

http://pubs.acs.org/journal/acsodf

Article

Effect of Benzyl Alcohol on Biomethanation from Lignite

Ying Wang, Lichao Dong, Yanan Lu, Litong Ma,* Guanqun Gong, and Yaxiong Wang



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_{420} , 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_{420} , 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 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.¹ According to the degree of coalification, coal can be divided into peat, lignite, bituminous coal, and anthracite coal.² In China, the verified lignite resource reserves are 130.3 billion tons.³ However, as fuel, lignite is utilized difficultly due to its high moisture content, low calorific value, easy-weathering, and ease of spontaneous combustion.⁴ Due to its moisture content, lignite can produce valuable gaseous products such as H₂, CO, and CH₄ through H₂O or CO₂ gasification processes.^{6,7} 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,⁸ 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 nutrients⁹ and adding bacteria^{10,11} for the anaerobic fermentation system. For biomethane production from lignite, Xia et al.¹² found that hydrogenase and methanogen activity was advanced through the addition of 10 mg/L Fe²⁺ in the fermentation system. Wang et al.¹³ reported that 0.2 mol/L sodium acetate solution activated

Received: August 17, 2022 Accepted: October 26, 2022 Published: November 22, 2022





© 2022 The Authors. Published by American Chemical Society

Table 1. Basic Properties of the Lignite Sample^a

	industry analysis				analysis of physical and chemical properties		
material	$M_{\rm t}/{ m wt}$ %	$A_{\rm d}/{ m wt}$ %	$V_{\rm d}/{ m wt}$ %	$F_{\rm c}/{ m wt}$ %	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
${}^{a}M_{v}$ moisture; A_{d} , ash; V_{d} , volatile; and F_{c} , fixed carbon.							

methanogen activities and improved the efficiency of the enzymatic reaction, which significantly increased the biomethane quantity. Moreover, Bucha et al.⁸ 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.^{14,15} 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 F_{420} 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.¹⁶ Humic acid content was determined by the 1% sodium hydroxide extraction-potassium dichromate volumetric method;¹⁷ the content of water-soluble humic acid was determined by the volumetric titration method.¹⁸ 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.¹⁹ Table 2 shows the parameters of lignite and anaerobic activated sludge used in this study.

Table 2. Parameters of Lignite and Anaerobic Activated Sludge $\!\!\!\!\!\!\!^a$

parameters	lignite	anaerobic activated sludge	
TS	91.27%	0.66%	
VS	77.81%	0.38%	
VS/TS	0.85	0.58	
^{<i>a</i>} TS, total solids; VS, volatile solid.			

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 μ m, 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

Table 3. Different Concentrations of Benzyl Alcohol Added

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

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 F_{420} 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.²⁰ 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 mm was measured by a UV-vis spectrophotometer (756, Youke, China). The concentration of coenzyme F₄₂₀ was calculated according to the equation $C = (A_1 - A_0) \times f/\varepsilon \times L$, where ε 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. $FeCl_3 \cdot 6H_2O$ (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 ($V_{sulfuric acid}/V_{distilled water} = 1:1$). 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

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 multiparameter comprehensive water quality (ET99731, Germany).²²

2.6. Determination of pH and Surface Morphology. The pH value was measured with a pH meter (PHS-25, 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 $p \le 0.01$ are considered "highly significant", $p \le 0.05$, "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.

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 ($p \ge 0.05$) 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 CO₂ removal from benzyl alcohol to form catechol, and then pyruvic acid and acetyl

coenzyme A (acetyl-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.^{23,24} 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.²⁵ Therefore, the total biomethane yield of the P1 group was lower than that of the control group. CO₂ 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



Figure 2. Effects of adding different concentrations of benzyl alcohol on the daily biomethane yield.

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 ($p \le 0.01$). 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.²⁹ 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.³⁰ 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



Figure 3. Effects of adding different concentrations of benzyl alcohol on coenzyme $\rm F_{420}$ activity.

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 F420 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 F₄₂₀ 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 ($p \le 0.05$), 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.³¹ The organic matter of lignite is converted into VFA, which is used as a raw material to produce CH_4 by methanogens in the anaerobic fermentation process.³² 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 ($p \le 0.05$).

In the process of fermentation, the overall concentration of VFA first increased, then decreased, and finally stabilized,



Figure 4. Changes in VFA on adding different concentrations of benzyl alcohol.

consistent with the theory that organic matter in anaerobic fermentation first decomposes into VFA, then gets converted into acetic acid and H₂, and finally forms CH₄.^{33,34} 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 CH₄ 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 CH₄ because of the conversion of benzyl alcohol into benzoic acid that participates in the TCA to generate VFA, such as acetic acid.35

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.³⁶ 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 CaCO₃, which increased to 710.00 mg/L CaCO₃ by 31.48% on day 6. This may be due to the increase of CO₂ 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 CO₂ from CH₄ at the beginning of fermentation.³⁷ Subsequently, VFA was converted into CH₄ 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 CaCO₃. On day 12, the alkalinity of group P3 increased to 706.67 mg/L CaCO₃, 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



Figure 5. Effects of adding different concentrations of benzyl alcohol on alkalinity.

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.

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.^{38,39}

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.⁴⁰ 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.¹³ 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.¹³ Ma et al.⁴¹ successfully increased biomethane yield after adding 1000 mg/L LaCl₃ and 100 mg/L NdCl₃, and biomethane yield was 48.07 and 11.70% higher than that of the control group, respectively. This is because La³⁺ and Nd³⁺ can enhance the permeability of cell membranes, so that microorganisms can better absorb and utilize the nutrients in the lignite biomethane fermentation system.⁴¹ 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



Figure 7. SEM of lignite and its fermentation residue.



raw material	exogenous substance	biomethane yield/(mL/g)	references
lignite		32.22	13
lignite	sodium acetate (1640 mg/L)	42.89	13
lignite		16.08	32
lignite	LaCl ₃ (1000 mg/L)	23.81	32
lignite	$NdCl_3$ (100 mg/L)	17.80	32
lignite		3.50	this article
lignite	benzyl alcohol (2000 mg/L)	4.03	this article

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

 Table 5. Technical and Economic Analysis of the Benzyl

 Alcohol Addition and the Control Group

	benzyl alcohol cost (¥)	increase in biomethane yield (¥)	net savings compared with those of the control group (¥)
P1	194.27	-0.24	-194.51
P2	289.33	0.81	-288.52
P3	383.53	1.59	-381.94
P4	462.93	-2.28	-465.21

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.⁴²

4. CONCLUSIONS

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

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 F_{420} , 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.

AUTHOR INFORMATION

Corresponding Author

Litong Ma – School of Chemistry and Chemical Engineering, Inner Mongolia University of Science and Technology, Baotou 014010, P. R. China; Inner Mongolia Engineering Research Center of Comprehensive Utilization of Bio-coal Chemical Industry, Baotou 014010, P. R. China; Laboratory of Low Rank Coal Carbon Neutralization, Inner Mongolia University of Science and Technology, Baotou 014010, P. R. China;
orcid.org/0000-0002-9850-2601; Email: mlt0916@ 126.com

Authors

- Ying Wang School of Chemistry and Chemical Engineering, Inner Mongolia University of Science and Technology, Baotou 014010, P. R. China
- Lichao Dong School of Chemistry and Chemical Engineering, Inner Mongolia University of Science and Technology, Baotou 014010, P. R. China
- Yanan Lu School of Chemistry and Chemical Engineering, Inner Mongolia University of Science and Technology, Baotou 014010, P. R. China

Guanqun Gong – School of Chemical Engineer & Technology, China University of Mining and Technology, Xuzhou 221116, P. R. China; © orcid.org/0000-0001-7896-9477 Yaxiong Wang – School of Chemistry and Chemical Engineering, Inner Mongolia University of Science and Technology, Baotou 014010, P. R. China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.2c05282

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors are grateful for the financial support from Chinese Academy of Sciences "Light of West China" Program (2019), Science and Technology Plan Project of Inner Mongolia Autonomous Region (2020GG0158), Talent Development Fund Project of Inner Mongolia Autonomous Region (2021), and Fundamental Research Funds for Inner Mongolia University of Science & Technology (2022).

REFERENCES

(1) Sekhohola, L. M.; Igbinigie, E. E.; Cowan, A. K. Biological degradation and solubilisation of coal. *Biodegradation* **2013**, *24*, 305–318.

(2) Ma, L.; Li, J. Resources and utilization of peat in Inner Mongolia. *Inn. Mongulia Petrochem. Ind.* **2014**, *40*, 33–35.

(3) Ren, H. Processing technology and development prospect of lignite. *Shandong Chem. Ind.* **2016**, *45*, 66–99.

(4) Jin, L.; Li, Y.; Lin, L.; Zou, L.; Hu, H. Drying characteristic and kinetics of Huolinhe lignite in nitrogen and methane atmospheres. *Fuel* **2015**, *152*, 80–87.

(5) Shafiee, S.; Topal, E. When will fossil fuel reserves be diminished? *Policy* **2009**, *37*, 181–189.

(6) Li, N.; Li, Y.; Zhou, H.; Liu, Y.; Song, Y.; Zhi, K.; He, R.; Yang, K.; Liu, Q. Direct production of high hydrogen syngas by steam gasification of Shengli lignite/chars: Significant catalytic effect of calcium and its possible active intermediate complexes. *Fuel* **2017**, *203*, 817–824.

(7) Li, N.; Te, G.; Liu, Q.; Ban, Y.; Wang, Y.; Zhang, X.; Wang, J.; He, R.; Zhi, K. Effect of metal ions on the steam gasification performance of demineralized Shengli lignite char. *Int. J. Hydrogen Energy* **2016**, *41*, 22837–22845.

(8) Bucha, M.; Detman, A.; Pleśniak, L.; Drzewicki, W.; Kufka, D.; Chojnacka, A.; Mielecki, D.; Krajniak, J.; Jędrysek, M. O.; Sikora, A.; Marynowski, L. Microbial methane formation from different lithotypes of Miocene lignites from the Konin Basin, Poland: Geochemistry of the gases and composition of the microbial communities. *Int. J. Coal Geol.* **2020**, *229*, 103558.

(9) Bucha, M.; Jędrysek, M.-O.; Kufka, D.; Pleśniak, L.; Marynowski, L.; Kubiak, K.; Błaszczyk, M. Methanogenic fermentation of lignite with carbon-bearing additives, inferred from stable carbon and hydrogen isotopes. *Int. J. Coal Geol.* **2018**, *186*, 65–79.

(10) Zhan, D.; He, H.; Liao, Y.; Zhao, S.; Yao, J.; Xiao, D.; Tang, J.; Tao, X. Community structure analysis of methanogenic flora and optimization for bioaugmentation methane generation from lignite. *Acta Microbiol. Sin.* **2018**, *584*, 684–698.

(11) Wang, B.; Tai, C.; Wu, L.; Chen, L.; Liu, J.; Hu, B.; Song, D. Methane production from lignite through the combined effects of exogenous aerobic and anaerobic microflora. *Int. J. Coal Geol.* 2017, 173, 84–93.

(12) Xia, D.; Huang, S.; Yan, X.; Yuan, R. Influencing mechanism of Fe2+ on biomethane production from coal. *J. Nat. Gas Sci. Eng.* **2021**, *91*, 103959.

(13) Wang, A.; Qin, Y.; Shao, P. Influences of different substrates on simulated lignite biogas production. *Int. J. Min. Sci. Technol.* **2015**, *25*, 991–995.

(14) Smidt, E.; Meissl, K.; Schmutzer, M.; Hinterstoisser, B. Cocomposting of lignin to build up humic substances-Strategies in waste management to improve compost quality. *Ind. Crop. Prod.* **2008**, *27*, 196–201. (15) Dawange, M.; Galkin, M. V.; Samec, J. S. M. Selective aerobic benzylic alcohol oxidation of lignin model compounds: Route to aryl ketones. *ChemCatChem* **2015**, *7*, 401–404.

(16) Sirucek, D.; Kalina, M.; Klucakova, M. Influence of the application of lignite on the distribution of organic carbon in soil. *12th International Conference on Nanomaterials*—Research and Application (NANOCON), 2020; pp 489–494.

(17) Lu, Y. N.; Ma, L. T. Effects of extractant and pretreatment on the structure of humic acid from methane fermentation peat residue. *Clean Coal Technol.* **2021**, *27*, 218–224.

(18) Yang, X.; Qiao, G.; Duan, J. Determination of fulvic acid content by volumetric analysis. *Henan Chem. Ind.* **2006**, *23*, 42–43.

(19) APHA. Standard Methods for the Examination of Water and Wastewater; American Public Health Association: Washington, DC, USA, 2005.

(20) Zhao, Y.; Li, X.; Du, G.; Chen, J. Effect of cobalt and its complexation on the key enzymes in methanogenesis. *Water Resour. Prot.* **2008**, *24*, 82–85.

(21) Dong, L. C.; Ma, L. T.; Wang, Y. X. Effect of humic acid precursor lignin on biomethanation of lignite. *Chem. Eng.* **2020**, *48*, 69–73.

(22) Farno, E.; Baudez, J.; Parthasarathy, R.; Eshtiaghi, N. Impact of thermal treatment on the rheological properties and composition of waste activated sludge: COD solubilisation as a footprint of rheological changes. *Chem. Eng. J.* **2016**, *295*, 39–48.

(23) Lin'kova, Y. V.; Dyakonova, A. T.; Gladchenko, M. A.; Kalyuzhnyi, S. V.; Kotova, I. B.; Stams, A.; Netrusov, A. I. Methanogenic degradation of (amino)aromatic compounds by anaerobic microbial communities. *Appl. Biochem. Microbiol.* **2011**, 475, 507–514.

(24) Johnson, C. W.; Beckham, G. T. Aromatic catabolic pathway selection for optimal production of pyruvate and lactate from lignin. *Metab. Eng.* **2015**, *28*, 240–247.

(25) Islam, M. A.; Morton, D. W.; Johnson, B. B.; Angove, M. J. Adsorption of humic and fulvic acids onto a range of adsorbents in aqueous systems, and their effect on the adsorption of other species: A review. *Sep. Purif. Technol.* **2020**, *247*, 116949.

(26) Pavlović, M.; Dimitrijević, A.; Bezbradica, D.; Milosavić, N.; Gavrović-Jankulović, M.; Šegan, D.; Veličković, D. Dual effect of benzyl alcohol on α -glucosidase activity: efficient substrate for high yield transglucosylation and non-competitive inhibitor of its hydrolytic activity. *Carbohydr. Res.* **2014**, 387, 14–18.

(27) Harwood, C. S.; Burchhardt, G.; Herrmann, H.; Fuchs, G. Anaerobic metabolism of aromatic compounds via the benzoyl-CoA pathway. *FEMS Microbiol. Rev.* **1998**, *22*, 439–458.

(28) Todini, O.; Pol, L. H. Anaerobic degradation of benzaldehyde in methanogenic granular sludge: the influence of additional substrates. *Appl. Microbiol. Biotechnol.* **1992**, *38*, 417–420.

(29) Zhuang, L.; Tang, J.; Wang, Y. Q.; Hu, M.; Zhou, S. G. Conductive iron oxide minerals accelerate syntrophic cooperation in methanogenic benzoate degradation. *J. Hazard. Mater.* **2015**, *293*, 37–45.

(30) Lu, X.; Wang, H.; Ma, F.; Li, A.; Zhao, G. Effects of an iron oxidezeolite additive on process performance of anaerobic digestion of swine waste at mesophilic, ambient and psychrophilic temperatures. *Environ. Sci-Wat. Res.* **2018**, *4*, 1014–1023.

(31) Bermúdez-Penabad, N.; Kennes, C.; Veiga, M. C. Anaerobic digestion of tuna waste for the production of volatile fatty acids. *Waste Manag.* **2017**, *68*, 96–102.

(32) Wijesinghe, D. T. N.; Suter, H. C.; Scales, P. J.; Chen, D. Lignite addition during anaerobic digestion of ammonium rich swine manure enhances biogas production. *J. Environ. Chem. Eng.* **2021**, *9*, 104669.

(33) Park, S. Y.; Liang, Y. Biogenic methane production from coal: A review on recent research and development on microbially enhanced coalbed methane (MECBM). *Fuel* **2016**, *166*, 258–267.

(34) Liu, H.; Chen, Y. Enhanced Methane Production from Food Waste Using Cysteine To Increase Biotransformation of l-Mono-saccharide, Volatile Fatty Acids, and Biohydrogen. *Environ. Sci. Technol.* **2018**, *52*, 3777–3785.

(36) Feizi, M.; Jalali, M.; Renella, G. Available alkalinity and N mineralization are key factors regulating soil pH value of an organically amended Iranian agricultural soil. *Arid Land Res. Manag.* **2017**, *31*, 140–158.

(37) Zhang, Z.; Zhang, L.; Zhou, Y.; Chen, J.; Liang, Y.; Wei, L. Pilotscale operation of enhanced anaerobic digestion of nutrient-deficient municipal sludge by ultrasonic pretreatment and co-digestion of kitchen garbage. *Int. J. Coal Geol.* **2013**, *1*, 73–78.

(38) Ritter, D.; Vinson, D.; Barnhart, E.; Akob, D. M.; Fields, M. W.; Cunningham, A. B.; Orem, W.; McIntosh, J. C. Enhanced microbial coalbed methane generation: A review of research, commercial activity, and remaining challenges. *Int. J. Coal Geol.* **2015**, *146*, 28–41.

(39) Wang, H.; Lin, H.; Dong, Y.; Sui, M.; Li, Y. Experiments on the gas production of brown coal degraded by exogenous methanogens. *Petrol. Explor. Dev.* **2012**, *39*, 813–817.

(40) Ahamd, M.; Zeshan, M. S. H.; Nasim, M.; Zahir, Z. A.; Nadeem, S. M.; Nazli, F.; Jamil, M. Improving the productivity of cucumber through combined application of organic fertilizers and pseudomonas fluorescens. *Pak. J. Agr. Sci.* **2015**, *52*, 1011–1016.

(41) Ma, L.; Hao, S.; Wang, Y.; Ji, X. Effect of Rare Earth Elements on Lignite Biomethanation. *Coal Convers.* **2020**, *436*, 33–39.

(42) Liu, Y. Y.; Zhao, W. Y.; Cheng, J. G.; Ma, L. T. Effect of lignite particle diameter on preparation of humic acid and fulvic acid by alkaline method. *Coal Convers.* **2020**, *431*, 42–46.