Anaerobic biogasification of NaOH-treated corn stalk

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Abstract: NaOH pretreatment was employed in order to improve anaerobic biodegradability and biogas yield of corn stalk. Corn stalk was first treated for 30 days at ambient temperature by sodium hydroxide (NaOH), NaOH amount added was 8% of dry matter of corn stalk. The untreated and NaOH-treated corn stalks were then anaerobically digested at mesophilic temperature (35℃) in batch reactors. For each corn stalk, four loading rates of 35, 50, 65 and 80 g/L were used. The results showed that NaOH pretreatment could significantly improve the biodegradability of corn stalk and increase biogas yield. The total biogas yield of NaOH-treated corn stalk was increased by 13.1%, 39.8%, 48.3%, and 47.8% over the untreated one for the loading rates of 35, 50, 65 and 80 g/L, respectively. The loading rates of 35 and 65 g/L achieved the highest biogas yield per gram of TS (total solid) loaded, for untreated and NaOH-treated corn stalk respectively. The contents and dry matter of main compositions of the corn stalk were changed significantly through NaOH pretreatment, approximate 1/2～2/3 of lignin, cellulose, and hemicellulose decomposed were converted into readily biodegradable soluble compounds. The biogas yield per gram of TS and VS (volatile solid) loaded for NaOH-treated stalk were increased by 13.1%～48.3% and 23.0%～61.3%, respectively, as compared with the untreated one. The average biogas yield per gram of VS reduced was the same for both untreated and NaOH-treated corn stalk, but not for the average biogas yield per gram of TS reduced. The results provided useful information for large-scale anaerobic digestion of corn stalk for production of renewable bioenergy and reduction of pollution associated with corn stalk.

Key words: corn stalk; sodium hydroxide; loading rate; biogas; anaerobic digestion
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0 Introduction

China is one of the largest agricultural countries in the world with 0.7 billion tons of crop stalks being generated annually. Corn is one of major crops mainly planted in northern China, and approximate 0.1 billion tons of corn stalk is produced yearly. Although there are a few methods available for corn stalk disposal and reutilization such as animal feed, cooking and house heating, and paper-making, quite a large amount of corn stalk is still burnt in open field currently, causing serious problems such as air pollution, fire disaster, and adverse impact on air craft and traffic safety. Therefore, it is imperative to find environmentally friendly alternatives for corn stalk utilization and pollution reduction.

Corn stalk is one kind of organic materials, which could be converted to biogas using anaerobic digestion technology. Anaerobic digestion has been widely applied for organic waste conversion into biogas, such as animal and human excrement, nevertheless, very few attempts have been made to investigate the potential of using corn stalk to produce biogas. The main reason is that corn stalk contains high percentage of lignocellulose, which is hard to be biodegraded by anaerobic bacteria, resulting in lower digestion rate and biogas yield. Pretreatment prior to anaerobic digestion is believed to be one of effective methods to improve corn stalk digestion efficiency and biogas yield. The microstructure and chemical compositions of lignocellulose in corn stalk would be changed obviously after chemical pretreatment, making corn stalk more accessible and biodegradable to the anaerobic microorganism and increasing digestion efficiency and biogas yield. There are various pretreatment methods, such as size reduction, steam explosion, fungi biodegradation, ammonification, urea and alkaline treatment. Muller[1] tested twenty-two basidiomycetes, and found that P. florida was the most effective fungus for improving biogas yield of wheat straw. Colleran[2] stated that the biogas yield could be increased by 50% after pretreated by NaOH

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and ammonia. Wilson and Chandra et al.[3,4] reported that NaOH pretreatment could increase the digestibility of wheat straw and coarse roughages considerably. Waiss[5] found that aqueous ammonia pretreatment improved digestibility of straws for ruminant feed. Yang et al.[6] conducted preliminary study on the effect of different types of chemicals on biogas yield of corn stalk, and found that NaOH was the best one. It seemed that most research in the past focused on improving the feed value other than biogasification efficiency of crop waste through chemical treatment.

The purpose of this study is to investigate the effect of NaOH pretreatment on anaerobic digestion efficiency and biogas yield of corn stalk and determine optimal loading rate for effective anaerobic conversion of corn stalk into biogas.

2 Materials and Methods

2.1 Experimental setup

The experimental setup for this study was comprised of three parts: an Erlenmeyer flask of 2 L, a jar of 1 L, and a beaker of 1 L, which functioned as anaerobic digester, biogas volume recorder and receiver for the water discharged from the recorder, respectively. All Erlenmeyer flasks were placed in shakers with temperature controlled as required. The biogas generated in the digester was introduced into the headspace of the jar by a rubber pipe and pressed the water in the jar into the receiver. The volume of the discharged water represented biogas production generated in the digester. Certain amount of treated and untreated corn stalk was put into the Erlenmeyer flask with a working volume of 1.5 L in order to obtain dry matter of four loading rates of 35, 50, 65 and 80 g/L, respectively. According to the research results from Gao[7], anaerobic digester operated at mesophilic temperature could achieve higher biogas yield, therefore, all flasks in the shakers were operated at mesophilic temperature of 35℃. All shakers were kept at the same constant speed of 120 r/min.

2.2 Materials

Corn stalk used in this research was collected from Tong District of Beijing. The corn stalk was first chopped and then ground into particles with a desired size (0.1 mm) through a hammer mill. Certain amount of NaOH was desolved into tap water, then the solution was added to the ground corn stalk in a container. The weight of NaOH added was 8% of corn stalk on dry matter basis. The ground corn stalk was mixed with the solution completely in the container, then corn stalk of 500 g was placed into each beaker with a volume of 1 L. Finally, all the prepared beakers were covered with plastic films and closed with rubber bands, then placed in a chamber for 30 days. By the end of the chemical treatment, the NaOH-treated corn stalk was analyzed for main compositions. The untreated corn stalk contained dry matter (DM) of 94.3% and the volatile solid was 76.0% of total solid. The corresponding values for NaOH-treated corn stalk were 97.6%, and 69.9%, respectively. The digester was seeded with the sludge taken from a mesophilic anaerobic digester in Gaobeidian Wastewater Treatment Plant of Beijing. The sludge contains 21879 mg/L TS, 10435 mg/L VS, and 20695 mg/L suspended solids. The concentration of mixed liquor suspended solid in each digester was adjusted to 15000 mg/L, which was chosen based on the research result from Zhang[8]. The original carbon-to-nitrogen ratio (C/N) of corn stalk is about 75, so 25 mg · g^{-1} (NH_4Cl dry matter) was added to adjust the C/N ratio of the mixed liquor to 25, which was believed to be optimal for anaerobic bacteria growth.

2.3 Sampling and analyzing methods

The daily biogas production for each anaerobic digester was recorded and the corresponding cumulative biogas production was calculated. The initial and final DM, TS, and VS in the digesters that included both corn stalk and anaerobic sludge were measured. All analyses were performed according to AHPA[9].

3 Results and discussion

3.1 Biogas production of untreated corn stalk

The daily biogas production of untreated corn stalk is shown in Fig. 1. Similar trends of daily biogas production were found for the four loading rates. Biogas started to be generated after seeding, and kept increase until peak value reached. Biogas production experienced several small peaks before finally ceased. However, the peak value of biogas production and the time of peak value-reaching were different for each loading rate. The biogas production reached its peak value of 1470 mL on 9th day for the loading rate of 35 g/L, while 1700 mL on the 19th day, 1310 mL on the 22th day, 1040 mL on the 35th day for the loading rate of 50, 65, and 80 g/L, respectively. It could be seen that the time of peak value-reaching was lagged as the loading rate increased. This indicated that it took longer time for anaerobic microorganism to adapt to

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the environment with more organic matter. The daily biogas production fluctuated considerably for all the loading rates, as indicated by several smaller peaks appeared. The reason for this phenomenon is not clear and needs to be further investigated.

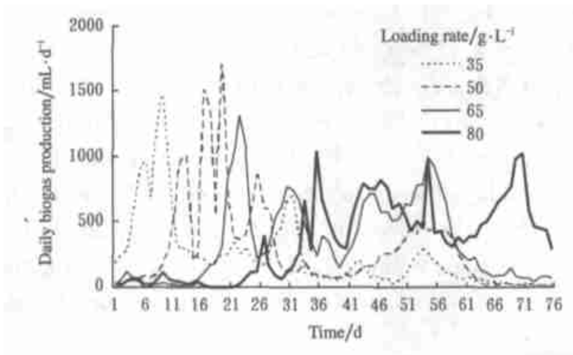

Fig. 1　Daily biogas production of untreated corn stalk

The cumulative biogas production of untreated corn stalk for the four loading rates is shown in Fig. 2. The cumulative biogas production for lower loading rates (35 and 50 g/L) were relatively higher in the early stage, but became lower in the later stage, due to the lack of available organic matter. For the higher loading rates (65 and 80 g/L), the reactors started to generate biogas later than those with lower loading rates in the early stage, but kept steady increase in the later time. The final cumulative biogas production was 17590, 21015, 26010, 26260 mL for the loading rates of 35, 50, 65 and 80 g/L, respectively. The loading rate of 80 g/L achieved highest biogas yield, but it does not mean that this loading rate is the best one since the biogas yield of the loading rate would be lower if based on per gram dry matter loaded. This will be discussed in detail in following section 3.3.

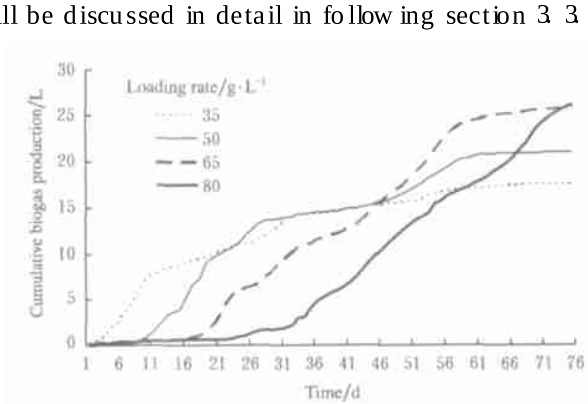

Fig. 2　Cumulative biogas production of untreated corn stalk

3.2　Biogas production of NaOH-treated corn stalk

The daily biogas production of NaOH-treated corn stalk is shown in Fig. 3. It was found that the trend of daily biogas production of NaOH-treated corn stalk was very similar to that of untreated one for all the loading rates. The biogas production reached its peak value of 1265 mL on 6th day for the loading rate of 35 g/L, while 2000 mL on 10th day, 1800 mL on 14th day, 1990 mL on 26th day for the loading rate of 50, 65, and 80 g/L, respectively. For the loading rate of 35, 50, 65, and 80 g/L, the time of peak value-reaching for NaOH-treated corn stalk were 3, 9, 8, and 9 days earlier than that of untreated one, respectively. It took approximate 40～60 days for NaOH-treated corn stalk to almost complete anaerobic digestion (Fig. 4), while 60～75 days for untreated one (Fig. 2), which was 15～20 days later than the former. This implies that the biodigestibility of NaOH-treated corn stalk was improved by chemical pretreatment, making it easier to be used by anaerobic microorganism and thus less time being needed for digestion. This finding has significant economical benefit since shorter time would lower the costs of both operation and management.

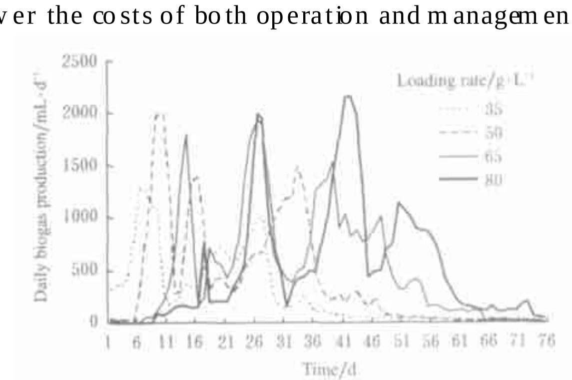

Fig. 3　Daily biogas production of NaOH-treated corn stalk

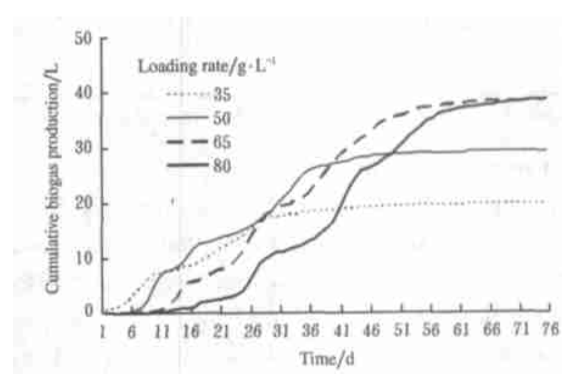

Fig. 4　Cumulative biogas production of NaOH-treated corn stalk

Besides the benefits mentioned above, NaOH-treated corn stalk achieved higher biogas production as compared with untreated one. The cumulative biogas production of NaOH-treated corn stalk is shown in Fig. 4. It could be seen that the trend of cumulative biogas production of NaOH-treated corn stalk was very similar to that of untreated one. The cumulative

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biogas production for lower loading rates (35 and 50 g/L) was relatively higher in the early stage, but did not increase obviously in the later stage, due to the lack of available organic mater. For the higher loading rates (65 and 80 g/L), the reactors started to generate biogas later than those with lower loading rates, but kept steady increase after that. The final cumulative biogas production was 19890, 29380, 38585 and 38820 mL for the loading rates of 35, 50, 65 and 80 g/L, respectively, an increase of 13.1%, 39.8%, 48.3%, and 47.8% over untreated one, indicating that NaOH pretreatment could significantly improve the biodegradability of corn stalk and increase biogas yield.

3.3 Comparisons of experimental results

The main results from the digestion experiments of untreated and NaOH-treated corn stalks are summarized in Table 1, so that comparisons could be made in order to investigate the effectiveness of NaOH pretreatment.

As compared with untreated corn stalk, NaOH-treated one increased total biogas yield by 13.1%～48.3%, correspondingly, increased TS and VS reduction by 15.3%～23.8%, and 34.0%～65.1%, respectively, indicating that NaOH pretreatment was capable of improving the digestibility and thus increasing the biogas yield of corn stalk significantly. The biogas yields based on the TS and VS loaded were increased by 13.1%～48.3%, and 23.0%～61.3%, respectively. The average biogas yields based on the TS and VS reduced for untreated and NaOH-treated corn stalks were 728.5 and 826.5 mL/gTS reduced, 1098.4 and 1120.6 mL/gVS reduced, respectively. This result showed that biogas production would be the same if the same amount of VS was digested, but not if the same amount of TS was digested, implying the important impact of VS digestion on biogas production.

For untreated and NaOH-treated corn stalk, the loading rates of 35 and 65 g/L achieved the highest biogas yield per gram TS loaded respectively. In other words, one gram of TS could produce the most biogas at the two loading rates, therefore, the two loading rates were believed to be the best for the digestion of untreated and NaOH-treated corn stalk respectively and thus recommended.

Table 1 Comparisons of experimental results

LR[a] /g·L^{-1}	total biogas yield /mL			TS reduction /%			VS reduction /%			biogas yield TS loaded /mL·g^{-1}			biogas yield VS loaded /mL·g^{-1}			biogas yield TS reduced /mL·g^{-1}		biogas yield VS reduced /mL·g^{-1}	
	Ut[b]	Nt[c]	Ch.[d] /+ %	Ut	Nt	Ch. /+ %	Ut	Nt	Ch. /+ %	Ut	Nt	Ch. /+ %	Ut	Nt	Ch. /+ %	Ut	Nt	Ut	Nt
35	17590	19890	13.1	36.6	42.2	15.3	33.2	44.5	34.0	335.0	378.8	13.1	440.8	542.0	23.0	915.3	898.1	1327.7	1218.4
50	21015	29380	39.8	39.3	45.9	16.8	34.9	48.3	38.4	280.2	391.7	39.8	368.7	560.4	52.0	712.5	854.0	1055.6	1161.1
65	26010	38585	48.3	39.0	48.3	23.8	31.5	52.0	65.1	266.8	395.7	48.3	351.0	566.2	61.3	684.6	819.9	1115.3	1089.5
80	26260	38820	47.8	36.4	44.0	20.9	32.2	45.6	41.6	218.8	323.5	47.8	287.9	462.8	60.7	601.6	734.1	894.9	1013.3

a—Loading rate; b—Untreated corn stalk; c—NaOH-treated corn stalk; d—Change rate

3.4 Changes of main compositions

The microstructure and chemical compositions of the corn stalk were changed during NaOH pretreatment process. The changes resulted from the complex physical and chemical roles of NaOH. The analyses were made to further investigate the reasons why biogas yield was improved after chemical pretreatment. The analyzing results of the main compositional contents and dry matter losses are shown in Table 2.

Table 2 Changes of main compositional contents after NaOH pretreatment %

	lignin	cellulose	hemi-cellulose	TC	TN	P	K	DM loss
raw corn stalk	6.9	43.6	27.8	41.7	1.2	0.12	1.87	
NaOH-treated corn stalk	4.1	29.4	11.8	31.1	1.3	0.07	1.33	
reduction by content/%	40.6	32.6	57.6	25.4	-8.3	41.7	28.9	
reduction by DM/%	53.2	46.9	66.6	41.3	14.7	54.1	44.0	21.3

After NaOH pretreatment, the contents of lignin, cellulose, and hemicellulose were reduced by 40.6%, 32.6%, and 57.6%, respectively, corresponding reduction of dry matter was 53.2%, 46.9%, and 66.6%, respectively, showing the significant effect of NaOH on main compositions. TC, TN, P, and K contents were changed considerably too. It was found that total dry matter loss was 21.3%, approximate 1/2～2/3 less than the losses of lignin, cellulose, and hemicellulose (46.9%～66.6%), implying that 1/2～2/3 of lignin, cellulose, and hemicellulose decomposed was actually converted into some matters else rather than be really lost. Although detailed analysis was not conducted in this study, it was believed that the matters ought to be mainly soluble compounds. The soluble compounds coming from the decomposition of corn stalk are usually some matters with low molecular weight and thus more easily used by

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anaerobic microorganism. This is one of the main reasons for the improvement of biodegradability and increase of biogas production after NaOH pretreatment. Another main reason is the broken-down of lignocellulose matrix due to the chemical role, leading to the change of microstructure of cell wall and making compositions more accessible to anaerobic microorganism.

4 Conclusions

NaOH pretreatment could significantly improve the biodegradability and increase biogas yield of corn stalk. The total biogas yield of NaOH-treated corn stalk was increased by 13.1%, 39.8%, 48.3%, and 47.8% over untreated one for the loading rates of 35, 50, 65 and 80 g/L, respectively. For untreated and NaOH-treated corn stalk, the loading rates of 35 and 65 g/L achieved the highest biogas yield per gram of TS loaded were recommended to be optimal for anaerobic digestion of untreated and NaOH-treated corn stalk respectively.

After NaOH pretreatment, the content and dry matter of main compositions of corn stalk were changed significantly, approximate 1/2～2/3 of lignin, cellulose, and hemicellulose decomposed were converted into soluble compounds, which contributed to the improvement of biodegradability of corn stalk and the increase of biogas production. Compared with untreated stalk, the biogas yields based on the TS and VS loaded for NaOH-treated one were increased by 13.1%～48.3%, and 23.0%～61.3%, respectively, indicating that NaOH pretreatment did improve the digestion efficiency. The biogas production would be the same if the same amount of VS was digested, but not if the same amount of TS was digested, therefore, VS digestion had more significant impact on biogas production than TS.

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NaOH 处理玉米秸秆厌氧生物气化试验研究

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摘　要: 提出通过NaOH 化学处理以改善玉米秸秆的可生物消化性能、提高玉米秸秆厌氧消化产气量的方法。NaOH 添加量为玉米秸秆干物质的 8%。对未处理和经NaOH 处理的玉米秸秆进行了厌氧消化对比试验研究, 厌氧消化负荷率为 35, 50, 65 和 80 g/L。分析并比较了两者在不同负荷率下的日产气量、累积产气量、单位TS 和VS 产气量等。结果显示, 与未处理玉米秸相比,NaOH 处理过的玉米秸的干物质消化率和产气量明显提高, 在 35, 50, 65, 80 g/L 负荷率下, 产气量分别提高了 13.1%, 39.8%, 48.3% 和 47.8%, 单位TS、VS 的产气率分别提高了 13.1%～48.3%、23%～61.3%; 两种玉米秸分别在 35 和 65 g/L 负荷率下获得了最高单位TS 产气量。NaOH 化学处理使玉米秸细胞壁结构和化学成分发生了明显的变化, 分别有 53.2%、46.9% 和 66.6% 的木质素、纤维素和半纤维素被分解, 其中 1/2～2/3 被转化成了易被厌氧菌利用的可溶性物质, 这是产气量提高的主要原因之一。研究结果对提高玉米秸的产气效率、实现大规模应用具有重要指导意义。

关键词: 玉米秸秆; NaOH; 负荷率; 生物气; 厌氧消化

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