

# Spiral-Pipe Gas Anaerobic Digester

Minghao Li, Xingling Zhao, Kai Wu, Chengyue Liang, Jing Liu, Hong Yang, Changmei Wang, Bin Yang, Fang Yin, and Wudi Zhang\*



Cite This: *ACS Omega* 2024, 9, 23202–23208



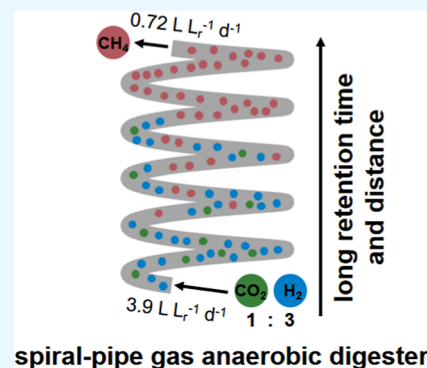
Read Online

ACCESS |

Metrics & More

Article Recommendations

**ABSTRACT:** The reduction of carbon dioxide to methane using hydrogen is an important process in biogas production. However, designing gas anaerobic digesters (GADs) based on this reaction presents several challenges. In this study, we developed an innovative spiral-pipe gas anaerobic digester (SGAD) to increase the displacement distance between the bubbles, thus prolonging the gas retention time and facilitating the reduction of CO<sub>2</sub> to CH<sub>4</sub> via H<sub>2</sub>. The process was successfully demonstrated by using a CO<sub>2</sub>/H<sub>2</sub> ratio of 1:3 and a gas-feeding rate of 3.9 L L<sub>r</sub><sup>-1</sup> d<sup>-1</sup>. During the experiment, more than 98% of the CO<sub>2</sub> and 96% of the H<sub>2</sub> were consumed, resulting in biogas containing ca. 86–96% CH<sub>4</sub>. Additionally, we applied our proposed evaluation methodology for assessing GAD performance to evaluate the performance of the SGAD. This methodology serves as a reference for evaluating and designing GAD systems. The innovative design of the SGAD and the corresponding evaluation methodology offer new insights into the design of reactors.



spiral-pipe gas anaerobic digester

## 1. INTRODUCTION

After the signing of the United Nations Framework Convention on Climate Change (UNFCCC), limiting the global temperature rise to 2 °C above preindustrial levels has become a common long-term goal for all countries. The European Union aims to create a climatically neutral society by 2050, defined as reducing greenhouse gas emissions by at least 40% compared to the 1990 baseline.<sup>1</sup> Achieving this would require an 80–95% reduction in greenhouse gas emissions. To mitigate the impact of global warming, increasing attention should be given to reducing carbon dioxide emissions and increasing the share of renewables in the energy mix.<sup>2</sup>

Anaerobic digestion (AD) is a biochemical process that occurs in oxygen-free environments, where complex metabolic pathways decompose organic waste, ultimately resulting in the formation of biogas.<sup>3</sup> Biogas, which typically comprises 55–70% CH<sub>4</sub> and 30–45% CO<sub>2</sub>, can be generated via the absorption of CO<sub>2</sub>. Many recent studies have focused on the biogas industry.<sup>4</sup> Compared with other sources of renewable energy, such as solar and wind energy, biogas can be stored more efficiently with minimal energy loss. Therefore, the production and use of biogas hold substantial promise for further development, with diverse applications.<sup>5</sup> Raw biogas can be used directly, such as in combustion or fusion processes. However, CO<sub>2</sub>, the primary impurity in biogas, severely reduces its practical value.<sup>5</sup> Hence, in most cases, biogas must be upgraded to improve its quality. The biomethane produced by upgrading biogas typically shares similar characteristics with natural gas, including high CH<sub>4</sub> content and purity, making it suitable as a fuel for compressed natural gas engine vehicles.<sup>6</sup>

Biomethane exhibits significantly better quality and calorific value than biogas. Despite the high investment and operational requirements associated with upgrading biogas, it represents a valuable source of renewable energy. Research into biogas-upgrade technology and its application is therefore becoming increasingly important.

Various chemical and physical methods can be used to remove CO<sub>2</sub> from biogas, thereby increasing the proportion of CH<sub>4</sub> in biogas. These methods include high-pressure water washing, pressure swing adsorption, and membrane separation.<sup>3,7</sup> Notably, although CO<sub>2</sub> is separated from biogas using these methods, the quantity of biogas is significantly lower after the upgrade. Upgrading biogas via hydrogenotrophic-based biological methanation (HBM) can resolve this problem. HBM refers to the conversion of CO<sub>2</sub> in the mixed gas into CH<sub>4</sub> by hydrogenotrophic methanogens (HMs) following the addition of H<sub>2</sub> to raw biogas. HBM-upgraded biogas generates significantly more energy than raw biogas. HBM has relatively low operational and energy costs and does not require expensive chemicals, making it one of the most efficient methods for converting excess energy into natural gas and avoiding energy loss.<sup>8</sup> Based on these findings, Luo and Angelidaki<sup>9</sup> proposed the conversion of excess hydrogen to

Received: November 8, 2023

Revised: December 9, 2023

Accepted: January 16, 2024

Published: May 20, 2024



methane via HBM. Therefore, HBM represents a more advanced approach.

HBM biogas upgrading can be divided into *in situ* and *ex situ* approaches, which differ in terms of the reactors and feed-gas injection methods used. Using *in situ* upgrading,  $H_2$  is directly injected into the AD reactor, allowing the simultaneous upgrading of biogas and AD in the reactor. Through the participation of HMs, the  $H_2$  and excess  $CO_2$  from AD are then converted into  $CH_4$ .<sup>3</sup> Conversely, *ex situ* upgrading requires a separate gas anaerobic digester (GAD). In this method, AD-generated biogas is combined with exogenous hydrogen and injected into the upgrading reactor, where HM enrichment occurs and the upgrading reaction takes place. In *ex situ* upgrading, HBM operates independently of AD, ensuring that the environment within the AD reactor remains unaffected by external hydrogenation. As a result, the stability of AD is not compromised, and potential problems related to the biological mechanisms are minimized.<sup>10</sup> In addition, owing to the simpler biochemistry and stability of *ex situ* HBM upgrading, which relies solely on carbon dioxide, hydrogen, and the activity and essential nutrients of HMs, the upgrading process is more controlled within the *ex situ* reactor.<sup>3,11</sup>

The effectiveness of *ex situ* upgrading depends on the design of the GAD. Achieving better results in the reduction of  $CO_2$  to  $CH_4$  via  $H_2$  requires a reactor in which the HMs are fully utilized within the GAD and exhibit excellent performance. However, the low solubility of hydrogen in aqueous media and the limited gas–liquid phase transfer of hydrogen hinder its bioavailability, thus limiting the efficiency of  $CO_2$  reduction to  $CH_4$  via  $H_2$ .<sup>3,12,13</sup> Due to the gas–liquid transfer limitation, few of the upgrading methods can achieve a high injection volume, conversion rate, and methane content. Jensen et al.<sup>14</sup> optimized biogas upgrading in bioreactors by increasing the gas–liquid contact area and extending the gas retention time, by incorporating fillers in the upflow anaerobic sludge blanket reactor, which reduced  $H_2$  diffusion and enhanced gas–liquid contact. In addition, the liquid was sprayed from top to bottom in a trickling filter bed, effectively increasing the contact area between the hydrogen and liquid. This liquid circulation strategy promoted biological reactions and increased the methane level to 98% of the biogas.<sup>15</sup>

A continuous stirred tank reactor can be integrated with various delivery and distribution devices (such as a bubble column, tube, or persistent pump) to increase biogas-upgrade capacity.<sup>16</sup> Membrane biofilm reactors have attracted considerable attention in recent years. The addition of a membrane enhances biofilm formation, improving the contact area between microbes, hydrogen, and the liquid, thus facilitating biogas upgrading. Hafuka et al.<sup>17</sup> achieved a methane content of 92.0% and methane yield of  $310.0 \text{ mL g}^{-1}$  volatile solids (VS) by using polyvinylidene fluoride hollow fibers with  $H_2$  supply. Zhang et al.<sup>18</sup> achieved a methane yield of  $0.36 \text{ L h}^{-1}$  (90.3%  $CH_4$ ) using an anaerobic membrane biofilm reactor. Using a porous gas distributor made from silicon carbide, Ghofrani-Isfahani et al.<sup>19</sup> were able to upgrade an artificially prepared synthetic gas mixture ( $H_2/CH_4/CO_2$ , 62%:23%:15%) to biomethane comprising 98%  $CH_4$ . Sun et al.<sup>16</sup> found that using a reasonable hydrogen flow rate and a moderate gas recirculation rate can make the biogas-upgrade process more efficient.

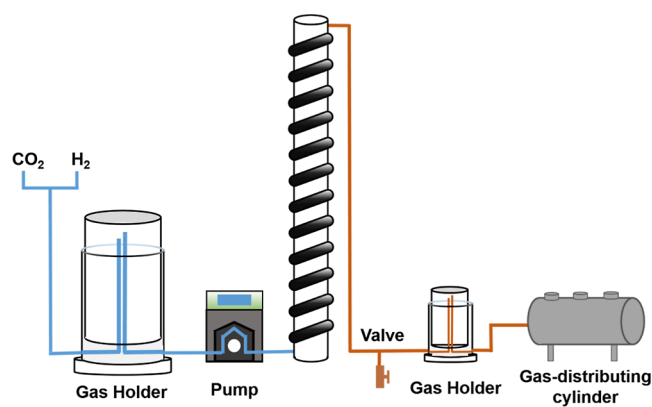
Although *ex situ* biogas upgrading is efficient, GAD construction requires an additional investment and operating expenses. In Germany, most of the biogas is generated by

small- and medium-sized AD plants in rural areas, while approximately 87% of the upgrading reactors are large facilities.<sup>20</sup> Although farmers generally have a positive attitude toward biogas and HBM,<sup>20–22</sup> they prefer to support only small- and medium-sized equipment owing to economic reasons.<sup>22,23</sup> Therefore, it is necessary to develop a GAD reactor that is small, has a low cost, and is highly efficient. The novel spiral-pipe gas anaerobic digester (SGAD) used in this study uses a low-cost spiral-pipe structure that can be wound directly around the AD reactor, enabling convenient *ex situ* biogas upgrading.

Methods for evaluating GAD performance have rarely been mentioned in the current studies. The methane production rate, which is typically used to evaluate the performance and efficiency of *ex situ* biogas-upgrade reactors, serves as a simple and effective evaluation indicator. While it directly reflects the relationship between the reactor and methane, it does not fully reflect the impact of the reactor on HMs. It is therefore necessary to evaluate the overall performance of the reactor. In this study, we propose an innovative methodology for evaluating the GAD, using a series of evaluation indicators to comprehensively assess reactor performance.

## 2. MATERIALS AND METHODS

**2.1. Reactor Setup.** The SGAD comprised a PVC silicone hose (length: 5 m; inner diameter: 14 mm; tube wall: 1 mm; working volume: 750 mL) wound around a 1 m plexiglass post at an angle of approximately  $20^\circ$  from the floor. The initial estimated volume of anaerobic sludge in the reactor was approximately 750 mL. The reactor had two entrances: a feed-gas inlet at the bottom and a biogas outlet at the top. The feed gas was prepared and stored in a wet-type gas holder (Plexiglas, 10 L) and was pumped into the reactor from the inlet using a peristaltic pump. The gas was collected in a wet-type gas holder (Plexiglas, 3.5 L) attached to the top of the reactor. To prevent clogging of the piping system, a valve was placed in front of the gas holder to drain the sludge. The reactor setup is shown in Figure 1.



**Figure 1.** Schematic diagram of the SGAD biomethanation reactor.

Prior to HM enrichment, sufficient  $CO_2$  was fed into the system to saturate the system solution with  $CO_2$ . The gas mixture ( $CO_2/H_2$ , 1:4) was fed into the SGAD to achieve HM enrichment. The gas mixture was prepared daily, stored in a gas holder, and thereafter continuously supplied to the bottom of the SGAD using a peristaltic pump at a gas-feeding rate (GFR) of  $1.5 \text{ L L}_r^{-1} \text{ d}^{-1}$ , where  $L_r$  refers to liters of reactor

volume. The enrichment process took 30 days to complete. Thereafter, to determine the optimal GFR and ratio of the feed gas, the gas mixture was fed into the SGAD at a rate of  $2.4 \text{ L L}_r^{-1} \text{ d}^{-1}$ , at a theoretical  $\text{CO}_2/\text{H}_2$  ratio of 1:4. Based on the composition of the biogas, the GFR and the  $\text{CO}_2/\text{H}_2$  ratio in the feed gas were continuously adjusted. The experiment was carried out at temperatures of  $20.2\text{--}26.5 \text{ }^\circ\text{C}$ .

**2.2. Analytical Methods.** Gas production was measured using a wet-type gas flow meter (Lv Qingqi LML-L, China), while the temperature was monitored using a centigrade thermometer.  $\text{CH}_4$ ,  $\text{H}_2$ ,  $\text{CO}_2$ , and  $\text{N}_2$  components were analyzed by using a meteorological chromatograph (GC-6890A, Zhejiang Fuli Precision Instrument Co., Ltd., Zhejiang, PR China). The column type: packed column (Porapak Q,  $30 \text{ m} \times 0.53 \text{ mm}$ ). The gasification chamber temperature was set at  $80 \text{ }^\circ\text{C}$ , column temperature at  $80 \text{ }^\circ\text{C}$ , and the thermal conductivity detector temperature at  $50 \text{ }^\circ\text{C}$ . The carrier gas used was argon (99.999%) with a flow rate of  $40 \text{ mL/min}$ .

**2.3. Inoculum and Substrate.** The hydrogen (in a cylinder, 99.999%) was produced by Chengdu Jinkesing Gas Co., Ltd. The carbon dioxide (in a cylinder, 99.999%) was produced by Kunming Messer Gas Products Co., Ltd. The standard gas composition for gas chromatography (Foshan KODI Gas Chemical Co., Ltd.) was as follows:  $\text{CH}_4$  ( $90.2 \times 10^{-2} \text{ mol mol}^{-1}$ ),  $\text{H}_2$  ( $1.98 \times 10^{-2} \text{ mol mol}^{-1}$ ),  $\text{N}_2$  ( $2.98 \times 10^{-2} \text{ mol mol}^{-1}$ ), and  $\text{CO}_2$  ( $5.02 \times 10^{-2} \text{ mol mol}^{-1}$ ). The inoculum was obtained from pig manure (from long-term domesticated pigs) with a total solid (TS) content of  $4.19 \pm 0.10\%$  and a VS content of  $41.37 \pm 1.14\%$ ; the manure was first sufficiently anaerobically fermented to no longer produce biogas.

**2.4. Calculations.** In this study, SGAD performance was demonstrated using the  $\text{H}_2$  conversion rate ( $\eta_{\text{H}_2}$ ),  $\text{CO}_2$  conversion rate ( $\eta_{\text{CO}_2}$ ), methane production rate ( $R$ ), methane formation rate from TS ( $R_{\text{ts}}$ ), and methane formation rate from VS ( $R_{\text{vs}}$ ). Flow rates are shown in units of  $\text{L L}_r^{-1} \text{ d}^{-1}$ .  $\eta_{\text{H}_2}$  is defined as

$$\eta_{\text{H}_2} = \frac{H_{2\text{in}} - H_{2\text{out}}}{H_{2\text{in}}} \times 100\% \quad (1)$$

where  $H_{2\text{in}}$  and  $H_{2\text{out}}$  represent the  $\text{H}_2$  flow rate fed into the reactors and the  $\text{H}_2$  flow rate in the output biogas, respectively.  $\eta_{\text{CO}_2}$  is defined as

$$\eta_{\text{CO}_2} = \frac{\text{CO}_{2\text{in}} - \text{CO}_{2\text{out}}}{\text{CO}_{2\text{in}}} \times 100\% \quad (2)$$

where  $\text{CO}_{2\text{in}}$  and  $\text{CO}_{2\text{out}}$  represent the  $\text{CO}_2$  flow rate fed into the reactors and the  $\text{CO}_2$  flow rate in the output biogas, respectively.  $R$  is defined as

$$R = \frac{\text{CH}_{4\text{out}}}{V_R \times I_d} \quad (3)$$

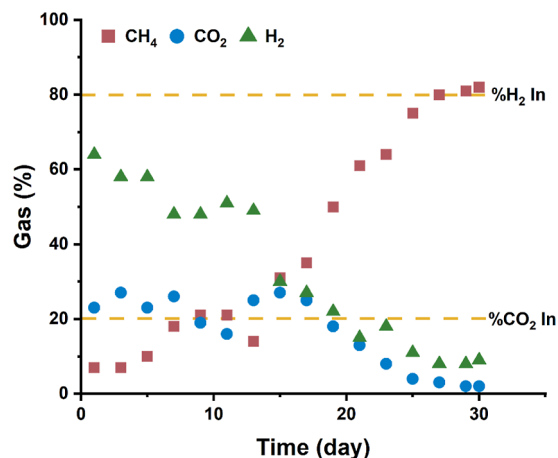
where  $\text{CH}_{4\text{out}}$  represents the  $\text{CH}_4$  flow rate in the output biogas and  $V_R$  represents the working volume of the reactor.  $R_{\text{ts}}$  and  $R_{\text{vs}}$  are defined as follows

$$R_{\text{ts}} = \frac{\text{CH}_{4\text{out}}}{V_R \times I_d \times \text{TS}} \quad (4)$$

$$R_{\text{vs}} = \frac{\text{CH}_{4\text{out}}}{V_R \times I_d \times \text{TS} \times \text{VS}} \quad (5)$$

### 3. RESULTS AND DISCUSSION

**3.1. Reactor Performance.** This study presents a novel HBM reactor that achieves a high conversion rate by incorporating a spiral structure that increases the bubble path length and the overall retention time. During the microbial enrichment stage,  $\text{CO}_2$  and  $\text{H}_2$  were injected into the SGAD at a ratio of 1:4, at  $1.5 \text{ L L}_r^{-1} \text{ d}^{-1}$ . After 30 days of operation, a methane content of approximately 80% was achieved (Figure 2).



**Figure 2.**  $\text{CH}_4$ ,  $\text{H}_2$ , and  $\text{CO}_2$  contents in the biomethanation reactor (SGAD over time). Operational conditions: GFR of  $1.5 \text{ L L}_r^{-1} \text{ d}^{-1}$ ;  $\text{CO}_2/\text{H}_2$  ratio, 1:4.

Next, the feed gas was pumped in at different rates (Table 1). Notably, when the GFR was increased to  $3.1 \text{ L L}_r^{-1} \text{ d}^{-1}$ , the methane yield in the biogas decreased, and the amount of excess  $\text{H}_2$  exceeded that of  $\text{CO}_2$  by approximately 7 times, indicating a high ratio of  $\text{H}_2$  in the feed gas. Burkhardt et al.<sup>24</sup> reported that the optimum  $\text{H}_2/\text{CO}_2$  ratio was 4. However, the current findings suggest a slightly lower  $\text{H}_2$  requirement, at just below 4 parts. This implies that a fraction of the  $\text{CO}_2$  was consumed by microorganisms for biomass build-up. These findings align with the conclusions of Rachbauer et al.<sup>25</sup> Similarly, an  $\text{H}_2/\text{CO}_2$  ratio below 4:1 was reported in a study investigating the influence of different pressures on biological hydrogen methanation.<sup>26</sup> Wahid et al.<sup>27</sup> showed that excess  $\text{H}_2$  would increase the pH to  $>8.0$  and destabilize the system, leaving the excess  $\text{H}_2$  unutilized and diluting methane levels. The impact of the feed-gas ratio requires further investigation.

To explore the optimal conversion rate using the SGAD and to obtain high-quality biogas while adjusting the GFR, it is essential to modify the feed-gas ratio based on the current load and the composition of the gas that is produced. Next, we increased the  $\text{CO}_2/\text{H}_2$  ratio in the feed gas (Table 1). The maximum content of  $\text{CH}_4$  ( $\text{CH}_4$  97%,  $\text{H}_2$   $< 1\%$ ,  $\text{CO}_2$  2%) was obtained at a GFR of  $3.9 \text{ L L}_r^{-1} \text{ d}^{-1}$ . Increasing the GFR further did not achieve better results, revealing that  $3.9 \text{ L L}_r^{-1} \text{ d}^{-1}$  is the optimal GFR for the SGAD. In order to assess the stability of the SGAD, the system was operated under optimal load conditions ( $3.9 \text{ L L}_r^{-1} \text{ d}^{-1}$ ) for a duration of 15 days, maintaining a  $\text{CO}_2/\text{H}_2$  ratio of 1:3. The obtained results revealed an average methane content of  $91 \pm 4.5\%$  in the produced biogas, with average hydrogen and carbon dioxide conversion rates of  $96 \pm 3.0$  and  $98 \pm 0.4\%$ , respectively. Importantly, the data exhibited minimal fluctuations over the



Table 1. Performance of the SGAD Biomethanation Reactor under Steady-State and Operating Conditions<sup>a</sup>

GFR		2.4	3.1	3.6	3.9	4.2
CO <sub>2</sub> /H <sub>2</sub>	L L <sub>r</sub> <sup>-1</sup> d <sup>-1</sup>	1:4	1:4	1:3.5	1:3	1:3
outflow gas composition						
CH <sub>4</sub>	%	69 ± 9.9	66 ± 5.3	85 ± 5.4	91 ± 4.5	84 ± 2.3
H <sub>2</sub>	%	14 ± 6.4	29 ± 8.5	7.3 ± 4.3	7.8 ± 5.2	10 ± 1.7
CO <sub>2</sub>	%	17 ± 4.5	4.4 ± 2.6	7.7 ± 2.3	1.5 ± 0.5	5.9 ± 1.1
conversion rate						
η <sub>H<sub>2</sub></sub>	%	90 ± 5.7	82 ± 5.7	95 ± 2.8	96 ± 3.0	94 ± 1.1
η <sub>CO<sub>2</sub></sub>	%	80 ± 7.0	94 ± 3.0	92 ± 2.9	98 ± 0.4	93 ± 1.3
methane production rate						
R	L L <sub>r</sub> <sup>-1</sup> d <sup>-1</sup>	0.41 ± 0.07	0.57 ± 0.1	0.69 ± 0.1	0.72 ± 0.03	0.88 ± 0.08
R <sub>TS</sub>	L kg <sup>-1</sup> TS d <sup>-1</sup>	9.79 ± 1.1	13.60 ± 1.7	16.47 ± 1.0	17.18 ± 0.5	21.00 ± 1.3
R <sub>VS</sub>	L kg <sup>-1</sup> VS d <sup>-1</sup>	23.69 ± 2.5	32.94 ± 4.1	39.87 ± 2.3	41.61 ± 1.1	50.85 ± 3.2

<sup>a</sup>η<sub>H<sub>2</sub></sub> and η<sub>CO<sub>2</sub></sub>, conversion rates of H<sub>2</sub> and CO<sub>2</sub>; R, methane production rate; R<sub>TS</sub> and R<sub>VS</sub>, methane formation rate from TS and VS; L<sub>r</sub>, effective volume of the reactor.

observation period, providing compelling evidence of the robust stability of the SGAD.

The gas contents of the SGAD for different GFR values are presented in Figure 3. An average of 91 ± 4.5% CH<sub>4</sub> was

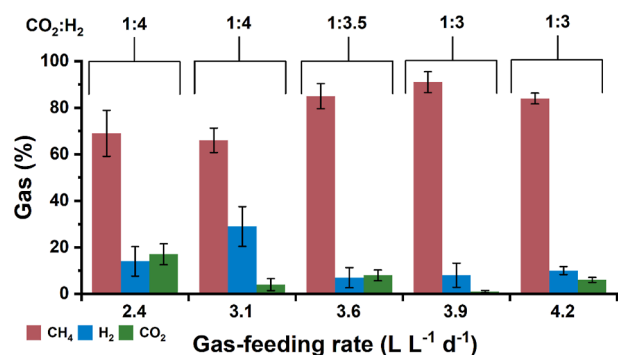


Figure 3. CH<sub>4</sub>, H<sub>2</sub>, and CO<sub>2</sub> contents in the SGAD biomethanation reactor under different operating conditions. The CO<sub>2</sub>/H<sub>2</sub> ratios are shown above the bars.

obtained at a GFR of 3.9 L L<sub>r</sub><sup>-1</sup> d<sup>-1</sup>. The levels of excess H<sub>2</sub> and CO<sub>2</sub> were found to be low, at 7.8 ± 5.2 and 1.5 ± 0.5%, respectively. In the experimental process, the combined volumes of CH<sub>4</sub>, H<sub>2</sub>, and CO<sub>2</sub> exceed 98% of the total gas volume, thus excluding the discussion of other impurity gases such as N<sub>2</sub>, H<sub>2</sub>S, and CO. The high CH<sub>4</sub> content could be attributed to the design of the SGAD, which prolongs the bubble retention time owing to its 5 m total length. Ullrich et al.<sup>26</sup> examined the effects of different pressures on the effectiveness of biogas-upgrade processes, suggesting that high pressures may improve H<sub>2</sub> gas–liquid transfer. Increasing the retention time might have a similar effect on gas–liquid transfer. Our findings are consistent with those of Ghofrani-Isfahani et al.,<sup>19</sup> who reported that increasing the gas retention time increased the CH<sub>4</sub> content.

Figure 4 illustrates the CO<sub>2</sub> and H<sub>2</sub> conversion rate in the SGAD. The highest η<sub>CO<sub>2</sub></sub> and η<sub>H<sub>2</sub></sub> were obtained at a GFR of 3.9 L L<sub>r</sub><sup>-1</sup> d<sup>-1</sup>, at which the CH<sub>4</sub> content was consistently maintained above 95%. This CH<sub>4</sub> content surpasses that achieved by the novel process of Baransi-Karkaby et al.,<sup>28</sup> which yielded 80–89% CH<sub>4</sub> but consumed >93% of the H<sub>2</sub>. Ghofrani-Isfahani et al.<sup>19</sup> investigated the impact of diffusers with different pore sizes on biogas-upgrade capacity. Miehle et

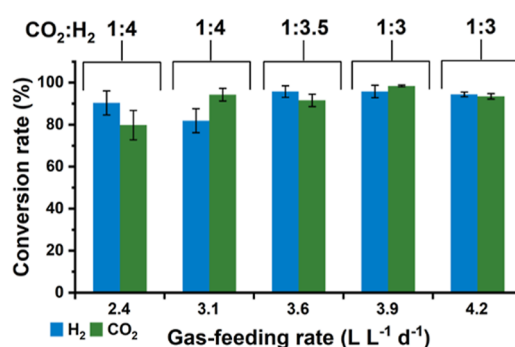
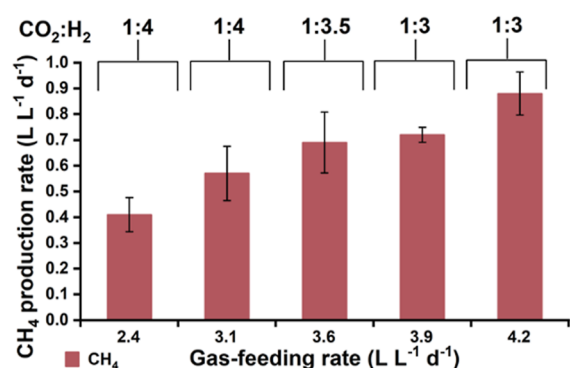


Figure 4. H<sub>2</sub> and CO<sub>2</sub> conversion rates in the SGAD biomethanation reactor under different operating conditions.

al.<sup>29</sup> used a diffuser with small pores (0.2 μm) to achieve high-quality biogas (99% CH<sub>4</sub>) with a high conversion rate. Gas diffusers evenly distribute the bubbles in the reactor, optimizing the use of HMs in the reactors, and better results are obtained with diffusers that have smaller pore sizes. The SGAD achieves a similar effect via its spiral structure, small cross section, and long length, which enable the bubbles to be distributed more evenly in the reactor than in a normal cylindrical reactor. This may explain the high conversion achieved here. As the GFR increases beyond the optimal rate, the conversion rate declines potentially because the loading exceeds the capacity of the SGAD, leading to inadequate reaction of the feed gas.

Figure 5 reveals an increase in R with the rise in GFR. At a GFR of 3.9 L L<sub>r</sub><sup>-1</sup> d<sup>-1</sup>, R was 0.72 ± 0.03 L L<sub>r</sub><sup>-1</sup> d<sup>-1</sup>, while at a GFR of 4.2 L L<sub>r</sub><sup>-1</sup> d<sup>-1</sup>, R was 0.88 ± 0.1 L L<sub>r</sub><sup>-1</sup> d<sup>-1</sup>, although the former GFR resulted in higher methane levels. To produce high-quality biogas, a GFR of 3.9 L L<sub>r</sub><sup>-1</sup> d<sup>-1</sup> is more appropriate for SGAD-based biomethanation. This study used a lower GFR to ensure the methane content and improve the CO<sub>2</sub> and H<sub>2</sub> conversion rates. In contrast, previous studies employed higher GFRs to maximize the biogas production efficiency. Voelklein et al.,<sup>11</sup> using a continuous supply of gas into a sequential *ex situ* reactor system, found that the availability of low-methane biogas increased with increasing GFR. To enhance biogas production efficiency in future applications, in the absence of strict requirements for methane content, a higher GFR can be used based on specific needs.



**Figure 5.** Methane production in the SGAD biomethanation reactor under different operating conditions.

The operating temperature of the reactor plays a crucial role in determining the methane production performance of HMs. Mesophilic methanogens exhibit optimal activity at 35–45 °C, while thermophilic methanogens prefer temperatures of up to 55 °C, and hyperthermophilic species prefer temperatures up to 65 °C.<sup>30,31</sup> Therefore, the activity of HMs has the potential to increase in SGAD biomethanation.

These findings indicate that the feed gas was evenly distributed in the reactor and that its residence time was extended by the innovative SGAD design, which allows for the full conversion of hydrogen and carbon dioxide. For future GAD designs, our time is considering innovations such as extending the bubble residence time and improving bubble distribution to achieve better results.

**3.2. GAD-Evaluation Methodology.** Methods to evaluate GAD design have been lacking till now. Most studies have relied solely on the methane production per unit volume as an indicator of reactor performance. This approach not only hinders the evaluation of reactor performance but also fails to establish a standardized design. This study aims to propose an evaluation methodology for the GAD that enables quantification and assessment of bubble residence time and distribution, providing a reference for GAD design. In the AD of gases, the methane production efficiency is determined by the gas residence time and distribution in the inoculum. These parameters are both influenced by the reactor structure. If the bubbles remain in the reactor long enough and are distributed evenly enough, HM activity is stimulated throughout the reactor and methane production per unit of inoculum is high in terms of  $R_{ts}$  and  $R_{vs}$ . Conversely, the inefficient use of space in the reactor results in relatively low  $R_{ts}$

and  $R_{vs}$ , indicating a poor reactor performance and design. In this study,  $R_{ts}$  and  $R_{vs}$  were used to evaluate the ability of the reactor to utilize HM. These indicators demonstrate how effectively the reactor utilizes different concentrations of the inoculum. The lower the TS and VS of the inoculum, the higher the  $R_{ts}$  and  $R_{vs}$ , indicating a higher utilization rate of the microorganisms in the reactor. Additionally, these indicators can characterize the residence time and bubble distribution.

For the SGAD, the  $R_{ts}$  and  $R_{vs}$  obtained were  $21.00 \pm 1.3$  L kg<sup>-1</sup> TS d<sup>-1</sup> and  $50.85 \pm 3.2$  L kg<sup>-1</sup> VS d<sup>-1</sup>, respectively, at a GFR of 4.2 L L<sup>-1</sup> d<sup>-1</sup> (Table 1). Each kilogram of the solid inoculum produced 21.00 L of methane per day in the SGAD (whereas 1 L of solid organic matter generates 50.85 L of methane per day). These results directly reflect the relationship between methane and its source (i.e., the HMs). Various studies have evaluated the reduction of CO<sub>2</sub> to CH<sub>4</sub> using H<sub>2</sub> (Table 2); in that of Jiang,<sup>32</sup> a similar  $R$  was obtained using a two-stage tandem fixed-bed and a trickle-bed reactor. However, in the former, the inoculum had a higher water content, resulting in higher  $R_{ts}$  and  $R_{vs}$  values, indicating that HMs were more fully utilized by the two-stage tandem fixed-bed reactor. Hao<sup>33</sup> used a lower GFR and a thinner inoculum to obtain biomethane; despite the low  $R$  obtained, the positive evaluation results confirm the viability of that design. In contrast, our evaluation of the SGAD method verified the merits of using smaller amounts of HMs to produce more methane. Our evaluation methodology correctly describes the relationship between the reactor and HMs. However, considering that normal operating conditions are not ideal experimental conditions, this evaluation method possesses certain limitations. For instance, a low-quality inoculum can result in a lower  $R_{ts}$ , which does not necessarily indicate inadequate reactor performance. In the future, the development of an improved evaluation methodology could provide more reference values for the evaluation of the GAD.

## 4. CONCLUSIONS

The SGAD biomethanation reactor successfully reduced CO<sub>2</sub> to CH<sub>4</sub> using H<sub>2</sub>. The spiral-pipe design significantly increased the contact time between the gas and liquid phases, effectively utilized microbes within the reactor, and provided favorable conditions for the gas reactions. Despite the high methane content of the biogas obtained from hydrogen and carbon dioxide, this did not constitute a biogas upgrade. Moreover, we presented a novel evaluation methodology for the GAD and assessed its performance. The innovative design of the SGAD

**Table 2.** Evaluation of Various Types of GADs, Including the SGAD Biomethanation Reactor<sup>a</sup>

references	reactor configuration	temperature (°C)	TS (%)	VS (%)	GFR (L L <sup>-1</sup> d <sup>-1</sup> )	$R$ (L L <sup>-1</sup> d <sup>-1</sup> )	$R_{ts}$ (L kg <sup>-1</sup> TS d <sup>-1</sup> )	$R_{vs}$ (L kg <sup>-1</sup> VS d <sup>-1</sup> )	CH <sub>4</sub> (%)
this study	SGAD	normal (20.2–26.5)	4.19	41.37	3.9	0.72 ± 0.03	17.18 ± 0.5	41.61 ± 1.1	91
			4.19	41.37	4.2	0.88 ± 0.08	21.00 ± 1.3	50.85 ± 3.2	84
(Jiang, 2021) <sup>32</sup>	two-stage tandem fixed bed	30	15.23	26.04	7.3	1.47	9.65	37.07	91
	trickle bed	normal (6.4–27.5)	25.85	28.30	4.7	0.93	3.60	12.71	91
(Hao, 2018) <sup>33</sup>	continuous stirred tank reactor	30	25.85	28.30	7.4	1.48	5.73	20.23	91
		37	6.23	33.26	1.9	0.36	5.78	17.37	96
		37	6.23	33.26	2.1	0.40	6.48	19.50	91

<sup>a</sup> $R$ , methane formation rate;  $R_{TS}$  and  $R_{VS}$ , methane formation rate from TS and VS; GFR, gas-feeding rate.

and its promising results suggest a potential alternative to biogas upgrading. Further optimization of the SGAD reactor and of this evaluation methodology is required to enable its widespread application.

## ■ ASSOCIATED CONTENT

### Data Availability Statement

Data is available in the Supporting Information for review only.

## ■ AUTHOR INFORMATION

### Corresponding Author

**Wudi Zhang** – Yunnan Normal University, Kunming, Yunnan 650500, PR China; Yunnan Research Center of Biogas Technology and Engineering, School of Energy and Environment Science, Yunnan Normal University, Kunming, Yunnan 650500, PR China; Yunnan Yunyu Technology Co., LTD, Kunming 650117, PR China; [orcid.org/0000-0002-1542-1196](https://orcid.org/0000-0002-1542-1196); Email: [wootichang@163.com](mailto:wootichang@163.com)

### Authors

**Minghao Li** – Yunnan Normal University, Kunming, Yunnan 650500, PR China; Yunnan Research Center of Biogas Technology and Engineering, School of Energy and Environment Science, Yunnan Normal University, Kunming, Yunnan 650500, PR China

**Xingling Zhao** – Yunnan Normal University, Kunming, Yunnan 650500, PR China; Yunnan Research Center of Biogas Technology and Engineering, School of Energy and Environment Science, Yunnan Normal University, Kunming, Yunnan 650500, PR China

**Kai Wu** – Yunnan Normal University, Kunming, Yunnan 650500, PR China; Yunnan Research Center of Biogas Technology and Engineering, School of Energy and Environment Science, Yunnan Normal University, Kunming, Yunnan 650500, PR China

**Chengyue Liang** – Yunnan Normal University, Kunming, Yunnan 650500, PR China; Yunnan Research Center of Biogas Technology and Engineering, School of Energy and Environment Science, Yunnan Normal University, Kunming, Yunnan 650500, PR China

**Jing Liu** – Yunnan Normal University, Kunming, Yunnan 650500, PR China; Yunnan Research Center of Biogas Technology and Engineering, School of Energy and Environment Science, Yunnan Normal University, Kunming, Yunnan 650500, PR China

**Hong Yang** – Yunnan Normal University, Kunming, Yunnan 650500, PR China; Yunnan Research Center of Biogas Technology and Engineering, School of Energy and Environment Science, Yunnan Normal University, Kunming, Yunnan 650500, PR China

**Changmei Wang** – Yunnan Normal University, Kunming, Yunnan 650500, PR China; Yunnan Research Center of Biogas Technology and Engineering, School of Energy and Environment Science, Yunnan Normal University, Kunming, Yunnan 650500, PR China

**Bin Yang** – Yunnan Normal University, Kunming, Yunnan 650500, PR China; Yunnan Research Center of Biogas Technology and Engineering, School of Energy and Environment Science, Yunnan Normal University, Kunming, Yunnan 650500, PR China; Yunnan Yunyu Technology Co., LTD, Kunming 650117, PR China

**Fang Yin** – Yunnan Normal University, Kunming, Yunnan 650500, PR China; Yunnan Research Center of Biogas

Technology and Engineering, School of Energy and Environment Science, Yunnan Normal University, Kunming, Yunnan 650500, PR China; Yunnan Yunyu Technology Co., LTD, Kunming 650117, PR China

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acsomega.3c08872>

### Author Contributions

Minghao Li: Conceptualization, Methodology, Writing-original draft, Writing-review and editing. Xingling Zhao: Data administration. Kai Wu: Investigation. Chengyue Liang: Data administration. Jing Liu: Investigation. Hong Yang: Investigation. Changmei Wang: Data administration. Bin Yang: Investigation. Fang Yin: Supervision, Project administration. Wudi Zhang: Conceptualization, Methodology, Writing-review and editing, Project administration, Funding acquisition.

### Funding

We would like to thank the following funding agencies for their generous grants that funded this study: Yunnan Ten Thousand Talents Plan Industrial Technology Champion Project (20191096), Yunnan Basic Research Program (202001AT070094), International Science and Technology Cooperation Project of Yunnan Province (202003AF140001), Yunnan Province Basic Research Special Youth Project (202201AU070058), Scientific Research Fund Project of Education Department of Yunnan Province (2022J0127), Yunnan Normal University PhD Project (xj2021102918), and Kunming International (Foreign) Science and Technology Cooperation Base (GHJD-2020026).

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

The authors are grateful to Yunnan Normal University, School of Energy and Environment Science, Yunnan Model Worker Innovation Studio, and the Open Fund from the Yunnan Key Laboratory of Rural Energy Engineering for their support in this work.

## ■ ABBREVIATIONS

AD, anaerobic digestion; GAD, gas anaerobic digester; SGAD, spiral-pipe gas anaerobic digester

## ■ REFERENCES

- (1) Scarlat, N.; Dallemand, J. F.; Fahl, F. Biogas: Developments and Perspectives in Europe. *Renew. Energy* **2018**, *129*, 457–472.
- (2) Scarlat, N.; Dallemand, J. F.; Monforti-Ferrario, F.; Banja, M.; Motola, V. Renewable Energy Policy Framework and Bioenergy Contribution in the European Union - An Overview From National Renewable Energy Action Plans and Progress Reports. *Renewable Sustainable Energy Rev.* **2015**, *51*, 969–985.
- (3) Angelidaki, I.; Treu, L.; Tsapekos, P.; Luo, G.; Campanaro, S.; Wenzel, H.; Kougias, P. G. Biogas Upgrading And Utilization: Current Status And Perspectives. *Biotechnol. Adv.* **2018**, *36* (2), 452–466.
- (4) Abdeen, F. R. H.; Mel, M.; Jami, M. S.; Ihsan, S. I.; Ismail, A. F. A Review of Chemical Absorption of Carbon Dioxide for Biogas Upgrading. *Chin. J. Chem. Eng.* **2016**, *24* (6), 693–702.
- (5) Lorant, B.; Tardy, G. M. Current Status of Biological Biogas Upgrading Technologies. *Period. Polytech., Chem. Eng.* **2022**, *66* (3), 465–481.
- (6) Muñoz, R.; Meier, L.; Diaz, I.; Jeison, D. A Review on the State-of-the-Art of Physical/Chemical and Biological Technologies for



- Biogas Upgrading. *Rev. Environ. Sci. Biotechnol.* **2015**, *14* (4), 727–759.
- (7) Nguyen, L. N.; Kumar, J.; Vu, M. T.; Mohammed, J. A. H.; Pathak, N.; Commault, A. S.; Sutherland, D.; Zdarta, J.; Tyagi, V. K.; Nghiem, L. D. Biomethane Production From Anaerobic Co-Digestion at Wastewater Treatment Plants: A Critical Review on Development and Innovations in Biogas Upgrading Techniques. *Sci. Total Environ.* **2021**, *765*, 142753.
- (8) Lecker, B.; Illi, L.; Lemmer, A.; Oechsner, H. Biological Hydrogen Methanation - A Review. *Bioresour. Technol.* **2017**, *245*, 1220–1228.
- (9) Luo, G.; Angelidaki, I. Integrated Biogas Upgrading and Hydrogen Utilization in an Anaerobic Reactor Containing Enriched Hydrogenotrophic Methanogenic Culture. *Biotechnol. Bioeng.* **2012**, *109* (11), 2729–2736.
- (10) Sposob, M.; Wahid, R.; Fischer, K. Ex-Situ Biological CO<sub>2</sub> Methanation Using Trickle Bed Reactor: Review and Recent Advances. *Rev. Environ. Sci. Biotechnol.* **2021**, *20* (4), 1087–1102.
- (11) Voelklein, M. A.; Rusmanis, D.; Murphy, J. D. Biological Methanation: Strategies for In-Situ and Ex-Situ Upgrading in Anaerobic Digestion. *Appl. Energy* **2019**, *235*, 1061–1071.
- (12) Guiot, S. R.; Cimpoaia, R.; Carayon, G. Potential of Wastewater-Treating Anaerobic Granules for Biomethanation of Synthesis Gas. *Environ. Sci. Technol.* **2011**, *45* (5), 2006–2012.
- (13) Kougiass, P. G.; Treu, L.; Benavente, D. P.; Boe, K.; Campanaro, S.; Angelidaki, I. Ex-Situ Biogas Upgrading and Enhancement in Different Reactor Systems. *Bioresour. Technol.* **2017**, *225*, 429–437.
- (14) Jensen, M. B.; Kofoed, M. V. W.; Fischer, K.; Voigt, N. V.; Agneessens, L. M.; Batstone, D. J.; Ottosen, L. D. M. Venturi-Type Injection System as a Potential H<sub>2</sub> Mass Transfer Technology for Full-Scale In Situ Biomethanation. *Appl. Energy* **2018**, *222*, 840–846.
- (15) Thapa, A.; Park, J. G.; Jun, H. B. Enhanced Ex-Situ Biomethanation of Hydrogen and Carbon Dioxide in a Trickle Bed Reactor. *Biochem. Eng. J.* **2022**, *179*, 108311.
- (16) Sun, Z. F.; Zhao, L.; Wu, K. K.; Wang, Z. H.; Wu, J. T.; Chen, C.; Yang, S. S.; Wang, A. J.; Ren, N. Q. Overview of Recent Progress in Exogenous Hydrogen Supply Biogas Upgrading and Future Perspective. *Sci. Total Environ.* **2022**, *848*, 157824.
- (17) Hafuka, A.; Fujino, S.; Kimura, K.; Oshita, K.; Konakahara, N.; Takahashi, S. In-Situ Biogas Upgrading With H<sub>2</sub> Addition in an Anaerobic Membrane Bioreactor (AnMBR) Digesting Waste Activated Sludge. *Sci. Total Environ.* **2022**, *828*, 154573.
- (18) Zhang, J. F.; Li, Y.; Wu, B. L.; Huang, X. Y.; Hou, Z. Y.; Chen, R. Performance and Mechanism of In-Situ Biogas Upgrading Using Anaerobic Membrane Bioreactor Effluent. *J. Water Process Eng.* **2021**, *44*, 102323.
- (19) Ghofrani-Isfahani, P.; Tsapekos, P.; Peprah, M.; Kougiass, P.; Zhu, X. Y.; Kovalovszki, A.; Zervas, A.; Zha, X.; Jacobsen, C. S.; Angelidaki, I. Ex-Situ Biogas Upgrading in Thermophilic Up-Flow Reactors: The Effect of Different Gas Diffusers and Gas Retention Times. *Bioresour. Technol.* **2021**, *340*, 125694.
- (20) Daniel-Gromke, J.; Rensberg, N.; Denysenko, V.; Stinner, W.; Schmalfuß, T.; Scheftelowitz, M.; Nelles, M.; Liebetrau, J. Current Developments in Production and Utilization of Biogas and Biomethane in Germany. *Chem. Ing. Tech.* **2018**, *90* (1–2), 17–35.
- (21) Liu, W. L.; Wang, C.; Mol, A. P. J. Rural Public Acceptance of Renewable Energy Deployment: The Case of Shandong in China. *Appl. Energy* **2013**, *102*, 1187–1196.
- (22) Zemo, K. H.; Panduro, T. E.; Termansen, M. Impact of Biogas Plants on Rural Residential Property Values and Implications for Local Acceptance. *Energy Pol.* **2019**, *129*, 1121–1131.
- (23) Zemo, K. H.; Termansen, M. Farmers' Willingness to Participate in Collective Biogas Investment: A Discrete Choice Experiment Study. *Resour. Energy Econ.* **2018**, *52*, 87–101.
- (24) Burkhardt, M.; Koschack, T.; Busch, G. Biocatalytic Methanation of Hydrogen and Carbon Dioxide in an Anaerobic Three-Phase System. *Bioresour. Technol.* **2015**, *178*, 330–333.
- (25) Rachbauer, L.; Voitl, G.; Bochmann, G.; Fuchs, W. Biological Biogas Upgrading Capacity of a Hydrogenotrophic Community in a Trickle-Bed Reactor. *Appl. Energy* **2016**, *180*, 483–490.
- (26) Ullrich, T.; Lindner, J.; Bar, K.; Mors, F.; Graf, F.; Lemmer, A. Influence of Operating Pressure on the Biological Hydrogen Methanation in Trickle-Bed Reactors. *Bioresour. Technol.* **2018**, *247*, 7–13.
- (27) Wahid, R.; Mulat, D. G.; Gaby, J. C.; Horn, S. J. Effects of H<sub>2</sub>:CO<sub>2</sub> Ratio and H<sub>2</sub> Supply Fluctuation on Methane Content and Microbial Community Composition During In-Situ Biological Biogas Upgrading. *Biotechnol. Biofuels* **2019**, *12*, 104.
- (28) Baransi-Karkaby, K.; Hassani, M.; Muhsein, S.; Massalha, N.; Sabbah, I. Innovative Ex-Situ Biological Biogas Upgrading Using Immobilized Biomethanation Bioreactor (IBBR). *Water Sci. Technol.* **2020**, *81* (6), 1319–1328.
- (29) Miehle, M.; Hackbarth, M.; Gescher, J.; Horn, H.; Hille-Reichel, A. Biological Biogas Upgrading in a Membrane Biofilm Reactor With and Without Organic Carbon Source. *Bioresour. Technol.* **2021**, *335*, 125287.
- (30) Ahring, B. K.; Ibrahim, A. A.; Mladenovska, Z. Effect of temperature increase from 55 to 65 °C on performance and microbial population dynamics of an anaerobic reactor treating cattle manure. *Water Res.* **2001**, *35* (10), 2446–2452.
- (31) Guneratnam, A. J.; Ahern, E.; FitzGerald, J. A.; Jackson, S. A.; Xia, A.; Dobson, A. D. W.; Murphy, J. D. Study of the Performance of a Thermophilic Biological Methanation System. *Bioresour. Technol.* **2017**, *225*, 308–315.
- (32) Jiang, J. Methane Production from Hydrogen and Carbon Dioxide and its Microbial Composition and Diversity in Anaerobic Digestion System, Ph.D. Dissertation, Yunnan Normal University, Kunming, China, 2021.
- (33) Hao, W. Study On H<sub>2</sub>/CO<sub>2</sub> Biological Methanation Process, Master's Dissertation, China University Of Petroleum, Beijing, China, 2018.