Enhanced anaerobic digestion of corn stover by thermo-chemical pretreatment

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Abstract: In order to solve the problem of lignocellulose degraded speedily and efficiently in anaerobic digestion, the thermo-chemical pretreatment was applied to enhance biogas production from corn stover. Corn stover was thermo-chemical pretreated with a fluidized bed pyrolysis reactor at 180℃, 200℃ and 220℃, respectively. Lignin degradations during pretreatment were 15.07%, 32.57% and 33.31%, respectively. The Scanning Electron Microscope (SEM) images and (Fourier Transform Infrared Spectroscopy (FTIR) spectra confirm that the thermo-chemical pretreatment can change the structure of corn stover and make lignin content decrease. The thermo-chemical pretreated corn stover was digested using a 2-L fermentation reactor. Experimental results showed thermo-chemical pretreatment could improve biodegradability and enhance biogas production. The highest total biogas production was 23 319 mL for 20 d which was 10.0% higher than that of the untreated corn stover.

Keywords: biogas production, corn stover, anaerobic digestion, fast pyrolysis, thermo-chemical, pretreatment
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1 Introduction

Lignocelluloses materials, such as agricultural wastes and agro-industrial by-products, have a complicated structure, which consist of carbohydrates such as lignin, cellulose and hemicellulose, pectin, proteins, salt and minerals[1]. Nowadays, there is a great interest in re-using lignocellulosic materials for renewable energy production, both from economical and environmental viewpoints. Among several renewable resources, biogas produced from anaerobic digestion remains a promising alternative for renewable energy.

Cellulose, hemicellulose and lignin are the three main components of lignocellulosic biomass. The cellulose and hemicellulose are largely protected from attack by cellulolytic enzymes. The inaccessibility to attack is mainly owing to the association of these polysaccharides with lignin and with each other, all of which act as a barrier shielding the polysaccharides[1,2]. Due to its resistance to enzymatic attack, cellulosic biomass must be pretreated before it can be enzymatically hydrolyzed.

A number of pretreatment methods have been reported, which mainly include mechanical pretreatment, thermal pretreatment, chemical pretreatment, biological pretreatment and some combinations[3]. Biswas et al.[4] evaluated the effects of steam explosion pretreatment on the elementary quality and ash properties of salix wood chips. They concluded that steam explosion could enhance carbon content and reduce oxygen amount in the

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pretreated materials which enhanced the heating value of it. A twin-screw extruder physical-chemical combination pretreatment was proposed by Cui et al.[5]. It was divided into twin-screw physical-chemical combination pretreatment group, unique twin-screw physical pretreatment group and unique chemical pretreatment group. Its results showed that the straw via physical-chemical combination pretreatment had the highest biogas yield and the transformation of the straw's form can meet the need of accessing and discharge for CSTR. Moreover, Zhong et al.[6] compared the chemical and biological pretreatment of corn stover for biogas production. They found both chemical and biological pretreatment can enhance biogas productivity of corn stover. And the highest biogas yield was obtained from corn stover treated by NaOH.

Overall, in these pretreatment methods, a variety of acids, alkaline, organic solvents, and oxidizing agents have been applied, which can cause several problems such as environment pollution, high cost and other technical difficulties[7]. Therefore, there is a need to develop sustainable, environmental and resource friendly technology to pretreat lignocellulosic biomass for valuable energy production. Thermo-chemical pretreatment represents a feasible solution to improve digestion efficiency and biogas production as it has shown several advantages, including no chemical required, mild conditions and environment-friendly. Additionally, previous research reported that the cellulose, hemicellulose and lignin of corn stover could be pyrolyzed in proper conditions. In general, lignin decomposition occurs within the wide temperature range of 160°C to 900°C[8]. While, the thermal stability of cellulose is stronger than lignin[9]. Therefore, the objective of this study was to investigate the effects of thermo-chemical pretreatment on the biogas production from corn stover via anaerobic digestion as well as the physicochemical structure change of the corn stover. Corn stover was thermo-chemical pretreated by a pyrolysis reactor and then subjected to the anaerobic digestion process. Lignin, cellulose, and hemicelluloses degradation of corn stover during the thermo-chemical pretreatment was studied. The structure change of corn stover during pretreatment was also investigated.

2 Materials and method

2.1 Feedstock and inoculum

Corn stover was collected from Zibo district of Shandong Province, China, and the moisture content was less than 10% after being air-dried. The dried corn stover was then pulverized to particles with the particle size less than 3 mm.

The dry anaerobic fermentation solid for anaerobic digestion was obtained from a laboratory at Shandong University of Technology and used as inoculum. The inoculum was put into fermentation reactor after being enriched with the enrichment medium[10] for seven days. The total solid (TS) of inoculum was 12.38%.

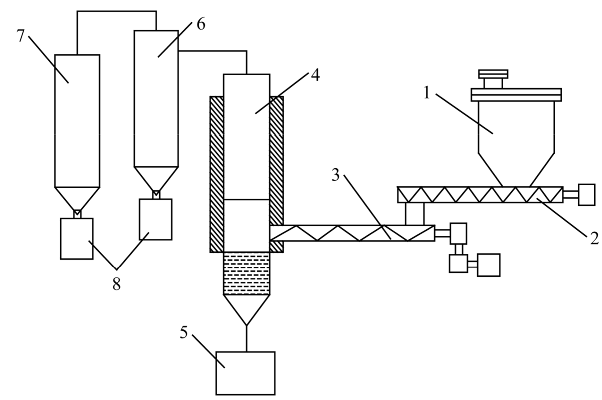
The characteristics of corn stover and fermentation solid are presented in Table 1.

Table 1 Characteristics of corn stover and fermentation solid

	Corn stover (Standard deviation)	Fermentation solid (Standard deviation)
Total carbon/% (wet basis)	40.16 ±0.550	9.17±0.354
Total nitrogen/% (wet basis)	0.79 ±0.012	0.68 ±0.017
Total solid/%	91.24 ±0.009	22.47 ±0.006
Volatile solid/%	73.93±0.047	15.24 ±0.007

2.2 Thermo-chemical pretreatment procedure

A fluidized bed pyrolysis reactor was used for thermo-chemical pretreatment of corn stover at 180°C, 200°C and 220°C, respectively. The schematic of the fluidized bed reactor is shown in Figure 1. The reactor was usually performed at atmospheric pressure, a short gas residence time (about 1 s) and a relatively high efficiency of heat transferring with low oxygen burnable gas as heat carrier gas.



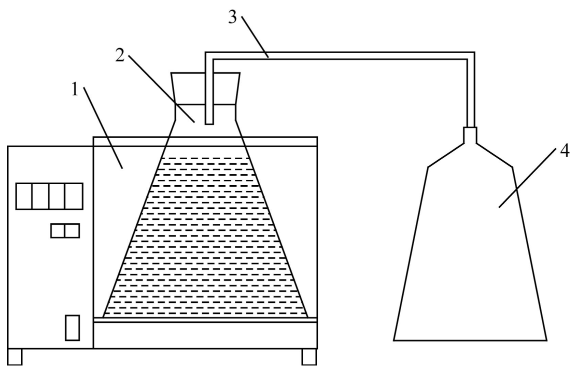
1. Feedbox 2. First screw feeder 3. Second screw feeder 4. Fluidized bed reactor 5. Preheating arrangement 6. First cyclone separator 7. Second cyclone separator 8. Collecting box

Figure 1 Schematic of fluidized bed reactor

Approximately 3-5 kg of ground corn stover particles were put into the feedbox. Then the corn stover particles were fed into the fluidized-bed reactor via two speed adjustable screw feeders. Quartz sands were used as bed material. Before the experiment start, the screw feeders and reactor were heated up by preheating arrangement. The temperature in the reactor was measured by thermocouples and controlled by a control device. After corn stover particles were pyrolyzed in the reactor, the pyrolyzed particles were blown into cyclone separators. Materials with larger particle size were collected in the first cyclone separator and the materials with smaller particle size were collected in the second cyclone separator, respectively. After the experiment, the pretreated corn stover particles were collected in sealed bags for componential and the structural analysis before the anaerobic digestion experiments.

2.3 Anaerobic digestion experiment

The untreated and thermo-chemical pretreated corn stovers were digested in a 2-L digester shown in Figure 2. The installation mainly consisted of a constant temperature vessel, 2-L conical flasks worked as digesters and biogas collecting bags.



1. Constant temperature vessel 2. Digester 3. Tracheal tube 4. Biogas collecting bag

Figure 2 Experimental setup of anaerobic digestion

The anaerobic digestion worked as liquid state fermentation at a TS content of 8.5%. The content of inoculum was 30% in the digester, and the organic loading rates of fermentation liquid was 65 g/L[11]. The C/N ratio was adjusted to 25:1 with ammonium bicarbonate solution and the pH value was adjusted to around 7.0 with dilute sodium hydroxide solution and dilute sulfuric acid[12]. The digestion tests were conducted in triplicate and performed at 35°C for 20 d. Biogas was collected daily with 3 L gas bags throughout the digestion process for gas composition and production analysis.

2.4 Analytical methods

2.4.1 Cellulose, hemicellulose and lignin analysis

The cellulose, hemicellulose, and lignin contents of the untreated and thermo-chemical treated corn stover samples were determined by an extraction unit (FIWE6, VELP Co., Italy), following the laboratory analytic procedure developed by Van Soest et al.[13].

2.4.2 Physicochemical structure analysis

A Sirion 200 (Holland) scanning electron microscopy (SEM) was used to examine the physical structure change of corn stover before and after pretreatment. The SEM was operated at acceleration voltage between 0.2-30 kV with a resolution of 1.5 nm. Before observation, the samples were coated with carbon using a vacuum sputter-coater to improve the conductivity of the samples and the quality of the SEM images[2].

The functional groups present in the untreated and thermo-chemical treated corn stover were also investigated by Fourier transform infrared spectroscopy (FTIR) using a Nicolet 5DXC FTIR spectrophotometer with a KBr disk containing 5% finely ground samples. The spectra were recorded between 4 000 cm^{-1} and 400 cm^{-1} with a resolution of 0.01 cm^{-1}.

2.4.3 Biogas analyses

The volume of biogas was measured by wet gas meter (LMF-1) and the composition of biogas was measured by BIOGAS Check (Geotechnical Instrument).

2.4.4 Data analyses

All the thermo-chemical pretreatment and digestion tests were conducted in triplicate and the average values were reported. The standard deviations and statistical differences were analyzed by using statistical software SPSS 13.0 for Windows.

3 Results and discussion

3.1 Degradation of corn stover during pretreatment

Thermo-chemical pretreated corn stover at three different temperatures all caused significant degradation of corn stover (Table 2). A preliminary judgment was made by reductions of lignin[14], which were 15.07%, 32.57% and 33.31%, respectively. However, the contents of cellulose and hemicellulose also relatively decreased with destruction of the lignocellulose. The results showed that the thermo-chemical pretreatment could break down protection of lignin in corn stover. Because the softening temperature of dry lignin is between 127°C and 129°C, and the temperature even higher when the molecular mass of lignin is larger[15]. As the temperature continues to rise, lignin can change to phenolic compounds. Xylans, one of dominant components of hemicellulose, are thermally the least stable[3], which lead to the decrease of hemicellulose after pretreated. And when cellulose was heated (200-280°C)[15], it would be dehydrated cellulose that could result in cellulose decreasing also. Based on the destruction of each ingredients of corn stover, 200°C was a proper temperature for the chemical pretreatment.

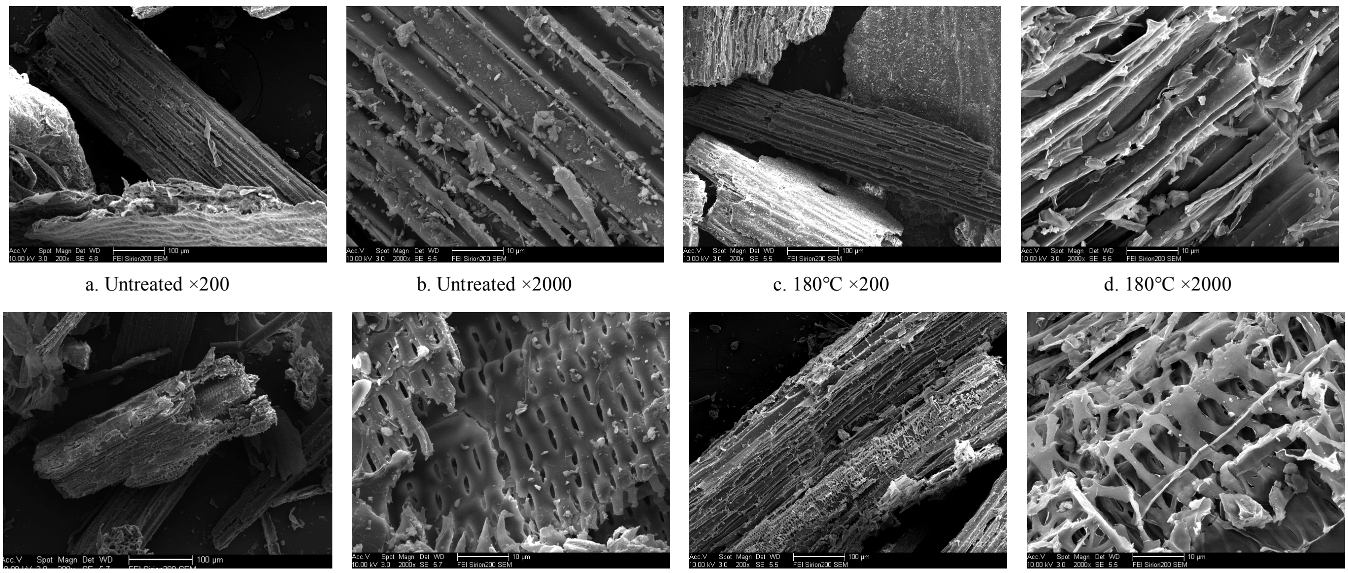
Table 2 Composition changes of corn stover after thermo-chemical pretreatment

Treatment	Cellulose (standard deviation)/%	Reduction /%	Hemicellulose (standard deviation)/%	Reduction/%	Lignin (standard deviation)/%	Reduction /%
Untreated	34.31(±0.28)		26.68(±0.25)		15.94(±0.65)	
180°C	28.67(±0.70)	16.43	24.23(±0.92)	9.20	13.54(±0.75)	15.07
200°C	28.58(±0.70)	16.70	23.73(±0.54)	11.86	10.75(±0.57)	32.57
220°C	25.28(±0.59)	26.32	22.95(±0.80)	13.98	10.63(±0.32)	33.31

3.2 Structure change during pretreatment

3.2.1 SEM

The SEM (scanning electron microscopy) images of untreated and treated corn stover under different magnifications were shown in Figure 3. The SEM images of the treated samples in different temperatures (Figure 3 c-h) indicate that the micro-fibrils are separated from the initial connected structure which became loose and disordered after the treatment, and with the temperature increasing, the structure of corn stover became more severely disordered. In consequence the porosity and external surface area of the corn stover were significantly increased, which certainly increased the accessibility of enzymes to the biomass.



a. Untreated ×200 b. Untreated ×2000 c. 180°C ×200 d. 180°C ×2000

e. 200°C ×200 f. 200°C ×2000 g. 220°C ×200 h. 220°C ×2000

Figure 3 SEM images of untreated and thermo-chemical treated corn stover

3.2.2 FTIR analysis

Figure 4 shows the FTIR spectra of untreated and pretreated corn stover. The chemical groups that correspond to the observed peaks in the IR spectrum were identified according to the literatures[16-18] in Table 3.

The characteristic bands at 1 499 cm^{-1} all disappeared in the three pretreated corn stover spectra, indicating the reduction of aromatic ring skeleton in the lignin. Moreover, it was also found that the intensity of the band at 1 514 cm^{-1} (aromatic ring) and 1 424-1 426 cm^{-1} (C-H with aromatic skeleton) become weaker than the untreated corn stover. The above waves are all related to lignin in the corn stover. It can be concluded that the relative content of lignin was reduced in the thermo-chemical pretreatment corn stover. On the other hand, the characteristic bands at 873 cm^{-1} also disappeared in the three pretreated corn stover spectra. The bands at 1 156-1 163 cm^{-1} (C-O-C vibration in cellulose and hemicellulose) and 897 cm^{-1} (C-H deformation in cellulose) in pretreated corn stover spectra had a weak reduction in relative intensity compared to the untreated, which indicated that, the relative content of cellulose and semi-cellulose also decreased after pyrolyzed. As the temperature increased, the decrement of cellulose and hemicellulose was big.

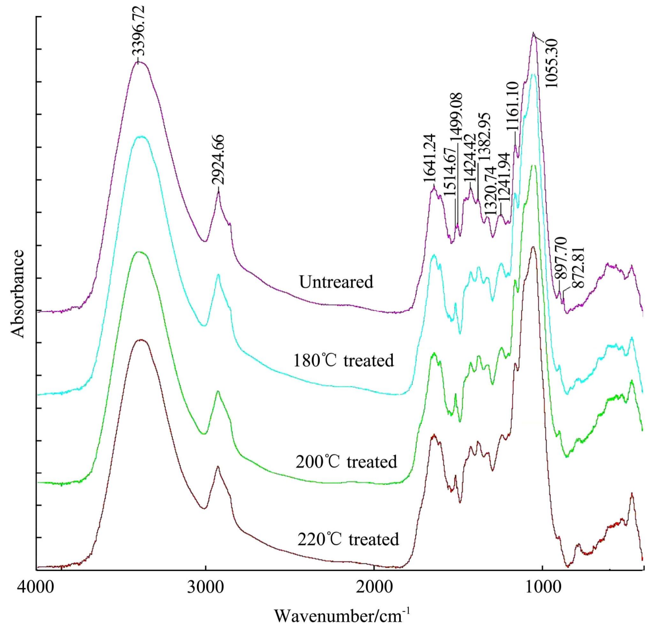


Figure 4 FTIR spectra of treated and untreated corn stover

Table 3 FTIR band assignments of corn stover

Wavenumber /cm^{-1}	Attribution of FTIR absorption
3395-3397	O-H stretching vibration
2924	C-H symmetrical and asymmetrical stretching in $-CH_3$ and $-CH_2$
1641	Lignin and aromatic ring conjugated C=O stretch
1499-1514	Lignin and other aromatic ring skeletal stretch
1424-1426	aromatic skeletal vibration and C-H in-plane bending vibration
1377-1383	$-CH_3$ asymmetrical vibration in aliphatic compound
1318-1324	C-H vibration in cellulose and C-O vibration in syringyl derivatives
1241	Methoxyl, C-C and C-O stretching vibration; C=O stretching vibration
1156-1163	C-O-C vibration in cellulose and hemicellulose
1054-1059	C-O stretch in cellulose and hemicellulose; Si-O stretch in amorphous SiO_2
873-901	C-H deformation in cellulose and saccharide

3.3 Anaerobic digestion

3.3.1 Biogas production

Figure 5 shows the daily changes of biogas production of pretreated and untreated corn stover, respectively. As shown in Figure 5, the daily biogas production of all pretreated corn stover was concentrated in the days 2-11 and declined gradually after 12 d. It can be observed that the daily biogas production of the pretreated corn stover was notably higher than that of the untreated samples in the first 10 d, except for the one pretreated at 220°C, indicating the biogas production was enhanced by thermo-chemical pretreatment at the beginning of the experiment. Twelve days later, the biogas productions of pretreated corn stover were all lower than the untreated for the lack of materials, because part of cellulose and hemicellulose was also pyrolyzed in pretreatment. A rapid initial biogas production was observed for the treated corn stover during the first 24 h of digestion. And the biogas production of the pretreated corn stover reached the peak values ahead of the untreated.There are two reasons: one is the thermo-chemical pretreatment broke down the structure of lignocelluloses, which made pretreated corn stover more easily accessible to hydrolytic; the other is the high temperature of thermo-chemical pretreatment could kill the majority of bacteria in corn stover, which helps the reproduction of methanogenic bacteria.

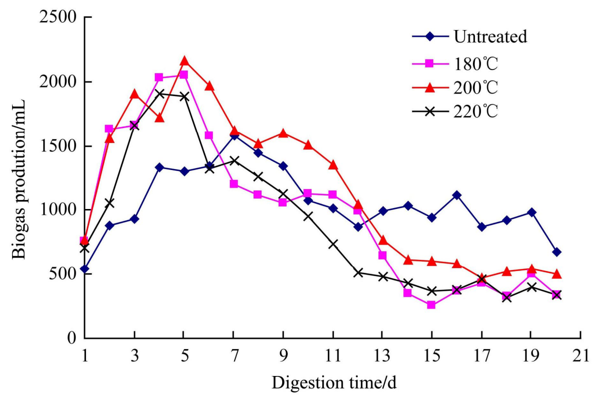


Figure 5 Daily biogas production of corn stover

The cumulative biogas yields of pretreated and untreated corn stover are presented in Figure 6. It was observed that the cumulative biogas yields of pretreated corn stover increased rapidly in the first 10 d, while the cumulative rate trended to be less than that of the untreated after 10 d. From the cumulative biogas yields, 200°C was the most suitable temperature for thermo-chemical pretreatment. The highest cumulative biogas yield for 20 d digestion was 23 319 mL, which was

10.0% higher than that of the untreated corn stover.

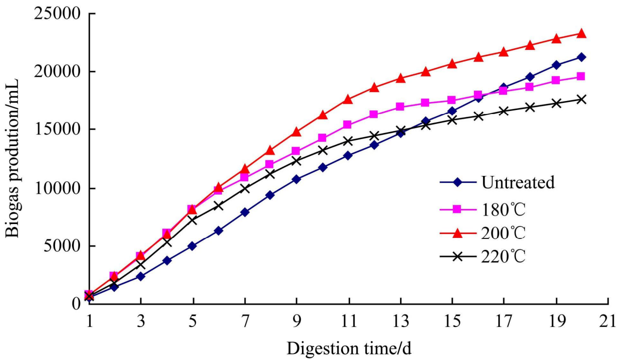


Figure 6 Temporal changes of cumulative biogas yields of corn stover

3.3.2 Biogas component analysis

The methane contents of biogas for 20 days digestion were presented in Figure 7. In the first three days, all of the pretreated and untreated corn stover generated a small amount of methane due to the air existed in the digester. The methane contents of pretreated corn stover were kept at a relatively higher level than that of the untreated corn stover in the first six days. From the 7th day, there were variations of methane content among pretreated and untreated samples, but they were not significantly different until the 12th day. However, after the 12th day, the methane contents of pretreated corn stover became slightly lower than that of the untreated corn stover, especially the corn stover pretreated by 220°C. The highest methane contents of the treated and untreated corn stover were 51.9%, 53.0%, 50.5% and 50.7%, respectively. The loss of cellulose and hemicelluloses during the pretreatment could contribute to the lower methane production at the end of fermentation as there were no inadequate raw materials for the subsequent digestion.

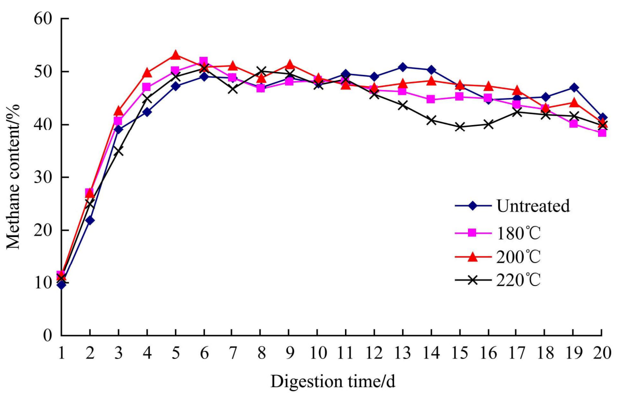


Figure 7 Methane contents of biogas during anaerobic digestion

4 Conclusions

Thermo-chemical pretreatment was proved to be effective in improving biodegradability and enhancing biogas production of corn stover. After thermo-chemical pretreatment, the contents of total lignin, cellulose, and hemicelluloses were reduced. Lignin has the highest reduction of 33.31% after the pretreatment. The SEM images indicated that structure of the corn stover was deformed and its fibers were exposed by the pretreatment. Meanwhile, the chemical structures were also changed. Further in-depth analysis indicates that the changes of chemical compositions and physicochemical structure were contributed to the improvement of biodegradability and the enhancement of biogas production.

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