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Effects of Thermodynamically Regulated Modified Biochar on Energy Conversion Efficiency in Anaerobic Digestion of Agricultural Waste

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ABSTRACT

The efficient treatment and resource utilization of agricultural waste have long been research hotspots in environmental protection and renewable energy. Anaerobic digestion (AD), as a well-established waste treatment technology, converts organic waste into renewable energy such as methane through microbial metabolism. However, the energy conversion efficiency of AD is influenced by multiple factors, among which temperature plays a critical role in regulating microbial activity, ammonia nitrogen (AN) accumulation, and volatile fatty acids (VFAs) production efficiency. In recent years, modified biochar has been increasingly applied to enhance AD efficiency due to its excellent adsorption properties and its role in providing a favorable microbial habitat. However, existing studies lack a systematic analysis of the effects of temperature on energy conversion efficiency in AD of agricultural waste, as well as the specific mechanisms by which modified biochar functions under different temperature conditions. This study aims to explore thermodynamic regulation strategies and investigate the role of modified biochar in the AD of agricultural waste, such as sludge and corn straw. The study focuses on analyzing the impact of different temperature conditions on energy conversion efficiency, examining the regulatory effects of temperature on AN and VFAs transformations, and further enhancing energy conversion efficiency through the introduction of modified biochar. A series of temperature-gradient experiments and biochar modification techniques are designed to provide theoretical insights and experimental support for improving energy conversion efficiency in AD of agricultural waste.

1. INTRODUCTION

With the growth of the global population and the expansion of agricultural production, the amount of agricultural waste generated has been increasing annually [1, 2]. How to efficiently treat and utilize this waste has become an important topic in environmental science and energy research [3]. Agricultural waste, especially sludge and corn straw, is typically rich in organic matter [4] and has high biodegradability [5], making it possible to be converted into renewable energy through AD technology [6], such as methane and other biogases. However, the energy conversion efficiency of AD of agricultural waste is influenced by multiple factors, among which temperature serves as a key regulatory factor in the AD process [7, 8], playing an important role in microbial activity, AN accumulation, and VFAs production. Therefore, optimizing temperature control conditions to improve the energy conversion efficiency of AD of agricultural waste has become one of the research hotspots.

Research on the energy conversion efficiency of AD of agricultural waste has made some progress in recent years. Reference [9] suggests that the introduction of modified biochar can play a positive role in improving organic matter degradation efficiency, reducing nitrogen accumulation, and increasing gas production. Modified biochar can not only adsorb and slowly release AN but also enhance microbial activity in the AD process by providing a stable microbial habitat [10]. Reference [11] states that proper temperature control can optimize microbial metabolism in AD, thereby improving methane production efficiency and organic matter degradation efficiency. However, most existing studies still lack systematic thermal regulation strategies [12-15], and there is still a lack of in-depth discussion on how modified biochar affects the energy conversion efficiency of agricultural waste under different temperature conditions.

Although existing studies have shown that temperature has a significant impact on the AD process and that modified biochar has potential in improving energy conversion efficiency, most current research focuses on the exploration of single factors [16], lacking a comprehensive analysis of the effects of temperature variation on the AD efficiency of agricultural waste. In particular, research remains insufficient regarding the mechanism of modified biochar, microbial metabolism changes under different temperature conditions, and the transformation details of AN and VFAs [17-19]. Additionally, issues such as temperature gradient optimization and the influence of temperature control on different types of agricultural waste have not been fully addressed [20, 21]. Therefore, the existing methods in the literature have certain limitations, and there is an urgent need for a more systematic and refined thermodynamic regulation strategy to further improve the energy conversion efficiency of AD of agricultural waste.

This study aims to explore in depth the effects of thermodynamically regulated modified biochar on the energy conversion efficiency of AD of agricultural waste. The research mainly includes two aspects: first, the effect of temperature on the energy conversion efficiency of AD of agricultural waste, focusing on the regulatory effect of modified biochar on the transformation efficiency of AN and VFAs under different temperature conditions; second, the specific design of experimental materials and methods, including sample selection, experimental setup, and optimization of analytical methods. Through this study, the aim is to provide a thermodynamically regulated modified biochar application strategy, offering new theoretical support and practical guidance for improving the energy conversion efficiency of AD of agricultural waste.

2. INFLUENCE OF TEMPERATURE ON THE ENERGY CONVERSION EFFICIENCY OF AD OF AGRICULTURAL WASTE

2.1 Thermodynamic regulation-oriented thermal power calculation

The study of thermodynamic regulation is crucial in the AD process because the reaction temperature directly affects the activity of AD microbial communities, and different agricultural wastes, such as sludge and corn straw, exhibit significant differences in thermal response characteristics. To better understand the energy conversion behavior of these agricultural wastes under different thermal environments, the study first needs to perform thermal power calculations to determine the thermal energy demand and thermal balance of each type of waste at different temperatures. This calculation is based on a thermostatic device with different temperature water baths, i.e., by determining through simulation and experimentation the thermal power input required for the waste at each temperature interval, thereby analyzing its conversion efficiency.

According to the experimental requirements, the temperature range of the thermostatic device is set. For example, the commonly used AD temperature is usually set between 30℃ and 55℃. Within this range, microbial activity and the decomposition rate of organic matter are relatively optimal. Then, based on the thermodynamic properties and heat conduction efficiency of the thermostatic device, the required thermal power input is calculated. The formula for thermal power calculation is:

$$P = m \cdot C \cdot \Delta T \tag{1}$$

where, P is the required thermal power, m is the mass of the liquid to be heated, C is the specific heat capacity of the liquid, and ΔT is the required temperature rise. According to different temperature settings, the input power is adjusted to maintain a stable system temperature.

Under different experimental conditions, the key to thermal power calculation lies in temperature differences and heat loss during the heating process. Typically, the thermostatic device needs to compensate for heat losses, such as heat exchange with the environment and heat conduction through the container walls. Therefore, in the calculation process, the influence of thermal efficiency and heat loss must be considered. For this purpose, heat power compensation is often employed in experiments, ensuring precise regulation of the thermostatic device through a feedback control system. For example, if an input power of X is required at 30℃, increasing to 40℃ requires more power to maintain the temperature. Considering heat loss compensation, an additional 20% power input is needed.

The input of thermal power directly affects the AD process of agricultural waste. Under thermodynamic regulation, an appropriate temperature can significantly promote microbial activity and the AD rate. Therefore, reasonable thermal power calculation ensures that no temperature fluctuations occur during the experiment, thereby optimizing the energy conversion process. Specifically, as the temperature increases, the organic matter in sludge and corn straw decomposes more rapidly, releasing more gaseous products and improving energy conversion efficiency. Through precise thermal power input, researchers can simulate and optimize these processes to ensure conversion efficiency.

In thermal power calculation, in addition to temperature, mass, and specific heat capacity, another important parameter is thermal conductivity. Different substances have different thermal conductivity properties, which affect heat distribution within the system. For the digestion reactions of these wastes, thermal power input must be adjusted according to their specific physical properties. Additionally, factors such as heating time, the insulation properties of the reactor, and the circulation effect of the heat transfer fluid must be considered, as these factors collectively influence the actual thermal power demand.

2.2 Influence of Temperature ON AN and VFAs distribution

2.2.1 Influence of temperature on AN and VFAs concentration and uniformity distribution

At higher temperatures, the metabolic rate of microorganisms is usually higher, which can accelerate the degradation process of agricultural waste, especially organic matter in sludge and corn straw. At this time, as the decomposition of organic matter accelerates, the concentration of AN and VFAs usually increases. However, if the temperature is too high, especially exceeding 50℃, the activity of some anaerobic microorganisms decreases, leading to uneven distribution of AN and VFAs in the reactor. This uneven distribution negatively affects the energy conversion efficiency because, in certain areas, microbial activity is inhibited due to unsuitable temperatures, thereby affecting product generation. To better understand the influence of temperature on concentration and uniformity distribution, the addition of modified biochar can, to some extent, alleviate the impact of temperature on system uniformity. Due to its high specific surface area and excellent adsorption capacity, modified biochar can help distribute AN and VFAs more evenly, reducing situations where the local concentration is too high or too low. Assuming the number of grid sections in the cross-section is represented by v, the parameter value at grid node u is represented by Z_u, and the average value of the parameters at the nodes is represented by $\bar{Z}$, the uniformity coefficient is defined as:

$$\varepsilon = 1 - \frac{1}{2v} \sum_{u=1}^{v} \frac{\sqrt{Z_u - \bar{Z}_u}}{\bar{Z}} \tag{2}$$

2.2.2 Influence of low temperature on AN and VFAs distribution

The impact of low temperature on the AD process of agricultural waste is generally manifested in a significant reduction in reaction rate, particularly in the decomposition of complex organic matter such as sludge and corn straw. Under low-temperature conditions, the activity of AD microorganisms significantly declines, slowing down the generation rate of AN and VFAs, which in turn affects their concentration and distribution. At lower temperatures, the ability of microorganisms in the AD system to convert AN and VFAs decreases, leading to the accumulation of AN in the reactor. This results in a high concentration of nitrogen sources, posing potential environmental pollution risks. Studies have shown that modified biochar can adsorb and slowly release AN, thereby preventing excessive nitrogen accumulation at low temperatures and reducing environmental pollution. Additionally, the surface structure and pore structure of modified biochar can provide more microbial habitats, ensuring stable growth conditions for microorganisms in low-temperature environments, which helps improve the generation rate and uniform distribution of VFAs.

2.3 Influence of temperature on AN and VFAs conversion efficiency

2.3.1 Influence of temperature on AN conversion efficiency

AN is one of the primary nitrogen sources produced during the AD of agricultural waste. The conversion efficiency of AN is directly related to the nitrogen removal efficiency during AD and the environmental impact of the reaction system. Temperature significantly influences AN conversion efficiency in the following aspects.

Under higher temperature conditions, the metabolic rate of anaerobic microorganisms increases, facilitating the decomposition of organic matter and the conversion of nitrogen sources. Specifically, under mesophilic AD conditions around 50°C, nitrogen conversion efficiency is generally better. However, when the temperature exceeds 55°C, the activity of some anaerobic microorganisms is inhibited, leading to a decline in the conversion efficiency of AN. At this point, excessive AN accumulates in the reactor, increasing nitrogen concentration, which affects the overall stability and efficiency of the system. Under low-temperature conditions, the decrease in temperature typically slows the activity of anaerobic microorganisms, particularly those involved in AN conversion, thereby affecting the removal efficiency of AN. At low temperatures, the conversion rate of AN significantly declines, resulting in nitrogen accumulation during AD. The addition of modified biochar can help alleviate this issue to some extent. Modified biochar, with its large specific surface area and adsorption capacity, can effectively adsorb and slowly release AN, preventing its accumulation under low-temperature conditions and thereby improving AN conversion efficiency.

2.3.2 Influence of temperature on VFAs conversion efficiency

VFAs are important intermediate products in the AD of agricultural waste, particularly formic acid, acetic acid, and propionic acid. These compounds not only serve as critical carriers for energy conversion but also undergo subsequent gas production processes to be converted into methane and other usable energy sources. Temperature significantly influences VFAs conversion efficiency, and the generation and conversion rate of VFAs exhibit different dynamic changes under different temperature ranges.

At higher temperatures, the AD reaction rate accelerates, and the metabolic rate of microorganisms increases, leading to a faster generation rate of VFAs. In the temperature range of 30–50°C, VFAs conversion efficiency is generally high because, at this stage, the microbial community exhibits the highest activity, efficiently decomposing organic matter in agricultural waste to produce more VFAs. Particularly for corn straw, which has a high cellulose content, high-temperature conditions can effectively promote the degradation of cellulose and hemicellulose, generating more VFAs and improving energy conversion efficiency. However, when the temperature is excessively high, especially exceeding 55°C, the increased temperature inhibits the activity of certain microbial groups, particularly those involved in VFAs generation. This inhibition results in lower VFAs conversion efficiency. Although the initial decomposition rate of organic matter may be fast, microbial metabolism is suppressed, leading to the accumulation of VFAs. The accumulated VFAs may further be converted into harmful substances, reducing the overall efficiency of the AD process.

Low-temperature conditions also inhibit VFAs conversion efficiency. Under low temperatures, the metabolic rate of microorganisms significantly decreases, leading to a slower generation rate of VFAs. When the temperature is below 25°C, AD efficiency is notably low, and the generation rate of VFAs significantly declines, sometimes resulting in incomplete VFAs conversion. At this stage, adding modified biochar can effectively enhance VFAs conversion efficiency. Modified biochar provides a more stable microbial habitat, enhancing microbial metabolic activity. Particularly under low-temperature conditions, it helps accelerate the generation and conversion of VFAs, thereby improving energy conversion efficiency.

Specifically, assuming that the conversion efficiency of AN and VFAs in the system is represented by λ_u, the initial concentration of AN and VFAs in the AD process is represented by $Z(u)_B$, and the final concentration of AN and VFAs in the AD process is represented by $Z(u)_A$, the calculation formula for AN and VFAs conversion efficiency is as follows:

$$\lambda_u = \frac{Z(u)_B - Z(u)_A}{Z(u)_B} \times 100\% \tag{3}$$

2.4 Thermal regulation strategies for AD energy conversion efficiency

This paper proposes specific thermal regulation strategies from three aspects: temperature control, modified biochar property regulation, and temperature gradient optimization to improve the conversion efficiency of AN and VFAs in the AD process of agricultural waste.

2.4.1 Temperature control strategy: Fine temperature regulation to optimize microbial metabolism

The degradation process of agricultural waste can be regulated through staged temperature changes. In the initial stage, a lower temperature can be used to promote AN conversion and slow decomposition of organic matter in AD, preventing the accumulation of ammonium nitrogen under excessively high temperatures. At this stage, modified biochar can adsorb and slowly release ammonium nitrogen, preventing excessive accumulation and improving nitrogen conversion efficiency. Subsequently, in the mid-reaction stage, the temperature is gradually increased to 40–50℃ to activate more microbial communities, enhancing the generation rate and efficiency of VFAs. Particularly for high-cellulose-content waste such as corn straw, high-temperature conditions can effectively promote cellulose degradation, thereby improving VFAs conversion efficiency. Finally, in the late stage of AD, the temperature is controlled at around 50℃ to maintain efficient methane production and complete organic matter degradation.

2.4.2 Modified biochar property regulation: Enhancing thermal regulation effect through surface modification

The surface properties and pore structure of modified biochar are crucial to its role in temperature regulation. To optimize the thermal regulation effect of modified biochar, chemical or physical modifications can be applied to its surface to increase its specific surface area and porosity. This not only helps adsorb more ammonium nitrogen but also improves its adaptability to temperature changes. For example, by acidification, nitridation, or other modification methods, the biochar surface can acquire a stronger negative charge, enhancing its adsorption capacity for ammonium nitrogen, especially at higher temperatures, to prevent AN accumulation and promote its stable conversion. At the same time, the pore structure of modified biochar can provide more microbial habitats, increasing microbial activity under different temperature conditions and enhancing VFAs production.

2.4.3 Temperature gradient optimization: Optimizing reaction efficiency through temperature gradient in the reactor

In an AD reactor, temperature distribution often presents a gradient, especially in larger reactors, where temperature differences lead to uneven microbial activity, thereby affecting AN and VFAs conversion efficiency. To fully utilize this gradient effect, different temperature zones can be designed inside the reactor. Based on the degradation characteristics of agricultural waste, the temperature gradient can be matched with the optimal temperature range for microbial metabolism. Multiple temperature control zones can be set up within the reactor, using different temperature ranges to promote AN removal and VFAs generation separately. For agricultural waste with high fiber content, such as corn straw, the higher temperature regions can promote cellulose degradation and increase VFAs conversion efficiency. Meanwhile, for nitrogen-rich sludge, lower temperature regions help prevent excessive accumulation and retention of AN, improving nitrogen conversion efficiency.

3. EXPERIMENTAL MATERIALS AND METHODS

3.1 Experimental materials

The sludge was collected from a livestock farm in Baoding City, Hebei Province, and sealed in a refrigerator at 4℃ for storage. The corn straw was collected from a cornfield in a village in Baoding City. After being air-dried outdoors, the collected corn straw was crushed to 2–3 mm using a grinder and stored in sealed bags for later use. The inoculated biogas slurry was obtained from a biogas digester in the same village, which had been running stably for a long time with good gas production. After collection, 10 g/L of fresh sludge was added daily, and it was acclimated at (35±1)℃ for 7 days before being used as inoculum. The physicochemical properties of the digestive substrates are shown in Table 1.

Table 1. Digestive substrate characteristics

Characteristic Parameters	Sludge	Corn Straw
Total solid content TS/%	12.52	83.7
Volatile solid content VS/%	6.76	78.4
Total organic carbon TOC/%	32.28	46.46
Total nitrogen *TN*/%	6.4	0.57
Carbon to nitrogen ratio *C/N*	5.04	84.51

3.2 Experimental design and device

In this experiment, sludge and corn straw were selected as AD substrates. According to the determined substrate properties, a 1 L wide-mouth bottle was used as the reaction vessel. The AD system was set with a volume of 700 mL, and the total solid concentration of the digestive substrate was 8%. Digestate with a mass of 30% of the total digestive liquid mass was introduced as the inoculum. Anaerobic co-digestion of sludge and corn straw was carried out under mesophilic conditions (35±1)℃. The sludge and corn straw were mixed in a 3:1 ratio (based on TS), with a total solid addition of 56 g. The concentration of biochar additive was set at 0 g/L (0 g), 5 g/L (3.5 g), 10 g/L (7.0 g), and 15 g/L (10.5 g), with three replicates for each group. The AD cycle was set to 30 days, and the daily biogas production was measured at the same time each day. The temperature of the constant-temperature water bath was adjusted, and sampling was conducted every three days starting from the first day of digestion to measure the pH, AN, and VFAs content in the digestion system. The experimental setup is illustrated in Figure 1.

3.3 Preparation of biochar material

Preparation method of pyrolytic biochar (BC): The treated corn cobs were placed in a muffle furnace with a heating rate of 10℃/min and calcined at 500℃ for 2 hours. After cooling to room temperature, the biochar was taken out, repeatedly filtered and washed with deionized water, then dried at 105℃, ground, and passed through a 60-mesh sieve before being stored in a sealed bag for later use.

Preparation method of acid-modified biochar (SBC): A 1 mol/L H_2SO_4 solution was mixed with BC at a ratio of 5 mL:1, and shaken in a constant temperature shaker at 35℃ and 120 r/min for 4 hours. It was then repeatedly filtered and washed with deionized water until the filtrate was neutral, dried in an oven at 105℃ to a constant weight, taken out, and stored in a sealed container for later use.

Preparation method of alkali-modified biochar (HBC): A 1 mol/L NaOH solution was mixed with BC at a ratio of 5 mL:1, and shaken in a constant temperature shaker at 35℃ and 120 r/min for 4 hours. It was then repeatedly filtered and washed with deionized water until the filtrate was neutral, dried in an oven at 105℃ to a constant weight, taken out, and stored in a sealed container for later use.

3.4 Measurement indicators and analysis methods

3.4.1 Physicochemical property analysis

pH value: Sartorius pH meter (PB-10, Sartorius, Germany);

AN measurement: Nessler reagent spectrophotometry

(HJ535-2009);

VFAs measurement: Ultraviolet-visible spectrophotometry.

3.4.2 Data analysis

Origin 2021 was used for graph plotting.

Canoco 5 was used for principal component analysis (PCA) of biogas production and environmental factors during the digestion process.

The Gompertz modified equation was used to simulate the biogas production performance of the AD process and predict the maximum biogas production potential (*Pmax*), maximum daily methane production (*Rmax*), and lag phase (λ) of each experimental group.

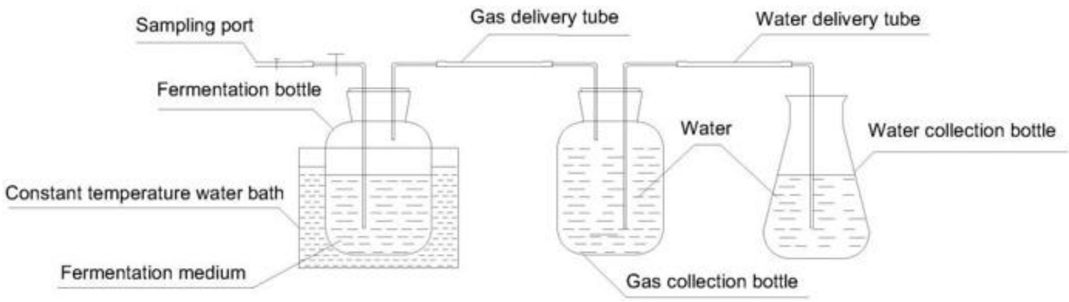


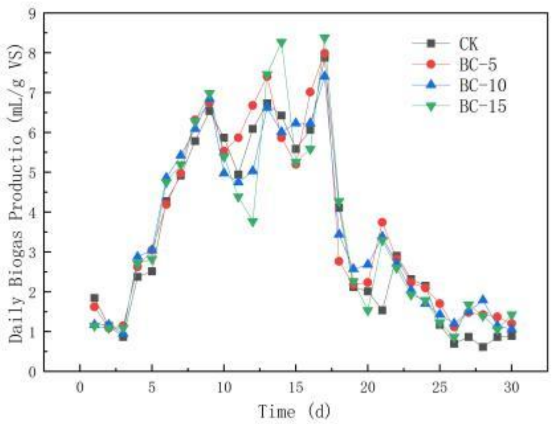
Figure 1. Installation drawing

4. RESULTS AND DISCUSSION

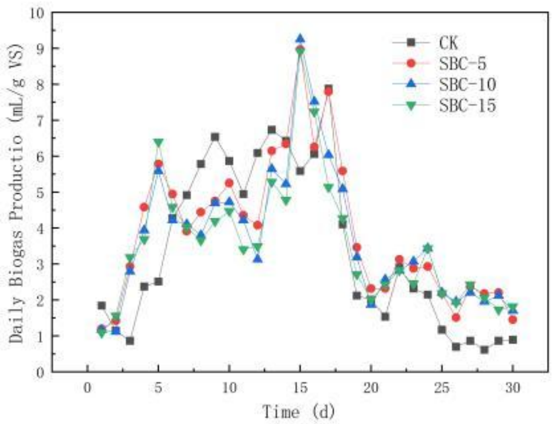
4.1 Analysis of the effect of biochar on biogas production performance in sludge-corn stalk AD under different temperature conditions

4.1.1 Characteristics of daily biogas production in AD

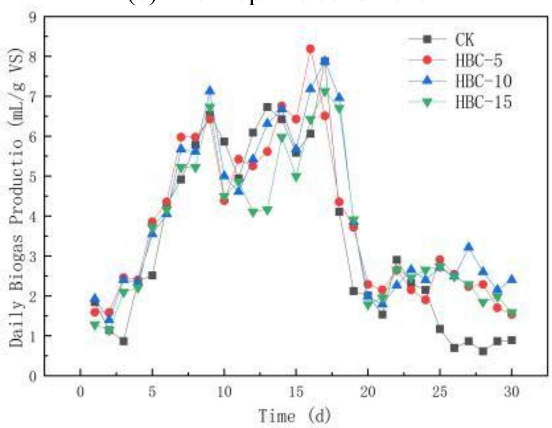
The effect of biochar on the daily biogas production of sludge-corn stalk AD under different temperature conditions is shown in Figure 2. The gas production trends of all experimental groups were generally consistent. Under normal temperature conditions, the promotion effect of biochar on daily biogas production was more significant. In the early stage of the experiment, all groups, along with the blank control (CK) group, showed a stable increase. In the middle stage, the production fluctuated dynamically due to the methanogenesis phase being dominant, which was caused by the differences in degradation of various components and adaptation of microbial communities in the digestion system. In the experimental groups with BC addition, the BC-5 group exhibited the smallest peak fluctuation, indicating that an appropriate amount of biochar could stabilize the AD system and improve digestion efficiency. The BC-15 group had the highest peak gas production and the lowest low peak value, reaching 8.2703 mL/g VS and 0.8661 mL/g VS, respectively, showing significant fluctuations in gas production and indicating instability in the digestion system.



(a) Mesophilic conditions



(b) Thermophilic conditions



(c) Psychrophilic conditions

Figure 2. Effect of biochar on daily biogas production in sludge-corn stalk AD

In the experimental groups with SBC addition, the first gas production peak appeared on the 5th day, four days earlier than the CK group, indicating that the appropriate addition of SBC could accelerate the startup of the sludge AD system. The maximum gas production peaks in the SBC-5, SBC-10, and SBC-15 groups were all higher than those in the CK group. In the experimental groups with HBC addition, the daily biogas production was significantly higher than in the BC and SBC groups. The variation trends among different groups were similar with smaller fluctuations, indicating that an appropriate amount of HBC addition could make the digestion system more stable and thus improve the efficiency of AD.

Under high-temperature conditions, the increased temperature accelerated the metabolic rate of microorganisms but also inhibited or even eliminated the activity of certain anaerobic microorganisms, making the impact of high temperature on AD more complex. The effect of biochar was enhanced under high-temperature conditions, especially in the HBC-added groups. Due to its larger specific surface area and superior adsorption performance, HBC effectively stabilized the AD system under high temperatures, mitigating the negative effects of excessive heat. The addition of SBC and BC helped regulate the temperature adaptability of the AD system, reducing system instability and improving daily biogas production under high-temperature conditions. Under low-temperature conditions, the significantly reduced activity of anaerobic microorganisms led to the suppression of the AD process and a slowdown in gas production rates. In this case, biochar addition exhibited a strong promoting effect, particularly SBC, which could facilitate the early initiation of the AD process and accelerate organic matter degradation in low-temperature environments. The gas production peaks in the SBC-5 and SBC-10 groups were higher than those in the CK group, indicating that biochar could effectively improve microbial adaptability and accelerate the reaction process under low-temperature conditions. The addition of BC and HBC also alleviated the inhibitory effect of low temperature on microbial activity and increased gas production stability. The appropriate addition of HBC enhanced microbial metabolic activity under low-temperature conditions, reduced gas production fluctuations caused by low temperatures, and helped maintain a more stable AD process.

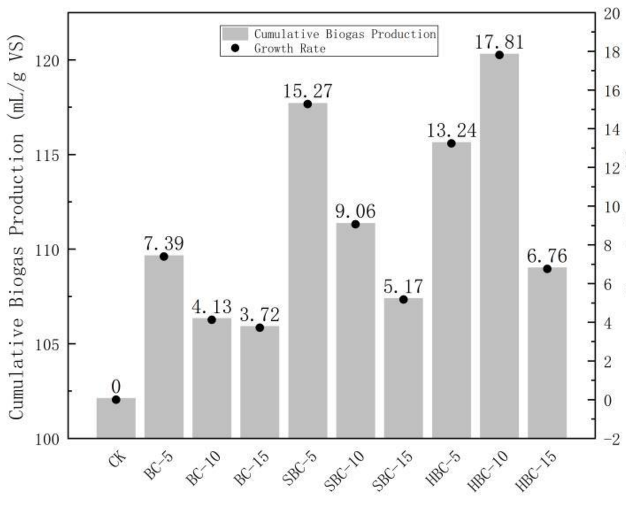


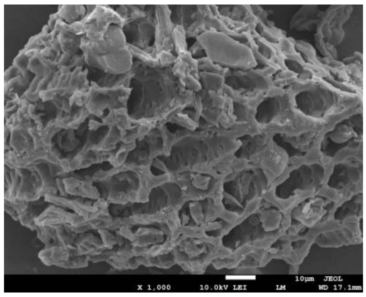
Figure 3. Effect of biochar on cumulative biogas production in sludgy corn stalk AD

The cumulative biogas production of sludge-corn stalk AD with biochar addition is shown in Figure 3. The cumulative biogas production in the CK group was 102.1212 mL/g VS. Among the BC-added groups, the highest gas production efficiency was observed in the group with 5 g/L BC, reaching 109.6651 mL/g VS, which was only a 7.39% increase compared to the CK group. The lowest cumulative biogas production was in the group with 15 g/L BC, which reached 105.9211 mL/g VS, representing only a 3.72% increase compared to the CK group. In the SBC-added groups, all experimental groups effectively improved cumulative biogas production. The highest total gas production was observed in the SBC-5 group, reaching 117.7118 mL/g VS, significantly higher than the CK group, with an increase rate of 15.27%. In the HBC-added groups, the addition of biochar had a noticeable impact on cumulative biogas production in sludge-corn stalk AD. The total gas production in the 10 g/L HBC group was 120.3103 mL/g VS, an increase of 17.81% compared to the CK group.

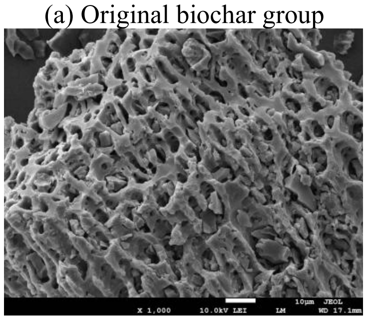
Overall, the appropriate addition of SBC and HBC helped mitigate severe fluctuations in the biogas production curve and improved the cumulative biogas production of sludge-corn stalk AD to varying degrees. However, excessive addition still led to a decrease in digestion system stability.

4.1.2 Morphological analysis of biochar

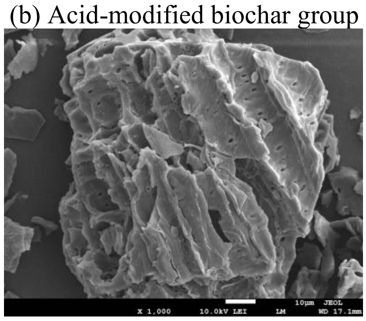
Figure 4 shows the scanning electron microscopy (SEM) images of each group of biochar at 1000 × magnification. The internal structure of the edge part of the untreated straw has been exposed due to the effect of physical and mechanical crushing. Such changes are beneficial for subsequent AD. The porosity and roughness of straw in the SBC and HBC groups increased significantly compared to the BC group, and the internal skeleton was partially exposed, forming many structurally disordered gaps, which promoted biogas production in subsequent AD experiments.



(a) Original biochar group



(b) Acid-modified biochar group



(c) Alkali-modified biochar group

Figure 4. SEM

4.1.3 Analysis of changes in biogas production kinetic parameters

The Gompertz fitting results of cumulative biogas production in different experimental groups under different temperature conditions are shown in Table 2. By using the modified Gompertz model, the effect of biochar on biogas production in sludge-corn stalk AD can be further reflected from multiple aspects, including cumulative biogas production (*T*), biogas production potential (P_{max}), maximum biogas production rate (R_{max}), and lag phase (λ). The R^2 value can measure the fitting degree of the kinetic equation, and when R^2 is greater than 0.990, the fitting result is good. The fitting results show that the R^2 values of all experimental groups are above 0.99, indicating that this equation can well predict the biogas production in sludge-corn stalk AD. According to related studies, the difference in *T* and P_{max} reflects the biodegradability of the substrate. In all experimental groups under normal temperature conditions, the T and Pmax of the biochar-added groups were significantly higher than those of the CK group, indicating that biochar improved the utilization rate of biodegradable compounds. The lag phase (λ) can indicate the impact intensity of the digestion substrate on microorganisms. The most effective treatment for shortening λ was the addition of the SBC-5 group, which shortened it by nearly half compared to the CK group, indicating that the addition of a high concentration of SBC enabled the system to quickly enter the methanogenic phase. However, Rmax was relatively low because excessive biochar adsorbed the digestion substrate, thereby reducing the biogas production potential of the digestion system.

Under low-temperature conditions, the addition of biochar significantly improved the biogas production kinetic parameters of sludge-corn stalk. The biogas production potential (P_{max}) of the BC-5 group reached 113.92 mL/g VS, higher than that of the CK group (106.56 mL/g VS), indicating that biochar could effectively promote substrate degradation and gas production. Although the differences in Rmax and λ values were not significant, the lag phase (λ) of the BC-5 group was 4.47 days, slightly shorter than that of the CK group (4.59 days), showing that biochar slightly promoted the system's transition to the gas production phase under low-temperature conditions. However, the relatively long lag phase still indicated the impact of low temperature on microbial activity. Under high-temperature conditions, the *Pmax* (127.67 mL/g VS) and *Rmax* (6.44 mL/g VS) of the *HBC*-10 group were the highest, and the lag phase (λ) was 4.05 days, slightly higher than that of the normal temperature group but still within a reasonable range. The high-temperature environment seemed to promote a more effective reaction between biochar and the substrate, thereby increasing the gas production rate and gas yield. Overall, the addition of biochar significantly enhanced the biogas production potential of sludge-corn stalk under different temperature conditions, but its effect was influenced by temperature changes, with the most significant effect observed under high-temperature conditions.

Table 2. Kinetics parameters of sludge-corn stalk gas production

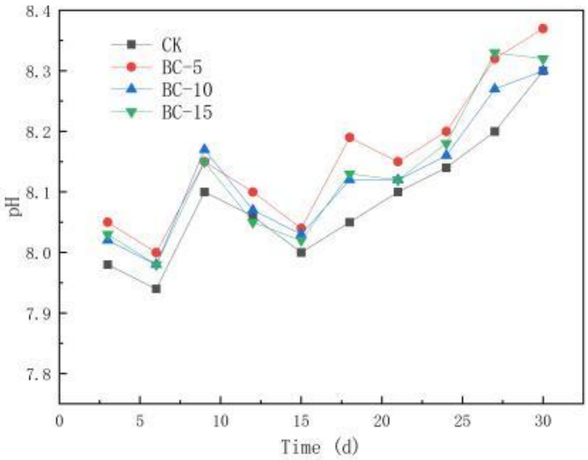
Temperature Condition	No.	Corrected *Gompertz Model*				
		T	P_{max}	R_{max}	λ	R^2
	CK	102.12122	106.5551±0.8259	6.6746±0.1140	4.5946±0.1261	0.9987
Psychrophilic conditions	*BC*-5	109.66505	113.9183±0.6705	6.7900±0.0811	4.4679±0.0914	0.9994
	BC-10	106.34018	111.3211±0.8114	6.4285±0.0907	4.2941±0.1106	0.9991
	BC-15	105.92107	110.1807±1.0110	6.6002±0.1241	4.4707±0.1433	0.9984
Mesophilic conditions	*SBC*-5	117.71181	128.3328±2.0879	6.1434±0.1398	3.5747±0.2039	0.9971
	SBC-10	111.3694	122.4810±2.1927	5.6811±0.1317	3.6524±0.2120	0.9969
	SBC-15	107.4019	117.9717±2.2265	5.3249±0.1286	3.1113±0.2263	0.9965
Thermophilic conditions	*HBC*-5	115.64424	122.2809±1.2782	6.3815±0.1091	3.8833±0.1442	0.9985
	HBC-10	120.31025	127.6732±1.6212	6.4351±0.1226	4.0490±0.1640	0.9981

4.2 Effect of biochar on the digestion process parameters of sludge-corn stalk under different temperature conditions

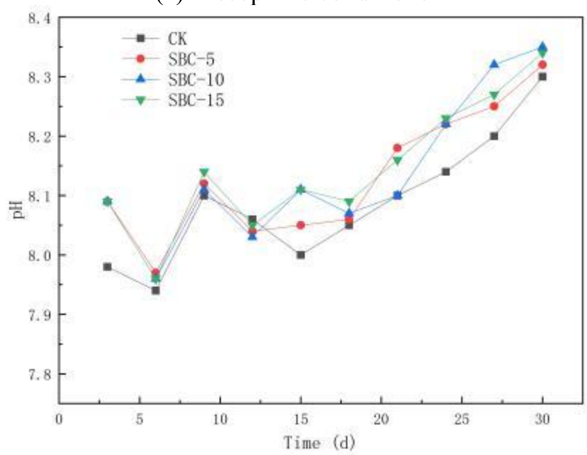
4.2.1 Changes in pH and VFAs during AD of sludge-corn stalk

The variations in pH values of each group during AD of sludge-corn stalk under different temperature conditions are shown in Figure 5. Under mesophilic conditions, in the experimental groups with BC addition, the highest pH value was observed in the BC-5 group, reaching 8.37. The other two groups exhibited significant fluctuations, indicating system instability. In the experimental groups with SBC addition, the initial pH value was 8.09, which was higher than that of the BC groups, and the overall fluctuations were smaller than those in the BC groups, suggesting that the addition of SBC improved the stability of the digestion system. In the groups with HBC addition, the pH fluctuations were smaller within the first 15 days, indicating a more stable system. After day 15, the pH value rose rapidly, reaching a peak on day 21, followed by a decline, but the pH value in the HBC group remained higher than that in the CK group. In all three biochar groups, the pH value decreased rapidly after the start of AD due to the accumulation of VFAs. Subsequently, as VFAs were gradually consumed and alkaline substances such as AN were produced, the pH value began to rise and eventually stabilized.

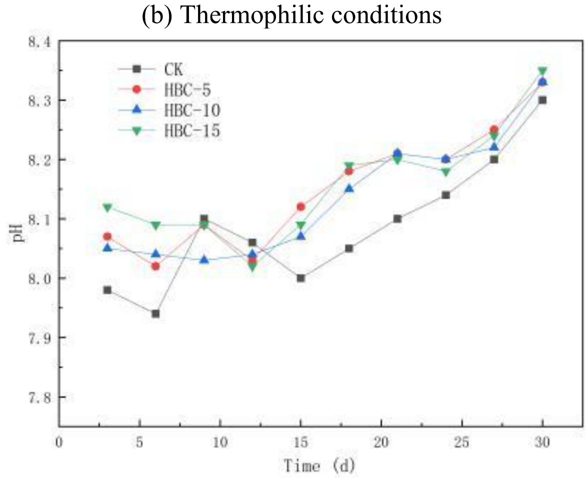
Under psychrophilic conditions, the experimental groups with biochar addition exhibited a relatively stable pH variation trend, especially in the BC-5 group, where the pH value remained at a high level of 8.37 with minimal fluctuations. This indicates that biochar can effectively mitigate pH fluctuations caused by low temperature. This result suggests that biochar addition in low-temperature environments helps enhance system stability and prevents severe pH fluctuations caused by excessive acidification or AN release. Meanwhile, although BC-10 and SBC-15 groups also exhibited some pH recovery in the early stages, their fluctuations were relatively larger, and they failed to maintain the stability observed in the BC-5 group. This may be related to the high adsorption capacity of biochar at higher concentrations and the mismatch between the substrate degradation rate. Under thermophilic conditions, the pH variations in the HBC group exhibited a more complex trend. In the first 15 days, the pH fluctuations were relatively small, and the system was stable. However, after day 15, the pH value began to rise rapidly, reaching a peak on day 21, and then slightly decreased. Despite this, the pH value in the HBC group remained higher than that in the CK group. This may be due to the enhanced adsorption of organic acids by biochar at high temperatures, which alleviated the accumulation of VFAs and the acidification effect. Overall, under thermophilic conditions, the addition of HBC resulted in a relatively smooth pH variation, indicating that biochar addition at high temperatures plays an important role in maintaining the pH stability of the AD system. In particular, HBC exhibited a strong buffering effect in high-temperature environments.



(a) Mesophilic conditions



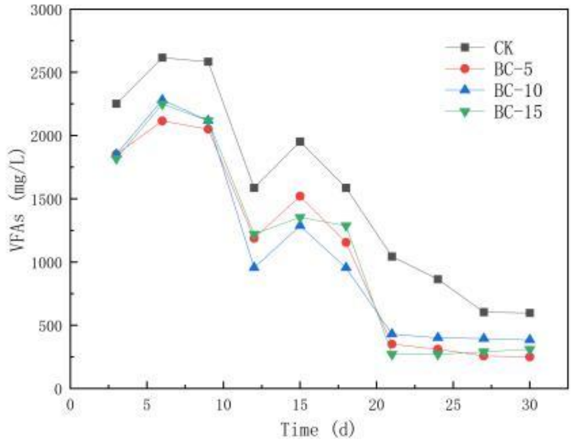
(b) Thermophilic conditions



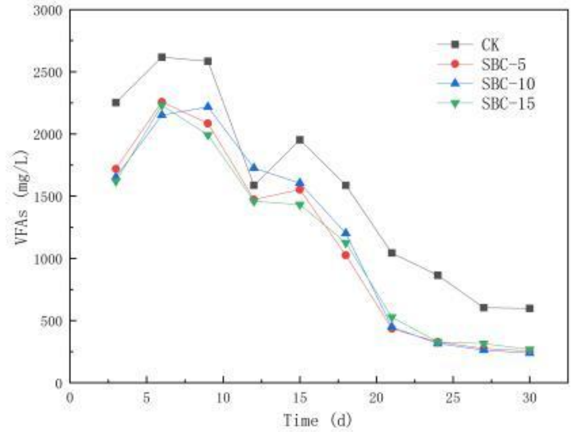
(c) Psychrophilic conditions

Figure 5. Effect of biochar on pH value of sludgy-corn stalk AD system

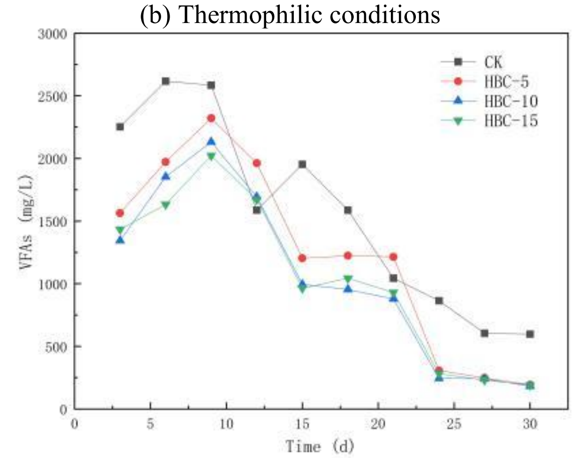
The variations in VFAs during the AD process of sludge-corn stalk under different temperature conditions are shown in Figure 6. Under mesophilic conditions, in the BC addition groups, the CK, BC-5, BC-10, and BC-15 groups reached peak VFAs concentrations on day 6.



(a) Mesophilic conditions



(b) Thermophilic conditions



(c) Psychrophilic conditions

Figure 6. Effect of biochar on VFAs concentration in sludgy-corn stalk AD system

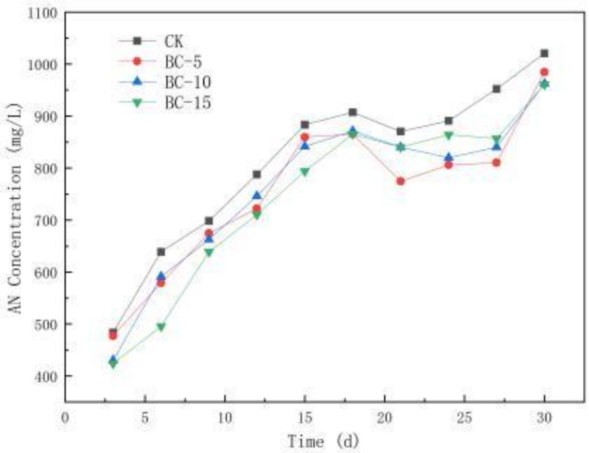
The final VFAs concentrations in each group were 597.40 mg/L, 250.84 mg/L, 384.33 mg/L, and 310.70 mg/L, respectively, demonstrating that appropriate BC addition could enhance both the generation and degradation of VFAs in the digestion system. In the SBC addition groups, the VFAs concentrations in the early digestion stage were lower than those in the CK group, and in the later digestion stage, the VFAs concentrations in each group became similar. The SBC addition groups showed smoother VFAs fluctuations compared to the CK group, indicating a more stable digestion system. In the HBC addition groups, the peak VFAs concentrations occurred on day 9, with HBC-5, HBC-10, and HBC-15 reaching 2321.02 mg/L, 2131.46 mg/L, and 2021.72 mg/L, respectively. The VFAs fluctuations were smaller than those in the CK group, and the fluctuations in the later stage were smoother than those in the CK group, indicating a stable digestion system. In the early digestion stage, the VFAs content in the biochar addition groups was lower than that in the CK group. This indicates that biochar effectively alleviates VFAs accumulation in the AD system and accelerates the biogas production process. By the end of digestion, the VFAs content in the biochar addition groups was significantly lower than that in the CK group, indicating that biochar addition promoted the conversion of macromolecular organic acids into acetic acid and accelerated the biogas production process.

Under psychrophilic conditions, the experimental groups with biochar addition exhibited a significant effect. In the BC addition groups (BC-5, BC-10, BC-15), VFAs concentrations peaked on day 6, followed by a rapid degradation trend, with final concentrations significantly lower than that in the CK group. Particularly, the VFAs concentration in the BC-5 group dropped to 250.84 mg/L, indicating that appropriate biochar addition under low temperatures can significantly promote VFAs degradation and prevent their accumulation in the system. This result suggests that in low-temperature environments, biochar can effectively mitigate VFAs accumulation, helping the system maintain a stable digestion process and accelerating biogas production. Additionally, under low temperatures, the SBC and HBC groups exhibited relatively low VFAs concentrations, especially in the early digestion stage, showing that biochar can reduce VFAs accumulation in the initial stage under low-temperature conditions and improve the stability of the AD system. Under thermophilic conditions, the HBC groups exhibited a significantly different VFAs variation trend. Particularly on day 9, the peak VFAs concentrations in the HBC-5, HBC-10, and HBC-15 groups reached 2321.02 mg/L, 2131.46 mg/L, and 2021.72 mg/L, respectively, much higher than those in the BC and SBC groups. This indicates that under thermophilic conditions, HBC addition led to rapid VFAs accumulation. However, as the digestion process progressed, VFAs concentrations gradually stabilized and decreased. Compared with the CK group, the VFAs fluctuations in the later stage of digestion in the HBC groups were smaller, indicating that biochar effectively mitigated VFAs accumulation under thermophilic conditions and helped maintain a more stable biogas production process. Additionally, although VFAs concentrations increased under high temperatures, biochar addition facilitated the conversion of organic acids into acetic acid, accelerating the biogas production process and improving biogas yield.

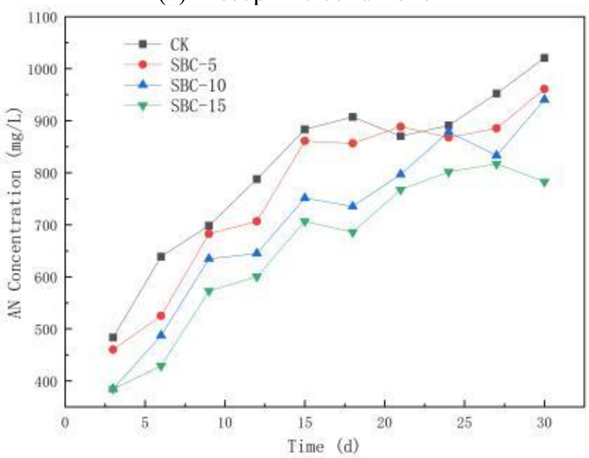
Overall, appropriate biochar addition can enhance both the generation and degradation of VFAs, increasing biogas production. However, both the type and dosage of biochar have minimal impact on the pH value of the system.

4.2.2 AN variation characteristics in sludge-corn stalk AD

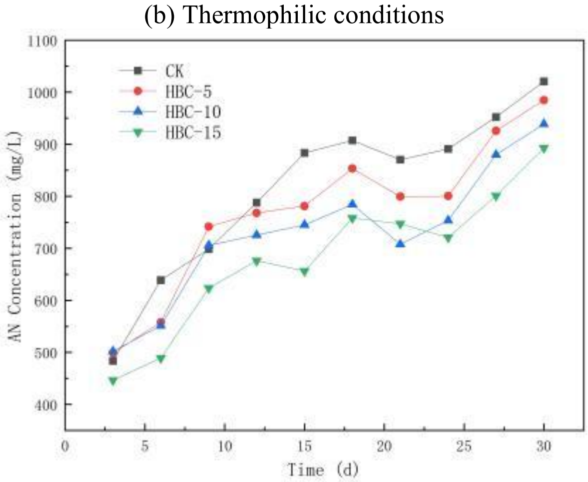
As shown in Figure 7, the effect of biochar on the AN concentration in the sludge-corn stalk AD system under different temperature conditions is presented. Under mesophilic conditions, the AN concentration in the CK group rapidly increased from the early stages of digestion, reaching its peak on day 18 (907.12 mg/L). At this point, the high AN concentration inhibited gas production, and it subsequently decreased rapidly with fluctuations, rising again to 1020.45 mg/L on day 27. In the BC-added experimental groups, the peak values were all lower than those of the CK group, with less fluctuation. In the SBC-added experimental groups, the AN concentration steadily increased without significant fluctuations, with the SBC-5 group being the most stable. In the HBC-added experimental groups, the overall trend of the AN curve showed a rising tendency with small fluctuations. Compared with the SBC group, the fluctuations were smaller, and the system was more stable, indicating that modified biochar could enhance the adsorption capacity for AN, making the digestion system more stable. Among them, the alkaline modification effect was better. Experimental data indicate that the AN concentration in the biochar-added groups was generally lower than that in the CK group during digestion.



(a) Mesophilic conditions



(b) Thermophilic conditions



(c) Psychrophilic conditions

Figure 7. Effect of biochar on AN concentration in sludgy-corn stalk AD system

Under psychrophilic conditions, the experimental groups with biochar showed clear advantages, especially in the BC and SBC groups, where the AN concentration fluctuated less and the peak values were relatively low. The AN concentration in the BC group did not reach the high peak value observed in the CK group and maintained a relatively steady increasing trend during digestion. This may be because, under psychrophilic conditions, biochar can more effectively adsorb AN, slowing its accumulation in the system, thus alleviating the impact of ammonia inhibition on gas production. In the SBC group, the AN concentration increased relatively steadily, without dramatic fluctuations, indicating that the addition of SBC further enhanced the stability of the digestion system and alleviated the potential AN accumulation issue under low temperatures. Under thermophilic conditions, the HBC group exhibited the most stable AN variation trend. Although the AN concentration continued to rise, its fluctuations were minimal, indicating that the modification effect of HBC effectively reduced the accumulation of AN under high temperatures and maintained system stability. Particularly under thermophilic conditions, the alkaline modification of HBC significantly improved its AN adsorption capacity, thereby preventing ammonia inhibition effects caused by high temperatures. Compared with other biochar-added groups, the HBC group exhibited the least fluctuation in AN concentration, and the digestion system showed a more stable operation state. This indicates that under thermophilic conditions, the addition of HBC can effectively alleviate ammonia inhibition and improve the stability and gas production efficiency of the AD process.

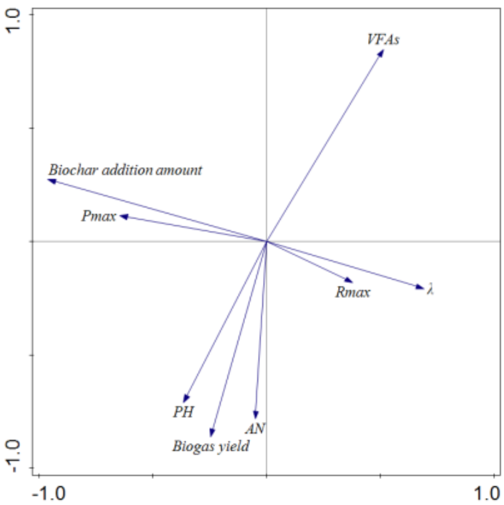
4.3 Influence of biochar on the methane production factors in sludge-corn stalk AD under different temperature conditions

Based on the data in Table 3, the addition of different types of biochar under different temperature conditions significantly affects the characteristic values and cumulative explanatory amounts of methane production in the sludge-corn stalk AD process. Whether under normal, high, or low temperature conditions, the first two principal components of axis 1 and axis 2 explain the majority of the changes in methane production, with the cumulative explanatory amounts of the first two axes being 97.09% under normal temperature conditions, 97.17% under high temperature conditions, and 96.70% under low temperature conditions. This indicates that under all three temperature conditions, the first two principal axes are still the main contributors to the changes in methane production and related parameters, especially the first principal component (Axis 1), which is particularly important in explaining the data. The experimental results also show that the effect of temperature changes on the characteristic values is relatively limited, especially regarding the explanatory amounts of the first two axes, with the impact of temperature changes on these characteristic values being quite consistent. From the explanatory amounts of the experimental data, the different types of biochar have a slight effect on the changes in methane production during the AD process, but the overall trend is relatively stable. Under normal, high, and low temperature conditions, the results of adding acid-modified biochar and alkaline-modified biochar were slightly different but displayed similar patterns, with the cumulative explanatory amounts of the first two axes remaining close to 97%. This suggests that although different types of biochar may contribute differently to methane production during the process, the impact of temperature conditions on different types of biochar is minimal. For the main system changes, Axis 1 still dominates, and temperature changes do not significantly alter this trend.

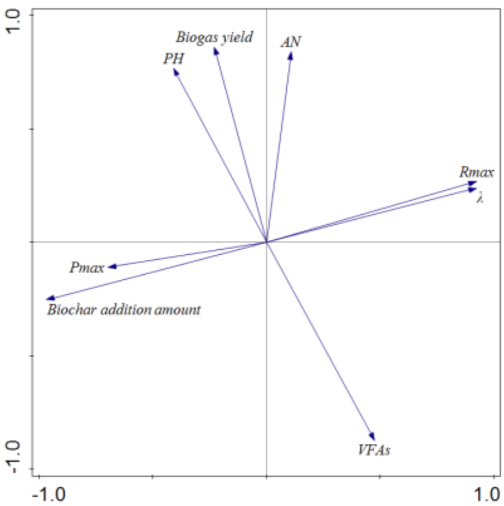
Based on the PCA results in Figure 8, the correlation between gas production kinetics parameters and process parameters showed a relatively consistent pattern, mainly influenced by the type of biochar and the dosage added. The modification conditions had little impact on the correlation differences between parameters. Under different temperature conditions, subtle changes in the correlations between these parameters were observed, especially under different biochar types and dosages, where the correlation between gas production kinetics parameters and the dosage of HBC was particularly strong. Temperature variations exerted a regulatory effect on the relationships between these parameters, especially the correlation between biogas production, pH, and AN, reflecting the impact of temperature on microbial metabolic activities during AD. Moreover, the negative correlation between biogas production and VFAs remained significant under all temperature conditions. Temperature had a varying degree of impact on the relationships between biochar and the various parameters in the sludge-corn stalk AD process. Under room temperature conditions, the correlation between biochar dosage and biogas production was more apparent, with a stronger positive correlation between pH and AN and the most notable AN adsorption by unmodified biochar. Under high and low temperature conditions, temperature had a smaller effect on the relationships between biogas production and other parameters, but it was still possible to observe changes in the positive correlation between pH and AN with different biochar additions. The negative correlation between VFAs and biogas production persisted, indicating that under both high and low temperature conditions, the gas production mechanism of AD was still dominated by these key parameters.

Table 3. Characteristic values and explanatory quantities of different biochar changes in biogas production in sludgy-corn stalk AD

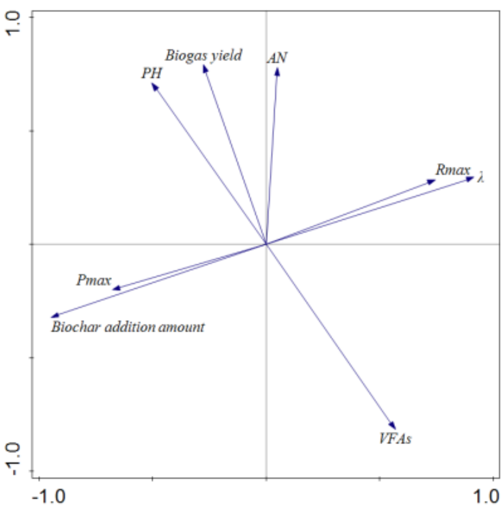
Sorting Axis	Mesophilic Conditions		Thermophilic Conditions		Psychrophilic Conditions	
	Eigenvalue	Characteristics of Biogas Yield Variation Cumulative Explanation Rate (%)	Eigenvalue	Characteristics of Biogas Yield Variation Cumulative Explanation Rate (%)	Eigenvalue	Characteristics of Biogas Yield Variation Cumulative Explanation Rate (%)
Axis 1	0.6316	63.16	0.6219	62.19	0.6270	62.70
Axis 2	0.3394	97.09	0.3499	97.17	0.3399	96.70
Axis 3	0.0277	99.87	0.0257	99.75	0.0307	99.77
Axis 4	0.0011	99.98	0.0015	99.90	0.0017	99.94



(a) Mesophilic conditions



(b) Thermophilic conditions



(c) Psychrophilic conditions

Figure 8. PCA among AD condition parameters, gas generation kinetic parameters and process parameters of sludge-corn stalk group

5. CONCLUSION

This study explored the influence of thermodynamically regulated modified biochar on the energy conversion efficiency in the AD process of agricultural waste. The research is divided into two main parts: on one hand, the regulatory effect of modified biochar under different temperature conditions on the energy conversion efficiency of agricultural waste AD was explored, with a focus on analyzing the effects of modified biochar on AN and VFAs conversion efficiency under different temperatures; on the other hand, the experimental materials and methods were designed in detail, including sample selection, experimental setup, and optimization of analysis methods, to ensure the reliability and validity of the experimental results. Through this research, the goal is to provide a thermodynamically regulated modified biochar application strategy to improve the energy conversion efficiency in agricultural waste AD, offering theoretical basis and practical guidance for future agricultural waste resource utilization and waste treatment technologies.

The main contribution of this study lies in revealing the regulatory effect of thermodynamically regulated modified biochar on the energy conversion efficiency in the AD process of agricultural waste under different temperature conditions. The results show that temperature and biochar type significantly affect AN adsorption, VFAs conversion, and biogas production, providing new theoretical support for improving the energy conversion efficiency of agricultural waste AD. The application of modified biochar, especially its impact on AN and VFAs conversion efficiency, has the potential to enhance biogas production and overall energy conversion efficiency in AD. However, there are some limitations in this study, mainly due to the experimental conditions, especially the relatively narrow temperature range. Future studies could expand the temperature range for verification. Moreover, although this study explores the influence of different biochar types on the AD process, further research is needed to investigate their stability and practical benefits during long-term operation. Finally, this study focuses on the regulatory role of temperature on modified biochar, but other factors such as pH, salinity, etc., may also impact the AD process. Therefore, future research can explore the impact of additional environmental factors on AD efficiency.

Future research directions can include the following aspects: first, expanding the temperature range to explore the effects of modified biochar under extreme temperature conditions; second, combining other environmental factors, such as salinity and humidity, to study their interactions with biochar; further optimizing experimental materials and methods to improve the reproducibility and accuracy of the results; and finally, integrating actual agricultural waste resource utilization needs to explore the long-term application and practical economic benefits of thermodynamically regulated modified biochar in agricultural waste resource utilization.

ACKNOWLEDGMENT

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