Effect of hydrothermal carbon on biogas production from agricultural waste by anaerobic fermentation

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Abstract. In this study, biogas residue was used as raw material to prepare biogas residue by hydrothermal carbonization at 190℃ with different treatment time. The effects of hydrothermal carbon addition on gas production characteristics during medium temperature anaerobic fermentation (straw, straw + chicken manure, chicken manure) were studied, and the differences of surface formation of biogas residue hydrothermal carbon were observed by SEM. The results showed that the duration of gas generation peak was prolonged in the straw + chicken manure fermentation group and the chicken manure fermentation group after adding biogas residue hydrothermal charcoal, and the total gas production in the 8h, 12h and 24h hydrothermal charcoal groups increased more ($P < 0.05$), and the total gas production increased 39.2% at most. There was no significant difference in cumulative gas production among groups in straw fermentation group. According to the actual production, the optimal HTC process for anaerobic fermentation is 8 h at 190℃.

Keywords: Hydrothermal carbon, Anaerobic fermentation, Renewal, biogas.

1. Introduction

Hydrothermal carbonization method (HTC) refers to the process of synthesizing carbon-rich products in a sealed high-pressure reaction kettle with compounds as raw materials, water as solvent and reaction medium, under autogenic pressure and reaction temperature of 150-260 ℃. In anaerobic digestion process, the material will produce some such as heavy metals (Cu, zinc, Cr, Cd and Hg, etc.), salt (Na, K, Ca, Al, etc.), phenol and halogenated hydrocarbon compounds, pesticides and antibiotics, such as inhibitor, in the process of producing gas also can produce some of the volatile fatty acids, long chain fatty acids, inorganic nitrogen and sulfide indirect inhibitor, These have seriously affected the gas production rate and production benefit of biogas projects [1]. Hydrothermal charcoal can be used for anaerobic fermentation, which can reduce the influence of organic load at the initial stage of anaerobic digestion, adsorb and inhibit sulfides, accelerate the accumulation of methanogenic bacteria, and improve the anaerobic digestion rate and methanogenic effect.

2. Materials and methods

2.1. Test materials

Fermentation materials were naturally dried corn straw and fresh chicken manure, which were taken from the scientific research base of Shenyang Agricultural University, and biogas residue was taken from the anaerobic fermentation tank of the Energy base of Shenyang Agricultural University, as shown in Table 1.

Table 1. Properties of raw materials

Materials	TS (%)	VS (%)	Carbon content (%)	TNitrogen content (%)	C/N
Corn stover	93.1	88.5	72.4	1.1	67.6
Chicken manure	56.3	29.7	22.5	1.7	13.2

2.2. Preparation of hydrothermal carbon

The biogas slag hydrothermal charcoal was prepared in a stainless steel reactor (Shanghai Jinbo Electronic Technology Co, LTD.), and about 20g of biogas slag sample was weighed. Put the biogas residue sample into the reaction kettle, screw the stainless steel sheath, place it in the oven, set the oven to heat up to 190℃, and heat for 2h, 4h, 8h, 12h, 24h respectively. After heating, take it out and place it so that the reaction kettle naturally drops to room temperature. After taking out the sample, conduct extraction and filtration, and place the extracted hydrothermal charcoal in 105℃ oven to dry for 12h. The product is biogas slag hydrothermal charcoal.

2.3. Test design

Batch fermentation was used in this experiment and the TS load was set at 15%. In the above fermentation tank, the mass ratio of inoculum to fermentation raw materials was 1:2, and in the straw + chicken manure group, the mass ratio of chicken manure to straw was 2:1. The addition amount of hydrothermal carbon accounted for 10% of the dry matter weight of the system respectively, and the treatment without hydrothermal carbon was set as the control group. See Table 2 for the addition of each material. Before canning, fermentation raw materials should be fully mixed in advance, and the added raw materials, hydrothermal charcoal and inoculants should be fully stirred and mixed during canning. After that, biogas slurry should be added for constant volume, and anaerobic fermentation should be carried out after sealing. Each group was treated with 3 repetitions, and the average value was finally taken for analysis.

The corn straw groups were expressed as CS-0, CS-2, CS-4, CS-6, CS-12 and CS-24. The maize straw + chicken manure experiment was expressed as SM-0, SM-2, SM-4, SM-6, SM-12 and SM-24, and the chicken manure experiment was expressed as CM-0, CM-2, CM-4, CM-6, CM-12 and CM-24. CS was Corn straw, SM was Corn straw + Chicken manure, and CM was Chicken manure. The number represents the carbonization time of the added hydrothermal charcoal.

2.4. Analysis method

Total solid content (TS) and volatile solid content (VS) were measured by national standard method. PH value was measured by pH meter (HQ40d-PHC101). Viscosity was measured with a digital rotational viscometer (SNB-1). The elemental content of the material was determined using Elementar, Germany. The morphology of hydrothermal carbon samples after different heat treatment was described by scanning electron microscope. Gas production was measured by drainage gas collection method. Use portable biogas analyzer to measure gas composition..

2.5. The data analysis

The data obtained from the experiment were analyzed and processed by Microsoft Excel and SPSS software.

3. Results and analysis

3.1. Effects of biochar addition on biogas production from anaerobic fermentation of livestock and poultry manure

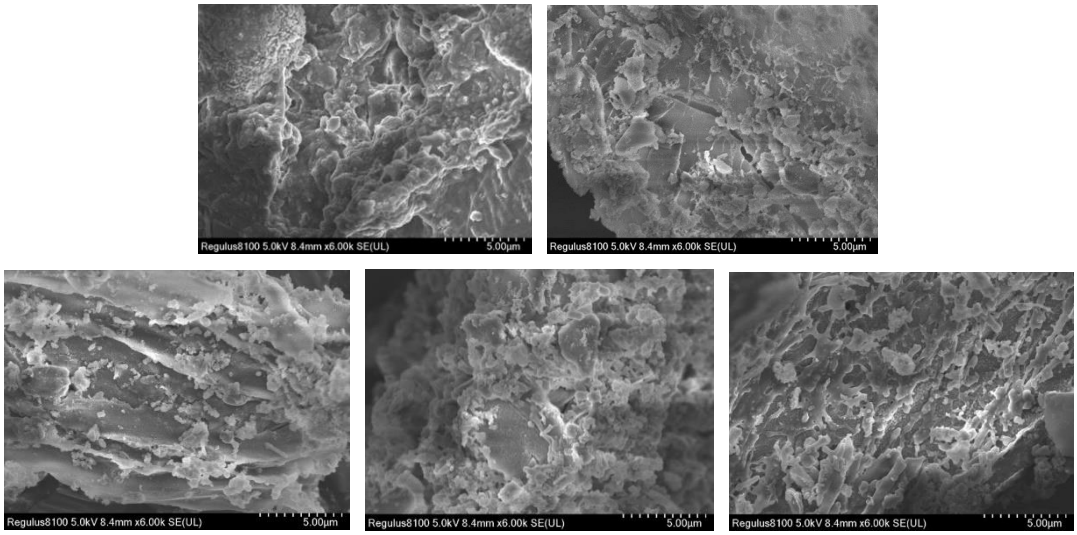
The pH of the liquid phase products during the preparation of hydrothermal carbon was detected, and the pH values were shown in Table 2.

Table 2. pH of liquid products at different treatment times

Standing time /h	pH	Standing time /h	pH	Standing time /h	pH
1	7.57	6	4.77	12	5.02
2	5.36	8	4.52	24	4.99
4	4.94	10	4.77		

As the water thermal response, at the beginning of the reaction, the incomplete due to polymer water is hot, system of pH decreases gradually along with the production of organic acid, and 8 h, to minimize the liquid product pH 4.52, after the water thermal response process, some intermediates occur further polymerization, produce large amounts of water at the same time, make the pH value in the system gradually picks up, In view of this, the experiment used hydrothermal charcoal with treatment time of 2h, 4h, 8h, 12h and 24h as additive to explore its influence on the anaerobic fermentation process.

Scanning electron microscopy is a potential technique to study the morphology of samples after different heat treatments. Scanning electron microscopy (SEM) showed that the physical properties and surface morphology of the samples were changed after HTC treatment. After the straw biogas residue is hydrothermal carbonized at 190℃, the surface characteristics of hydrothermal carbon change is shown in FIG. 1



a. 2h hydrothermal treatment b. 4h hydrothermal treatment
c. 8h hydrothermal treatment d. 12h hydrothermal treatment e. 24h hydrothermal treatment

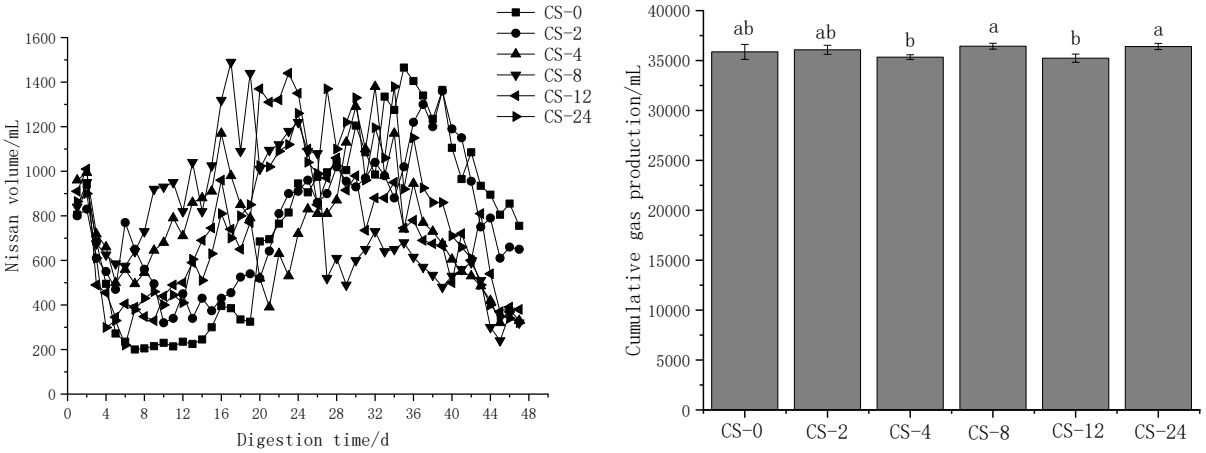
Figure 1. Surface characteristic changes of hydrothermal carbon

It can be clearly seen from Figure 2 that cracks and grooves began to appear on the surface of 2h hydrothermal carbon, and many irregular protrusions formed on the surface. The surface of the hydrothermal carbon generated was very rough. At 4h, the surface of hydrothermal carbon began to fracture, and some structures similar to carbon microspheres were produced, and the surface also began to fragment. 8h hydrothermal carbon surface collapse is more serious, the number of carbon microspheres began to increase significantly, the internal structure began to become complex. In the 12h hydrothermal carbon diagram, the hydrothermal carbon itself was broken seriously, and a large number of irregular microspheres and fragments began to be generated. The raw carbon skeleton was slightly damaged, resulting in more developed and complex pore structure, and gelatinous materials appeared at the edges of some large particles. A large number of colloidal substances attached to the surface of hydrothermal carbon appeared in the 24h hydrothermal carbon, and the surface of the carbon was relatively smooth. With the increase of residence time, many micron sphere particles form on the surface of hydrothermal carbon, which is conducive to improving the specific surface area of hydrothermal carbon [3]. After 12h and 24h, the colloidal substance appeared on the surface of hydrothermal carbon, which was speculated to be due to the longer residence time leading to slight hydrolysis of lignin, polymerization and other reactions of some intermediates, and the carbon material similar to hydrothermal carbon was produced. Gao et al. [2] showed that a longer residence time had a visual impact on the surface topography, because cellulose and hemicellulose did not fully react within a shorter residence time. With the increase of residence time, cellulose and hemicellulose may be completely decomposed, increasing the number of microspheres [4,8].

The special surface characteristics of hydrothermal charcoal promote the growth of microorganisms in anaerobic fermentation process: hydrothermal charcoal can absorb harmful inhibitors (such as ammonia molecules, ammonium hydroxide, sulfide, etc.) generated in the fermentation process, and reduce their damage to methane generation. At the same time, the complex structure of hydrothermal carbon can be used as the carrier of microbial growth, which is conducive to the formation of biofilm on the surface of carbon. Direct electron transfer (DIET) in methane production can be promoted by changing the interactions between methanogens [5,6,7].

3.2. Effects of different hydrothermal carbon additions on gas production

The daily gas production and cumulative gas production of each straw group were shown in Figure 2.



a. Change of daily gas volume in straw group

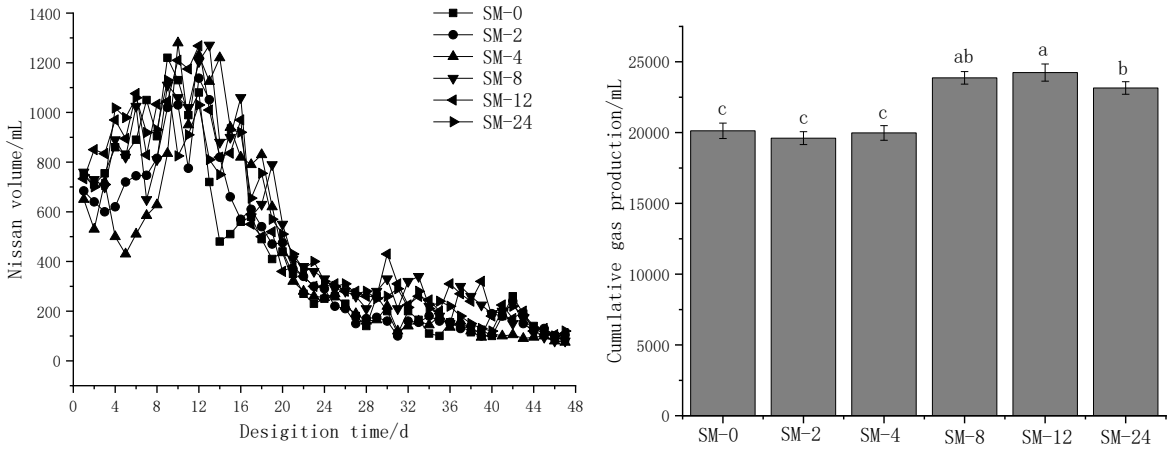
b. Change of cumulative gas production in straw group

Figure 2. Gas production of each straw group

It can be seen from the daily gas chart that each group can start quickly in the early stage of fermentation. The gas production rate of CS-4, CS-8, CS-12 and CS-24 groups was significantly different from that of the control group. The peak of gas production of CS-4, CS-8, CS-12 and CS-24 groups was concentrated in the first 25 days, and the gas production rate was low in the middle and late stage of the reaction, presenting a trend of gradual decline. The gas production trend of CS-0 and CS-2 groups is basically similar, and the peak of gas production is behind the other four groups. The variation of gas production in CS-4 group was larger in the middle fermentation period, and the fermentation effect in CS-8 group was better in the early and middle fermentation period. Daily gas production decreased rapidly in the late fermentation period and tended to be stable in the late fermentation period.

In terms of cumulative gas production, except CS-4 and CS-12 groups, the total gas production of straw group with different hydrothermal carbon was slightly larger than that of straw control group, and the total gas production of straw group with 8h and 24h carbon was almost the same, but the total gas production of straw group with 2h hydrothermal carbon had no obvious increasing trend. This indicates that the addition of hydrothermal carbon has little effect on gas production in the pure straw fermentation group, which may be because straw itself has characteristics similar to hydrothermal carbon, and its principle needs further exploration.

Daily gas production and cumulative gas production of straw + chicken manure groups were shown in Figure 3.



a. Daily gas volume of straw + chicken manure groups

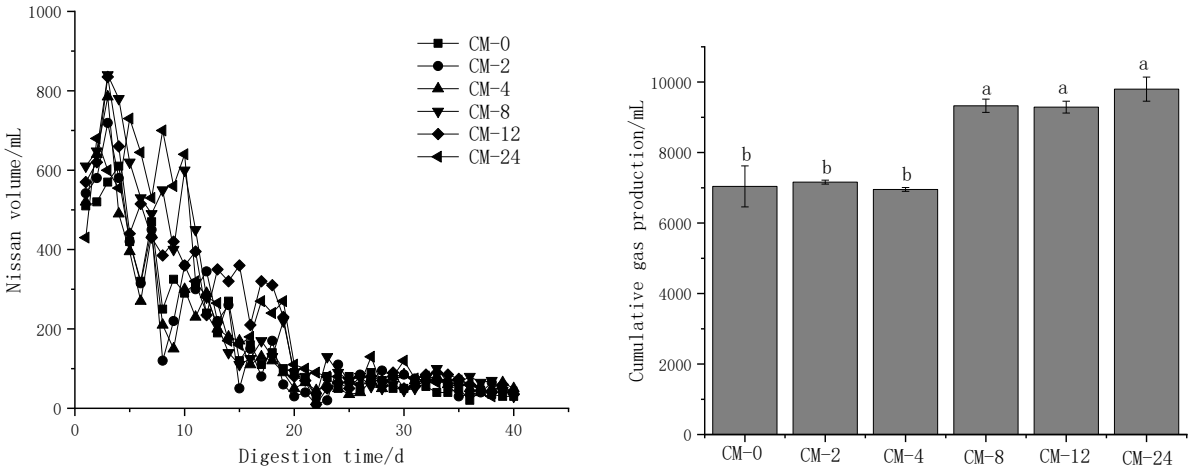
b. Cumulative gas production diagram of straw + chicken manure groups

Figure 3. Gas production of straw + chicken manure groups

As shown in figure 3, the straw + chicken manure group in the control group and other adding different hydrothermal carbon group compared to the change trend of difference is small, the early stage of the fermentation with the increase of number of days, the gas production rate shock rise, gas trend is basically the same and each group can fast start, but the control group 10 d before start of gas is better than add 2 h, 4 h hydrothermal carbon group, in the middle of the fermentation, The gas production peak lasted for a long time in each group with hydrothermal carbon addition, appearing on day 9 to 15. At the late fermentation stage, the gas production decreased slowly in all groups, and the gas production effect was almost the same after 20 days.

Compared with the control group, the cumulative gas production of SM-2 and SM-4 groups was not significantly different, but the total gas production of SM-8, SM-12 and SM-24 was significantly higher than that of the control group ($P < 0.05$). By adding hydrothermal charcoal, the duration of the middle gas production peak was increased, which was the main reason for the increase in total gas production.

The daily gas production and cumulative gas production of chicken manure groups were shown in Figure 4.



a. Daily gas chart of chicken manure group

b. Cumul ative gas production diagram of chicken manure group

Figure 4. Gas production in each group of chicken manure

The gas production of the chicken manure group is shown in FIG. 4. Each group reaches the peak of gas production about the 4th day; the gas production rate of the chicken manure control group drops rapidly after reaching the peak of gas production; the gas production rate of the experimental

group with hydrothermal charcoal drops by shock; after 20 days, the change trend is roughly the same as that of the control group. The results showed that in the chicken manure group, due to the high content of ammonium nitrogen in chicken manure, the ammonium nitrogen in solid anaerobic fermentation chicken manure was easier to concentrate and thus inhibited gas production, so the peak value reached in the early stage of gas production.

In the chicken manure control group, the total gas production was the least due to the relatively low gas production in the first 6 days. The gas production of CM-2 and CM-4 was roughly the same, while the gas production of CM-8, CM-12 and CM-24 was higher ($P < 0.05$), and the three had little fluctuation.

The results showed that in the straw group, the gas production of CS-4, CS-8, CS-12 and CS-24 decreased rapidly at the later stage of gas production, presumably because the buffer capacity and microbial activity of the system were enhanced after the addition of hydrothermal carbon, and the rate of substrate consumption was increased. Straw and chicken manure in the group, as a result of contains some straw, which will also produce similar straw group phenomenon, but as a result of inoculum and hydrothermal carbon are floating in the biogas slurry, so conducive to the growth of the microorganisms in water hot coals surface, thus greatly improve the water burning charcoal to the effect of anaerobic fermentation, prolong the duration of the gas peak, also did not produce a similar group of straw fermentation effect of prophase. In the chicken manure group, the addition of hydrothermal charcoal increased the gas production of chicken manure, and the hydrothermal charcoal was the only carrier for microbial adhesion and growth, which greatly promoted the interaction between microorganisms in the process of anaerobic digestion. The results show that hydrothermal carbon, like granular activated carbon and carbon cloth, can be used as electron transport material in anaerobic fermentation process to promote direct electron transport (DIET), which is very beneficial to methanogenesis process. In addition, the special surface structure of hydrothermal carbon can absorb inhibitory sulfides produced during anaerobic fermentation. It has also been reported that carbonyl groups on the surface of hydrothermal carbon may also bind to CO_2, which is conducive to methane gas production.

4. Conclusion

1) In the medium temperature anaerobic fermentation system with TS=15%, the gas production of SM group and CM group anaerobic fermentation system with hydrothermal carbon was increased. According to data analysis, the hydrothermal carbonization treatment time with the best improvement effect on the fermentation process was 8 h, 12 h, 24 h. According to the actual production, the optimal HTC process for anaerobic fermentation is 8 h at 190℃.

2) Adding straw biogas residue hydrothermal charcoal can improve digestion efficiency of medium temperature fermentation and promote degradation of cellulose and hemicellulose in anaerobic fermentation. Hydrothermal charcoal can enrich a large number of microorganisms on the surface and form biofilm, especially its resident effect on methanogens can improve gas production efficiency in the fermentation process. In this study, hydrothermal carbon was proved to significantly increase gas production and shorten the lag period for methane production. Biochar selectively enriched functional microorganisms closely attached to it, which played an optimal role in anaerobic fermentation. The cost efficiency and treatment technology of hydrothermal charcoal make it feasible in anaerobic digestion engineering of organic waste.

Acknowledgments

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