Hot Water Extraction of Corn Stover: Hemicellulose Fractionation and its Effect on Subsequent Soda-AQ Pulping

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Fractionation of lignocellulosic biomass is an important process in producing biofuels. In this study, hot water extraction of corn stover hemicellulose was carried out at 150, 160, and 170 °C. Variations of sugar content in the hydrolysate under different holding time were detected. The contents of furfural and 5-hydroxymethyl-2-furaldehyde generated during the extraction were also determined. Results showed that the main composition of the hydrolysate was xylo-oligosaccharide; the yield of oligosaccharides first increased as holding time was prolonged. After extraction at 160 °C for 210 min, 70.2% of the total xylan was dissolved, with the generation of furfural (0.90 g/L) and 5-hydroxymethyl-2-furaldehyde (0.10 g/L). The effects of extraction on alkali pulping and bleaching were also investigated. Results indicated that soda-AQ pulp obtained from the extracted material had poorer tensile and burst strengths but better tear strength.

Keywords: Hemicellulose; Hot water extraction; Xylan; Pulping

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INTRODUCTION

Recently, lignocellulosic biomass, including agricultural residues, forestry wastes, and energy crops, has received great attention due to its potential to produce renewable biofuels and bioenergy. Additionally, utilization of biomass is environmentally friendly (Himmel *et al.* 2007). Lignocellulosic biomass is primarily constituted by three major polymers: cellulose, hemicellulose, and lignin, all of which can serve as sources of bioenergy. A universal case that converts biomass to energy on an industrial scale is the combustion of spent liquor in traditional chemical pulp mills. Since pulping liquors contain a significant amount of hemicelluloses and their derivatives besides lignin, and the heat value of hemicellulose is much lower than that of lignin (Yoon and van Heiningen 2008), this part of hemicellulose cannot be fully utilized if they are burned to recover heat energy together with lignin. Therefore, extraction of hemicellulose prior to pulping for generation of fuels or bioethanol provides a viable option for revenue generation in the pulp industry (Sattler *et al.* 2008). The Portuguese pulp and paper industry has already seen success in combining biomass conversion with high-quality pulp production (Mendes *et al.* 2009).

There are many methods for pre-extraction of hemicellulose from biomass, including dilute acid extraction, steam-explosion extraction, alkali extraction, and liquid hot water extraction (Huang *et al.* 2008; Mosier *et al.* 2005; Teng *et al.* 2010). These methods are considered to be effective in the removal of hemicellulose. However, acid

and steam-explosion extraction may require extra investment of equipment. Alkali extraction can remove most of the hemicellulose with high molecular weight from lignocellulosic biomass (Egüés *et al.* 2012), but it still requires chemicals. Hot water extraction has widely been studied recently (Leppänen *et al.* 2011; Duarte *et al.* 2011). The mechanism for hot water extraction is similar to that for acid extraction. During extraction, with the increase of temperature and holding time, acetyl/uronic acid groups detach from hemicellulosic monomers and form acid in the extract. This acid (in the form of hydrogen ions) catalyses the hydrolysis and results in glycosidic bond cleavage between sugar units. The hot water extraction is an autocatalytic acid hydrolysis process and requires no extra chemicals. Thus it can be regarded as costless and friendly to the environment (Aguilar *et al*. 2002). Previous studies have shown that kraft pulp from hot water-extracted materials had a lower kappa number, higher brightness, and better bleaching behavior than the reference pulp (Lei *et al.* 2010; Lu *et al.* 2012; Vila *et al.* 2011).

In this study, factors affecting hemicellulose dissolution of corn stover by hot water extraction were investigated. The pre-extracted corn stover was then pulped with a soda-AQ process and bleached with alkaline peroxide. The main purpose of this work was to produce a certain amount of saccharides as well as traditional chemical pulp with good quality, particularly strength properties.

EXPERIMENTAL

Materials

Corn stover was collected from Shandong province, China. The material was depithed and cut into pieces of 2 cm in length prior to use. The initial chemical composition of corn stover was determined to be 50.7% glucan, 18.1% xylan, 2.2% arabinan, 15.5% Klason lignin, 1.4% acid soluble lignin, 7.4% benzene-alcohol extractives, and 0.5% ash (Cheng *et al.* 2011).

D-xylose, D-galactose, D-glucose, D-mannose, L-arabinose furfural, and HMF were purchased from Sigma-Aldrich (USA). Other chemicals used in this study were of analytical grade.

Hot Water Extraction

Extraction of the corn stover hemicellulose was carried out in an M/K 609-2-10 reactor (USA) equipped with an internal liquid reflux system and a discharging valve at the bottom. Corn stover (400 g, dry matter basis) was soaked in water overnight at a liquid-to-solids ratio 10:1. Then, the mixture was placed in the reactor and heated to the maximum temperature (150, 160, or 170 °C) at a rate of 2 °C/min. The holding time was 540 min at 150 °C and 300 min at 160 and 170 °C. About 10 mL of the extract was unloaded from the reactor every 15 min during the insulation stage. The pH was determined after the extract cooled to room temperature.

Sugar Analysis

The total polysaccharides and monosaccharides contents were determined by ionic chromatography (Dionex ICS3000) with a CarboPac TM PA20 anion exchange column and an electrochemical detector. Samples for determination of monosaccharides were diluted with deionized water and filtered through a syringe filter (0.22 μm) before

being subjected to the automatic injection system. Samples for total sugars measurements were pre-hydrolyzed with 4% H_2SO_4 at 121 °C for 1 h.

Furfural and HMF Analysis

All samples were filtered through a syringe filter with pore size of 0.22 μm before analysis. The contents of furfural and HMF were determined by HPLC with an Agilent C18 universal column and an ultraviolet detector. The mobile phase was 5% methanol solution (pH 2.5, adjusted by acetic acid) at a flow rate of 1 mL/min. Since furfural and HMF were converted by pentose and hexose, respectively, the yields of furfural and HMF were calculated according to the following formula,

$$Y_{Fur} = \frac{132}{96} \times \frac{C_{Fur} \times V}{m_{pentosan}} \times 100\% \quad (1)$$

where C_{Fur} is the concentration of furfural in the hydrolyzate (g/L), V is the volume of hydrolyzate (L), $m_{pentosan}$ is the mass of pentosan, (g), and 132/96 is the stoichiometric conversion coefficient between furfural and pentosan, while the stoichiometric conversion coefficient between HMF and hexosan is 162/126.

Pulping

Pulping was carried out in a 15-L ZQS_1 electrothermal slewing digester (Machinery Factory of Shaanxi University of Technology) using a soda-AQ method. Pulping conditions were as follows: alkali charge 12% (w/w, calculated by NaOH); AQ charge 0.05% (w/w); liquor-to-solid ratio 4:1 (v/w); maximum temperature 150 °C; time to 150 °C, 120 min; and time at 150 °C, 60 min. Corn stover without pre-extraction was also pulped under the same conditions as the control.

Bleaching

Pulps were bleached with hydrogen peroxide after alkaline pulping. The operating conditions were: (i) in Q stage, pulp consistency 10% (w/w), EDTA dosage 0.3% (w/w), temperature 60 °C, time 60 min; and (ii) in P stage, pulp consistency 10% (w/w), H_2O_2 3%, NaOH 2%, $MgSO_4$ 0.15%, Na_2SiO_3 2%, temperature 90 °C, reaction time 240 min.

RESULTS AND DISCUSSION

Variation of pH during Hot Water Extraction

The pH value of the hydrolysate decreased with increasing temperature and extraction time, as illustrated in Fig. 1. After heating to the extraction temperature, the pH values of the extracts decreased from neutral to 5.24, 5.03, and 4.86 at 150, 160, and 170 °C, respectively. This suggests that the liquor was not neutral when the insulation stage began. With further extraction, the pH value continued decreasing; the higher the extraction temperature, the lower the pH was obtained, at a certain holding time. After extraction at the set temperature for 300 min, the pH decreased to 4.15, 3.74, and 3.57 at 150, 160, and 170 °C, respectively. A lower pH was obtained at a higher temperature at the same holding time. Even when prolonging the holding time to 540 min at 150 °C, the pH value was just 3.90. It can be inferred from these results that temperature plays a more important role in hot water pre-extraction than holding time.

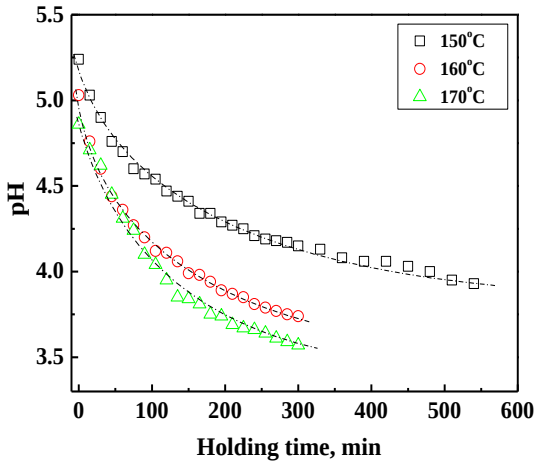

Fig. 1. Effect of temperature and holding time on pH value

Dissolution of Saccharides during Hydrolysis

Xylan is the main composition of corn stover hemicellulose; therefore, the yield of xylan determines the efficiency of the extraction. During extraction, most of the xylan was dissolved in the form of oligosaccharides, and some were further degraded into monosaccharides. Therefore, the total pentose content in the extract comprises of both oligosaccharides and monosaccharides.

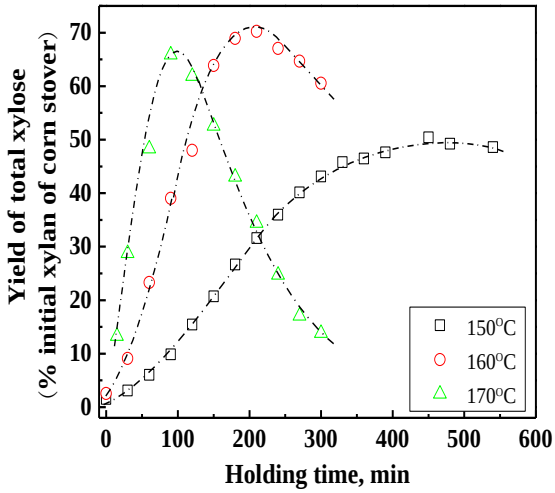

Fig. 2. Effect of temperature and holding time on the yield of total xylose

The yield of total xylose extracted at 150, 160, and 170 °C was dependent on holding time, as shown in Fig. 2. For instance, the content of total xylose dissolved in the extract increased to a maximum value after 90 min when extracted at 170 °C and then decreased as the extraction proceeded. This can be explained by the fact that acidic conditions enable xylooligosaccharides to dissolve in the extract. These oligomers were then degraded to monosaccharides, or even to furfural, depending on the severity of the extraction conditions. When the rate of degradation exceeded the rate of dissolution, the yield of total xylose decreased, as shown in Fig. 2. The maximum yield of total xylose was 70.2% after being pretreated for 210 min at 160 °C, with a corresponding xylose concentration of 12.73 g/L, while xylan yield was 68.9% at 160 °C for 180 min. At 150

and 170 °C, the maximum yields were 50% and 65.8%, when the holding time was 450 min and 90 min, respectively.

The yield of xylose (monosaccharides) increased with holding time at 150 and 160 ºC, as shown in Fig. 3. The highest yields of xylose under the experimental conditions were 18% and 25% at 150 and 160 °C, respectively. The time-dependent yield at 170 ºC was quite different, as shown in Fig. 3. After extraction for 210 min, a maximum yield of 19% was reached. From then on, the yield of xylose decreased, probably because 170 °C provided a relatively severe pre-extraction condition. It can also be inferred from Figs. 3 and 4 that total xylose is primarily composed of xylooligosaccharide.

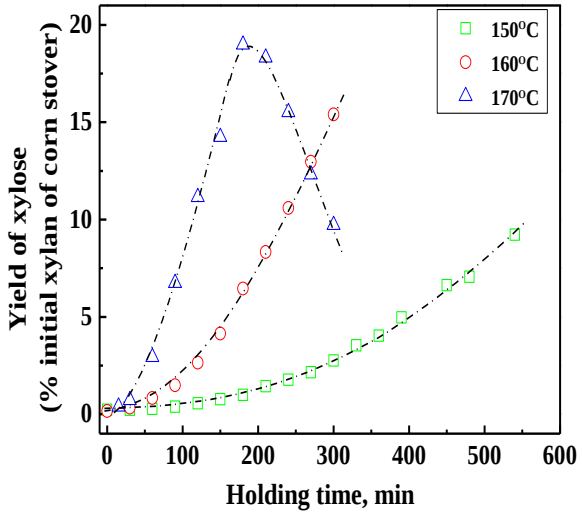

Fig. 3. Effect of temperature and holding time on the yield of xylose (monosaccharide)

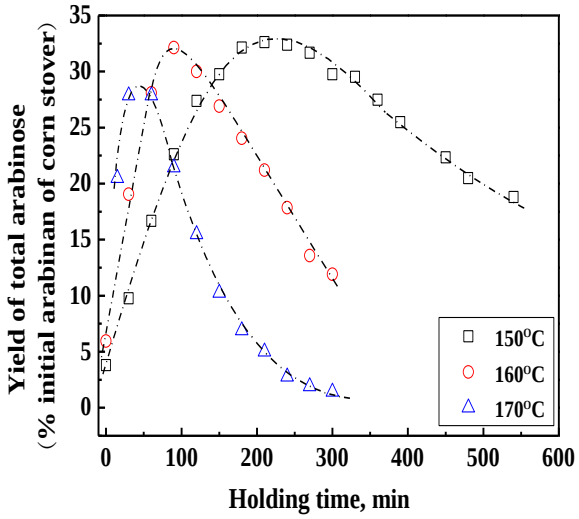

Fig. 4. Effect of temperature and holding time on the yield of total arabinose

The yields of total arabinose at different temperatures are shown in Fig. 4. The maximum yields at 150, 160, and 170 °C were 32%, 30%, and 28%, respectively, obtained at corresponding holding times of 210, 120, and 60 min. The time-dependent yield of arabinose monosaccharide was similar to that of xylose. According to the results shown in Figs. 4 and 5, the total arabinose in the extract was mostly composed of arabinose, rather than arabinooligosaccharides.

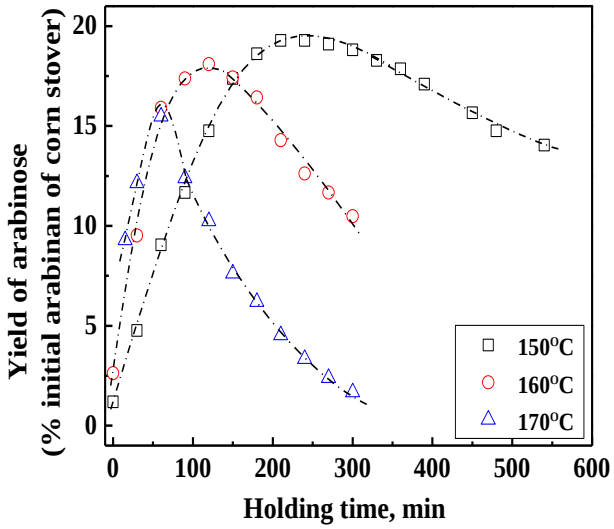

Fig. 5. Effect of temperature and holding time on the yield of arabinose (monosaccharide)

Generation of Furfural and HMF

As the extraction proceeded, weak organic acid continuously originated from de-acetylation of the hemicellulose. The pentose and hexose dissolved in the extract were then degraded into furfural and HMF, respectively. The formation of furfural and HMF not only reduced the yield of hemicellulose, but could also inhibit the efficiency of sugar fermentation by microorganisms for bioethanol production, if they reached a certain concentration (Banerjee *et al.* 1981; Klinke *et al.* 2004). Therefore, the concentration of furfural and HMF during the extraction was monitored; the results are shown in Figs. 6 and 7. Obviously, the content of furfural and HMF increased with the holding time. Moreover, the higher the extraction temperature was adopted, the more furfural/HMF was generated. When the holding time was 210 min at 160 °C, the yields of furfural and HMF were 5.56% and 0.26%, corresponding to concentrations of 0.90 g/L and 0.10 g/L, respectively. At 160 °C for 180min, the concentration for furfural and HMF were just 0.68 g/L and 0.08g/L.

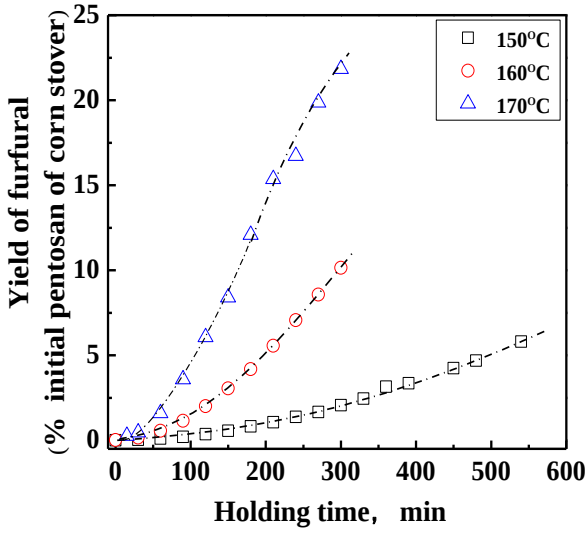

Fig. 6. Effect of temperature and holding time on the yield of furfural

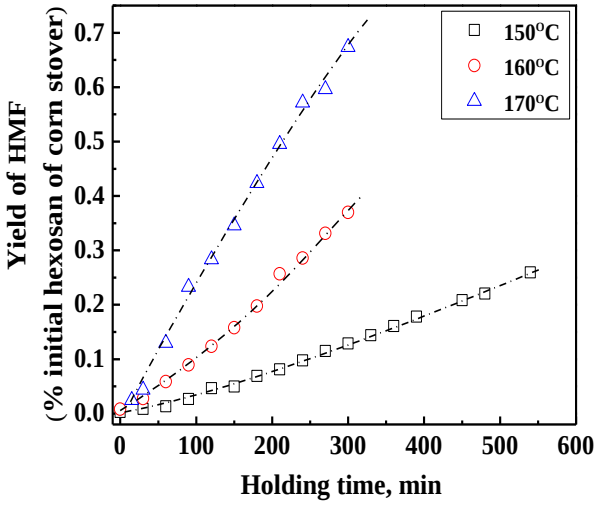

Fig. 7. Effect of temperature and holding time on the yield of HMF

Effect of Hot Water Extraction on Soda-AQ Pulping

Since the yield of xylan at 160 °C for 180 min was close to 160 °C for 210 min, and the concentration of furfural under 160 °C for 180 min was much lower than for 210 min, corn stover pretreated for 180 min at 160 °C was adopted to investigate its alkaline pulping properties. As a comparison, raw material without hot water pretreatment was also subjected to alkaline pulping under the same conditions. The results (Table 1) showed that the tear index of the soda-AQ pulp from hot water-extracted corn stover (HEP) increased greatly compared with the reference pulp (BP), while the viscosity of the HEP (1199 mg/L) had a slight increase compared with the BP (1135 mg/L). However, the kappa number of the HEP pulp was much higher than that of the BP pulp, whereas the brightness and strength properties of the HEP, like density, breaking length, and burst index, were all lower.

During hot water extraction, the color of corn stover gradually turned from pale yellow to deep brown. The mass loss was about 30% when the holding time was 180 min at 160 °C, which suggested that hemicellulosic sugars were responsible for the mass loss, and most of the lignin remained in the solids under the experimental conditions. Chromophore groups formed with increasing holding time. These groups were responsible for the deep color of the residual solids, and might be the reason for the higher kappa number of the HEP pulp.

Table 1. Property Comparison between the Reference Soda-AQ Pulp (BP) and HEP Pulp

	BP	HEP
Kappa number	21.9	28.9
Residue alkali (g/L)	1.7	1.3
Yield (%)	55.1	37.5
Brightness (%ISO)	28	22
Beating degree (°SR)	43	42.5
Density ($g \cdot cm^{-3}$)	0.8	0.7
Breaking length (km)	9.5	6.0
Tear index ($mN \cdot m^2 \cdot g^{-1}$)	8.6	13.9
Bursting index ($Pa \cdot m^2 \cdot g^{-1}$)	6.8	4.3

Effect of Hot Water Extraction on Peroxide Bleaching

Both BP and HEP pulps were bleached with alkaline peroxide. Pulp properties are listed in Table 2. The strength properties, including burst index and breaking length, were lower for both HEP-b and BP-b pulps, as compared with their corresponding soda-AQ pulp, while the tear index was greater.

The brightness of HEP-b was lower than that of BP-b; about 3.4% ISO brightness was lost after hot water pre-extraction. Considering the greater difference in kappa number, the bleachability of the HEP pulp was improved after hot water extraction.

Table 2. Property Comparison between the Reference QP Bleached Pulp (BP-b) and HEP-b Pulp

	BP-b	HBP-b
Beating degree (°SR)	41.5	43
Brightness (%ISO)	81.6	78.2
Density ($g \cdot cm^{-3}$)	0.8	0.7
Breaking length (km)	9.18	5.6
Tear index ($mN \cdot m^2 \cdot g^{-1}$)	9.4	15.6
Bursting index ($KPa \cdot m^2 \cdot g^{-1}$)	6.1	4.3

CONCLUSIONS

1. The effects of hot water extraction of hemicellulose on soda-AQ pulping of corn stover were investigated. The contents of total xylose and arabinose in the extract were determined to study the efficiency of the extraction. With increasing holding time and temperature, the yields of total xylose and total arabinose first increased to a maximum value and then decreased. About 70.2% of the total xylose was obtained at 160 °C after 210 min.
2. As the extraction proceeded, furfural and HMF were generated from pentose and hexose in the extract. The concentrations of furfural and HMF in the extract were 0.90 g/L and 0.10 g/L, respectively, at an extraction temperature of 160 °C after 210 min.
3. Soda-AQ pulping was carried out on corn stover pre-extracted at 160 °C for 180 min. The performance of HEP pulp was not as good as expected. The yield and brightness were decreased as compared with the reference BP pulp produced under the same cooking conditions. The kappa number increased and strength properties such as burst index and breaking length decreased; this was probably because the chromophoric groups formed during hot water extraction consumed extra cooking chemicals. Results of QP bleaching suggest that the bleachability of pulp from hot water-extracted corn stover was improved compared to the reference pulp.

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