deformation within the methoxyl groups of lignin (Hsu, Guo, Chen, & Hwang, 2010). These peaks were disappeared in FT-IR of corn stalks after treatment with the combined

Table 1
The solid–liquid phase compositions in corn stalk before and after treatment with different methods.

Component content	Corn stalk	5% H_2SO_4	5% NaOH	Steam explosion + 5% H_2SO_4 (MPa)			Steam explosion + 5% NaOH (MPa)		
				0.4	0.6	0.8	0.4	0.6	0.8
Solid phase fraction (%)									
Cellulose	31.54	60.51	76.15	50.16	54.51	65.16	80.41	79.84	70.91
Hemicellulose	29.10	7.02	6.86	14.61	11.13	11.15	8.27	5.94	4.61
Lignin	38.12	32.21	16.52	34.57	33.79	23.01	10.74	13.6	23.87
Liquid phase fraction (mg/mL)									
TSY[a]	/	6.83	1.86	5.78	5.42	4.96	2.14	1.89	2.19
Glucose	/	0.73	0.36	0.16	0.08	0.11	0.65	0.55	0.73
Xylose	/	3.79	0.98	3.49	3.15	3.27	1.19	1.05	1.23
Arabinose	/	0.70	0.09	0.64	0.47	0.43	0.12	0.10	0.06
Oligosaccharides (XOS + GOS + AOS)[b]	/	1.54	0.38	1.41	1.67	1.10	0.14	0.15	0.11
Acetic acid	/	1.14	0.51	1.12	1.08	0.81	0.86	1.37	0.72
Furfural	/	0.069	0.077	0.059	0.065	0.047	0.120	0.086	0.054
5-HMF[c]	/	0.013	0.026	0.0028	0.0041	0.0016	0.044	0.031	0.011
Phenolic acid (FA + P-CA)[d]	/	0.0612	0.428	0.051	0.088	0.068	0.863	0.357	0.245

[a] TSY: total sugar yield.
[b] XOS: xylooligosaccharides, GOS: glucooligosaccharides, AOS: arabinooligosaccharides.
[c] 5-HMF: 5-hydroxymethyl furfural.
[d] FA: ferulic acid, P-CA: P-coumaric acid.

process of steam explosion and acid or alkaline (see Fig. 1B and C). But based on the efficient removal of lignin, the depolymerization effect of steam explosion and alkali was better than that of steam explosion and acid, suggesting that the release of acid-soluble lignin in pretreated solid residue occurred. Moreover, the adsorption peak due to aromatic hydroxyl groups was observed at 1300 cm^{-1}. This peak might be generated by cleavage of ether bonds within the lignin. These results implied that the partial lignin was removed.

3.2. Characterization of the pretreated solid and liquid fraction

The chemical compositions in corn stalk before and after treatment with the different methods is given in Table 1. The untreated corn stalks were composed of 31.54% cellulose, 29.10% hemicellulose, and 38.12% lignin. It was found that the cellulose yields of 60.51% and 76.15% were achieved when corn stalks were pretreated with H_2SO_4 and NaOH at 60 °C for 24 h, respectively. It may be attributed to the removal of lignin, hemicellulose and other soluble substance because the contents of hemicellulose and lignin in the treated stalk were lower than those in raw material. These results were in agreement with the investigation from FT-IR (see Fig. 1).

Table 1 showed that most of hemicellulose and lignin could be removed while treating corn stalk with a combination of steam explosion and acid or alkali. For example, 84.16% of hemicellulose and 71.83% of lignin in corn stalk were removed after treatment with 0.8 MPa steam explosion + alkali and 0.4 MPa steam explosion + alkali, respectively. Similarly, the collaborative approach of steam explosion and H_2SO_4 could also remove hemicellulose and lignin and thereby resulted in the increase of cellulose content in corn stalk. These results suggest that steam explosion coupled with acid or alkali resulted in a certain depolymerization to the molecular structure of corn stalk, but considering the removal of hemicellulose and lignin, the depolymerization effect of steam explosion and alkali is better than that of steam explosion and acid. Zhang, Fu and Chen (2012) reported that treatment corn stalk with steam explosion improved the conversion efficiency of lignocellulose to xylose. Generally, an increase in cellulose content and/or a decrease in hemicellulose and lignin contents could improve the catalytic efficiency of cellulase for lignocellulosic materials. Additionally, during pretreatment, corn stalk degrades into sugars and other chemicals (mainly acetic acid, furfural, 5-HMF, and phenolic acid). Acetic acid was produced during degradation of hemicellulose and lignin (Qin, Liu, Li, Dale, & Yuan, 2012), it was generated in the hydrolysis of acetyl groups in hemicellulose. The partial glucose could be transformed into 5-HMF under acidic or alkaline condition. However, the amounts of 5-HMF were very low (0.001–0.04 mg/mL) in liquid phase fraction in this research. Two pentoses (xylose and arabinose) could be transformed into furfural. Table 1 showed that the maximum concentration of furfural was 0.12 mg/mL. The by-products of phenolic acid (mainly FA and P-AC) were detected in the liquid phase fraction of corn stalk after treatment using steam explosion coupled with acid or alkali. These organic compounds were mainly degraded from the lignin-carbohydrate-complex (LCC) and lignin. Therefore, pretreatment influence can be partly evaluated by composition of the liquid phase fraction, mainly composed of glucose, xylose, arabinose, degradation production and by-products. As listed in Table 1, monosaccharide took the main part of recovered sugars in the liquid phase fraction. With the increase of treating bursting pressure, the pentose (mainly xylose and arabinose) and acetic acid, normally generated from hemicellulose degradation, were detected. The result showed that total sugar content changed from 1.86 mg/mL to 6.83 mg/mL with different pretreatment methods. This offers a good account for the removal of hemicellulose with the combination of steam explosion and acid/alkali.

The concentration of the total solubilized sugars (both oligomers and monomers) from biomass is an important indicator of the suitability of a pretreatment process. Table 1 depicts the comparison of steam explosion coupled with acid or alkali hydrolysis of corn stalk for production of the total solubilized sugars, it shows data concerning the conversion of lignocellulose into their respective monomers and oligomers (mainly xylooligosaccharides (XOS), glucooligosaccharides (GOS) and arabinooligosaccharides (AOS). It was found that a difference in amount of oligomers and monomers produced through steam explosion coupled with acid or alkali pretreatment was described comparatively. The result indicates the effect of steam explosion + acid pretreatment in contrast to steam explosion + alkali under the same experiment conditions (0.4–0.8 MPa). As observed, there were obtained the higher quantities of monomers (1.4–5.2 mg/mL) than oligomers (0.1–1.6 mg/mL) in steam explosion coupled with acid or alkali pretreatment process, however, the difference was much bigger in steam explosion + acid pretreatment, which was obtained the higher concentration of oligomers (1.1–1.6 mg/mL) than that of steam explosion + acid pretreatment (0.1–0.3 mg/mL). The combined methods with steam explosion + acid are more effective than

Table 2
The enzyme hydrolysis of the treated sample under different conditions.

Treatment method	Total sugar and glucose contents in the enzymatic hydrolysis[a] (mg/mL)						
	6 h	12 h	24 h	36 h	48 h	60 h	72 h
5% H_2SO_4	8.69 (2.34)	10.21 (3.12)	13.00 (3.34)	15.07 (4.19)	16.44 (4.09)	17.44 (4.28)	17.89 (3.96)
5% NaOH	16.64 (5.28)	24.14 (7.02)	28.66 (7.66)	31.38 (8.15)	41.11 (9.77)	38.49 (7.77)	39.27 (9.14)
0.4 MPa steam explosion + 5% H_2SO_4	7.29 (2.32)	9.92 (3.31)	11.60 (3.57)	17.37 (3.86)	17.46 (4.35)	19.60 (4.61)	17.33 (4.65)
0.6 MPa steam explosion + 5% H_2SO_4	8.12 (2.11)	9.30 (3.10)	11.85 (3.64)	14.65 (3.65)	17.21 (4.22)	17.78 (4.14)	15.82 (3.54)
0.8 MPa steam explosion + 5% H_2SO_4	7.05 (1.90)	9.14 (2.72)	10.21 (3.12)	16.88 (3.50)	19.93 (3.78)	18.11 (3.85)	16.31 (3.82)
0.4 MPa steam explosion + 5% NaOH	16.54 (5.69)	22.94 (7.54)	28.17 (8.31)	32.45 (9.76)	42.67 (10.22)	39.52 (10.31)	39.31 (9.39)
0.6 MPa steam explosion + 5% NaOH	17.29 (5.09)	16.43 (6.93)	28.00 (7.87)	35.83 (9.56)	40.20 (10.82)	37.25 (9.58)	38.37 (9.46)
0.8 MPa steam explosion + 5% NaOH	16.71 (5.42)	19.85 (6.80)	27.67 (7.21)	35.83 (9.13)	39.44 (9.83)	37.66 (3.79)	39.45 (8.72)

[a] The value in brackets express glucose content in enzymatic hydrolysis process (mg/mL).

steam explosion + alkali hydrolysis for production of the total solubilized sugars.

3.3. Effect of pretreatment on enzyme hydrolysis

The enzyme hydrolysis of the treated sample under different conditions is summarized in Table 2. The result showed that enzymatic hydrolysis sugar contents were improved by steam explosion coupled with acid or alkali pretreatments. The higher total sugar contents (16–40 mg/mL) was obtained in the alkali or steam explosion + alkali treatment samples compared with the acid treatment samples for the enzymatic hydrolysis within 72 h. The lower total sugar contents of the treated sample by H_2SO_4 or steam explosion + acid can be observed from 7 mg/mL to 17 mg/mL with the enzymatic hydrolysis time from 6 h to 72 h. It is because proper hemicellulose and lignin were removed under alkali/acid pretreatment condition, and also the physicochemical properties of corn stalk was interrupted. Additionally, increasing the pretreatment pressure resulted in a higher removal rate of hemicellulose and lignin since this released more sugar from the conversion of hemicellulose and cellulose.

3.4. X-ray diffraction analysis

The X-ray diffraction patterns of the treated and untreated corn stalks are depicted in Fig. 2. The intensities of the amorphous region at $2\theta = 18^\circ$ and the crystalline region at $2\theta = 22^\circ$ were used to calculate the crystallinity index (CrI) (Kim & Holtzapple, 2006).

$$\mathrm{CrI} = \frac{[\text{intensity at } 2\theta = 22^\circ - \text{intensity at } 2\theta = 18^\circ]}{[\text{intensity at } 2\theta = 22^\circ]} \quad (1)$$

As shown in Fig. 2, the diffraction peak of the untreated corn stalk at (0 0 2) was wide and round. However, this peak became sharper and narrower when the tested material was treated with acid or alkaline. In addition, a shoulder peak at (1 0 1) and a weak peak at (0 4 0) appeared when corn stalks were treated with acid and alkaline. These peaks are assigned to the cellulose phase, suggesting the removal of most of lignin and hemicellulose from corn stalk. By a calculation of Eq. (1), CrI values of corn stalk after treatment with H_2SO_4 and NaOH increased to 63.5% and 67.0% as compared with 51.8% of the untreated stalk, respectively. The reason might be that the amorphous hemicellulose was hydrolyzed while crystalline structure was change thus increasing of crystallinity index in biomass. Moreover, the swelling ability of alkali to the amorphous region of lignocellulose was relatively strong as compared to that of acid and resulted in the increase of the dissolution rate of lignin and hemicellulose. Zheng et al. (2012) reported that the crystallinity, porosity and inner surface area of corn stalk were increased when the ordered rearrangement and the secondary crystallization were proceeding in the non-crystallized portion and the imperfect part of cellulose crystal structure.

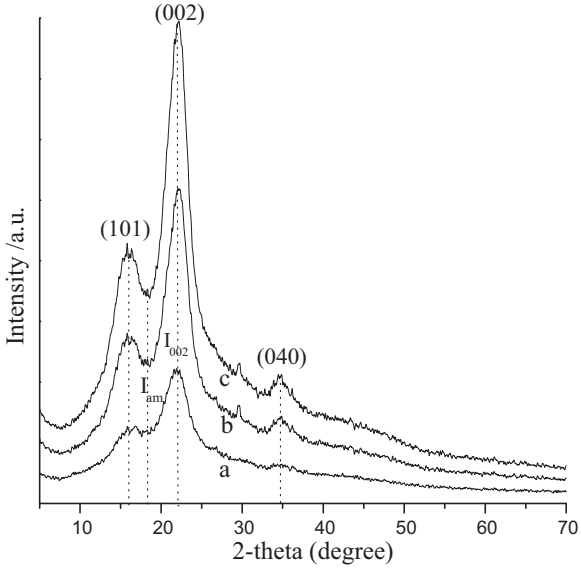


Fig. 2. X-ray diffraction pattern of untreated and treated corn stalk: (a) corn stalk; (b) acid; (c) alkali.

3.5. The thermal stability analysis

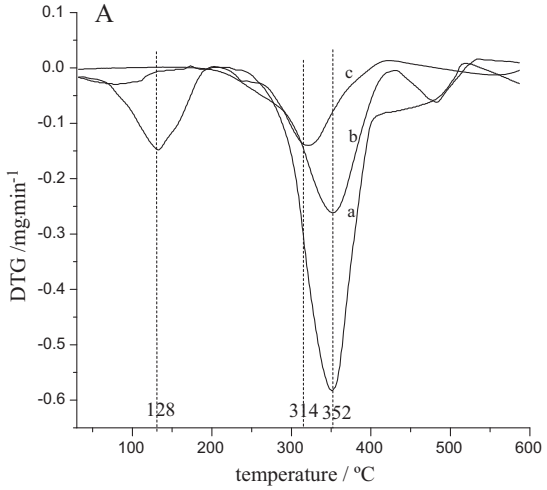
DTG curve was usually used to reflect the degradation of biomass. Generally, the decomposition reaction of lignocellulose is divided into three processes including (1) dehydration and drying stage in 25–250 °C, (2) the pyrolysis stage in 250–500 °C, and (3) the depth of the pyrolysis stage in 500–600 °C. In this paper, the pyrolysis characteristics and DTG curves of corn stalk before and after treatment with the tested methods are given in Table 3 and Fig. 3, respectively. As can be noted, the DTG curves contain a strong peak, which is attributed to the primary pyrolysis. This result is consistent with that of other studies on biomass materials (Jiang, Nowakowski, & Bridgwater, 2010). Physical and chemical pretreatment had little effect on the shape of DTG curves. The maximum weight loss rate and pyrolysis temperature of corn stalks after treatment with steam explosion, acid, and alkaline, alone or in combination, were higher than those of the untreated material.

When temperature was lower than 250 °C, the weight loss of corn stalk was mainly attributed to the removal of absorbed water and crystal water, the dehydration peak and drying curves were disappeared with the combined pretreatment using acid or alkali and steam explosion (Fig. 3B and C). This was also supported by the fact that the heat absorption and weight loss rate of dehydration and drying stage were changed in untreated and treated corn stalks (see Table 3).

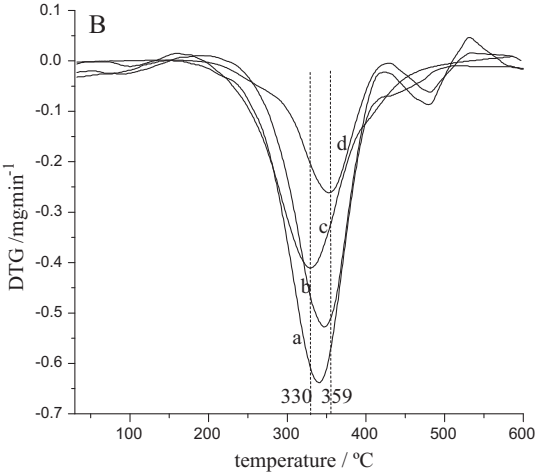
Table 3
Pyrolysis characteristics of corn stalk before and after treatment with different methods.

Treatment method	dehydration and drying stage		Pyrolysis stage			
	Heat absorption (J/g)	Weight loss rate (%)	Heat absorption (J/g)	Weight loss rate of stage 1 (%)	Weight loss rate of stage 2 (%)	Pyrolysis temperature (°C)
Untreated	113.37	29.62	241.94	35.11	6.44	332.11
5% H_2SO_4	53.26	0.21	195.90	71.80	10.06	365.56
5% NaOH	92.18	3.14	205.69	70.86	10.24	357.05
0.4 MPa steam explosion + 5% H_2SO_4	52.16	1.63	118.94	73.55	–	348.82
0.6 MPa steam explosion + 5% H_2SO_4	50.66	2.16	161.85	69.21	8.18	354.35
0.8 MPa steam explosion + 5% H_2SO_4	55.41	0.74	87.47	69.28	–	339.14
0.4 MPa steam explosion + 5% NaOH	75.56	2.08	225.09	89.31	–	356.08
0.6 MPa steam explosion + 5% NaOH	62.63	2.15	192.51	66.62	10.58	357.89
0.8 MPa steam explosion + 5% NaOH	72.17	1.58	114.79	69.99	–	354.59

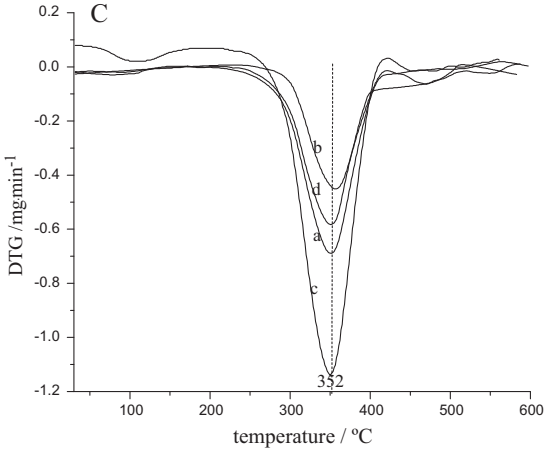
With the increase of temperature (>250 °C), the DTG profiles of the treated and untreated displayed a significant difference. Although the shapes of DTG curve did not exhibited a significant change under different pretreatment condition, the peaks of weight loss shifted towards the high temperature region. Because treatment corn stalk with acid or alkali could remove most of hemicelluloses and some lignin, the temperature of the maximum degradation rate shifted from 332 °C to 365 and 357 °C at 5 °C/min and the maximum weight loss rate from 41.5% to 81.8% and 81.0%, respectively. These results on the lateral shift to higher temperatures for the maximum region of weight loss are in agreement with those from other investigators on polypropylene, oil shale and their mixture (Deng, Zhang, & Wang, 2008). It also could be concluded that lower weight loss rate of dehydration stage and lower heat absorption of pyrolysis stage were obtained when corn stalks were treated with steam explosion coupled with acid or alkali as compared to those of acid or alkaline treatment alone. The main reason of this was related to partial removal of hemicelluloses and



(a) alkali; (b) acid; (c) untreated



(a) 0.4 MPa steam explosion + acid; (b) 0.6 MPa steam explosion +acid; (c) 0.8 MPa steam explosion + acid; (d) acid



(a) 0.4 MPa steam explosion + alkali; (b) 0.6 MPa steam explosion + alkali; (c) 0.8 MPa steam explosion + alkali; (d) alkali

Fig. 3. DTG curves of corn stalk before and after treatment with different methods. (A) acid and alkali; (B) steam explosion + acid; (C) steam explosion + alkali.

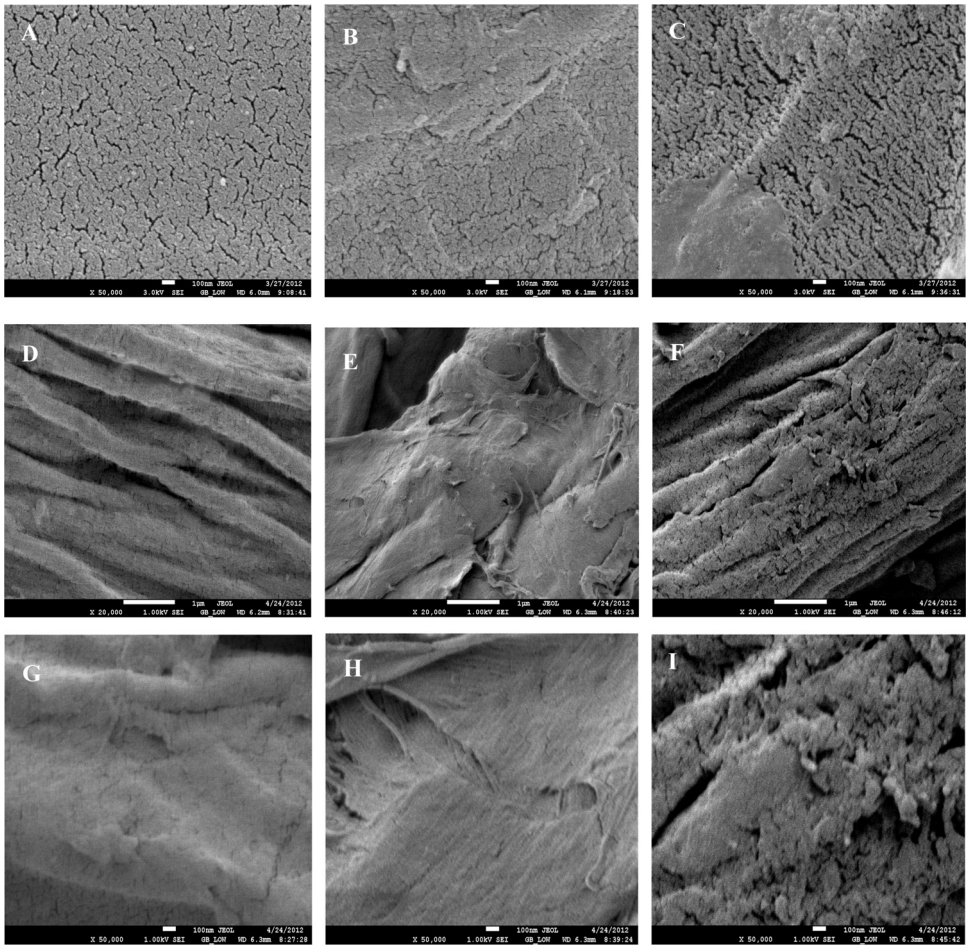


Fig. 4. SEM images of corn stalk before and after treatment with different methods. (A) Untreated; (B) acid; (C) alkali; (D) 0.4 MPa steam explosion + acid; (E) 0.6 MPa steam explosion + acid; (F) 0.8 MPa steam explosion + acid; (G) 0.4 MPa steam explosion + alkali; (H) 0.6 MPa steam explosion + alkali; (I) 0.8 MPa steam explosion + alkali.

lignin from the corn stalk and higher crystallinity of cellulose. These were consistent with the results obtained from XRD and FT-IR measurements (see Figs. 1 and 2).

In thermal analysis, the pyrolysis of hemicelluloses and cellulose in the untreated and treated corn stalks occurred quickly at about 225–325 °C, which is attributed to thermal depolymerisation of hemicelluloses or pectin. The major decomposition peak at about 300–430 °C was attributed to cellulose decomposition. However, lignin was more difficult to decompose, as its weight loss happened in a wide temperature range from 250 to 500 °C (Chen, Yu, Zhang, & Lu, 2011; Kaushik & Singh, 2011). Additionally, Fig. 3 showed that the pyrolysis temperature and thermal stability of corn stalk were enhanced after treatment with the combined method of steam explosion and acid or alkaline due to the removal of most of hemicellulose and lignin. These results suggest that dilute acid and dilute alkali lead to a certain depolymerization to the molecular of corn stalk, but the depolymerization effect of dilute alkali is better than that of dilute acid in terms of delignification.

3.6. Scanning electron microscopy

SEM micrographs of the untreated and treated rice straw fibers were shown in Fig. 4. The untreated sample showed an even and smooth flat surface, indicating a rigid and highly ordered surface structure (see Fig. 4A). However, the nature surface was broken into some large fragments and appeared porous structure and rift after treatment with alkaline or acid (see Fig. 4B and C). When corn stalks were treated with acid and steam explosion under different pressure, the treated sample had a rugged, rough, loose, and broken surface (see Fig. 4D–F). It was clearly found that morphologies of the treated corn stalks under different conditions were also obviously different. For example, the surface of raw samples by 0.8 MPa steam explosion + alkali looked more roughness than that by 0.4 MPa or 0.6 MPa steam explosion + alkali (see Fig. 4G–I). The reason is that lignin and hemicellulose of interwoven wrapped cellulose crystalline structure was broken and weakened the mutually binding force between holocellulose and lignin by the pretreatment with different burst pressure in acid–alkali. This would obviously favor the catalyst contacting the inner linkage, hence accelerating the biodegradation process.

4. Conclusions

Treatment with steam explosion and alkali could remove most of hemicellulose (84.16%) and lignin (71.83%) in corn stalk as compared to those of the untreated stalk. The surface morphology become loose and the thermal stability increased when corn stalks were depolymerized with steam explosion and acid or alkali. These results suggested that steam explosion coupled with acid or alkali could lead to a depolymerization of the molecular structure of corn stalk, but in consideration of removal of hemicellulose and lignin, the depolymerization effect of steam explosion and alkali was better than that of steam explosion and acid.

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References

Adney, B., & Baker, J. (1996). Measurement of cellulase activities. In *NREL analytical procedure*. National Renewable Energy Laboratory Golden, Co (NREL/TP-510-42628).

Bian, J., Peng, F., Xu, F., Sun, R. C., & Kennedy, J. F. (2010). Fractional isolation and structural characterization of hemicelluloses from *Caragana korshinskii*. *Carbohydrate Polymers*, *80*, 753–760.

Chen, X. L., Yu, J., Zhang, Z. B., & Lu, C. H. (2011). Study on structure and thermal stability properties of cellulose fibers from rice straw. *Carbohydrate Polymers*, *85*, 245–250.

Chundawat, S. P. S., Venkatesh, B., & Dale, B. E. (2007). Effect of particle size based separation of milled corn stover on AFEX pretreatment and enzymatic digestibility. *Biotechnology and Bioengineering*, *96*, 219–231.

Deng, N., Zhang, Y. F., & Wang, Y. (2008). Thermogravimetric analysis and kinetic study on pyrolysis of representative medical waste composition. *Waste Management*, *28*, 1572–1580.

Egüés, I., Sanchez, C., Mondragon, I., & Labidi, J. (2012). Effect of alkaline and autohydrolysis processes on the purity of obtained hemicelluloses from corn stalks. *Bioresource Technology*, *103*, 239–248.

Gullón, P., Romaní, A., Vila, C., Garrote, G., & Parajó, J. C. (2012). Potential of hydrothermal treatments in lignocellulose biorefineries. *Biofuels, Bioproducts and Biorefining*, *6*, 219–232.

Goering, H. K., & Van Soest, P. J. (1970). Forage fiber analysis. In *USDA-ARS agriculture handbook 379*. Washington, DC: U.S. Government Printing Office.

Hsu, T. C., Guo, G. L., Chen, W. H., & Hwang, W. S. (2010). Effect of dilute acid pretreatment of rice straw on structural properties and enzymatic hydrolysis. *Bioresource Technology*, *101*, 4907–4913.

Jiang, G. Z., Nowakowski, D. J., & Bridgwater, A. V. (2010). A systematic study of the kinetics of lignin pyrolysis. *Thermochimica Acta*, *498*, 61–66.

Karagöz, P., Rocha, I. V., Özkan, M., & Angelidaki, I. (2012). Alkaline peroxide pretreatment of rapeseed straw for enhancing bioethanol production by same vessel saccharification and co-fermentation. *Bioresource Technology*, *104*, 349–357.

Kaushik, A., & Singh, M. (2011). Isolation and characterization of cellulose nanofibrils from wheat straw using steam explosion coupled with high shear homogenization. *Carbohydrate Research*, *346*, 76–85.

Kumar, R., & Wyman, C. E. (2009). Cellulase adsorption and relationship to features of corn stover solids produced by leading pretreatments. *Biotechnology and Bioengineering*, *103*, 252–267.

Kim, S., & Holtzapple, M. T. (2006). Effect of structural features on enzyme digestibility of corn stover. *Bioresource Technology*, *97*, 583–591.

McIntosh, S., & Vancov, T. (2011). Optimisation of dilute alkaline pretreatment for enzymatic saccharification of wheat straw. *Biomass and Bioenergy*, *35*, 3094–3103.

Moharram, M. A., & Mahmoud, O. M. (2008). FTIR spectroscopic study of the effect of microwave heating on the transformation of cellulose I into cellulose II during mercerization. *Journal of Applied Polymer Science*, *107*, 30–36.

Oliveira, F. M. V., Pinheiro, I. O., Souto-Maior, A. M., Martin, C., Goncalves, A. R., & Rocha, G. J. M. (2013). Industrial-scale steam explosion pretreatment of sugarcane straw for enzymatic hydrolysis of cellulose for production of second generation ethanol and value-added products. *Bioresource Technology*, *130*, 168–173.

Peng, F., Peng, P., Xu, F., & Sun, R. C. (2012). Fractional purification and bioconversion of hemicelluloses. *Biotechnology Advances*, *30*, 879–903.

Pedersen, M., & Meyer, A. S. (2009). Influence of substrate particle size and wet oxidation on physical surface structures and enzymatic hydrolysis of wheat straw. *Biotechnology Progress*, *25*(2), 399–408.

Qin, L., Liu, Z. H., Li, B. Z., Dale, B. E., & Yuan, Y. J. (2012). Mass balance and transformation of corn stover by pretreatment with different dilute organic acids. *Bioresource Technology*, *112*, 319–326.

Qi, X. J., Gou, J. X., Han, X. J., & Yan, B. (2004). Study on measuring reducing sugar by DNS reagent. *Journal of Cellulose Science and Technology*, *12*, 17–19 (In Chinese).

Ranjan, A., & Moholkar, V. S. (2013). Comparative study of various pretreatment techniques for rice straw saccharification for the production of alcoholic biofuels. *Fuel*, *112*, 567–571.

Ruiz, H. A., Rodríguez-Jasso, M. A., Fernandes, B. D., Vicente, A. A., & Teixeira, J. A. (2013). Hydrothermal processing, as an alternative for upgrading agriculture residues and marine biomass according to the biorefinery concept: A review. *Renewable and Sustainable Energy Reviews*, *21*, 35–51.

Sun, Y. G., Ma, Y. L., Ma, X. X., & Chang, X. (2013). Experimental study on the molecular structure of corn stalk after depolymerization with acid or alkali. *Chemistry*, *76*(7), 645–649 (In Chinese).

Talebnia, F., Karakashev, D., & Angelidaki, I. (2010). Production of bioethanol from wheat straw: An overview on pretreatment, hydrolysis and fermentation. *Bioresource Technology*, *101*, 4744–4753.

Vegas, R., Alonso, J. L., Domínguez, H., & Parajó, J. C. (2004). Processing of rice husk autohydrolysis liquors for obtaining food ingredients. *Journal of Agricultural and Food Chemistry*, *52*, 7311–7317.

Zhang, Y. Z., Fu, X. G., & Chen, H. G. (2012). Pretreatment based on two-step steam explosion combined with an intermediate separation of fiber cells-optimization of fermentation of corn straw hydrolysates. *Bioresource Technology*, *121*, 100–104.

Zheng, M. X., Li, L. Q., Zheng, M. Y., Wang, X., Ma, H. L., & Wang, K. J. (2012). Effect of alkali pretreatment on cellulosic structural changes of corn stover. *Environmental Science and Technology*, *35*, 27–31.

Zhou, D. F., Ma, Y. L., Xie, L., & Cai, Y. (2011). Experimental study on pretreatment of maize stalk cellulose with H_2O_2 and alkaline. *Renewable Energy and Resources*, *29*(1), 19–22 (In Chinese).