

Comparison of the Delignifiability and Hydrolysability of Wheat Straw and Corn Stover in Aqueous Ammonia Pretreatment

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The impact of an aqueous ammonia pretreatment on the structural properties, delignifiability, and hydrolysability of wheat straw and corn stover was investigated. The results showed that the aqueous ammonia pretreatment had an excellent delignification ability and that the corn stover exhibited higher susceptibility to an aqueous ammonia attack than wheat straw. In total, 35.6% and 70.0% of the lignin in wheat straw and corn stover were removed, respectively, by the aqueous ammonia pretreatment at 75 °C with 21% ammonia and a solid:liquid ratio of 1:10 for 20 h. Both lignin and polysaccharides in the corn stover exhibited higher susceptibility to aqueous ammonia than those in wheat straw. In addition, the hydrolysability of corn stover was more susceptible to aqueous ammonia than it was to wheat straw. A chemical structure analysis of different substrates showed that the aqueous ammonia pretreatment removed lignin, broke ester bonds between lignin and hemicelluloses, increased the specific surface area and crystallinity index, and, finally, enhanced the hydrolysis yield.

Keywords: Aqueous ammonia pretreatment; Structure properties; Enzymatic hydrolysis; Wheat straw; Corn stover

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INTRODUCTION

At present, the economic dependency on fossil oil for energy and chemical production has placed focus on alternative resources. Unlike fossil fuel, biofuel is a renewable and clean energy source produced by lignocellulosic materials, and it can reduce both the consumption of crude oil and environmental pollution (Hamelinck *et al.* 2005; Alvira *et al.* 2010). Being abundant and widely distributed, lignocellulosic materials are a promising energy feedstock for bioethanol production. Wheat straw and corn stover are the most important agricultural residues in the world. In China, millions of tons of wheat straw and corn stover residues are produced annually, and they contain celluloses and hemicelluloses, which are polysaccharides that can be hydrolysed into fermentable sugars for the production of bioethanol and other chemicals. However, technologies for the conversion of lignocellulosic materials into bioethanol and other chemicals are still being investigated (Sun and Tomkinson 2001; Talebnia *et al.* 2010; Laluece *et al.* 2012).

Lignocelluloses primarily consist of cellulose, hemicellulose, lignin, extractives, and ash. Cellulose and hemicelluloses, typically making up two-thirds of the cell wall dry matter, can be hydrolysed into sugars and then fermented to bioethanol. Lignin is an aromatic polymer in which the phenyl propane units are connected by both ether and carbon-carbon linkages to hemicelluloses, bonded together by a set of linkages to form a complex matrix (Higuchi 1990). The production of ethanol from lignocelluloses includes

three processes: a pretreatment, the hydrolysis of cellulose and hemicelluloses in the lignocellulosic materials to fermentable sugars, and the fermentation of the sugars to ethanol. Various pretreatments have been used to overcome the recalcitrance of lignocellulosic materials so that the cellulose is more accessible to enzymes for enzymatic hydrolysis (Hamelinck *et al.* 2005; Balat 2011; Zhang *et al.* 2011). The enzymatic hydrolysis requires an effective pretreatment to improve the accessibility of the enzymes, to set free the cellulose fractions from the lignin-carbohydrate complex (LCC), to disrupt the crystalline structure of lignocellulosic materials, and to increase the total yield of liberated sugars in the hydrolysis step (Talebnia *et al.* 2010).

Acid- or alkali-based methods are the most commonly used chemical pretreatment systems. Drawbacks of the acid pretreatment are that it is corrosive, it requires high energy consumption, the reactors used for the pretreatment need to be highly resistant to corrosion, and the cost is relatively high compared to other physico-chemical pretreatments (Sun and Cheng 2002; Galbe and Zacchi 2002; Talebnia *et al.* 2010). Generally, lower temperatures and pressures are used in alkali pretreatment compared to acid pretreatment. Sodium hydroxide, ammonia, and lime are suitable alkaline agents for pretreatment, among which ammonia has been studied by many researchers (Gupta and Lee 2010; Nguyen *et al.* 2010; Rollin *et al.* 2010; Li and Kim 2011; McIntosh and Vancov 2011; Gao *et al.* 2012). Aqueous ammonia has been widely used for the pretreatment of lignocelluloses and is recyclable due to its volatility. As previous studies have reported, ammonia pretreatment allows the retention of most of the cellulose and hemicellulose components while removing a portion of lignin and altering its structure (Kim *et al.* 2003; Li *et al.* 2010; Rémond *et al.* 2010; Gao *et al.* 2012). An aqueous ammonia pretreatment can delignify lignocellulose by disrupting the C-O-C bonds in lignin as well as the ester bonds in the LCC (Hsu *et al.* 2010; Alvira *et al.* 2010; Balat 2011; Nguyen *et al.* 2010). Also, ammonia is a chemical reagent that is only about one-fourth as expensive as sulfuric acid (Kim *et al.* 2003).

In this work, the effects of aqueous ammonia pretreatment on the structural changes and chemical compositions of wheat straw and corn stover were determined. The solubilisation of glucan and xylan from the substrates with the aqueous ammonia pretreatment was also investigated. Suitable conditions for the aqueous ammonia pretreatment were evaluated by calculating the hydrolysis efficiency of cellulose with commercial enzyme preparations. The results of this work will be beneficial to evaluate the great potential application of the aqueous ammonia pretreatment for efficient hydrolysis of wheat straw and corn stover.

EXPERIMENTAL

Materials and Reagents

Wheat straw and corn stover were collected from a local farm in Yangling, Shaanxi Province, China. The materials were dried at 90 °C for 8 h and then milled to a size of about 1 mm. The milled materials were stored at -18 °C for further use. The initial chemical compositions of the wheat straw and corn stover were determined according to laboratory analytical procedures established by the National Renewable Energy Laboratory (Sluiter *et al.* 2005a, b, 2008). The chemical composition of the wheat straw was 31.8% glucan, 21.9% xylan, 20.8% lignin, 8.1% ash, and 6.7% water extractives. The chemical composition of the corn stover was 32.6% glucan, 20.5% xylan, 21.0%

lignin, 6.2% ash, and 11% water extractives. Ammonia solution (26±1%, w/w) was supplied by Sichuan Xilong Chemical Co., Ltd (Chendu, China). All other chemical reagents were of analytical grade.

Aqueous Ammonia Pretreatment

The milled wheat straw and corn stover were pretreated with 21% (w/w) of an aqueous ammonia solution in a screw-capped 1000-mL bottle under the conditions of 75 °C and a S:L (solid : liquid) ratio of 1:10 for 5, 20, and 50 h, respectively. The pretreatment conditions used in this work were based on previous work with minor revision (Kim *et al.* 2008; Ko *et al.* 2009). These conditions were selected because of their very good delignification ability. A control with low temperature was performed under the conditions of room temperature (18±2°C) and a S:L ratio of 1:10 for 20 h. No stirring occurred during the pretreatment. The slurry was separated by centrifugation, and the spent ammonia liquid (SAL) was collected, neutralised to a pH of 6 to 7 by hydrochloric acid (1 M), diluted to a constant volume, and stored at -18 °C for glucose and reducing sugars analysis. The solid was recovered using a filtration cloth and washed with distilled water until the pH of the filtrate was between 6 and 7. After that, the solid was air-dried and stored at -18 °C.

Enzymatic Hydrolysis

The enzymatic hydrolysis was performed at 2% dry matter (w/v) in screw-capped 10-mL tubes with a working volume of 5 mL in a 50 mM sodium citrate buffer (pH 5.0). The reaction mixtures were incubated at 50 °C on an orbital shaker at 200 rpm. The commercial enzyme preparations Celluclast 1.5L (Novo Nordisk A/S, Bagsværd, Denmark) and Novozyme 188 (Novo Nordisk A/S, Bagsværd, Denmark) were employed for the hydrolysis experiments. The filter paper activity (FPA) of Celluclast 1.5L was 74.7 filter paper units (FPU)/mL according to the standardised IUPAC filter paper assay (Ghose 1987). The β -glucosidase activity of Novozyme was 8451 nkat/mL (~380 IU/mL) as measured according to the method described by a previous study (Bailey and Linko 1990). The cellulase loading was 15 FPU/g of dry matter of the Celluclast 1.5L, which was supplemented with 500 nkat/g of dry matter of Novozyme 188. The samples were withdrawn at 6 and 48 h and boiled for 10 min to stop the enzymatic hydrolysis. After cooling, the samples were centrifuged at 10,000 \times g for 10 min, and the supernatants were analysed for glucose and xylose by high performance liquid chromatography (HPLC). The conversion factors from glucose to glucan and xylose to xylan are 0.90 and 0.88, respectively, as a previous study has described (Irick *et al.* 1988). Two replicate tests were carried out in all of the hydrolysis experiments, and the average values are presented.

Analytical Procedures for Solid and Liquid Composition Analysis

Carbohydrates, water extractives, ash, and acid-insoluble lignin in the substrates were determined using laboratory analytical procedures established by the National Renewable Energy Laboratory (Sluiter *et al.* 2005a,b, 2008). The samples were hydrolysed with 72% sulfuric acid for 1 h and autoclaved after being diluted to 4% sulfuric acid for 1 h through the addition of water. The autoclaved samples were filtered, and the dried residue was weighed to give the Klason lignin content. The concentration of glucose and xylose in the filtrate was neutralised by calcium carbonate and determined on a Hitachi L-2000 HPLC system equipped with a RI-detector and an Aminex HPX-87P

column (Bio-Rad, USA) at 85 °C with HPLC-grade water as the eluent at a flow rate of 0.6 mL/min. SAL samples were neutralised to a pH of 7.0 with 4% (w/w) H₂SO₄ before the carbohydrate analysis. The reducing sugars were measured using the dinitrosalicylic acid (DNS) method with glucose as the standard (Miller 1959).

Scanning Electron Microscopy (SEM) Analysis

Physical changes in the samples and materials after hydrolysis were observed by SEM, operated at an accelerating voltage of 10 kV. The samples were air-dried and mounted on aluminum sample stubs. The mounted samples were then placed in the chamber of a sputter coater and coated with a thin layer of gold before the SEM examination. The samples were evaluated using a scanning electron microscope (JSM-6360LV, Jeol, Japan). Representative images were chosen to illustrate the physical changes caused by the aqueous ammonia pretreatment.

X-ray Diffraction (XRD) Analysis

The cellulose crystallinity index (CI) of the samples was measured with XRD using a Rigaku D/max-3C generator (Rigaku Corporation, Japan). The dried samples were scanned in a 2θ range from 5° to 50° using steps of 0.02° in width and using Cu/K α radiation (1.54 Å) generated at 35 kV and 35 mA. The CI of cellulose was calculated from the XRD spectra according to the XRD peak height (Park *et al.* 2010). Scherrer's equation was used for estimating the crystallite size (Mittal *et al.* 2011),

$$\beta = \frac{k\lambda}{\tau \cos \theta} \quad (1)$$

where λ is the wavelength of the incident X-ray (1.54 Å), θ is the Bragg angle corresponding to the (002) plane, β is the full-width at half maximum (FWHM) of the X-ray peak corresponding to the (002) plane, τ is the X-ray crystallite size, and k is a constant with a value of 0.89 (Lewin and Roldan 1971).

Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The samples for the FTIR spectra analysis were pressed into a disc with KBr and were analysed on a Thermo Nicolet 470 FTIR spectrophotometer (Thermo Nicolet Corporation, VA, USA). The background spectrum of the diamond window without the sample was subtracted from that of each sample spectrum. In total, 32 scans were collected for each measurement over the wavelength range of 4000 to 400 cm⁻¹.

RESULTS AND DISCUSSION

Effect of Aqueous Ammonia Pretreatment on Chemical Composition

It has been reported that the temperature and the duration of an aqueous ammonia pretreatment were decisive factors in determining the crystal lattice and degree of crystallinity of cellulose, affecting the hydrolysis rate and yield of cellulose in biomass (Saapan *et al.* 1984; Mittal *et al.* 2011). After aqueous ammonia pretreatment, the lignin reduction increased with the duration time and the pretreatment temperature (Table 1); this was in agreement with a previous study that determined that there was a positive correlation between the intensity of an alkaline pretreatment and the efficiency of the

delignification (Xu *et al.* 2011). In this work, 75 °C was chosen as the pretreatment temperature, because it was reported that a high delignification could be obtained at above 70 °C and no supercharge equipment was required (Kim *et al.* 2008; Ko *et al.* 2009). After 5 h of pretreatment, the lignin contents of the wheat straw and corn stover decreased from 20.8% and 21.0% to 14.1% and 8.4%, respectively (Table 1). When the pretreatment time increased to 20 h, the lignin contents of the wheat straw and corn stover decreased to 13.4% and 6.3%, corresponding to 35.6% and 70.0% of lignin removal, respectively. The highest lignin removal (40.9% and 80.0%, respectively) was obtained from the wheat straw and corn stover after 50 h of pretreatment, indicating that lignin in the wheat straw was harder to remove with the aqueous ammonia pretreatment than that in the corn stover. Low delignification abilities were obtained both in wheat straw (12.0%) and corn stover (18.6%) at room temperature. In this work, the aqueous ammonia pretreatment showed a high delignification ability for lignocellulosic materials, which is in agreement with the research conducted by Ko and coworkers, who found that 60.6% and 88.0% of lignin was removed from rice straw and wheat straw, respectively, using an aqueous ammonia pretreatment (Ko *et al.* 2009; Hsu *et al.* 2010). The data presented here indicated that the lignin fraction in both materials was selectively removed, and the lignin in the wheat straw exhibited lower susceptibility to an aqueous ammonia attack than that in corn stover.

Table 1. Compositions of Glucan, Xylan, and Lignin (% Dry Matter) in Wheat Straw and Corn Stover after Aqueous Ammonia Pretreatment

Raw Material	Temperature (°C)	Time (h)	Composition (%)		
			Glucan	Xylan	Lignin
Wheat Straw	Non-pretreatment		31.8±0.0	21.9±0.0	20.8±0.1
	75	5	44.2±0.7	26.0±0.5	14.1±0.45
	RT	20	39.0±0.5	26.1±1.2	18.3±0.55
	75	20	49.6±0.4	26.0±0.4	13.4±0.1
	75	50	50.4±0.3	25.2±1.6	12.3±0.02
Corn Stover	Non-pretreatment		32.6±0.0	20.5±0.0	21.0±0.1
	75	5	54.3±0.1	26.6±0.9	8.4±0.03
	RT	20	44.2±0.3	25.6±1.4	17.1±0.7
	75	20	53.7±0.8	26.6±0.3	6.3±0.01
	75	50	58.4±1.0	26.6±0.7	4.2±0.03

* RT: Room Temperature (18±2 °C)

SAL is an aqueous solution that dissolves a majority of lignin residues, hemicellulose, and some inorganic chemicals (Mussatto *et al.* 2007; Ghatak 2008; Minu *et al.* 2012; Xu *et al.* 2012). More glucose was released from the corn stover than from the wheat straw after the aqueous ammonia pretreatment, indicating that glucan in the corn stover could be solubilised more easily than that in wheat straw. After the aqueous ammonia pretreatment (75 °C, 5 h, 21% ammonia, S:L 1:10), the reducing sugars in SAL collected from the wheat straw and corn stover were 1.98 and 3.05 g/L (Table 2), corresponding to 3.4% and 5.2% of the polysaccharides in the substrates, respectively.

Table 2. Concentrations of Glucose and Reducing Sugars in Spent Ammonia Liquid from Wheat Straw and Corn Stover after Aqueous Ammonia Pretreatment

Raw Material	Temperature (°C)	Time (h)	Concentration (g/L)	
			Reducing sugars	Glucose
Wheat straw	75	5	1.98	0.87
	75	20	1.80	0.80
	RT	20	1.21	0.40
	75	50	2.25	1.40
Corn stover	75	5	3.05	1.60
	75	20	3.18	1.93
	RT	20	2.16	0.87
	75	50	4.11	2.33

* RT: Room Temperature (18±2 °C)
All of the standard errors are within 0.30.

When the pretreatment time was extended to 20 h, 3.0% and 5.4% of the polysaccharides in the wheat straw and corn stover were solubilised during the pretreatment, respectively. After 50 h of pretreatment, the glucose in SAL from the wheat straw and corn stover reached 1.40 and 2.33 mg/mL, respectively, indicating 4.0% and 6.5% of the glucan in the wheat straw and corn stover were solubilised. Except for glucose, the reducing sugars in SAL may include some xylose and xylo-oligosaccharides (Gupta and Lee 2010). The contents of glucose and reducing sugars in SAL were very low, and the recovery of those sugars could be performed by membrane separation technology. The results revealed that the polysaccharides were mostly solubilised in the first 5 h of the pretreatment and that the polysaccharides in the corn stover were more susceptible to the aqueous ammonia than those in the wheat straw.

SEM analysis

Because a large fraction of the lignin was removed by the aqueous ammonia pretreatment, it became of interest to examine the structural morphology of the wheat straw and corn stover substrate surfaces (Fig. 1). The fibers before the pretreatment were smooth, compacted, and well-ordered. After the aqueous ammonia pretreatment, the surface of the wheat straw and corn stover fibers became rough and coarse, which could be due to the loss of a large amount of the lignin and other carbohydrate contents, which were dissolved in the SAL (Figs. 1b and 1e), as confirmed previously. When the pretreatment time increased to 50 h, the surface of the fiber became rougher, most of the outer surface layer was stripped off, the inside of the fiber was exposed, and the surface area of the fiber clearly increased compared to the control (Fig. 1c and 1f). Kim *et al.* reported that the microfibrils of corn stover that were pretreated with a recycled ammonia percolation treatment were separated from the initial connected structure and fully exposed (Kim *et al.* 2003). This phenomenon is in agreement with the results presented here.

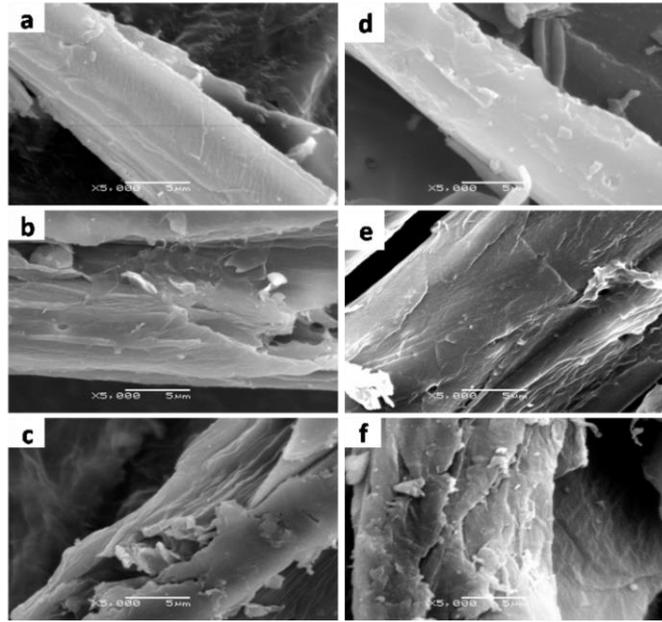


Fig. 1. SEM images of materials before hydrolysis under 5000 magnification (a) non-pretreated wheat straw, (b) wheat straw after pretreatment at 75 °C for 5 h, (c) wheat straw after pretreatment at 75 °C for 50 h (d) non-pretreated corn stover, (e) corn stover after pretreatment at 75 °C for 5 h, (f) corn stover after pretreatment at 75 °C for 50 h

XRD Analysis

Previous studies have shown that a decrease in substrate crystallinity is accompanied by characteristics such as a particle size reduction and an increase in the available surface area (Schuerch 1963; Wada *et al.* 2006; Alvira *et al.* 2010). The CI of celluloses can be measured using several techniques, including XRD, solid-state ^{13}C NMR, and FTIR (Hsu *et al.* 2010; Park *et al.* 2010). Four different crystalline amorphous phases of cellulose (cellulose I, II, III, IV) were identified in previous studies using XRD (Ishikawa and Okano 1997). Lewin and Roldan reported that ammonia penetrated the cellulose and reacted with the hydroxyl groups after breaking the hydrogen bonds. The interaction between cellulose and aqueous ammonia can cause changes in the interplanar distances of the 101 planes (Lewin and Roldan 1971; Mittal *et al.* 2011).

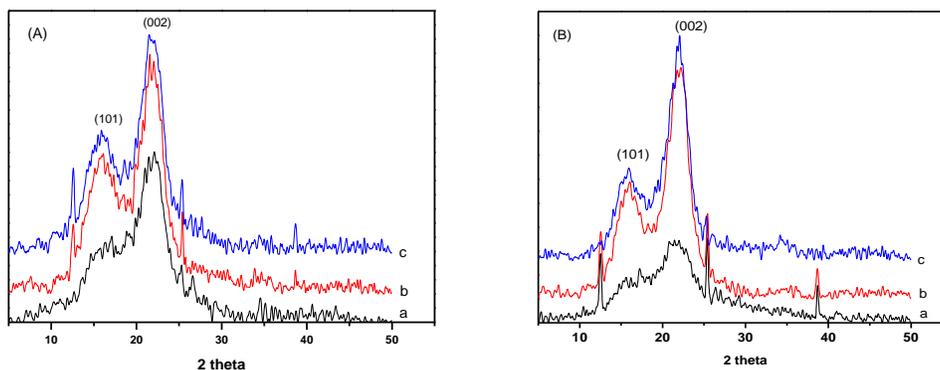


Fig. 2. XRD patterns of (A) wheat straw and (B) corn stover. Pretreatment conditions: (a) non-pretreatment; (b) 75 °C for 5 h; (c) 75 °C for 50 h

Figure 2 shows the X-ray diffractograms from the wheat straw and corn stover before and after pretreatment. The increased peak height and decreased peak width of the 002 peak indicated a decrease in the amorphous fraction of the samples. For lignocellulosic materials, the CI value indicates the relative amount of the crystalline cellulose in the total solid. A lower CI value indicates a larger proportion of amorphous components present in the biomass (Park *et al.* 2010). Aqueous ammonia pretreatment mainly removes xylan and lignin, which are amorphous components in lignocellulosic materials (Kim *et al.* 2003; Alvira *et al.* 2010). As can be seen in Table 3, substrate treated with aqueous ammonia resulted in an increase in the values of the CI. The CI values of the wheat straw and corn stover after the pretreatment for 50 h increased from 62% and 51% to 69% and 78%, respectively. However, there was no obvious regular pattern in the crystallite size of these samples. Mittal and coworkers observed that under the conditions of a final treatment temperature of 130 °C for 1 h, the crystallite size of corn stover increased from 30 Å to 56 Å (Mittal *et al.* 2011). The results here indicated that after the ammonia pretreatment, the CI of the substrates increased and the crystallite size changed. Higher CI values of the substrates were associated with the removal of amorphous contents like lignin and hemicelluloses; therefore, the physical structure of the samples became porous during the aqueous ammonia pretreatment process, making them suitable for the subsequent enzymatic hydrolysis. A larger increase in the CI value and the crystallite size was observed in the corn stover, indicating that more amorphous contents were removed from the corn stover than from the wheat straw.

Table 3. Crystallinity Index (CI) and Crystallite Size from XRD Analysis of Untreated and Pretreated Wheat Straw and Corn Stover. Pretreatment was Performed by 21% (w/w) Aqueous Ammonia at S:L 1:10

Raw Materials	Temperature (°C)	Time (h)	CI (%)	Crystallite size (Å)
Wheat straw	Control	-	62	29
	75	5	66	36
	75	50	69	28
Corn stover	Control	-	51	26
	75	5	72	33
	75	50	78	37

FTIR Analysis

The ester linkage C=O with an absorption peak at 1730 cm⁻¹ is usually defined as the acetyl group in the hemicellulose structure or the linkage between hemicelluloses and lignin (Kumar *et al.* 2009; Hsu *et al.* 2010). An adsorption peak at 1730 cm⁻¹ was weaker after pretreatment of the wheat straw (Fig. 3). These adsorptions may be generated by cleavage of the acetyl group, and the ester linkage between the lignin and hemicelluloses may be broken after the aqueous ammonia pretreatment (Gao *et al.* 2012). According to previous research (Kim *et al.* 2003), the lignin characteristic peaks are at 1218 cm⁻¹, 1268 cm⁻¹ (C-O of the guaiacyl ring), 1315 cm⁻¹ (C-O of syringyl ring), and 1502 to 1600 cm⁻¹ (aromatic skeletal vibration). As shown in Fig. 3, the band intensities at all of the lignin peaks of the control were higher than those from the aqueous ammonia pretreated substrates. This phenomenon demonstrates that the aqueous ammonia pretreatment had efficient delignification ability.

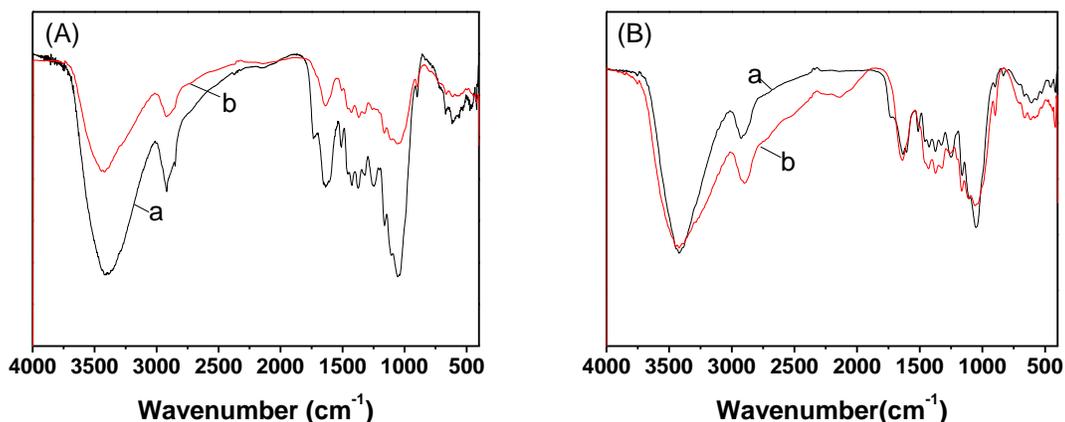


Fig. 3. FTIR spectra of wheat straw (A) and corn stover (B). (a) Raw materials; (b) substrates after pretreatment at 75 °C for 50 h

Enzymatic Hydrolysis

To investigate the effect of aqueous ammonia pretreatment on enzymatic hydrolysis, the hydrolysis of different substrates of wheat straw and corn stover by cellulase preparation was carried out (Fig. 4). The glucan conversions of non-pretreated wheat straw and corn stover were as low as 21% and 15%, respectively, after 48 h of hydrolysis by cellulases. In this work, the calculation of glucan conversion was defined as the ratio of glucan hydrolyzed ($0.9 \times \text{glucose}$) to the glucan in the pretreated wheat straw or corn stover. Under the conditions of 75 °C, S:L 1:10, when the pretreatment time increased from 5 to 50 h, the glucan conversion of the wheat straw and corn stover increased by 3.8% and 45.4%, respectively. It was found that the maximum glucan conversion yields of wheat straw and corn stover were 63% and 96%, respectively. Higher glucan conversion was always found in the hydrolysis of the pretreated corn stover, which was due to its higher delignifiability in the pretreatment (Table 1), resulting in much less non-productive adsorption of cellulases on lignin. In the hydrolysis of aqueous ammonia pretreated (75 °C, 48 h, 15% ammonia, S:L 1:12) barley hull, a glucan conversion of 83% was obtained (Kim *et al.* 2008), which is higher than that of wheat straw but lower than that of corn stover in this work. The increment of glucan conversion was significant after extension of hydrolysis time from 24 to 48 h (Fig. 4), which was due to the efficient delignification, swelling, and disruption of cellulose crystallinity of the pretreatment, resulting in high accessibility of cellulases to glucan in the substrates (Kim *et al.* 2008). For the wheat straw and corn stover pretreated by aqueous ammonia at room temperature with a S:L ratio of 1:10 for 20 h, the glucan conversions after 48 h of hydrolysis were about 28% and 20%, respectively. When the pretreatment temperature was 75 °C, the glucan conversion yields of the wheat straw and corn stover clearly increased to around 60% and 82%, which were lower and higher than the glucan conversion (76%) from the 24 h aqueous ammonia pretreated barley hull, respectively (Kim *et al.* 2008). After pretreatment by aqueous ammonia, the contact areas on the surface of lignocellulosic materials have been magnified; hence, the accessibility of the enzymes was improved significantly, in good agreement with previously published reports (Kim and Lee 2005; Kim *et al.* 2008). The results here revealed that the hydrolysability of the corn stover was more susceptible to pretreatment time and temperature than that of the wheat straw.

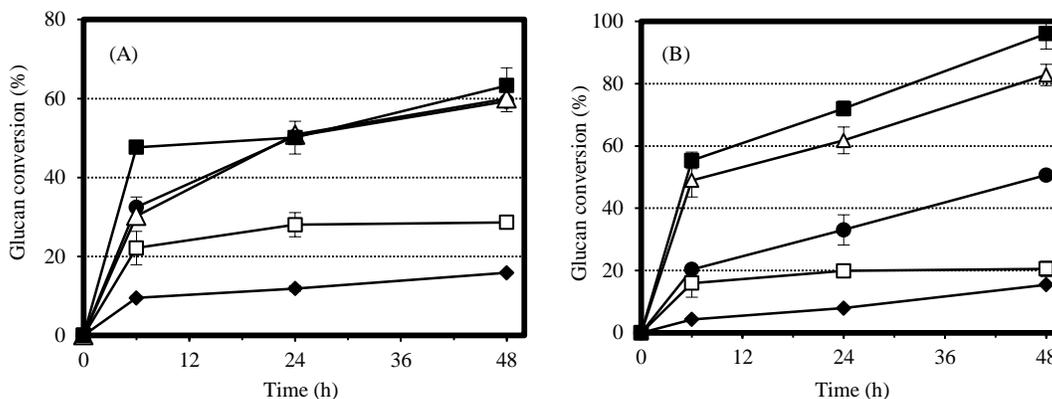


Fig. 4. Hydrolysis of aqueous ammonia-pretreated wheat straw (A) and corn stover (B). (◆) Non-pretreatment; (●) after pretreatment at 75 °C for 5 h; (△) after pretreatment at 75 °C for 20 h; (□) after pretreatment at room temperature for 20 h; (■) after pretreatment at 75 °C for 50 h. Error bars represent standard errors.

CONCLUSIONS

1. An aqueous ammonia pretreatment of wheat straw and corn stover showed effective delignification ability, while the corn stover showed higher susceptibility to the aqueous ammonia attack than the wheat straw.
2. Most lignin and polysaccharides were removed from the corn stover and wheat straw in the first 5 h of the aqueous ammonia pretreatment. Both lignin and polysaccharides in the wheat straw were less easily removed by aqueous ammonia than those in the corn stover.
3. The results of XRD, SEM, and FTIR showed that after the aqueous ammonia pretreatment, the CI and the surface area of the substrates increased. Disruption of the linkage between the hemicellulose and lignin was demonstrated by the results.
4. Both the time and temperature of the aqueous ammonia pretreatment had a greater effect on the hydrolysability of the corn stover than they did on that of wheat straw.

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