Experimental study on gas production optimization of pig manure and wheat straw under different pig manure levels

Yajun Chu\textsuperscript{1,2}, Shengyong Liu\textsuperscript{1,2*}, Hao Bai\textsuperscript{3}, Shuqing Zhang\textsuperscript{1,2}, Lei Peng\textsuperscript{1,2}, Dongdong Wei\textsuperscript{1,2}, Jie Lu\textsuperscript{1,2}, Libin Jie\textsuperscript{1,2}, Yibo Pan\textsuperscript{1,2}

\textsuperscript{1} Collaborative Innovation Center of Biomass Energy, Henan Agricultural University, Zhengzhou, Henan, 450002, China
\textsuperscript{2} Key Laboratory of New Materials and Facilities for Rural Renewable Energy, Henan Agricultural University, Zhengzhou, Henan, 450002, China
\textsuperscript{3} Zhengzhou Gewo Environmental Protection Development Co, Zhengzhou, Henan, 450002, China

* Corresponding author’s e-mail: liushy@vip.sina.com

Abstract. In order to explore the optimal ratio of pig manure and wheat straw mixed fermentation process, the experiment controlled the temperature of the fermentation control fermentation process to 35 °C, the total mass of the fermentation liquid was 700 g, and the total solid (TS) was 8%. The effect of pig manure content on fermentation. Based on the analysis of the gas production per unit of TS, when the pig manure content is 80%, the unit TS produced has the highest gas yield of 344 ml/g, which is 58.9% higher than that of pure wheat straw fermentation. Fermentation increased by 11.43%. In order to explore the best pig manure content in the fermentation process, regression analysis was performed on the gas production per unit of TS by origin. The result was that when the content of pig manure was 79%, the gas production was the highest, 336.3 ml/g, which was higher than that of wheat straw fermentation. 55.51%, 9.05% higher than pure pig manure fermentation. The methane content was used as the analysis result: when the pig manure content was 75%, the highest average methane content after start-up was 60.33%, which was 15.24% higher than that of wheat straw alone, and 3.4% higher than that of pig manure alone. Therefore, during the fermentation process of pig manure and wheat straw, when the content of pig manure is controlled at about 75%, the biogas production in the fermentation process and the methane content in the biogas can be effectively improved.

1. Introduction

According to the China Statistical Yearbook 2018, China's pig breeding has a net output of 702 million heads, and the annual planting area of wheat is 24,500,000 hectares\textsuperscript{[1]}. At present, livestock manure is mainly treated as organic fertilizer and returned to the field after simple treatment. The method of straw utilization mainly includes making fuel and crushing the field\textsuperscript{[2,3]}. When livestock manure is used as organic fertilizer, the stench or sewage generated is likely to have a serious impact on the living of the surrounding residents; when the shaped fuel is produced, the energy consumption is high, and the smoke after combustion also has an impact on the atmospheric gas production. The process of returning to the field is due to the slow decomposition of microorganisms in the ground, and the problem of pests after returning to the field is becoming more and more serious. Biogas
fermentation uses organic matter such as livestock and poultry manure, crop straw, and kitchen waste as fermentation raw materials. The raw materials are abundant, and the energy consumption of the fermentation process is low. The biogas is clean renewable energy, and the biogas residue is high-quality organic fertilizer. It is an effective way to integrate energy and environmental protection. However, the current efficiency of biogas fermentation is still not high, which restricts the large-scale promotion of biogas. Straw in crop straw is composed of lignocellulose and hemicellulose. The C/N of wheat is generally high, and the C/N of livestock manure is generally low, which is also not suitable for microorganisms in fermentation process requirements for C/N. Therefore, many domestic and foreign scholars have done a lot of research on biogas mixed fermentation.

Weiland[9] mixed fermentation of different raw materials, and the fermentation efficiency of the mixed raw materials was higher than that of the single raw materials. Jiang et al.[10] studied the best gas production when cow dung and corn stalks were 2:1. Parkin et al.[11] found that when the C/N ratio is between 20 and 30, the gas production effect is better, and the C/N control is at 25, and the gas production effect is the best. Lehtomäki et al.[12] used different straw and cow dung for mixed anaerobic fermentation. When the content of straw accounted for 30%, the yield per unit volume of methane increased by 16%-65% compared with the fermentation of cow manure alone. Wang et al.[13] in the continuous fermentation reactor at 55 °C, adding 1t pig manure and 4.6kg wheat straw for fermentation, the results showed that the methane content in the mixed fermentation was 10% higher than the methane content in the pig manure fermentation alone. Chen et al.[14] found in the study of pig manure and rice straw, adding pig manure to the straw can greatly increase the ammonia nitrogen content in the fermentation feed liquid, which is conducive to the smooth progress of fermentation. Liu et al.[15] studied the anaerobic fermentation effect of the ratio of manure to grass in dry fermentation at 35 °C. The peak gas production of fermented pig manure and rice straw mixed fermentation appeared 11 to 15 days earlier than the separate fermentation of manure and stalk. The peak gas production is also increased by 85~265ml.

The above experiments only analyze the gas produced in the mixed fermentation, and the research on the methane content in the mixed fermentation is less. In this experiment, pig manure and wheat straw were used as fermentation raw materials. Based on the unit gas production rate and methane content, polynomial fitting was used to explore the optimal ratio of pig manure and wheat straw in mixed fermentation, and provide data reference for biogas fermentation engineering operation.

2. Experimental materials and methods

2.1. Experimental materials and pretreatment

In the experiment, pig manure and wheat straw were used as fermentation raw materials, and the normal fermentation of the biogas slurry in the laboratory was used as an inoculum. The pig manure was taken from the Zhengzhou breeding farm in Henan Province. After collection, it was naturally air-dried and stored for use in the experimental process. The straw was from the third living experiment area of Henan Agricultural University. After the straw was collected, it was crushed to a length of 5-10 mm and added to the biogas slurry. The clear liquid is made to have a water content of about 70%, and is stacked, and the stacking process is stirred once a day until the surface of the straw grows white hyphae. The C/N, TS and VS contents of each raw material and inoculum before the experiment are as shown in Table 1.

| Raw material  | C/N     | TS (%) | VS (%) |
|--------------|---------|--------|--------|
| Pig manure   | 7.3152  | 86.38  | 70.04  |
| Wheat straw  | 35.264  | 29.30  | 79.97  |
| Inoculum     | 2.96    | 59.42  |        |

Table 1. The C/N, TS and VS contents of each raw material and inoculum.
2.2. Experimental device
The experimental device is composed of a thermostat device, a fermentation device and a gas collecting device. The thermostat is provided by a 250 L incubator in the laboratory. The fermentation device consists of a 1000 ml volumetric flask, the bottle mouth is sealed with a rubber stopper, a rubber stopper and a conduit; the gas collection device is collected by a drainage gas collection method. A conduit link is used between the fermentation unit and the gas collection unit, as shown in Figure 1.

2.3. Experimental design
The experiment used pig manure and wheat straw as fermentation raw materials. The experiment was divided into 8 groups, and each group was set up in two parallels. In the 8 groups of experiments, pig manure and wheat straw were used as raw materials for separate fermentation and pig manure and wheat straw were mixed and fermented according to pig manure content. The materials of each group were shown in Table 2. The test adopts a feeding method to add pig manure and wheat straw to the fermentation bottle according to a certain dry matter ratio, and 210 g of the inoculum is added to the fermenter, and the total mass of the fermentation liquid is 700 g with distilled water, and the total TS content is 8%. The pH value, gas production and corresponding methane content of the fermented feed liquid were measured regularly every day, and the average value was used as the result for analysis.

2.4. Test items and methods
The total solids and volatile solids were determined by drying and burning. The nitrogen (N) and carbon (C) contents were determined using a C-N elemental analysis (vario EL cube). pH was measured using a pH meter (PHS-3E). Gas yields were measured using drainage gas gathering method. Methane content was measured by gas chromatography (Agilent 6820) equipped with a FID detector.
and a carbosieve S II packed column. Nitrogen as carrier gas and the carrier gas, The temperature of carrier gas, column and the detector were adopted 60℃,80℃ and 150℃ respectively.

3. Results and analysis

3.1. Changes in methane content of each group during fermentation

The variation trend of methane content in each group during fermentation was as shown in Figure 2. During the first five days of fermentation, the methane content of each group increased rapidly, reaching about 40%, and then the rate of increase of methane content slowed down, about 15 days after fermentation. During the fermentation process, the peak gas production of each group and the average methane content of the whole process and the methane content after startup are shown in Table 3. When the pig manure content is lower than 66%, the peak value of methane in each group increases with the increase of pig manure content. When the pig manure content is above 66%, the peak value of methane in each group is basically stable at about 70%. The peak value of methane in pure straw fermentation was 58.2%, and the peak value of methane in pure pig manure fermentation was 74.08%. The average methane content after start-up (A methane content of 50% is considered to be activated), when the pig manure content is less than 50%, the average methane content increases with the increase of pig manure. When the pig manure content is above 50%, the methane content of each group after start-up is around 59%. Which is the highest when the pig manure content is 75%, which is 60.33%, 15.24% higher than the pure wheat straw fermentation (52.35%), and 3.4% higher than the pig manure (58.34%). It shows that the mixed fermentation of pig manure and wheat straw in a certain ratio can increase the methane content of fermentation.

Table 3. Peak methane content, average methane content, and average methane content after start-up.

| Groups | Peak methane content (%) | Average methane content (%) | Average methane content after start-up (%) |
|--------|--------------------------|-----------------------------|-------------------------------------------|
| R1     | 58.20                    | 50.21                       | 52.35                                     |
| R2     | 61.02                    | 50.50                       | 54.81                                     |
| R3     | 62.73                    | 52.22                       | 55.93                                     |
| R4     | 63.03                    | 53.71                       | 57.26                                     |
| R5     | 69.25                    | 53.77                       | 58.19                                     |
| R6     | 70.62                    | 55.70                       | 60.33                                     |
| R7     | 69.81                    | 55.76                       | 59.94                                     |
| R8     | 74.08                    | 54.52                       | 58.34                                     |

Figure 2. Trend of methane content in each group during fermentation.
3.2. Changes in gas production of each group during fermentation

3.2.1. Trends in daily production rate of each group. The gas production rate is the most direct manifestation of fermentation. The higher the gas production rate, the shorter the fermentation cycle and the higher the fermentation efficiency. Figure 3 shows the trend of daily gas production rate during the fermentation process. During the whole fermentation process, there are two distinct gas production peaks in the daily gas production rate of each group. But there are some differences in the peak of gas production in different groups. The peak of gas production in each group appeared for the first time on the 3rd to 7th day of fermentation, and the second time on the 12th to 18th day of fermentation. The R1 group is pure straw fermentation, the maximum gas production rate is 800 ml/d, the pig manure content in the R2 and R3 groups is less than 50%, and the peak value is relatively low, 825 ml/d and 1050 ml/d, respectively, and the peak appears relatively late. The pig manure content in the R4, R5, R6 and R7 groups is between 50% and 80%, and the maximum gas production rate is relatively high, respectively 1580 ml/d, 1350 ml/d, 1500 ml/d, 1395 ml/d, the peak appeared relatively early, on the sixth and seventh days of fermentation. R8 is pure pig manure fermentation, the maximum gas production rate is 1470 ml/d. The peak gas production and time of each group are shown in Table 4. Table 4 shows that when the pig manure content is less than 50%, the gas production peak is lower, and the peak appears later. When the pig manure content is above 50%, the gas production peak is relatively high, and the occurrence time is earlier. It is indicated that an appropriate increase in pig manure content can increase the peak gas production and the peak time.

![Figure 3](image-url)  
Figure 3. Trend of daily gas production rate during fermentation in each group.

| Groups | First peak (ml) | First peak time (d) | Second peak (ml) | Second time (d) |
|--------|----------------|-------------------|-----------------|----------------|
| R1     | 740            | 5                 | 800             | 12             |
| R2     | 415            | 3                 | 825             | 13             |
| R3     | 900            | 7                 | 1050            | 14             |
| R4     | 1585           | 6                 | 1125            | 13             |
| R5     | 1350           | 6                 | 1280            | 15             |
| R6     | 1500           | 7                 | 1400            | 15             |
| R7     | 1395           | 6                 | 890             | 18             |
| R8     | 1470           | 6                 | 1150            | 15             |

3.2.2. Trends in cumulative gas production and trends in unit TS. Figure 4 and Figure 5 shows the trend of cumulative gas production during fermentation and the gas production per unit TS of each group. In the first five days of fermentation, the cumulative gas production of each group began to rise rapidly. After, the cumulative gas production trend between different groups changed significantly.
The cumulative gas production of R1, R2 and R3 is relatively slow, and the rate of R5, R6 and R7 rising is relatively fast. After 18 days, the gas production rate decreased, and the cumulative gas production rate of each group gradually slowed down until the end of fermentation. During the whole fermentation process, the final cumulative gas production of R5, R6 and R7 is relatively high, and R1 is the lowest.

The total gas production of pure wheat straw (R1) fermentation process is 12110 ml, the gas production per unit TS is 216ml/g; the total gas production of pure pig manure (R8) fermentation is 17270 ml, and the gas production per unit TS is 308ml/g. During the mixed fermentation of pig manure and wheat straw, the total gas production of each group increased with the increase of pig manure content. When the pig manure content was 80%, the total gas production was the highest, being 19245 ml, and the corresponding unit TS gas production was 344ml /g, the total gas production by pure wheat straw fermentation increased by 58.9%, which was 11.43% higher than the total gas production of pig manure alone. It indicates that increasing the content of pig manure during mixed fermentation can increase the cumulative gas production of mixed fermentation of pig manure and wheat straw.

![Graph](image1.png)

**Figure 4. Trend of cumulative gas production in each group during fermentation.**

![Graph](image2.png)

**Figure 5. Unit TS gas production of each groups.**

**3.2.3. Polynomial fitting of unit TS gas production.** In order to obtain the optimal ratio of the fermentation process of pig manure and wheat straw more accurately, the final unit gas production of the fermentation was analyzed by regression analysis. Figure 7 and Figure 8 show the quadratic polynomial fitting and cubic polynomial fitting of the unit TS gas production. The closer \( R^2 \) is to 1 during the polynomial fitting process, the higher the degree of fit.

The fitting results are shown in Table 5, where X is the pig manure content and Y is the total gas production. Table 5 shows that the \( R^2 \) of the quadratic polynomial fitting model is 0.91. When the content of pig manure is 87%, the highest unit TS gas production rate is 326.69ml/g; the \( R^2 \) of the cubic polynomial fitting model is 0.9938, the whole model had the largest unit TS gas production rate of 336.3 ml/g when the pig manure content was 79%. Compared with the quadratic fitting, the \( R^2 \) of the cubic term fit is closer to 1, resulting in higher reliability.

| Polynomial fitting | Fitting equation | \( R^2 \)  | \( R_{adj}^2 \) | \( Y_{max} \) | X   |
|--------------------|-----------------|----------|----------------|-------------|-----|
| Binomial fit       | \( Y=204.92+278.58X-159.32X^2 \) | 0.9193   | 0.887          | 326.69      | 0.87|
| Trinomial fit      | \( Y=216.73+45.98X+457.75X^2-410.61X^3 \) | 0.9938   | 0.9895         | 336.3       | 0.79|
4. Conclusions

(1) Mixed raw material fermentation can improve gas production efficiency. Mixed fermentation process, the unit TS gas production rate of each group increased as the pig manure content in the fermentation material increased. When the pig manure content is 25%, the unit TS gas production rate is 250.94 ml/g, which is 16.04% higher than the wheat straw fermentation alone, 18.62% lower than the pig manure fermentation alone; the mixed fermentation efficiency is the highest when the pig manure content is 80%, it is 343.66 ml/g, which is 58.92% higher than the straw alone, and 11.44% higher than the pig manure alone. When the pig manure content is less than 50%, the peak appears first, but the peak value is also low. When the pig manure content is higher than 50%, the peak height does not differ significantly from the time of occurrence. Therefore, an appropriate increase in pig manure content can effectively increase the amount of gas produced by fermentation and the peak time of gas production.

(2) Fermentation of mixed raw materials can increase the methane content in the gas. When the pig manure content is less than 50%, the increase of pig manure content during the mixed fermentation process can increase the methane content in the fermentation process. When the pig manure content is higher than 50%, the methane content is relatively high, there is no significant difference. When the pig manure content is 75% after start-up, the average methane content is highest, which is 60.33%, and which is 15.24% higher than that of wheat straw is alone, and 3.4% higher than that of pig manure alone.

(3) The best ratio of mixed raw materials. Binomial and trinomial fittings were performed on the unit TS gas production rate of each group using the original 8.0 software. The R² of the three terms is 0.9193, and the R² of the three-phase is 0.9938. The trinomial fit is better than the binomial fit. As a result of the trinomial fitting, when the content of pig manure was 79%, the fermentation had the best gas production rate of 336.3 ml/g, which were 55.51% higher than that of wheat straw fermentation and 9.05% higher than that of pig manure fermentation.

Acknowledgement
Thanks to the tutor for their assistance in the experimental process. And financial support from the key technology research project of biomass mixed anaerobic fermentation (No. 2018015); Henan Science and Technology Open Cooperation Project (182106000012)

Reference
[1] National Bureau of Statics. (2018) China Statistical Yearbook[R], Beijing: China Statistics Press
[2] Tian S F, Luo W G, Jing Y Y, et al. (2008) Combustion process and kinetic sanalysis of cornstalk[J]. Acta Energiae Solaris Sinica, 29(12): 1570-1572.
[3] Tian X Y, Hou Z D, Xu Y. (2011) Microstructure of corn stover briquette[J]. Transactions of the Chinese Society for Agricultural Machinery, 42(3): 105-108
[4] Lei Z F, Chen J Y, Zhang Z Y. (2010) Methane production from rice straw with acclimated
anaerobic sludge: Effect of phosphate supplementation[J]. Bioresource Technology, 101(12): 4343-4348.

[5]  Ai P, Zhang Y L, Sheng K, et al. (2010) Pretreatment for biogas production by anaerobic fermentation of rice straw[J]. Transactions of the Chinese Society of Agricultural Engineering, 26(7): 266-271.

[6]  Zhu H, Hu Q C, Tang X Y, et al. (2017) Current Development and Progress of Fuelization of Agricultural Straw in China[J]. China Biogas, 35(02): 115-120.

[7]  Zhang W, Li X J, Pang Y Z, et al. (2008) A pilot study on mesospheric dry anaerobic digestion of rice straw[J]. Journal of Agro-Environment Science, 5:2075-2079.

[8]  Ning G X, Shen H, Wen Y B, et al. (2009) Experimental study on anaerobic digestion of straw[J]. Journal Of Agro-Environment Science, 28(6): 1279-1283..

[9]  Weiland P. (2000) Anaerobic waste digestion in Germany–Status and recent developments[J]. Biodegradation, 11(6): 415-421.

[10]  Jiang Z S, Ping J P, Guo Y K, et al. (2016) Effect of different ratios of cow manure and corn straw on the mixed anaerobic fermentation rate[J]. Journal of Hebei University of Science and Technology, 37(04): 396-405..

[11]  Parkin G F, Owen W F. (1986) Fundamentals of anaerobic digestion of wastewater sludges[J]. Journal of Environmental Engineering, 112(5): 867-920.

[12]  Lehtomäki A, Huttunen S, Rintala J A. (2007) 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 and Recycling, 51(3): 591-609.

[13]  Wang G, Gavala H N, Skiadas I V, et al. (2009) Wet explosion of wheat straw and codigestion with swine manure: effect on the methane productivity[J]. Waste Management, 29(11): 2830-2835.

[14]  Chen G Y, Zheng Z, Zou X X, et al. (2009) Anaerobic Co-digestion of Rice Straw and Swine Feces[J]. Journal of Agro-Environment Science, 28(01):185-188.

[15]  Liu Z, Zhu H G, Wang B, et al. (2009) Effect of ratios of manure to crop on dry anaerobic digestion for biogas production[J]. Transactions of the Chinese Society of Agricultural Engineering, 25(4): 196-200.