Application of Pressure Swing Adsorption for Carbon Dioxide and Methane Enrichment in Biogas Mixture Produced from Animal Manure and Organic Waste

Raveethida Srimalanon*, Pongsakorn Kachapongkun*‡, Parnuwat Usapein*

* Rattanakosin College for Sustainable Energy and Environment, Rajamangala University of Technology Rattanakosin, Phutthamonthon, Nakhon Pathom, 73170

(raveethida.s@gmail.com, pkerdchang@gmail.com, parnuwat.usa@rmutr.ac.th)

‡ Corresponding Author; Pongsakorn Kachapongkun, Rattanakosin College for Sustainable Energy and Environment, Rajamangala University of Technology Rattanakosin, Phutthamonthon, Nakhon Pathom, 73170, Tel: +66 2 441 6000, pkerdchang@gmail.com

Received: 07.09.2022 Accepted:13.10.2022

Abstract- Purified biogas is the way to enhance biogas utilization for many applications. Pressure Swing Absorption (PSA) is a promising technique for separating methane from carbon dioxide. The goal of this study is to evaluate the effectiveness of methane and carbon dioxide separation from biogas stream by utilizing MSC-3K 172 as an adsorbent. Biogas is produced from the anaerobic fermentation of animal manure and organic waste. A 150-liter gas storage tank is connected to a 200-liter gas fermenter tank in a biogas digester. The system has a batch capacity of 0.112 m3 of biogas. To separate methane and carbon dioxide, the PSA technique was used. As solid absorbents, Molecular Sieve (SHIRASAGI MSC 3K-172) were employed. The effects of pressure, flow rate, and time of experiment were investigated. The outcome showed that CO_2 captured behaviour is influenced by pressure and flowrate. The fraction of CO_2 captured increases with pressure. The behaviour of CO_2 captured is inversely correlated with the gas flow rate. The amount of CO_2 captured increases as the flow rate decreases. The findings indicate that 99.23% of CO_2 may be captured utilizing the PSA technique using molecular sieve (SHIRASAGI MSC 3K-172) as solid absorbent. The methane content in biogas was found to be between 65 and 68 percent; however, after going through the PSA process, the concentration of CH_4 rose to 98.26%. As a result, if the separated methane gas is stored properly, it can be used for a variety of purposes, such as household cooking gas and vehicle fuel.

Keywords Pressure Swing Adsorption, Biogas Purification, Carbon Dioxide.

1. Introduction

The current global energy crisis has turned attention to the development of renewable energy from diverse indigenous resources that may be available in order to meet the growing global energy demand [1, 2]. To address environmental problems and reduce reliance on fossil fuels, numerous sustainable and renewable energy sources have been developed [3, 4]. As a reliable energy source, biogas has made notable advancements in the field of renewable energy [5]. It can be produced from anaerobic digestion of organic matter. The main component of biogas is methane, which is another form of renewable energy that replaces fossil fuels and has the environmental benefit of reducing methane emissions into the atmosphere. Biogas production from organic matter involves a complex process and multiple bacterial groups [6, 7]. The production can be divided into four phases: 1) hydrolysis phase, the complex organic molecules are hydrolysed into subunits (sugars, amino acids, alcohols, fatty acids, etc.); 2) acidogenesis phase, soluble monomers are broken-down into small volatile fatty acids - NH_3, H_2S, and H_2; 3) acetogenesis/dehydrogenation phase, acetogenic bacteria assault the intermediates of acidogenesis and convert its molecules into CO_2, H_2 and mostly acetic acid; and 4) methanation phase, many reactions occur using the intermediate products from the previous phases. Methane is the major product of a number of reactions [8].

About 50–65 percent of the world's total methane emissions are caused by human activity. Main sources of methane emissions come from natural gas and petroleum systems, enteric fermentation, and landfills [9]. Since methane gas decomposes more quickly than carbon dioxide, it has a greater adverse effect on the climate (27.2 times compared to CO_2) [10, 11]. An efficient use of biogas, especially methane gas and carbon dioxide contained in biogas, will be used to reduce greenhouse gas emissions into the atmosphere and make use of it as a renewable energy source. Biogas can be utilized in different ways, such as electricity generation, heat, and vehicle fuel. Biogas can be cleaned of CO_2 and other pollutants to create an enhanced methane stream, which has more energy than raw biogas [12]. Carbon dioxide in biogas can diminish biogas calorific value, cause corrosion in piping and equipment, and contribute to the greenhouse impact. In addition, the separated carbon dioxide can be applied for industrial use as well.

Despite the fact that biogas production technology is well-established globally, the commercial applications of biogas are still restricted because biogas must first be purified before being used on-site [5]. For the technology of biogas purification, there are various techniques, i.e., membrane [13], absorptions [14], chemical [15], physical [16], and pressure swing adsorption (PSA) processes [17]. Due to its energy efficiency, cheap operational and installation costs, very compact equipment, and ease of operation, PSA is one of these technologies that is being investigated more and more for biogas upgrading. In order to meet the requirements of the natural gas grid and fuel quality regulations, PSA can achieve methane purity of more than 97 percent [18]. In this process, biogas was compressed to a pressure of between 0.5 and 3 bars and fed to the separation tank where it came into contact with an adsorbent which would choose to store CO_2.

Many types of adsorbents were investigated for capturing CO_2 from biogas mixtures i.e., activated carbon, silica, metal organic framework, zeolites, and carbon molecular sieve [19]. A carbon molecular sieve is the remarkable performance of a kinetic process that, depending on pore size, eliminates methane molecules and captures carbon dioxide molecules. [20] reported that when trace amounts (100 ppmv) of H_2S and 35% vol CO_2 are taken up by a molecular sieve 13X in a biogas stream, both sulfur and carbon dioxide can be captured. The carbon molecular sieve (CMS) KP-457 was used to study the performance of CH_4 and CO_2 separation using a thermally regenerative adsorbent-packed heat exchanger. The result showed that the CH_4 concentration was as high as 75% [21]. Molecular sieving carbon MSC-3K 172 was used to investigate the adsorption equilibria and kinetics of CH_4 and N_2 [22, 23]. However, there is no study on the performance of separation between CH_4 and CO_2 from the biogas stream. Therefore, the objective of this study is to investigate the performance of CH_4 and CO_2 separation from the biogas stream using MSC-3K 172 as an adsorbent.

2. Methodology

2.1. Anaerobic Digester Equipment

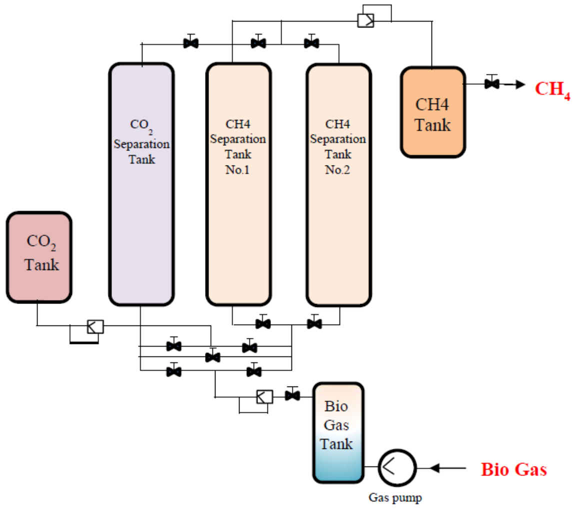
In this research, biogas fermentation from animal manure was performed by using 2 sets of anaerobic biogas digesters: (1) 200-liter gas fermenter tanks; and (2) 150-liter gas storage tanks. Firstly, 30 kg of pig manure and 30 liters of water were put in the first tank. Gas would be produced in about 7-15 days. The results showed that the inside of the gas storage tank had more air than methane, so the vent valve was opened. After that, 60 liters of water and pig manure were added for 15 days. Later, biogas production from pig manure was 0.112 cubic meters per batch. The composition of biogas is shown in Table 1. After getting biogas, such gas will be used in the process of separating CO_2 and other gases from biogas in order to increase the purity of CH_4.

Table 1. Biogas composition in this study

Gas composition	Unit
CH_4	65-68 %
H_2	0-3 %
CO_2	15-50 %
N_2	5-40 %
O_2	0-5 %
H_2S	0-310 ppm
Heating value	15.5 MJ/Nm^3

2.2. Pressure Swing Absorption (PSA)

The PSA apparatus consists of an adsorption column and a reciprocating compressor. The adsorption bed is 2 feet long and 3 inches in internal diameter, made of stainless steel, and fitted with thermocouples, pressure gages, rota meters, and sampling ports on all inlet and outlet lines, as shown in Fig. 1. Table 2 shows the details of the PSA equipment in this study. The solid adsorbents are SHIRASAGI MSC 3K-172 by Osaka Chemical Group. Some characteristics of sieve properties are shown in Table 3.



(a) Biogas separation system

(b) Pressure swing absorption set

Fig 1. Schematic diagram of PSA in this study.

Table 2. PSA characteristics

Item	Unit	Description
Appearance	-	Cylindrical
Color	-	Black
Particle diameter	mm	1.8
Loss on Drying *	%	1.0 max
Particle Size * (2.800 – 1.180 mm) (7 - 14 mesh)	%	99.0 min.
Hardness *	%	98.0 min.
PSA performance of 99 % Nitrogen at 30°C, 0.588MPa		
Cycle time	sec	60
Adsorption pressure	barG	7-15

Table 3. Molecular sieve characteristics [24]

	SHIRASAGI 3R-172
Pellet diameter	18 mm φ
Bulk Density (g/mL)	0.680～ 0.720
Particle size (%)	2.360～1.000
Hardness (wt%)	93.0～

The operating condition of PSA is inlet pressure 1 to 3 bars. The flowrate was controlled at 1, 3, and 5 liter per minutes. The temperature is ambient temperature. As shown in Figure 1 (a), the biogas is initially compressed before being fed into the compressor from the storage tank. Then, biogas was fed from the bottom of the PSA column. The PSA vessel is then used to purify the methane and carbon dioxide after the biogas has been poured into it.

The PSA columns were thoroughly cleaned by pumping just air into them prior to the experiment's start. To ensure there are no residues of CH_4, CO_2, O_2, or any other gases or pollutants, this process took roughly 20 minutes to complete. In order to accomplish the objective of the study, the target flow rate, pressure inlet, and pressure outlet were also set or calibrated during this process. A biogas analyzer (Geotech Biogas 5000 portable analyser) was utilized to determine the composition of the biogas directly from the storage tanks [25].

To accomplish the objective of this experiment, a comparison of the biogas composition before and after the experiment is essential.

3. Result and discussions

3.1 Effect of pressure

When the experiment operated under a pressure of 1–3 bar, at 4 °C, and a flow rate of 1 L/min, the result was shown in Fig.2. It can be seen that the molecular sieve can capture 70.72% of methane gas. When the system pressure was increased to 2 and 3 bars, the percentage of methane adsorption increased to 77.55 and 78.68, respectively. The percentage of methane adsorption becomes purer at higher pressures, as well as carbon dioxide. In this experiment, a pressure greater than 3 bars was not possible due to the insufficient amount of fermentable gas for the experiment. From the results, it can be concluded that the percentage of methane adsorption of the molecular sieve 3R-172 was directly proportional to the pressure.

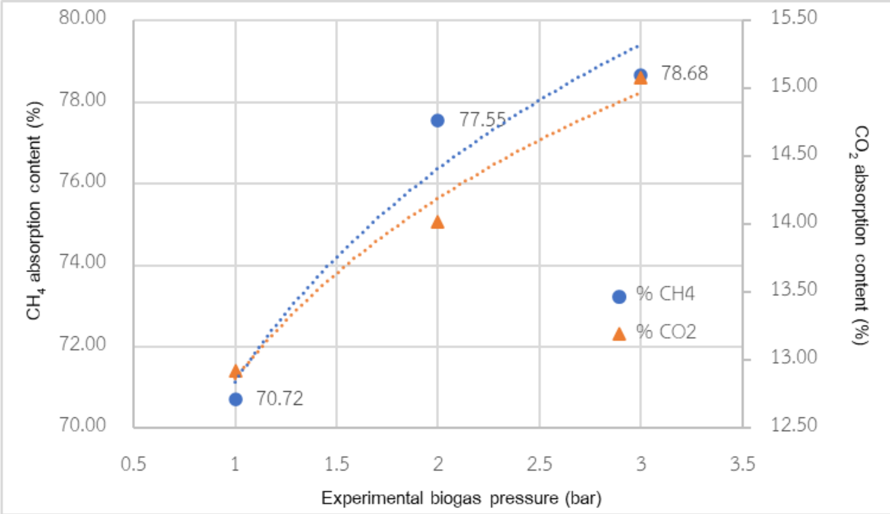


Fig 2. Comparison of methane and carbon dioxide adsorption at different pressure

3.2 Effect of Flow Rate

The comparison of the percentage of methane with different flow rates is shown in Fig. 3. It can be seen that the feed flow rate of 5 liters per minute gave the highest percentage of methane (98.23%) at 20 minutes of the experiment. The feed flow rates of 3 and 1 liter per minute are 98.26% and 98.52% of methane concentrations, respectively, but use a longer period of experiment at 30 and 35 mins, respectively. Increasing the flow rate has similar but different methane separation efficiency at the time. The flow rate of 5 L/min takes the least time compared to other flow rates.

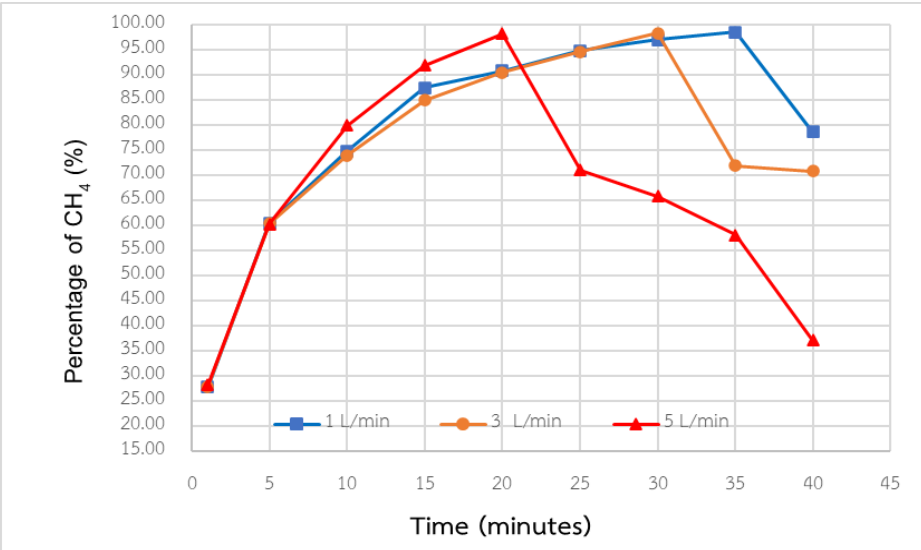


Fig 3. The influences of feed flow rates on the CH_4 purity

3.3 Effect of Experiment Time

As shown in Fig. 4, the carbon dioxide adsorption behavior is directly proportional to the pressure and duration of the experiment. Carbon dioxide adsorption increases when pressure is increased. It can be noticed that, at pressures of 2 and 3 bar, the efficiency of carbon dioxide adsorption is similar. At pressures of 1, 2, and 3 bar, the average percentage of CO_2 captured is 26%, 29%, and 30%, respectively. At the 25th minute of the experiment, almost no CO_2 was left in the system.

In the case of methane gas, at a pressure of 1 bar, the highest methane concentration was 86.13%, while the pressures of 2 and 3 bars gave the highest percentage of 97.18% and 98.26%, respectively. Therefore, the suitable pressure is 2 bars, as its efficiency is close to 3 bars, but the cost is less.

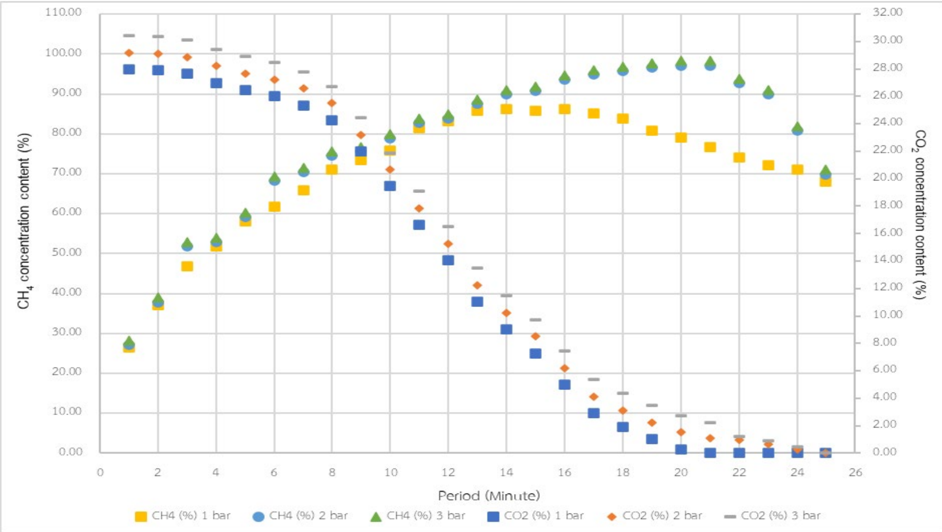


Fig 4. The concentrations of CH_4 (left side) and CO_2 (right side) of biogas at different total pressures

4. Conclusion

In this study, biogas was produced by an anaerobic digestion system using manure as feedstock. Biogas digester has a 200-liter gas fermenter tank and is connected to a 150-liter gas storage tank. The system can produce biogas at a rate of 0.112 m^3/batch. A Pressure Swing Absorption (PSA) technique was applied to separate CH_4 and CO_2. As a solid absorbent, a molecular sieve (SHIRASAGI MSC 3K-172) was used. The effects of pressure, flowrate, and time of experiment on CO_2 separation were investigated. The result indicated that the pressure and flowrate affect CO_2 capture behavior. When pressure increases, the percentage of CO_2 captured increases. The gas flow rate has an inverse effect on the CO_2 capture behavior. The percentage of CO_2 captured increases as the flow rate decreases. From the results, it can be concluded that the PSA technique using molecular sieve (SHIRASAGI MSC 3K-172) as solid absorbent can capture CO_2 for 99.23%. The CO_2 separated from the PSA process can be utilized for various applications, which results in a way to reduce greenhouse gas emissions. In the case of methane, the methane concentration in biogas was observed at 65-68%; however, after biogas has passed through the PSA process, the concentration of CH_4 has increased to 98.26%. Therefore, if the separated methane gas is stored appropriately, it can be used in many applications, for example, fuel for automobiles, cooking gas in households.

Acknowledgements

The authors would like to thank for the support from Rattanakosin College for Sustainable Energy and Environment, Rajamangala University Technology of Rattanakosin.

References

[1] M. Asif and T. Muneer, "Energy supply, its demand and security issues for developed and emerging economies," *Renewable and Sustainable Energy Reviews,* vol. 11, no. 7, pp. 1388-1413, 2007.

[2] Y. Utsugi, S. Obara, Y. Ito, and M. Okada, "Planning of the optimal distribution of renewable energy in Hokkaido, Japan," in *2015 International Conference on Renewable Energy Research and Applications (ICRERA)*, pp. 495-499, IEEE, 2015.

[3] F. Blaabjerg, Y. Yang, K. Ma, and X. Wang, "Power electronics - the key technology for renewable energy system integration," in *2015 International Conference on Renewable Energy Research and Applications (ICRERA)*, pp. 1618-1626, IEEE, 2015.

[4] A. Harrouz, D. Belatrache, K. Boulal, I. Colak, and K. Kayisli, "Social Acceptance of Renewable Energy dedicated to Electric Production," in *2020 9th International Conference on Renewable Energy Research and Application (ICRERA)*, pp. 283-288, IEEE, 2020.

[5] M. H. V. Bahrun, A. Bono, N. Othman, and M. A. A. Zaini, "Carbon dioxide removal from biogas through pressure swing adsorption – A review," *Chemical Engineering Research and Design,* vol. 183, pp. 285-306, 2022.

[6] M. A. Salamanca-Valdivia, L. Cardenas-Herrera, J. E. Barreda-Del-Carpio, G. M. Moscoso-Apaza, R. E. Gárate-de-Dávila, and C. A. Munive-Talavera, "Production of biogas in a dry anaerobic digestion reactor of residues generated in the processing of sheep and alpaca wool," in *2021 10th International Conference on Renewable Energy Research and Application (ICRERA)*, pp. 152-154, IEEE, 2021.

[7] V. Yilmaz, "A straightforward method: Biochemical methane potential assay," in *2015 International Conference on Renewable Energy Research and Applications (ICRERA)*, pp. 148-150, IEEE, 2015.

[8] C. B. Clifford, "Anaerobic Digestion," *Lesson 12: Additional Processes for Fuels from Biomass*. [Online]. Available: https://www.e-education.psu.edu/egee439/node/727. (accessed October 9, 2022).

[9] "Overview of Greenhouse Gases," United States Environmental Protection Agency

https://www.epa.gov/ghgemissions/overview-greenhouse-gases (accessed October 9, 2022).

[10] "IPCC Sixth Assessment Report Global Warming Potentials," ERC Evolution Ltd. [Online] Available: https://www.ercevolution.energy/ipcc-sixth-assessment-report/ (accessed June 25, 2022).

[11] P. Usapein and O. Chavalparit, "Life cycle assessment of bio-sludge for disposal with different alternative waste management scenarios: a case study of an olefin factory in Thailand," *Journal of Material Cycles and Waste Management,* vol. 19, no. 1, pp. 545-559, 2017.

[12] K. Starr, X. Gabarrell, G. Villalba, L. Talens, and L. Lombardi, "Life cycle assessment of biogas upgrading technologies," *Waste Management,* vol. 32, no. 5, pp. 991-999, 2012.

[13] Y. Liu, J. Sim, R.H. Hailemariam, J. Lee, H. Rho, K.D. Park, D.W. Kim, and Y.C. Woo, "Status and future trends of hollow fiber biogas separation membrane fabrication and modification techniques". *Chemosphere*, vol 303 p.134959, 2022.

[14] A. Ayub, S. Ahsan, D. Meeroff, and M. Jahandar Lashaki, "Amine-grafted mesoporous silica materials for single-stage biogas upgrading to biomethane," *Chemical Engineering Journal,* vol. 445, 2022.

[15] A. A. Abd, M. R. Othman, Z. Helwani, and H. J. K. Shabbani, "Role of heat dissipation on carbon dioxide capture performance in biomethane upgrading system using pressure swing adsorption," *Separation and Purification Technology,* vol. 280, 2022.

[16] S. Gao, C. Bo, J. Li, C. Niu, and X. Lu, "Multi-objective optimization and dynamic control of biogas pressurized water scrubbing process," *Renewable Energy,* vol. 147, pp. 2335-2344, 2020.

[17] G. Shah, E. Ahmad, K. K. Pant, and V. K. Vijay, "Comprehending the contemporary state of art in biogas enrichment and CO2 capture technologies via swing adsorption," *International Journal of Hydrogen Energy,* vol. 46, no. 9, pp. 6588-6612, 2021.

[18] A. A. Abd, M. R. Othman, H. J. K. Shabbani, and Z. Helwani, "Biomethane upgrading to transportation fuel quality using spent coffee for carbon dioxide capture in pressure swing adsorption," *Journal of Environmental Chemical Engineering,* vol. 10, no. 2, p. 107169, 2022.

[19] E. Mulu, M. M. M'Arimi, and R. C. Ramkat, "A review of recent developments in application of low cost natural materials in purification and upgrade of biogas," *Renewable and Sustainable Energy Reviews,* vol. 145, p. 111081, 2021.

[20] P. Pagliai and R. Di Felice, "Biogas clean-up and upgrading by adsorption on commercial molecular sieves," in *Chemical Engineering Transactions*, vol. 29, pp. 871-876, 2012.

[21] N. I. Zainol, Y. Osaka, T. Tsujiguchi, M. Kumita, and A. Kodama, "Separation and enrichment of CH4 and CO2 from a dry biogas using a thermally regenerative adsorbent-packed heat exchanger," *Adsorption,* vol. 25, no. 6, pp. 1159-1167, 2019.

[22] G. Xiao, Z. Li, T. L. Saleman, and E. F. May, "Adsorption equilibria and kinetics of CH4 and N2 on commercial zeolites and carbons," *Adsorption,* vol. 23, no. 1, pp. 131-147, 2017.

[23] G. Xiao, T. L. Saleman, Y. Zou, G. Li, and E. F. May, "Nitrogen rejection from methane using dual-reflux pressure swing adsorption with a kinetically-selective adsorbent," *Chemical Engineering Journal,* vol. 372, pp. 1038-1046, 2019.

[24] Osaka Gas Chemical Ltd. *Carbon molecular sieves (CMS)*, Activated Carbon Business Division Osaka, Japan 2018. [Online]. Available: https://www.ogc.co.jp/shirasagi/biz/e/cms.html (accessed June 28, 2022).

[25] I. Geotechnical, "BIOGAS 5000 Gas Analyser Operating Manual," no. DS43-ISSUE.13.