Effects of Exogenous Biochar Addition on High Solid Anaerobic Fermentation of Livestock Manure for Environmental Pollution Control

Jiamin Zhao¹, Yang Gao¹, Jiaxing Sun¹, Zhen Wang¹ and Ling Zhao¹,*

¹College of Engineering, Shenyang Agricultural University, Shenyang, China

*Corresponding author: zhaoling@syau.edu.cn

Abstract. In order to explore the effects of adding biochar on biogas production by high solid concentration anaerobic fermentation of livestock and poultry manure and agricultural safety, this study used pig manure, cow manure and chicken manure as fermentation raw materials, and carried out experiments on biogas production by mesophilic temperature anaerobic fermentation with high solid concentration. The changes of cumulative biogas production, biogas production rate, methane (CH₄) content, volatile fatty acid (VFA) and hydrogen sulfide (H₂S) content in three kinds of livestock manure with or without biochar were analyzed. The results showed that the addition of biochar had different effects on anaerobic fermentation of livestock and poultry manure with high solid concentration, increased the content of CH₄ and decreased the content of H₂S. The addition of biochar provided enough granular surface to absorb a large number of inoculated microorganisms, which shortened the start-up time, increased the biogas production rate of high-solid anaerobic fermentation of livestock and poultry manure, and advanced the peak period of biogas production; reduced the content of VFA, reduced the inhibition of methanogens, so the methane content increased. The addition of biochar had the most obvious effect on anaerobic fermentation of cow manure and chicken manure with high solid content.

Keywords: biochar, livestock manure, anaerobic fermentation, methane.

1. Introduction
Anaerobic fermentation of livestock and poultry manure is an effective way to solve environmental pollution and produce energy. According to statistics, in 2018, China's livestock and poultry manure production volume was 22.35×10⁸ t, the main source is swine, cattle and poultry breeding, biogas production potential of 1072.75×10⁸m³, energy potential accounted for 60% of the year's natural biogas consumption [1]. There have been many reports about high solid anaerobic fermentation of livestock and poultry manure at home and abroad. Liu Zhanguang [2] and others used pig manure and rice straw as raw materials for anaerobic fermentation at the concentration of TS (total solid) of 30%. The results showed that mixed dry anaerobic fermentation could significantly increase the biogas production rate, but had no significant impact on fermentation potential of raw materials. Pranas et al. [3] studied that biochar additives increased the concentration of CH₄ in biogas and reduced the concentration of biogas impurities (CO₂ and H₂S) in biogas. The highest concentration of CH₄ in biogas
produced by chicken manure with biochar additive is higher than that produced by chicken manure without biochar additive. Lehtomäki et al. [4] used cow dung mixed with different crop straw to ferment. When 30% of crop straw was mixed, methane yield per unit volume increased by 16%-65% compared with cow dung fermented alone. Liangwei et al. [5] used pig manure as fermentation substrate, set anaerobic fermentation in groups with high solid content and low solid content, and studied the influence of substrate concentration on anaerobic fermentation. Finally, high substrate concentration can improve the efficiency of anaerobic fermentation system.

In this paper, the promotion of biochar on high solid anaerobic fermentation was studied. As a type of black carbon, biochar is a kind of highly aromatic and refractory solid substance produced by pyrolysis and carbonization of plant substances under complete or partial anoxia. In addition to providing a certain carbon source, biochar has high stability, strong adsorption and well-developed pore structure, which can be used as a carrier for microbial aggregation, maintain an environment conducive to microbial growth and accelerate the consumption of volatile acids. Therefore, it is of great significance to study the mixed fermentation of biochar and livestock manure, and to explore the effect of biochar addition on its biogas production, so as to solve environmental pollution and improve the utilization rate of agricultural solid waste.

2. Materials and methods

2.1. Test materials
Fermentation materials: fresh swine manure, cow manure and chicken manure from a farmer near Shenyang Agricultural University; Biochar made from corn straw made 500℃pyrolysis carbonization 30 min; The inoculation material came from anaerobic fermentation tank of a household in the suburbs of Shenyang.

Physicochemical indexes such as total solid (TS) mass fraction, volatile solid (VS) mass fraction, nitrogen content and phosphorus content of fermentation raw materials are shown in Table 1.

| Fermentation raw material | TS (%) | VS (%) | Total nitrogen content (%) | Total phosphorus content (%) |
|--------------------------|--------|--------|----------------------------|-----------------------------|
| Swine manure             | 21.6   | 78.4   | 3.3                        | 4.0                         |
| Cow manure               | 18.5   | 73.3   | 3.1                        | 0.9                         |
| Chicken manure           | 31.4   | 69.7   | 4.5                        | 2.8                         |

2.2. Test apparatus
The devices are mainly composed of fermentation bottle, biogas collecting bottle and water collecting bottle. The fermentation flask is a 1L wide-mouth flask. The glass tube is connected with the latex tube to form a small anaerobic fermentation device and the biogas is collected by drainage method. Continuous fermentation of the device in a constant temperature water bath at 35 ℃.

2.3. Test design
The experiment was divided into three groups: group I(Swine manure test group), group II(Cow manure test group) and group III(Chicken manure test group). Each group had one control group (without biochar) and one experimental group (with biochar). The total solid concentration of each test group was 20%. Each group was repeated three times.

2.4. Analysis method
Total Solid Content (TS): Drying Method; Volatile Solid Content (VS): Drying Method; Gas Production: Drainage Method; pH Value: Composite Electrode Method; Biogas Composition: Biogas Portable Biogas Analyser; Volatile Fatty Acids: Titration [6].
2.5. The data analysis
The measured data were processed and plotted with Sigma Plot 10.0 software.

3. Results and analysis

3.1. Effects of biochar addition on biogas production from anaerobic fermentation of livestock and poultry manure
During the fermentation process, the biogas production rates of the three kinds of livestock and poultry manure with and without biochar were shown in figure 1.

Figure 1. Biogas production rates of company's animal manure
It can be seen from figure 1 that the three types of livestock and poultry manure can start up rapidly under different adding states. The separate fermentation of cow manure with biochar and chicken manure starts to produce biogas on the first day, and the other four groups start to produce gas normally on the second day. There was a significant difference in the biogas production rate between different livestock and poultry manure. The gas production rate in the swine manure group was not significantly different. The peak of biogas production was concentrated in the first 15 days, and the gas production rate in the middle and late stages of the reaction was low, showing a gradual downward trend. The variation trend of the two groups with and without biochar in the cow manure group was basically similar. There were two small peaks of biogas production after the peak of gas production, and then the biogas production fluctuated and decreased until the end of biogas production. However, the peak of the group with biochar was 5 days earlier than that of the control group. The variation trend of chicken manure group was significantly different. In the control group, there was a small peak of gas production after the peak of biogas production, and then the biogas production fluctuated and decreased until the end of the biogas production. In the experimental group, there were multiple peaks of biogas production during the fermentation process, and the biogas production rapidly decreased in the later stage of fermentation.

In this experiment, the biogas production peak of the swine manure group occurred between 5 and 10 days, the biogas production peak of the cow manure group started slowly occurred between 15 and 20 days, and the biogas production peak of the chicken manure group rapidly reached between 1 and 5 days. In the experiment of swine manure group, the biogas production rate was low in the early stage of fermentation, and the peak value appeared late, which indicated that the fermentation material liquid produced acidification in the early stage, and the value measured by the precision pH test paper gradually decreased. Then the biogas production rate rose and peaked, mainly because methanogens gradually adapted to such an environment through reproduction and became active. Due to the high content of ammonium nitrogen in chicken manure, the ammonium nitrogen in high solid anaerobic fermentation chicken manure was more easily concentrated and thus inhibited the biogas generation [7]. Therefore, the peak value was reached at the early stage of biogas generation and was lower than that of the other two groups. It can be seen from the above analysis that the addition of biochar in swine manure and cow manure group accelerated the gas production rate, while the addition of biochar in chicken manure group adsorbed ammonium nitrogen in chicken manure, and the maximum daily biogas production of each group increased.

3.2. The effect of biochar addition on methane (CH4) in anaerobic fermentation of livestock and poultry manure

During the anaerobic fermentation process of the three groups of experiments, the methane content in the produced gas increased gradually with the progress of the fermentation. As can be seen from figure 2, the variation trend of the experimental group and the control group was basically the same, with a small change range. The methane content of the experimental group was slightly higher than that of the control group at the initial stage of the reaction, and reached the maximum in both groups on the 12th day. The experimental group reached 48.3% and the control group 46.5% [24], indicating that the swine manure fermentation and decomposition was fast. Then the methane content in the control group decreased sharply to 36.8%, but the experimental group presented a slow decline trend, making the methane content in the experimental group greater than that in the control group. After a small peak in the middle and late stage of the experimental group, the methane content in the experimental group fluctuated steadily between the experimental group and the control group, fluctuating between 39%-45%.
a. The methane content of swine manure

b. The methane content of cow manure

c. The methane content of chicken manure

Figure 2. Changes of methane content in anaerobic fermentation of different animal manure

The variation trend of methane content in the cow manure group was basically the same as that in the control group. The methane content in the produced biogas showed a significant increase trend with the extension of fermentation time. After reaching a peak, the methane content decreased sharply and then slowly rose to another peak, showing a stable fluctuation, fluctuating between 41% and 55%. The
The overall trend of methane content in the experimental group was about 5 days higher than that in the control group. The highest methane content in the experimental group was 56.5%, which was 2.3% higher than that in the control group.

From Figure 2, it can be seen that the change trend of chicken manure group is basically the same and the methane content of the experimental group is higher than that of the control group. From the beginning of fermentation, the methane content gradually increases to the peak value, then it fluctuates steadily, and fluctuates between 40% and 56%. The methane content in the experimental group reached the maximum 57.6% on 29 days, which was 4 days earlier than that in the control group and the peak value increased by 8.3%, and the methane content in the experimental group was higher than that in the control group as a whole.

3.3. Effects of biochar addition on VFA and pH in anaerobic fermentation of livestock and poultry mar

The effect of biochar addition on VFA content in high solid anaerobic fermentation of three kinds of animal manure is shown in figure 3, the influence of swine group in the control group and experimental group at the beginning of the fermentation VFA content is 1380 mg·L⁻¹ and 930 mg·L⁻¹, pH value is 6.8 and 7.2 respectively. The VFA content in the control group decreased in the first 28 days and then increased, reaching 1 380 mg/L at the end of fermentation. The pH value in the control group increased in the first 28 days, then decreased slowly, and reached 6.7 at the end of fermentation; The content of VFA in the experimental group decreased in the first 21 days, and then increased in fluctuation. At the end of fermentation, it reached 720 mg·L⁻¹. The pH value in the experimental group increased in the first 21 days, then decreased. At the end of fermentation, the pH value was 7.1. the content of VFA was as high as 5340 mg·L⁻¹ and 5520 mg·L⁻¹ at the initial stage of fermentation in the control group and the experimental group of cow group, and the pH values were 6.4 and 6.3, respectively.
b. Changes of VFA content of cow manure

c. Changes of VFA content of chicken manure

d. Changes of the pH of swine manure
As the reaction went on, the content of VFA in cow manure without biochar gradually decreased to the end of the reaction, and the content of VFA was 450 mg·L\(^{-1}\), the pH value fluctuated and increased to 7.4 at the 56th day of fermentation. With the progress of the reaction, the content of VFA in cow manure with biochar decreased rapidly, dropping to 320 mg·L\(^{-1}\) at the lowest point on the 28th day, and then recovered slightly. At the end of the reaction, the content of VFA was 600 mg·L\(^{-1}\), and the pH value increased to 7.6 at the first 28 days, and then decreased, reaching 7.2 at the end of the reaction.

Chicken manure group in the control group and experimental group at the beginning of the reaction of VFA content is 5940 mg·L\(^{-1}\) respectively and 6000 mg·L\(^{-1}\), pH value is 6.3 and 6.2 respectively, as the response to the control group content of VFA layer increased to 35 d reaction, 9300 mg/L, and showed a trend of gradual decline at the end of the reaction of VFA content is 6510 mg·L\(^{-1}\) respectively, the pH in small amplitude fluctuation state response at the end of 6.2; In the test group, the VFA content presented a steady decline of 2,640 mg·L\(^{-1}\) on the first 35d, and then slightly increased to 3,240 mg·L\(^{-1}\). The pH value increased to 7.1 on the first 35d, and then decreased, and the pH value was 7 at the end of the reaction. From the overall analysis, the content of VFA in the anaerobic fermentation of livestock and poultry manure with added biochar was lower than that in the separate fermentation of livestock and poultry manure, and the content of VFA was inversely proportional to the pH value. The results of the study analyzed the results of this experiment, because methanogens are sensitive to pH value, the
appropriate pH value range is 6.8 ~ 7.8. In this experiment, the pH value of chicken manure group was too low, the activity of methanogens was inhibited, and the biogas production was low.

3.4. Effect of biochar addition on hydrogen sulfide (H2S) in anaerobic fermentation of livestock and poultry manure

The effects of biochar addition on H2S content in high solid anaerobic fermentation of three kinds of animal manure are different. As shown in Figure. 4, the content of H2S in the control group increased to 640 mg·L⁻¹ at the beginning of fermentation, then decreased sharply, and nearly reached zero at the end of reaction. The content of H2S in the experimental experimental group smells weaker. It can be seen that the addition of biochar reduces the content of hydrogen sulfide. The overall trend of H2S content in cow manure was the same, and the content of H2S decreased gradually and fluctuated to a certain extent until the end of the reaction. In the first 10 days of fermentation, the content of H2S was higher, and then decreased sharply to zero in the experimental group and the control group, showing a small fluctuation state. The content of H2S in the experimental group was almost zero and lower than that in the control group. The addition of biochar in the reaction reduced the content of H2S to a certain extent and almost zero.

![Graph showing changes in H2S content with and without biochar addition](image)

**a. Changes of H2S content of swine manure**

![Graph showing changes in H2S content with and without biochar addition](image)

**b. Changes of H2S content of cow manure**
c. Changes of H\textsubscript{2}S content of chicken manure

Figure. 4 Changes of H\textsubscript{2}S content during the anaerobic fermentation of animal manure

In the chicken manure group, the content of hydrogen sulfide gradually decreased to zero in the first five days, then rose sharply to 11987 mg·L\textsuperscript{-1}, showing a trend of decreasing fluctuation; in the control group, the content of H\textsubscript{2}S was 0 mg·L\textsuperscript{-1} in the first 10 days, and then rose sharply to 4668 mg·L\textsuperscript{-1}, showing a fluctuation state. The content of H\textsubscript{2}S in the experimental group was always lower than that in the control group, and the biogas produced in the control group was particularly odorous, while the odor in the experimental group was much less odorous. It can be seen that the addition of biochar had a certain effect on the reduction of hydrogen sulfide content in high solid anaerobic fermentation of chicken manure, but its content was zero at first and then increased by a large fluctuation.

3.5. Effect of biochar addition on heavy metals content in biogas residue

After mixed fermentation of biochar and livestock and poultry manure, the content of heavy metals in residual biogas residue was determined. The results were shown in Table 2:

| Fermentation raw material     | Cu (mg·kg\textsuperscript{-1}) | Zinc (mg·kg\textsuperscript{-1}) | Cd (mg·kg\textsuperscript{-1}) | Pb (mg·kg\textsuperscript{-1}) |
|------------------------------|-------------------------------|---------------------------------|-------------------------------|-------------------------------|
| swine                        | 47.804                        | 134.953                         | 0.405                         | 9.547                         |
| Swine + biochar              | 31.487                        | 116.407                         | 0.385                         | 7.92                          |
| Cow manure                   | 433.045                       | 599.669                         | 0.414                         | 6.853                         |
| Cow manure + biochar         | 249.341                       | 360.998                         | 0.383                         | 5.169                         |
| Chicken manure               | 51.576                        | 307.363                         | 0.494                         | 9.204                         |
| Chicken manure + biochar     | 50.712                        | 294.84                          | 0.379                         | 7.325                         |

At present, the harmless standard for heavy metals in livestock and poultry manure composting is sludge application. The maximum limit values of total contents of copper, zinc, cadmium and lead are 250 mg·kg\textsuperscript{-1}, 500 mg·kg\textsuperscript{-1}, 10 mg·kg\textsuperscript{-1} and 100 mg·kg\textsuperscript{-1}, respectively. It can be seen in Table 4 that the contents of copper and zinc in bovine manure fermented separately exceed the standard, and the contents of copper exceed 73.2% and zinc exceed the standard by 20%. However, the contents of heavy metals in bovine manure fermented with biochar are within the standard range, and there is no phenomenon of exceeding the standard. It shows that biochar plays an adsorptive role in the anaerobic fermentation process, and plays an adsorptive role in the heavy metal content of biogas residue. The chemical properties of biochar are stable, and the heavy metals adsorbed are not easy to escape. Therefore, the
mixed fermentation of biochar and livestock and poultry manure provides an effective method for returning biogas residue to the field.

4. Conclusions
1) High-solid anaerobic fermentation of livestock and poultry manure started slowly, and the addition of biochar provided enough granular surface to absorb a large number of inoculated microorganisms, which shortened the start-up time, increased the biogas production rate of high-solid anaerobic fermentation of livestock and poultry manure, and advanced the peak period of biogas production; reduced the content of VFA, reduced the inhibition of methanogens, so the methane content increased.

2) The addition of biochar has a great influence on the production of H\textsubscript{2}S by high solid anaerobic fermentation of livestock and poultry manure. After mixed fermentation of biochar and pig manure, cow manure and chicken manure, the content of H\textsubscript{2}S decreased significantly, and the odor of fermentation broth was weak.

3) The addition of biochar reduces the content of heavy metals in biogas residue, which indicates that the addition of biochar can adsorb heavy metal pollutants in passive fermentation residues.

4) Comprehensive analysis of the anaerobic fermentation effect of livestock and poultry manure showed that the addition of biochar had the most obvious effect on anaerobic fermentation of cow manure and chicken manure with high solid content. biogas production rate increased significantly, methane content increased, H\textsubscript{2}S content decreased, and biogas and biogas residue were purified.

Acknowledgments
This work was financially supported by the Natural Science foundation of Liaoning Province.

Reference
[1] J.J.Wu, L.M.Geng, Analysis and Research on biomass energy utilization in Rural China, Chinese Forestry economy. (05) (2019) 70-72.
[2] Z.G.Liu, J.G.Zhu, B.Zhang, et.al, Effect of the ratio of faecal grass to dry anaerobic fermentation on biogas production , J. Journal of Agricultural Engineering.25(04) (2009) 196-200.
[3] P. Baltrėnas, D. Paliulis, V. Kolodynskij, The experimental study of biogas production when digesting chicken manure with a biochar additive, Greenhouse Gases: Science and Technology. 9(4) (2019).
[4] A. Lehtomäki, S. Huttunen, J.A. Rintala, Laboratory investigations on co-digestion of energy crops and crop residues with cow manure for methane production: Effect of crop to manure ratio, J. Resources, Conservation & Recycling, 51(3) (2006).
[5] L. Deng, Y. Li, Z. Chen, et.al, Separation of swine slurry into different concentration fractions and its influence on biogas fermentation, Applied Energy. 114 (2014).
[6] X.M.Liu, Discussion on methods for Monitoring and Analysis of Water and Wastewater, J. China Environmental Monitoring. (01) (1993) 63-64.
[7] Z. Suli, L. Qian, Y. Fengxia,et.al, How methane yield, crucial parameters and microbial communities respond to the stimulating effect of antibiotics during high solid anaerobic digestion, Bioresource Technol .283 (2019).