Effect of Benzyl Alcohol on Biomethanation from Lignite

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ABSTRACT: Currently, biomethane obtained from coal resources, such as lignite and peat, serves as a sustainable biofuel urgently needed by the energy economy. To improve biomethane yield from lignite, the effects of different concentrations of benzyl alcohol, a degraded product of humic acid, on a biomethanation fermentation system were analyzed. The total biomethane yield, daily biomethane yield, coenzyme F<sub>420</sub>, VFA (volatile fatty acids) concentration, alkalinity, and pH were used to determine the optimal benzyl alcohol concentration. The biomethanation fermentation system with 2000 mg/L benzyl alcohol produced up to 4.03 mL/g of biomethane, which was 1.15 times that produced from the control group. The coenzyme F<sub>420</sub>, VFA, alkalinity, and pH of the system after adding 2000 mg/L benzyl alcohol were more preferable after adding other concentrations during the lignite biomethanation process. In summary, 2000 mg/L benzyl alcohol had a significantly positive effect on the lignite biomethanation fermentation system. When benzyl alcohol is added to the fermentation system, it accelerates the tricarboxylic acid cycle, which in turn produces more biomethane. Additionally, the self-supply of lignite microbial transformation nutrients from the perspective of chemical composition was explored as a novel approach in solving the common problem of low biomethane yield from a single lignite raw material. This also laid a foundation for subsequent steps through the adjustment of pretreatment conditions to ensure that the lignite pretreatment liquid contained increased benzyl alcohol, and a greater yield of biomethane can be produced after activated sludge addition.

1. INTRODUCTION

Coal accounts for more than 70% of fossil fuel use globally, while petroleum and biogas account for only 17 and 2%, respectively. According to the degree of coalification, coal can be divided into peat, lignite, bituminous coal, and anthracite coal. In China, the verified lignite resource reserves are 130.3 billion tons. However, as fuel, lignite is utilized difficultly due to its high moisture content, low calorific value, easy-weathering, and ease of spontaneous combustion. Due to its moisture content, lignite needs to be dried before use in power plants. In addition, lignite can produce valuable gaseous products such as H<sub>2</sub>, CO, and CH<sub>4</sub> through H<sub>2</sub>O or CO<sub>2</sub> gasification processes. These reactions require expensive catalysts, as well as high temperature with high pressure conditions. Therefore, finding a means to realize low cost and mild conversion for lignite has become an urgent matter.

Studies found that lignite can produce biomethane under anaerobic fermentation, but with low yield, as the complex organic compounds in lignite are not easy to degrade. To meet the needs of anaerobic microbial growth, reproduction, and metabolism, studies have focused on adding nutrients and adding bacteria for the anaerobic fermentation system. For biomethane production from lignite, Xia et al. found that hydrogenase and methanogen activity was advanced through the addition of 10 mg/L Fe<sup>2+</sup> in the fermentation system. Wang et al. reported that 0.2 mol/L sodium acetate solution activated
methanogen activities and improved the efficiency of the enzymatic reaction, which significantly increased the biomethane quantity. Moreover, Bucha et al. found that the methanogenic fermentation of lignite with the carbon-bearing additives of glucose, acetate, and methanol significantly increased the biomethane production. Lignite is rich in humic acid, and benzyl alcohol, a degradation product of humic acid, can be used as a nutrient for microorganisms in a fermentation system. Presently, there are no reports of biomethanation from lignite by adding benzyl alcohol.

In the present study, the effects of benzyl alcohol on the biomethanation of lignite were investigated by adding benzyl alcohol at different concentrations to the lignite biomethanation fermentation system. In addition, the changes in total biomethane yield, daily biomethane yield, coenzyme F₄₂₀ concentration, alkalinity, pH, and volatile fatty acid (VFA) concentration were studied.

2. MATERIALS AND METHODS

2.1. Materials. Activated sludge was taken from the sewage treatment plant located in the southern suburb of Baotou and stored in a refrigerator at 4 °C for anaerobic acclimation. Lignite was obtained from Pingzhuang coal mine, Chifeng city, Inner Mongolia Autonomous Region. Industry analysis of the procured lignite was performed by an automatic analyzer (YX-GYFX, Youxin, China). Lignite organic matter content was detected by thermogravimetry. Humic acid content was determined by the 1% sodium hydroxide extraction-potassium dichromate volumetric method; the content of water-soluble humic acid was determined by the volumetric titration method. The basic properties of the lignite sample are shown in Table 1. An intelligent muffle furnace (YX-WK/MFL7300, Youxin, China) was used to detect the total solids (TSs) and volatile solids (VSs) of the lignite. Table 2 shows the parameters of lignite and anaerobic activated sludge used in this study.

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2.2. Experimental Methods. The Automatic Methane Potential Test System (AMPTS II, Bioprocess, Sweden) was adopted. Fifteen sets of fermentation bottles, of which the total capacity was 500 mL, were divided into five groups to produce biomethane. Each bottle had 45 g of lignite crushed to 250 μm, 200 mL of activated sludge, varied concentrations of benzyl alcohol, and water added to keep the fermentation volume at 450 mL (Table 3). In addition, the initial pH was adjusted to 7.0 with 0.1% NaOH. The fermentation experiment was carried out in a water bath at a constant temperature of 50 °C. The TS content of the fermentation system was 8%. Stirring was automated using a motor, to be done every 6 h for 5 min. During the 33 day fermentation period, biomethane yield data were recorded daily, while the system VFA concentration, alkalinity, pH, and coenzyme F₄₂₀ concentration were measured every 3 days. All the experiments were carried out independently in triplicate.

2.3. Determination of Coenzyme F₄₂₀. Coenzyme F₄₂₀ was determined by an ultraviolet—visible (UV—vis) spectrophotometer by a previously described method. A certain amount of sample was centrifuged for 10 min at 6000 rpm to obtain precipitate 1 (precipitate from first centrifugation). The process was repeated to obtain precipitate 2 (precipitate from second centrifugation) from precipitate 1 mixed with physiological salt water. Accordingly, the separation procedures were repeated twice, and the supernatant was discarded to retain the final precipitation. After adding 50 or 100 mL of distilled water, the final precipitate was heated to 95 °C for 30 min. After cooling to 25 °C, the precipitate was dissolved in ethanol with a mass ratio of 3:1. The mixture was centrifuged again to obtain the supernatant. Thereafter, the pH of the supernatant was adjusted to 13.5 with 2 mol/L NaOH in order to eliminate all organic interference. Finally, the absorbance at 420 nm was measured by a UV—vis spectrophotometer (756, Youke, China). The concentration of coenzyme F₄₂₀ was calculated according to the equation $C = (A_1 - A_0) \times f/e \times L$, where $e$ is the molar extinction coefficient with a value of 45.3 (cm·L)/mmol; $A_1$ is the absorbance of the sample at 420 nm at pH = 13.5; $A_0$ is the absorbance of the reference sample at 420 nm; $f$ is the dilution multiple of the sample; and $L$ is the thickness of the colorimetric dish.

2.4. Determination of VFA. FeCl₃·6H₂O (20.00 g) was dissolved in 500 mL of distilled water to which 20 mL of concentrated sulfuric acid was added, and the volume was adjusted to 1 L with distilled water. The solution was allowed to stand for 12 h after which the precipitate was discarded.

The following were added into a colorimetric tube: 0.5 mL of fermentation liquid, 1.5 mL of ethylene glycol, and 0.2 mL of dilute sulfuric acid ($V_{\text{sulfuric acid}}/V_{\text{distilled water}} = 1:1$). The tube was heated in a boiling water bath for 3 min and cooled to 25 °C. Then, 0.5 mL of hydroxyamine sulfate (10%) and 2.0 mL of sodium hydroxide (4.5 mol/L) were added to the tube. After mixing, the solution was left to stand for 1 min. Subsequently, 10 mL of acidic ferric chloride was added in the colorimetric tube, and the volume was adjusted to 25 mL with distilled water. After

| Table 1. Basic Properties of the Lignite Sample |
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| **material** | **industry analysis** | **analysis of physical and chemical properties** |
| | **M/ wt%** | **Aᵦ/ wt%** | **Vₛ/ wt%** | **Fᵦ/ wt%** | **organic matter/ wt%** | **total humic acid/ wt%** | **water-soluble humic acid/ wt%** |
| lignite | 6.44 | 15.86 | 34.13 | 43.57 | 51.48 | 24.60 | 5.94 |

* M, moisture; Aᵦ, ash; Vₛ, volatile; and Fᵦ, fixed carbon.

| Table 2. Parameters of Lignite and Anaerobic Activated Sludge |
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| **parameters** | **lignite** | **anaerobic activated sludge** |
| TS | 91.27% | 0.66% |
| VS | 77.81% | 0.38% |
| VS/TS | 0.85 | 0.58 |

* TS, total solids; VS, volatile solid.

| Table 3. Different Concentrations of Benzyl Alcohol Added |
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| **test group** | **lignite/g** | **benzyl alcohol concentration/ (mg/L)** | **benzyl alcohol volume/mL** |
| control | 45 | 0 | 0 |
| P1 | 45 | 1000 | 0.47 |
| P2 | 45 | 1500 | 0.70 |
| P3 | 45 | 2000 | 0.94 |
| P4 | 45 | 2500 | 1.12 |
mixing, the solution was left to stand for 5 min. The optical density was determined at 500 nm. The measured optical density was calculated using a standard curve of acetic acid to obtain the VFA concentration.21

2.5. Determination of Alkalinity. 1 mL of fermentation liquid was diluted to 10 mL and placed in a circular cuvette (Φ 24 mm). An ALKA-M-HR PHOTOMETER tablet (Germany) was dissolved in the diluted fermentation liquid. The alkalinity of the fermentation liquid was detected by COD/TOC multi-parameter comprehensive water quality (ET99731, Germany).22,23

2.6. Determination of pH and Surface Morphology. The pH value was measured with a pH meter (PHS-2S, China). The surface morphology of lignite and its fermentation residue was observed by a QUANTA-400 (FEI, America) scanning electron microscope.

2.7. Data Processing and Analysis. SPSS 26.0 software was used to analyze the data for differences between the corresponding indexes of the experimental and control groups. Test results with \( p \leq 0.01 \) are considered “highly significant”, \( p \leq 0.05 \), “significant”, and \( p > 0.05 \), “no significant difference”.

3. RESULTS AND DISCUSSION

3.1. Effects of Adding Benzyl Alcohol on the Total Biomethane Yield. The effects of benzyl alcohol, on lignite biomethanation were explored. During the 33 day fermentation period of lignite, the total biomethane yields at different concentrations of benzyl alcohol are shown in Figure 1.

![Figure 1. Effects of adding different concentrations of benzyl alcohol on the total biomethane yield. Note: different lowercase letters indicate the significant differences between treatments at \( p < 0.05 \).](http://pubs.acs.org/journal/acsodf)

The results showed that adding different concentrations of benzyl alcohol resulted in varying amounts of biomethane yield. Compared with the control group yield of 3.50 mL/g, the total biomethane yields were 3.26, 3.77, 4.03, and 2.74 mL/g by adding 1000, 1500, 2000, and 2500 mg/L benzyl alcohol, respectively. There was no significant difference \( (p \geq 0.05) \) between the experimental groups and the control group. Group P3 showed the highest total biomethane yield, with an increase of 15.14% compared to the yield of the control group. This indicates that benzyl alcohol exerted significant effects on promoting biomethane yield during anaerobic fermentation, possibly because of benzoic acid mediated CO\(_2\) removal from benzyl alcohol to form catechol, and then pyruvic acid and acetyl coenzyme A (acyl-CoA) released after decomposition. Pyruvic acid and acetyl-CoA can participate in the tricarboxylic acid cycle (TCA cycle) to increase methanogenesis and promote biomethane production.25,26 Thus, benzyl alcohol can improve biomethane yield during fermentation. Furthermore, benzyl alcohol was adsorbed by humic acid in lignite and was adhered to the lignite surface, thereby inhibiting lignite hydrolysis.27 Therefore, the total biomethane yield of the P1 group was lower than that of the control group. CO\(_2\) production was increased by adding excessive benzyl alcohol, resulting in a decrease in the pH of the fermentation system, thus reducing both the methanogen activity and consequent biomethane yield.23 Excess benzyl alcohol also inhibited glucose degradation, resulting in less carbonaceous organic matter that could be converted into biomethane.26

3.2. Effects of Benzyl Alcohol on Daily Biomethane Yield. As one of the degradation products of humic acid, benzyl alcohol was added to explore its effects on the daily biomethane yield. Obvious effects were seen on biomethanation from lignite (Figure 2). During initial stages of anaerobic fermentation, the daily biomethane yield was maintained at a high level and a peak was attained on the 1st day. With the addition of 2000 mg/L benzyl alcohol, the biomethane yield of the P3 group reached 0.91 mL/g, while that of the control group was only 0.86 mL/g. During days 12–15, the daily biomethane yield of the anaerobic fermentation system increased significantly and reached the second peak. On day 13, the biomethane yield of the P3 group was 0.22 mL/g, 1.16 times higher than that of the control group. This result indicates that adding benzyl alcohol to produce biomethane produced positive effects, and in particular, the yield on adding 2000 mg/L was significantly higher than that of the control group \( (p \leq 0.01) \). However, the P1, P2, and P4 groups indicated no significant effect compared to the control group \( (p > 0.05) \). This may be attributed to the fact that microorganisms can convert 2000 mg/L benzyl alcohol into benzoic acid, which is an intermediate product of anaerobic metabolism of aromatic compounds.27,28 Subsequently, the methanogenesis system could possibly generate further more biomethane by decomposing acetic acid, a degradation product of benzoic acid.27 Due to the presence of less benzyl alcohol in the late fermentation period, the daily biomethane yields of P1, P2, P3, and P4 groups were similar to that of the control group.

3.3. Effects of Benzyl Alcohol on Coenzyme F\(_{420}\) Concentration. As a unique enzyme of methanogens,
coenzyme $F_{420}$ can directly reflect methanogen activity. In order to better illustrate the anaerobic digestion process of lignite, the effects of adding different concentrations of benzyl alcohol on coenzyme $F_{420}$ in the lignite biomethanation system are plotted in Figure 3. With the degradation of the lignite organic matter and the proliferation of methanogens in activated sludge, the coenzyme $F_{420}$ concentration of the control group increased from 0.000405 mmol/g on day 1 to a peak value of 0.001019 mmol/g on day 6. During the addition of different concentrations of benzyl alcohol, coenzyme $F_{420}$ concentration of the P3 group was the highest with 0.001550 and 0.001690 mmol/g on days 1 and 6, respectively. Subsequently, the proliferation of methanogens was inhibited with the change of pH value, resulting in a decrease of both the activity and concentration of coenzyme $F_{420}$ activity. The concentration of coenzyme $F_{420}$ during days 24–33 was maintained between 0.000675 and 0.000988 mmol/g, higher than that of other groups from days 1 to 12 and days 24 to 33. Notably, the P1 and P4 groups exhibited no significant effects compared with the control group ($p > 0.05$). However, the P2 group showed significantly higher activity than the control group ($p \leq 0.05$), and the P3 group was highly significantly higher than the control group ($p \leq 0.01$). These results indicate that the addition of 2000 mg/L benzyl alcohol could significantly promote the proliferation of methanogens in the activated sludge, leading to the increase of coenzyme $F_{420}$ activity in the fermentation system. This is likely due to benzyl alcohol, which can be used in the fermentation system as an organic matter to provide carbon source and improve the activity of microorganisms.

3.4. Effects of Adding Benzyl Alcohol on VFA Concentration. VFA concentration is the most common indicator to characterize the stability of organic matter in an anaerobic fermentation system. The organic matter of lignite is converted into VFA, which is used as a raw material to produce $\text{CH}_4$ by methanogens in the anaerobic fermentation process. The addition of various concentrations of benzyl alcohol had considerable effects on the VFA in the lignite biomethanation process (Figure 4). The VFA concentration of the P1, P2, and P4 groups were not significantly different from that of the control group ($p > 0.05$). However, the VFA level of the P3 group was significantly higher than that of the control group ($p \leq 0.05$).

In the process of fermentation, the overall concentration of VFA first increased, then decreased, and finally stabilized, consistent with the theory that organic matter in anaerobic fermentation first decomposes into VFA, then gets converted into acetic acid and $\text{H}_2$, and finally forms $\text{CH}_4$. In addition, the overall trend shows that the VFA concentration of the control group is relatively low. Due to the decomposition of the lignite organic matter, VFA began to accumulate during the initial stage of lignite biomethanation and reached 1204.84 and 1461.28 g/L in the control and P3 groups, respectively, on day 3. After that, VFA was converted into $\text{CH}_4$ by metabolism of methanogens, marking the commencement of the methanogenesis stage, leading to a decrease in the fluctuation of VFA concentration in the fermentation system. On day 33, VFA concentration decreased to 675.67 and 757.08 g/L in the control and P3 groups, which were 43.92 and 48.19% lower than that on day 3, respectively. This result suggests that on adding 2000 mg/L benzyl alcohol in the fermentation system, the biotransformation ability is stronger and more VFA gets converted into $\text{CH}_4$ because of the conversion of benzyl alcohol into benzoic acid that participates in the TCA to generate VFA, such as acetic acid.

3.5. Effects of Adding Benzyl Alcohol on Alkalinity. Alkalinity refers to the total amount of substances in water that can neutralize strong acids. Examples of alkaline substances include carbonates, bicarbonates, and hydroxides. Alkalinity may have played a buffering role in the system. In other words, the higher is the alkalinity of the fermentation broth, the stronger is the buffering capacity of the fermentation system. Marked effects on the alkalinity of lignite biomethanation were observed by adding different concentrations of benzyl alcohol. Results are plotted in Figure 5.

The initial alkalinity of the control group was 540.00 mg/L CaCO$_3$, which increased to 710.00 mg/L CaCO$_3$ by 31.48% on day 6. This may be due to the increase of CO$_2$ content in the fermentation system, which was dissolved to form bicarbonate in the fermentation broth. The bicarbonate increased the alkalinity of the biomethane fermentation system because of the yield of CO$_2$ from $\text{CH}_4$ at the beginning of fermentation. Subsequently, VFA was converted into $\text{CH}_4$ by the growth and metabolism of methanogens, resulting in the reduced accumulation of VFA and fluctuations in alkalinity. The initial alkalinity of group P3 was 480.00 mg/L CaCO$_3$. On day 12, the alkalinity of group P3 increased to 706.67 mg/L CaCO$_3$, a 47.22% increase. The alkalinity increase rates of P1, P2, and P4 groups were 27.06, 36.24, and 43.48%, respectively. In the fermentation system, the alkalinity of P1, P2, P3, and P4 groups were not...
respectively. The P3 group showed the least fluctuation, which significantly different compared with that of the control group ($p > 0.05$). Although there was no significant correlation between the P3 group and the control group, the alkalinity increase was the greatest in the P3 group ($p > 0.05$). This indicated that the P3 group had the strongest buffering capacity, and reaching an acid–base balance was unhindered so that the risk of rapid acidification was reduced in the fermentation process. This is due to the addition of benzyl alcohol that acts a carbon source for microorganisms, which degrade the acidic substances in the fermentation system and convert them into biomethane.

3.6. Effects of Adding Benzyl Alcohol on pH. The activities of microorganisms are closely related to the pH of their environment, an important influencing factor in the lignite biomethanation fermentation system. Figure 6 shows the effects of benzyl alcohol on pH during anaerobic fermentation.

![Figure 6. Effects of adding different concentrations of benzyl alcohol on pH.](image)

Lignite decomposes under anaerobic conditions to produce VFA, which leads to a decline in pH. The variation trends of pH in P1, P2, P3, and P4 were similar to that of the control group, with no significant difference ($p > 0.05$). The initial pH of the lignite fermentation reaction system was adjusted to 7.0. At the initial stage of fermentation, the pH of all groups decreased, reaching the minimum on day 6, after which the pH started to increase. After fermentation, the pH values of the control, P1, P2, P3, and P4 groups were 7.04, 6.92, 6.95, 7.01, and 6.92, respectively. The P3 group showed the least fluctuation, which was further supported by the alkalinity of the P3 group. These results indicate that the biomethanation of lignite is the result of the joint action of multiple microorganisms. During the degradation of lignite by bacterial flora, organic degradation results in concentration changes of acetic acid, CO$_2$, H$_2$, and other substances in the environment. This changes the dominant genera that thrive in the methanogenic system leading to the replacement of bacteria by methanogenic archaea causing subsequent fluctuation of pH.

3.7. Scanning Electron Microscopy of Lignite and Its Fermentation Residue. In order to intuitively understand the effects of microbial transformation on the surface morphology of lignite, the raw lignite and its fermentation residue were observed by scanning electron microscopy (SEM). Figure 7 (Pa) displays the SEM image of lignite without fermentation. As shown in Figure 7 (Pa), the lignite sample surface without fermentation was relatively smooth and flat. After anaerobic fermentation, the surfaces of P1, P2, P3, and P4 groups got damaged noticeably, with the appearance of cracked and spongy pores. After fermentation, although the surface of lignite in the control group was damaged, it was not to the same extent as that of the experimental groups. This observation indicated that during the process of lignite biomethanation, the microflora left morphological traces on the surface due to the consumption of the fixed carbon and volatile components of lignite. Notably, the surface of lignite in the P3 group was destroyed extensively, indicating that more fixed carbon and volatile substances in the lignite were transformed and utilized by the microbial flora in the P3 group, from which more biomethane was ultimately generated.

3.8. Effects of Adding Different Substances on Total Biomethane Production. Effects of adding different substances on the total biomethane yield of lignite are shown in Table 4. Wang et al. reported that sodium acetate could significantly enhance biomethane yield from lignite. With the addition of 1640 mg/L sodium acetate, the biomethane yield was 42.89 mL/g, which was 1.33 times that of the control group. This occurrence is likely due to sodium acetate being a common nutrient composition of anaerobic bacteria, which can quickly activate the process of methanogenesis and promote its proliferation. Ma et al. successfully increased biomethane yield after adding 1000 mg/L LaCl$_3$ and 100 mg/L NdCl$_3$, and biomethane yield was 48.07 and 11.70% higher than that of the control group, respectively. This is because La$^{3+}$ and Nd$^{3+}$ can enhance the permeability of cell membranes, so that microorganisms can better absorb and utilize the nutrients in the lignite biomethanation fermentation system. The present study found that adding benzyl alcohol could increase the biomethane yield, with optimal results yielded from the addition of 2000 mg/L. The biomethane yield of adding 2000 mg/L benzyl alcohol was 4.03 mL/g, which was 1.15 times higher than that of the control group. Benzyl alcohol increased fermenting materials and provided carbon source to methanogens, resulting in our conclusion that benzyl alcohol promotes increased biomethane yield from lignite. Although the biomethane yield efficiency of the present experiment is lower than that of sodium acetate, our study provides a new idea for the self-supply of nutrients in lignite microbial transformation.

3.9. Technical and Economic Analysis. While adding nutrients can increase the biomethane yield, it also increases the cost of fermentative methanogenesis. Therefore, a technical and economic analysis is needed to determine the feasibility of implementing the technology of adding nutrients to improve the...
biomethane yield. Results of the technical and economic analysis of the benzyl alcohol additions and the control group are shown in Table 5. The cost of benzyl alcohol required by different fermentation groups were 194.27, 289.33, 383.53, and 462.93¥, while the profit of the biomethane yield increase was −0.24, 0.81, 1.59, and −2.28¥. The profit for all fermentation groups were in deficit. Therefore, we carried out related research on the extraction of fulvic acid from lignite fermentation residues.

4. CONCLUSIONS

Adding benzyl alcohol is beneficial for the biomethane of lignite. The experiment results have shown the following:

(1) The total biomethane yield of the control group is 3.50 mL/g without adding benzyl alcohol. By adding 2000 mg/L benzyl alcohol, the system yielded 15.14% greater biomethane than that of the control group, indicating that 2000 mg/L benzyl alcohol is the optimal amount to improve the biomethanation of lignite. This is because benzyl alcohol is added to the fermentation system as an intermediate product of biomethane yield from lignite, which can accelerate the biomethane production reaction.

(2) Day 6 showed the peak value of 0.001690 mmol/g of the coenzyme F420, which indicated that the addition of 2000 mg/L benzyl alcohol allowed 1.66 times as much of the coenzyme as that of the control group. This indicates that adding 2000 mg/L benzyl alcohol can increase the activity of methanogens, which in turn makes lignite more easily degraded to produce biomethane. In addition, with adding benzyl alcohol, more VFA was transformed and more biomethane was subsequently produced.

(3) The overall results indicated that the addition of benzyl alcohol is beneficial to the biomethanation process of lignite, which provides groundwork for adding process products during fermentation to increase biomethane yield.

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Notes

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