Anaerobic Digestion Performance and Mechanism of Ammoniation Pretreatment of Corn Stover

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The objective of this study was to investigate the anaerobic digestion performance and mechanism of corn stover pretreated with ammonia at three ammonia concentrations (2, 4, and 6%) and four moisture contents (30, 50, 70, and 90%). The physical and chemical structures as well as the changes in its chemical compositions of ammonia-pretreated corn stover were analyzed to understand its biogas production performance. The results showed that ammonia pretreatment could effectively improve the anaerobic digestion performance of corn stover and that the optimal biogas production performance was achieved with 4% ammonia and 70% moisture content. The maximum biogas yield reached 427.1 mL/gVS. The conversion rates of cellulose and hemicellulose were 80.60 and 68.5%, respectively, which is about 30 and 26% higher than those of the untreated corn stover, respectively. The composition and structure analyses showed that ammoniation pretreatment could rupture chemical bonds such as ester and ether bonds in the lignocellulose, partially degrade aliphatic and carbohydrate compounds, and bring anaerobes into sufficient contact with corn stover material, therefore helping to increase biogas yield.

Keywords: Anaerobic digestion; Ammoniation pretreatment; Moisture content; Corn stover

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INTRODUCTION

China is one of the largest agricultural producers in the world. Its annual output of crop straw was around 810 million tons in 2013 (National Bureau of Statistics of China 2014); corn stover, wheat straw, and rice straw account for over 80% of this production. The production of corn stover has reached 293 million tons, accounting for about 36.9% of the total crop straw output. However, 50 to 60% of this straw is not effectively utilized in China every year. At present, uses of straw include energy generation, returning to the field, and forage. Use for energy purposes accounts for approximately 25% (Cui *et al*. 2008). Recently, the use of crop straw as the main raw material to produce biogas has received increasing research attention.

Corn stover consists mostly of cellulose, hemicelluloses, and lignin (Chen *et al*. 2010), which form complex, three-dimensional structures and are not very accessible to microorganisms. Thus, pretreatment prior to anaerobic digestion is quite important for corn stover. Chemical pretreatments (acidification and alkalization) have been widely applied in engineering practice because of their fast effects and short pretreatment times (Jiao *et al*. 2011). The C:N ratio in straw is typically 53:1 to 78:1, while the C:N ratio of anaerobic digestion is 20:1 to 30:1. It is obvious that acidification and alkalization pretreatment cannot concurrently provide the nitrogen required for the anaerobic digestion of straw. A nitrogen source is thus necessary during anaerobic digestion, which would greatly increase operating costs (Yadvika *et al*. 2004). At present, the ammoniation method has been used primarily for forage, and there are few relevant studies on ammonia pretreatment. The study by Caneque *et al*. (1998), using ammonia-pretreated rice straw for animal feed, found that ammoniation pretreatment yielded the best effect, not only increasing straw's digestion rate but also increasing its N content. Oji *et al*. (2007) found in research on ammonia forage that ammonia pretreatment could effectively increase the nitrogen content in corn stover and reduce its cellulose and hemicelluloses contents. However, there have been relatively few studies on ammoniation pretreatment for anaerobic digestion. Research carried out by Zhang and Zhang (1999) on anaerobic digestion *via* ammonia pretreatment of rice straw showed that 2% ammonia pretreatment effectively increased the total yield of methane by 17.5% over that from untreated straw. In experiments on the ammonia pretreatment of rice straw for anaerobic digestion, Ma *et al*. (2011) found that with 4% ammonia pretreatment, the biogas production per gram of volatile solids (VS) of rice straw increased by 34.8% over that of untreated straw.

The objectives of this study were to solve corn stover pretreatment problems and supplement the nitrogen source during the anaerobic digestion process, to investigate the anaerobic digestion performance of corn stover under different ammonia pretreatment conditions, and to determine its mechanism to provide a theoretical basis for the engineering practice of using ammoniated corn stover as the main raw material for biogas production.

EXPERIMENTAL

Materials

Corn stover was used as the raw material in these experiments. Corn stover from the suburbs of Shunyi, Beijing was air-dried and chopped to about 5 mm size for future use. The inoculant sludge used in the experiments came from a biogas station in Shunyi, Beijing. The physical and chemical properties of the corn stover and inoculant sludge are shown in Table 1.

Table 1. Basic Characteristics of Corn Stover and Sludge (%)

	Total Solids (TS)	Total Volatile Solids (VS)	Total Carbon	Total Nitrogen	Cellulose	Hemi-cellulose	Lignin
Corn Stover	94.50	86.50	42.29	0.60	34.33	26.62	7.56
Sludge Inoculant	8.45	5.29	30.13	3.27	Not Applicable	Not Applicable	Not Applicable

The experiments were in the form of batch anaerobic digestion. The reaction device consisted of a 1-L anaerobic digestion bottle, a 1-L gas collection bottle, and a 1-L beaker. Anaerobic digestion was carried out in a constant-temperature shaker with moderate internal temperature (35 ± 2 °C) rotating at 120 rpm for 3 min/h.

Methods

The pretreatment reagent was ammonia in water at a fraction of 25% (v/v). In the pretreatment process, the chopped corn stover was placed in a sealed bag, air was purged from the bag, and ammonia was added at charges of 2, 4, and 6% of the dry weight of corn stover. Water was added to this mixture to regulate the moisture content of the corn stover to 30, 50, 70, and 90% of the corn stover's dry weight. The bag was immediately sealed, and the contents were kneaded to fully mix the corn stover with the ammonia. When the pH of this system stabilized (pH±0.2), the pretreatment process was deemed complete. The number of days of pretreatment was determined (Zheng *et al*. 2009). The sealed bags were then stored at 30 ± 2 °C for later use.

A load of 65 g TS/L of pretreated corn stover was used for 1-L anaerobic digestion bottle, and untreated corn stover was taken as the control. For each reactor, 15 MLSS g/L of inoculant sludge was added. Water was then added to reach the effective volume (0.8 L) of the bottle. The reactor was fixed in the constant-temperature shaker and connected to the gas collecting and water drainage devices. The anaerobic digestion time was 65 d. Biogas production was recorded daily during the experiment, and the methane content was tested every 2 d to evaluate the pretreatment effects. The experiments for different pretreatment were repeated three times.

Analytical methods

The untreated and ammonia-pretreated corn stover samples were analyzed for their total solids (TS) and volatile solids (VS) contents according to APHA standard methods (American Public Health Association 1998). The total carbon (TC) and total nitrogen (TN) contents were determined with a TC analyzer (PrimacsSLC; Netherlands) and a Kjeldahl total nitrogen analyzer (FOSS SCINO KT260; Shanghai, China). The cellulose, hemicelluloses, and lignin contents were determined according to the procedure described by van Soest *et al*. (1991). A Hitachi S-4700 (Hitachi, Ltd. Tokyo, Japan) scanning electronic microscope was used to observe the surfaces of the untreated and 4%-ammonia-pretreated corn stover. The surface of corn stover sample was gold-plated prior to observation. The scanning electron microscope (SEM) (JEOL, JSM-6360A, Japan) was used to examine the morphology of both the raw biomass and ash particles. Fourier transform infrared (FTIR) spectra were obtained using an FTIR spectrophotometer (Nicolet 6700) using a KBr disk containing 1% finely ground samples. A total of 30 scans were taken with a resolution of 4 cm^{-1}.

RESULTS AND DISCUSSION

Determination of Pretreatment Time

Pretreatment time is an important factor (van Soest *et al*. 1991), as it affects the efficiency of actual production. Thus, it was necessary to determine the requisite pretreatment time in advance. The changes in pH with different pretreatments of corn stover with 2, 4, and 6% ammonia contents showed the same trend. Therefore, only the pH change trend for 4% ammonia is presented in Fig. 1 in order to make it clearer.

In the beginning (day 0), the pH values for four moistures were in the range of 9.6 to 10.1. Afterwards, all pH values started to decline and reached stable stage on day 4. However, during the initial period the pH values declined by varying degrees, depending on the moisture content.

The pH value at 90% moisture content decreased more rapidly than others and decreased to 8.2 on day 4, while the pH values for 30, 50, and 70% moistures reached 8.7, 8.9, and 8.8 on day 4, respectively. This finding indicated that more moisture seems to help facilitate pretreatment process. Though the pH values actually stabilized within 4 d in each case, 5 d pretreatment time was used for later experiments in order to be sure that the time was more than sufficient.

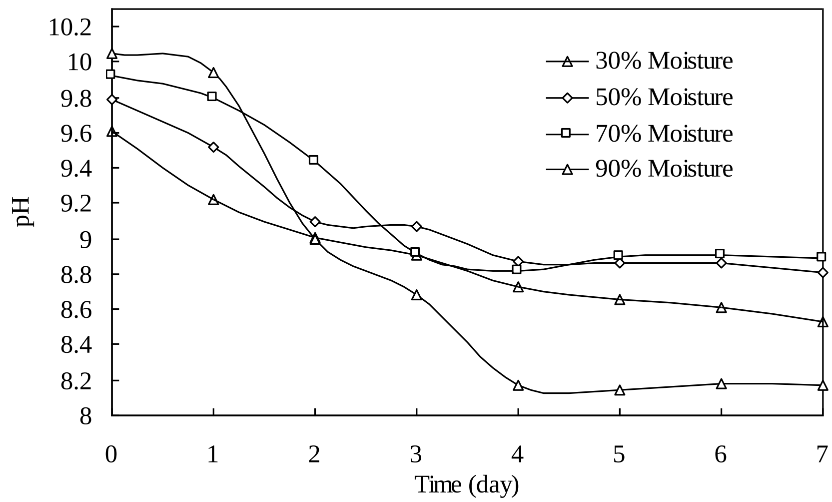


Fig. 1. Changes in pH during ammoniation of corn stover with 4% ammonia

Daily Biogas Production

Among the various ammonia treatments, similar trends with Zheng *et al*. (2009) in the daily biogas production were observed. The daily biogas production exhibited 3 to 4 peaks (Fig. 2) during the digestion process. The first peak occurred between days 1 and 4. At 30% moisture content, the daily biogas production peaked at 660 mL, which is higher than the peak value of the untreated corn stover. Afterward, the daily biogas production dropped rapidly to below 100 mL. System acidification was observed, as the pH decreased to 5.4 to 5.9. The pH was then readjusted to around 7.5 with $Ca(OH)_2$. However, changes were not significant at moisture contents of 70 and 90%.

The second biogas production peak at moisture contents of 70 to 90% and 30 to 50% occurred between the 11th and 13th days and the 19th and 23rd days, respectively. This was 15 to 17 d and 8 to 10 d earlier, respectively, than that of the untreated corn stover. The second peak in daily biogas production from the corn stover pretreated with 6% ammonia at 30% moisture content was the highest, at 1300 mL, 32.65% higher than that of the untreated corn stover.

For 70 % and 90 % moisture content, besides the early second peak, the third and fourth peaks also appeared 5 to 18 d earlier than those of 30% and 50% moisture contents and the untreatment ones. The daily biogas production of the third peak ranged from 680 ml to 840 ml, which were lower than that of the second peak. The above results showed that increasing moisture content can not only make the peaks appear early but also increase daily biogas production.

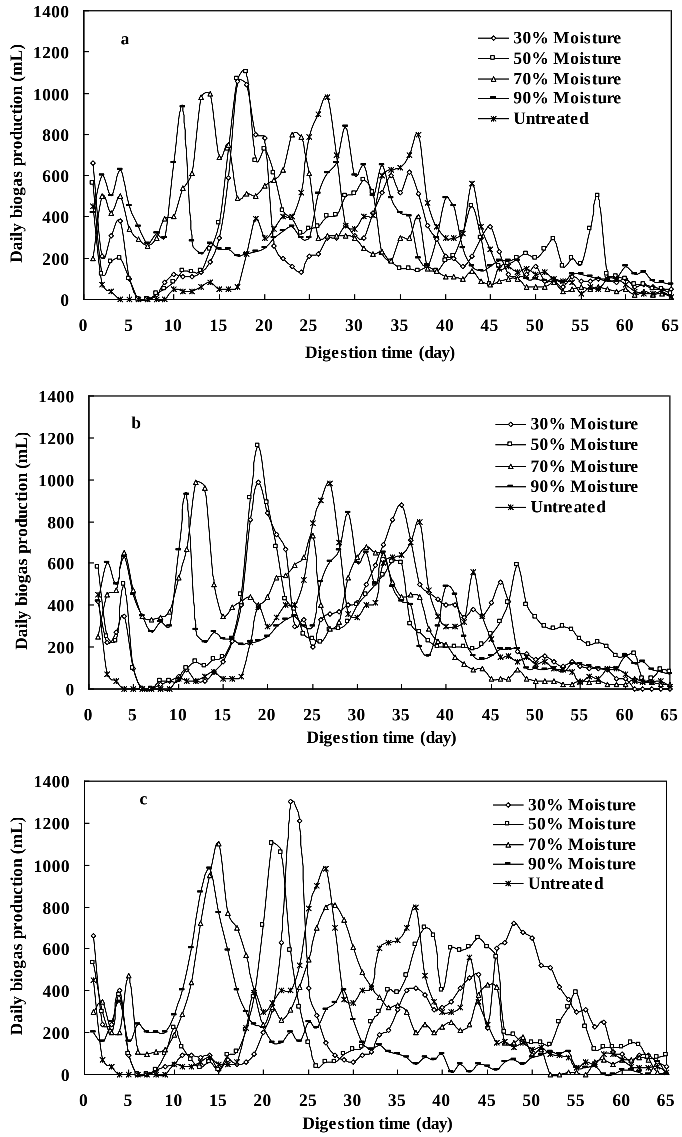


Fig. 2. Daily biogas production from corn stover pretreated with (a) 2, (b) 4, and (c) 6% ammonia

Biogas Yield of VS

The biogas yield per gram of VS is an important parameter for measuring the biodegradable properties of corn stover during the anaerobic digestion process. It can adequately represent the effectiveness of the pretreatment of corn stover. As shown in Fig. 3, the biogas yield per gram of VS of corn stover was significantly different ($p < 0.05$) with increasing pretreatment moisture content under various ammonia changes (2, 4, and 6%). The biogas yield per gram of VS of corn stover was 348.85 to 391.89 mL/g, 399.30 to 427.10 mL/g, and 249.33 to 413.71 mL/g at these ammonia charges, respectively. The biogas yield per unit of VS with various ammonia contents at 70% moisture content was the highest at 427.10 mL/g, 26.69% higher than that of the untreated stover and 9% more than that found in the research of Zhang and Zhang (1999) (17.5%).

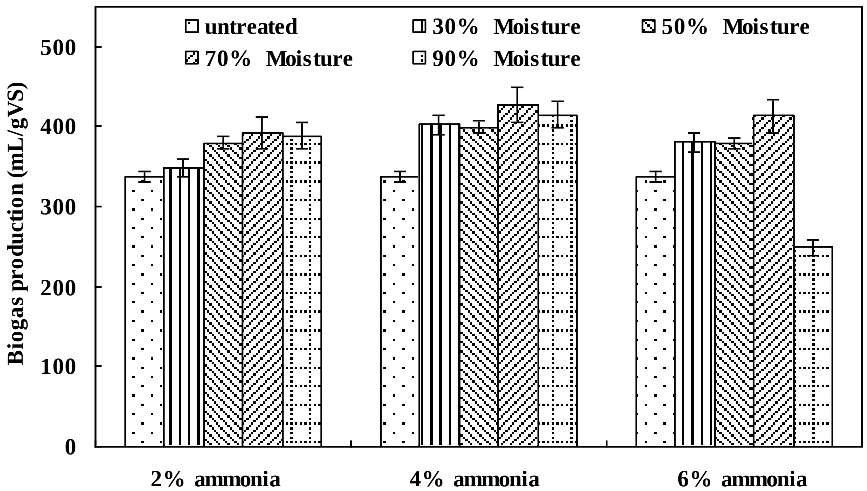


Fig. 3. Comparison of biogas yield per gram of VS with different corn stover pretreatments

Changes in the Physical Structure

The corn stover's color gradually darkened with increasing pretreatment moisture content. With 4% ammonia charge, the untreated corn stover was a white color, whereas that pretreated at 30% moisture content appeared yellowish in color. The color changed from white to brown-yellow at 70% pretreatment moisture content because of the combined effects of water infiltration and ammoniation. The corn stover exhibited no superfluous water leaching at 30 to 70% moisture content, whereas a large quantity of water was leached when the moisture content was increased to 90%. The corn stover pretreated at 70 to 90% moisture content had an acidic smell after the bag was opened, indicating that ammonia had a chemical reaction with the corn stover.

Scanning electron microscopy is effective for observing changes in the physical structure of substances (Xu *et al*. 2007b). Figure 4 shows scanning electron micrographs of untreated and ammonia-pretreated corn stover, highlighting the major changes in the corn stover's physical structure before and after pretreatment. The surface of untreated corn stover was more complete and smooth, the lignocellulose structure was aligned, and the structure was tight and without damage (Fig. 4a). The lignocellulose structure of different ammonia-pretreated corn stover was clearly fractured, and the internal structure was exposed.

The complete, smooth surface was destroyed with pretreatment with 4% ammonia at 30% moisture content, and some loose parts of the structure were dissolved and detached (Fig. 4b). The surface of the pretreated corn stover was more seriously damaged by pretreatment with 4% ammonia at 70% moisture, and obvious structural exfoliation appeared (Fig. 4c). In addition, with increasing moisture content, the loose surface structure was dissolved and exfoliated and the cellulose and hemicelluloses were exposed. The anaerobic microorganism could thus make contact with more cellulose and hemicelluloses, enhancing the anaerobic digestion ability of the corn stover. This is why the highest biogas yield per gram of VS was achieved *via* pretreatment at 70% moisture content with 4% ammonia.

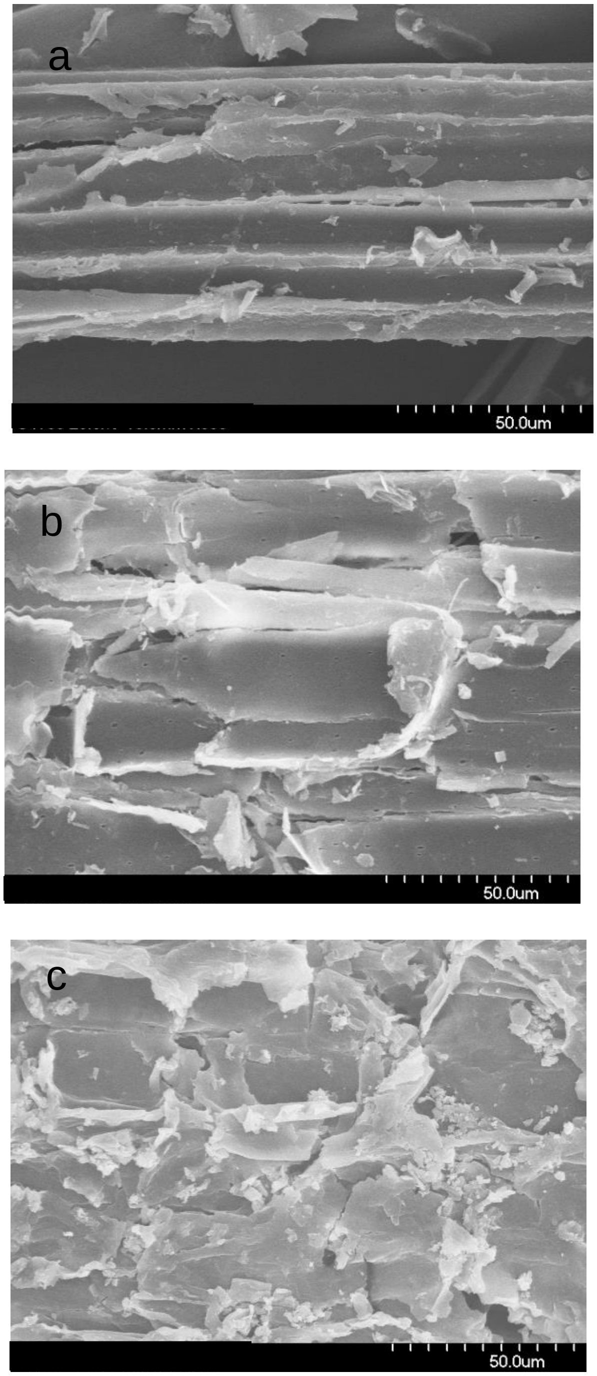


Fig. 4. Scanning electron micrographs of corn stover; (a) untreated, (b) 4% ammonia at 30% moisture, and (c) 4% ammonia at 70% moisture

Changes in Compositions

The contents of the main ingredients of lignocellulose were compared before and after ammonia pretreatment and after anaerobic digestion. Table 2 shows that cellulose and hemicelluloses were the main components of the corn stover, acting as the main carbon sources for the growth of the anaerobic microorganism. In the untreated corn stover, the total content of cellulose and hemicelluloses was 67.8%, of which the cellulose content was higher, accounting for about 38.8%.

Table 2. Changes in Composition after Ammonia Pretreatment and after Anaerobic Digestion (%DM, except Lignin/Cellulose Ratio)[a]

Pretreated Condition		After Ammonia Pretreatment					After Anaerobic Digestion		
Ammonia Content	Moisture Content	Cellulose	Hemi-Cellulose	Lignin	LCH	L/C	Cellulose Conversion Rate	Hemi-cellulose Conversion Rate	Lignin Conversion Rate
2	30	38.60±0.34	28.01±0.72	6.60±0.31	73.21±0.68	0.171	63.73±1.40	58.21±2.08	25.42±0.70
	50	36.92±0.07	27.41±0.19	6.55±0.11	70.88±0.23	0.177	68.54±2.46	63.51±2.48	17.21±3.60
	70	34.99±0.34	27.22±0.74	6.27±0.29	67.48±0.11	0.179	73.99±1.45	67.97±0.96	22.81±4.35
	90	32.99±0.26	26.72±0.26	5.57±0.33	65.28±0.85	0.169	76.56±3.37	67.32±1.10	18.36±2.04
4	30	37.51±0.41	27.68±0.94	6.47±0.13	71.66±0.40	0.173	70.10±1.43	61.94±3.03	14.53±2.54
	50	36.09±0.61	25.61±0.30	6.46±0.28	67.16±0.63	0.179	75.94±1.71	62.85±3.72	14.71±0.67
	70	34.67±1.67	24.81±0.20	5.88±1.39	62.39±0.47	0.170	80.60±1.05	68.52±0.25	16.32±0.84
	90	32.01±0.77	22.92±0.16	5.71±0.29	60.64±0.64	0.178	74.59±1.79	64.97±1.18	17.80±1.00
6	30	36.29±0.09	21.08±0.23	5.42±0.07	62.79±0.40	0.149	70.70±1.64	64.60±3.32	9.70±2.90
	50	35.47±0.23	20.72±0.35	5.45±0.21	61.64±0.37	0.154	74.90±0.13	65.25±1.25	12.68±1.67
	70	32.65±2.03	20.49±0.09	5.04±1.19	58.18±0.22	0.154	75.25±1.97	65.15±1.10	10.73±0.08
	90	32.80±2.83	20.91±0.60	5.73±1.04	59.44±1.39	0.175	52.10±0.39	58.76±1.51	18.34±1.23
Untreated		38.80±0.75	29.00±0.57	7.12±0.63	74.92±0.97	0.184	62.10±0.02	54.38±1.04	16.42±0.28

[a] Values are the means ± standard deviation (n≥3)

In comparison, the lignin content was low, about 7.1%. After ammonia pretreatment, the hemicellulose content in the corn stover was lowered from the original 29.0% to 20.5%, decreasing by 29.3%. The lignin content was also reduced to some extent compared to that of the untreated corn stover ($p>0.05$), indicating that lignin was partially removed by the ammonia pretreatment, releasing cellulose and hemicellulose and increasing the accessibility of the microorganism to the two. Compared with untreated corn stover, the total lignocellulose content decreased by 2.3% to 22.3% following pretreatment. Scharer and Moo-Young (1979) pointed out that the substrate biodegradability can be evaluated by the ratio of lignin-to-cellulose (L/C); the L/C ratio (Table 2) after ammonia pretreatment was less than that of the untreated corn stover ($p>0.05$). During ammonia pretreatment, lignin removal releases hemicelluloses and cellulose from the substrate, bringing anaerobes into contact with more digestible material and improving the anaerobic digestion performance of the corn stover.

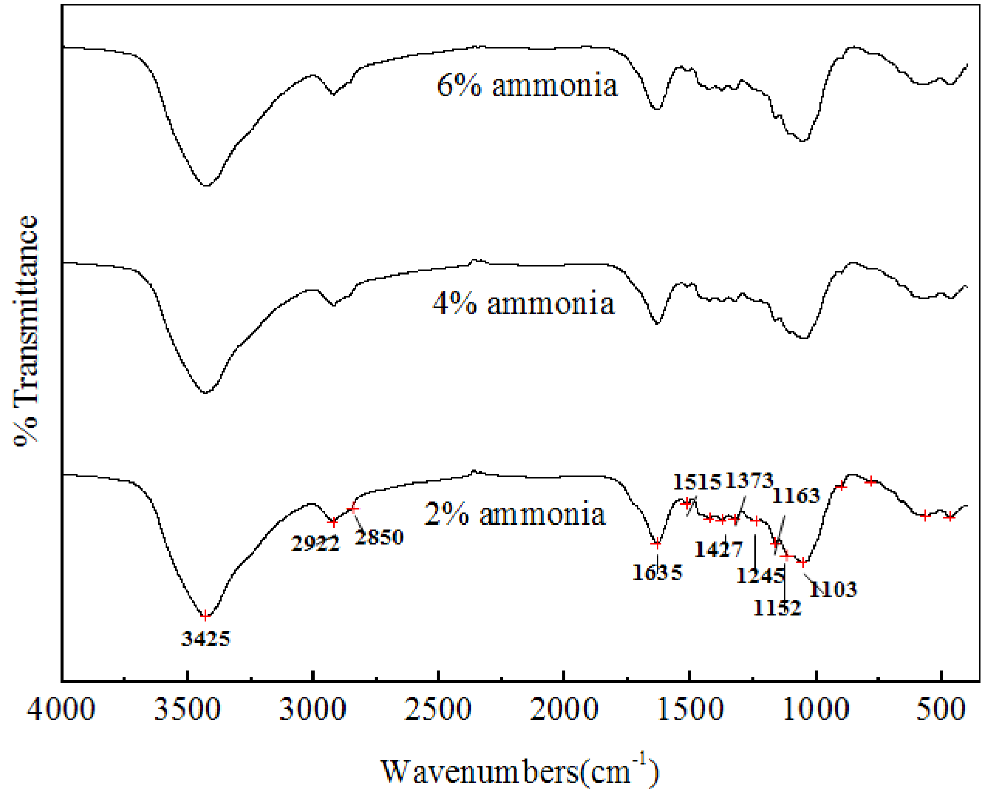
The conversion rates of cellulose, hemicelluloses, and lignin under different ammonia pretreatment conditions were 52.1% to 80.6%, 54.38 to 68.52%, and 9.7% to 25.42%, respectively. When the ammonia content was 4% and the moisture content was 70%, the conversion rates of cellulose and hemicellulose were the greatest ($p<0.05$), at 80.60% and 68.52%, higher than those of the untreated corn stover by 29.79% and 26% ($p<0.05$), respectively. This explains why the corn stover yielded the highest biogas yield per gram of VS under pretreatment at 70% moisture content with 4% ammonia.

Changes in Chemical Structure

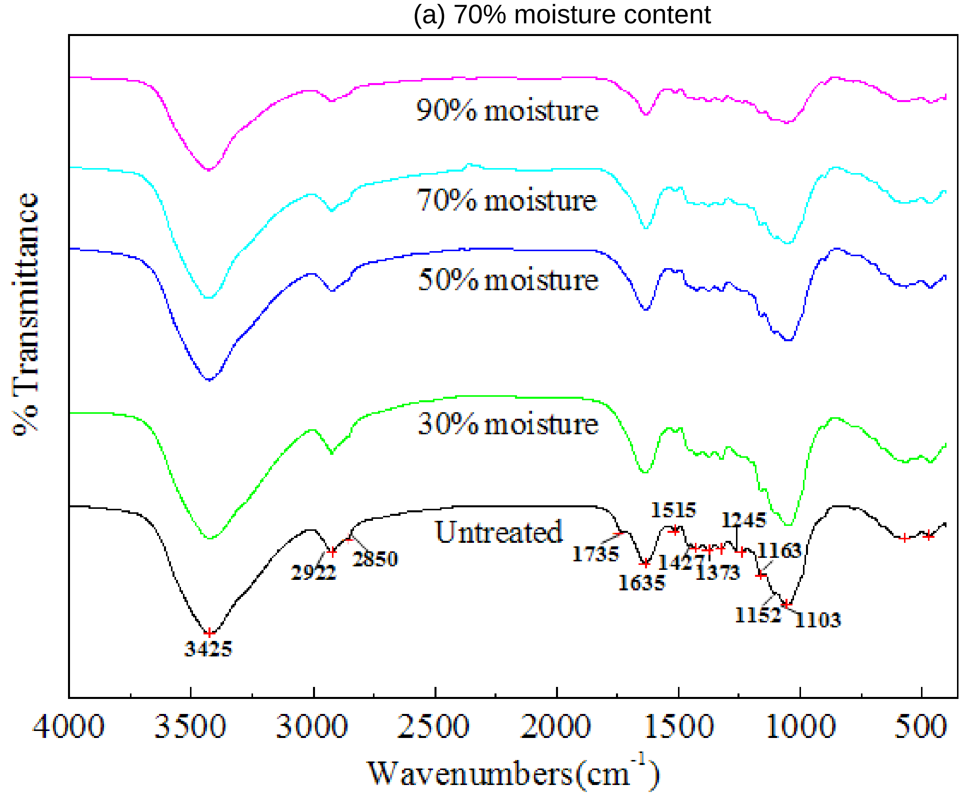
After ammonia pretreatment, corn stover's main constituents were degraded to a certain degree, and NH^{4+} and OH^{-} ionized from ammonia facilitated chemical reactions with lignocellulose, changing its chemical structure. The anaerobic digestion process further digested and decomposed the organic substances in the system. The structural organic changes were analyzed to better understand the effects of ammonia pretreatment on the functional groups and main organic compounds of the corn stover. Fourier transform infrared spectroscopy (FTIR) was used to analyze the change in the lignocellulose structure. The specific FTIR spectra frequencies of functional groups and chemical bonds in lignocellulose are known, so the structural changes can qualitatively and quantitatively be analyzed by comparing the changes in absorption intensities (Fig. 5).

After ammonia pretreatment, the absorption intensities of some characteristic peaks of the corn stover were weakened or strengthened, and some characteristic peaks disappeared completely, indicating that the chemical structure of the corn stover was changed. The corn stover was composed of cellulose, hemicelluloses, lignin, protein, starch, sugar, and wax ester compounds. According to the spectral features before and after ammonia pretreatment, the chemical structure changes during anaerobic digestion of the ammonia-pretreated corn stover were inferred.

The most distinguishing feature of the FTIR spectra of the ammonia-pretreated corn stover was that the absorption peak at 1735 cm^{-1}, representing non-conjugated hydroxyl C=O stretching vibration, disappeared. This functional group represented the ester bond between lignin and hemicellulose or the cutin of the epidermal wax layer, indicating that this bond or the wax epidermal layer in the ammonia-pretreated corn stover was destroyed. Because the ester bond was very sensitive to alkali, it was easy to rupture, even at low moisture and ammonia contents.



(a) 70% moisture content



(b) 4% ammonia

Fig. 5. FTIR spectra of different ammonia-pretreated corn stovers

The absorption peak representing C-O stretching vibration in lignocellulose (1163 cm^{-1}) also declined in intensity, indicating that some ether bonds in the lignocelluloses were also ruptured. In the corn stover's cell wall, ferulic acid is connected with hemicellulose *via* the ester bond and connected with lignin *via* the ether bond to formulate a hemicellulose-ester-ether-lignin cross-bridged structure (Xu *et al*. 2005) (Fig. 6). The rupture of these two functional groups (the ester and ether bonds) indicated that the ammonia pretreatment produced the same alkaline pretreatment effect. After ammonia pretreatment, acetic acid and phenolic substances were released and hemicellulose was converted into easily biodegradable ingredients such as free carboxyl groups, thereby improving the corn stover's biodegradability (Hendriks and Zeeman 2009).

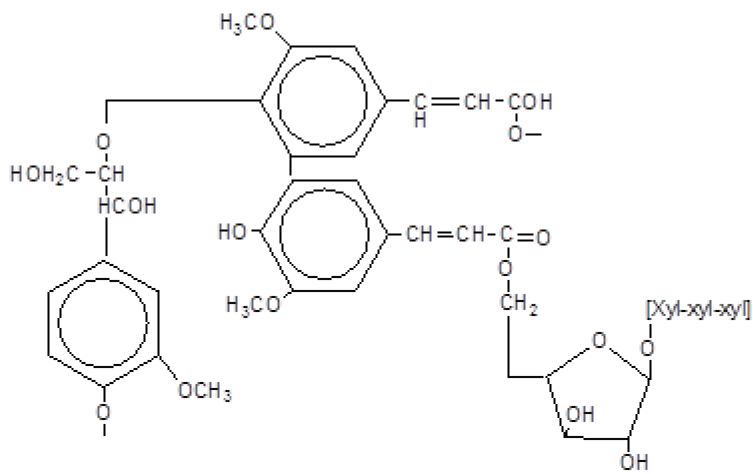


Fig. 6. Connection between hemicellulose and lignin in corn stover

The hemicellulose content significantly decreased following pretreatment, and the cellulose was also degraded. Figure 5 shows that after pretreatment, the absorption peak intensity significantly decreased at 3425 and 2922 cm^{-1}, indicating that carbohydrates in the ammonia-pretreated corn stover were gradually decomposed, leading to a constant decrease in the amounts of hydroxyl and methylene groups. The absorption peak intensity at 2850 cm^{-1}, representing symmetric methoxyl contraction vibration, and that at 1373 cm^{-1}, representing the stretching vibration of $-CH_3$ in aliphatic compounds, significantly decreased. With increasing ammonia and moisture contents, the absorption peak intensity decreased more significantly. The absorption intensity at 1373 cm^{-1} of the corn stover pretreated with 4% ammonia at 70% changed significantly, indicating that the methyl and methylene group contents in the corn stover were gradually reduced. During pretreatment, hemicelluloses and cellulose were both lost to a certain extent and aliphatic compounds were degraded somewhat, with simultaneous demethylation. At 1163 and 1245 cm^{-1}, the absorption peak intensities after ammonia pretreatment decreased significantly, indicating that cellulose, hemicelluloses, saccharides, and carbohydrates in the ammonia-pretreated corn stover were decomposed. The intensity of such absorption peaks decreased significantly with increasing moisture and ammonia contents, indicating that the carbohydrates, aliphatic compounds, and saccharides were completely degraded. This was consistent with the change in the chemical constituent contents in the ammonia-pretreated corn stover previously discussed.

The absorption peak intensity at 1204 cm^{-1}, representing polysaccharide characteristics, decreased after ammonia pretreatment, indicating that polysaccharides were also degraded by ammonia pretreatment. Hendriks and Zeeman (2009) pointed out that alkaline pretreatment could swell the straw's cell wall, increasing anaerobes' accessibility to the cell wall. When the pretreatment was very alkaline, terminal tissues were exfoliated, alkaline hydrolysis and degradation occurred, and soluble polysaccharides were degraded. The degradation of polysaccharide was caused mostly by the exfoliation and hydrolysis of the cell wall.

The absorption peaks at 1600, 1513, and 1424 cm^{-1}, representing the characteristic stretching vibration of the benzene ring skeleton, and that at 1460 cm^{-1}, representing carbohydrates and aliphatic compounds, both exhibited significant changes (Xu *et al*. 2007a). The peaks at 1324 and 1109 cm^{-1} represented typical guaiacyl and syringyl groups (Chi 2005). The strong absorption peak from 1200 to 890 cm^{-1} was the characteristic absorption of polysaccharides in the corn stover (Sun *et al*. 1995). The peak at 898 cm^{-1} was ascribed to ring vibrations of cellulose and saccharides such as β-glucan, galactose, mannose, arabinose, and polysaccharides (Chi 2005).

Carbohydrates, aliphatic compounds, and some polysaccharides in the ammonia-pretreated corn stover were all degraded to a certain degree, and the ester and ether bonds connecting the lignocellulose were ruptured, releasing cellulose and hemicelluloses. Carbonyl, methyl, and methylene groups between benzene rings were partially degraded. These structural changes released more carbohydrates and increased the accessibility of subsequent anaerobes. After ammonia pretreatment, the reaction between ammonia and lignocellulose formed ammonium salt and provided a nitrogen source for subsequent microbes, thereby improving the anaerobic digestion performance of the corn stover.

CONCLUSIONS

1. Ammonia pretreatment could improve biogas production during the anaerobic digestion of corn stover. The optimal performance was achieved with 4% ammonia at 70% moisture content. The highest biogas yield was 427.1 mL/gVS, 26.7% higher than that of the untreated stover.
2. After ammoniation pretreatment, the conversion rates of cellulose, hemicelluloses, and lignin were increased for all the pretreatment conditions. At the optimal condition, the conversion rates of cellulose and hemicellulose reached 80.6% and 68.5%, which was about 30% and 26% higher than those of the untreated corn stover, respectively, indicating improved biodegradability after pretreatment.
3. Ammonia pretreatment could break chemical bonds such as the ester and ether bonds in the lignocellulose, partially degrade aliphatic compounds and carbohydrates. The breakage of such chemical bonds and the degradation of chemical compositions could facilitate the access of anaerobic microorganisms to the corn stover substance, therefore improving the biodegradability and anaerobic digestion performance of corn stover.

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