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Development of Biogas Upgrading System with Membrane Separators

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ABSTRACT

In Japan, biogas generated from sewage treatment plants are mostly utilized as auxiliary fuel for sewage sludge combustion and Combined Heat and Power (CHP) fuel, however, some excess biogas is usually just burned without energy recovery. Since Japanese major gas companies are legally required to utilize 80 % or more of excess biogas by 2015, they are expected to promote on-site and off-site utilizations of biogas.

In general, biogas has a composition of around 60 vol % methane, 40 vol % carbon dioxide and trace impurities such as hydrogen sulfide, water vapor and siloxane. Even if these trace components are removed before fuel supply, available gas appliances are limited to boilers and CHPs with special specification because its calorific value is lower than city gas. In order to expand application of biogas, it is required to be upgraded to natural gas quality.

Today, there are several types of technologies for biogas upgrading and the most popular technologies are pressurized water scrubbing, pressure swing adsorption (PSA), organic physical scrubbing and chemical scrubbing. In Japan, pressurized water scrubbing and PSA are adopted for biogas upgrading before gas grid injection. However pressurized water scrubbing is suitable for only large-scale plants and PSA method is low in methane recovery rate. Currently membrane separation technology has gained attention because of its high performance in methane separation from biogas and its compactness suitable for smaller scale plants. In addition, capital and operational costs of membrane separation system are expected lower than other systems although there are few cases of biogas upgrading with membrane technology in Japan. Since membrane separators are not developed for biogas upgrading in usual, there is not enough data of upgrading digestion gas from sewage treatment plants with membrane separators to estimate long-term performance and membrane replacement cycle.

A long-term test of upgrading digestion gas with organic membrane separators was carried out on a pilot scale. Raw digestion gas generated from a sewage treatment plant in Yokohama city was provided for the test. Targeted values of the methane concentration and the recovery rate of the upgraded biogas were over 98 vol % and over 90 %, respectively.

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2.BODY OF PAPER

2.1. INTRODUCTION

In Japan, Sophisticated Methods of Energy Supply Structures was established in 2010 and major gas companies are legally required to utilize 80% or more of estimated amount of excess biogas by 2015.

Biogas can be generated by methane (CH_4) fermentation and it has a composition of around 60% CH_4, 40% carbon dioxide (CO_2) and impurities such as hydrogen sulfide (H_2S), siloxane and water vapor which depend on the materials of biomass. Impurity which is likely to cause damage on gas appliances is required to be removed from biogas. CO_2 is also removed as necessary. This removal process is usually called biogas upgrading system. Upgrading gas can be utilized as fuel for power generation such as CHP, gas turbine and fuel cell. Using upgraded gas is expected to generate electricity at higher efficiency than using non-upgraded gas. It is also expected that biogas applications such as air conditioning with absorption heat pump or gas heat pump (GHP), boiler, Natural Gas Vehicle (NGV) and city gas grid injection is expanded by biogas upgrading. Schematic flows of biogas utilization with upgrading system in several ways are shown in Figure 1. However, biogas upgrading systems are not widely used because their capital costs are high and/or methane recovery rates are not enough high with conventional technologies.

In Yokohama-city, biogas generated from sewage treatment plant is utilized for CHP. Because of the seasonal variation, excess biogas is generated in winter mainly and is just burned. It is desirable to utilize this excess biogas.

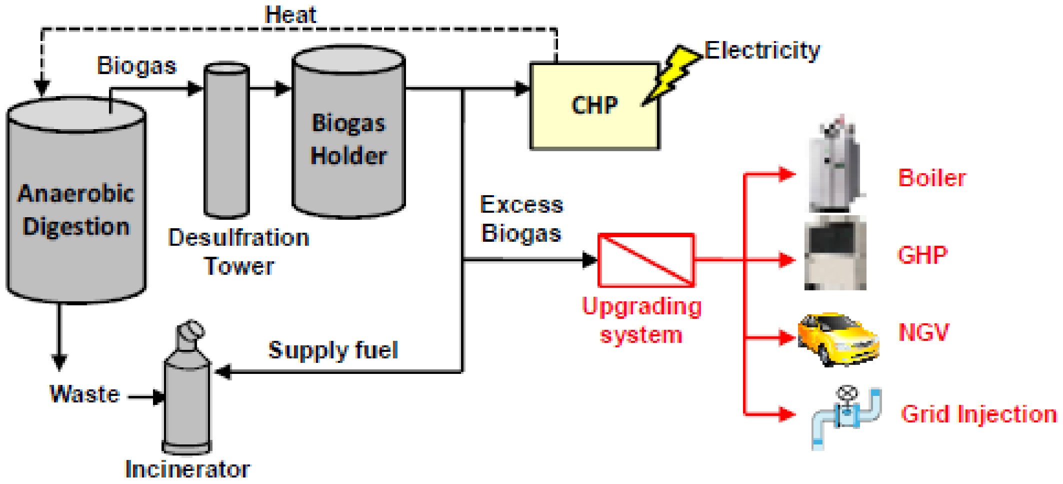


Figure 1 Schematic flow of biogas utilization with upgrading system.

Many types of biogas upgrading methods have been developed. Table 1 shows properties of four biogas upgrading technologies. In Japan, PSA (Pressurized Swing Adsorption) is adopted in Ota city, Tokyo, and pressurized water scrubbing is adopted in Kobe city, Hyogo for biogas upgrading before gas grid injection. However, PSA method is low in CH_4 recovery rate and pressurized water scrubbing is suitable for only large-scale plants. Chemical scrubbing method is used for chemical plants mainly. It is suitable for large-scale too, and its capital cost is high. The membrane separation method has attracted technology. Various kinds of membranes are developed, however they are applicable to small and medium scale plants. It is expected that the membrane separation method is lower in capital and operational cost for upgrading excess biogas from sewage treatment plants relative to existing technologies.

Table 1 Properties of biogas upgrading technologies.

Technology	CH_4 Purity	CH_4 Recovery	Capital cost	Operation cost	Main features
Pressurized water scrubbing	98%	97%	High	High	Removes H_2S together Using huge amounts of water
Pressure swing adsorption	98%	69%	Middle	Middle	Low CH_4 Recovery
Chemical absorption	98%	98%	High	Low	Heat required for solvent recycling
Membrane separation	98%	93%	Middle	Low	Great advantage of compactness Favorable to smaller scale plants Low capital and operation costs

The objectives of this study are to examine the capability and the stability of two types of membrane separators in long term experiments and to evaluate feasibility of excess biogas utilization with common city gas appliances.

2.2. Membrane separators

2.2.1. Types of membranes used for gas separation

Recently, many researchers have reported about membranes synthesized with new materials to improve the performance of gas separation [1] [2]. There are two main types of membranes, one is organic type and the other is inorganic type. The capability of CH_4-CO_2 separation is usually evaluated with permeability and selectivity. They depend on materials, structures, film thickness of membranes, and so on. The partial pressure of CO_2 also affects permeability. The difference in the principle of CH_4-CO_2 separation between organic type and inorganic type of membranes is illustrated in Fig. 2.

Generally, inorganic type membranes are known to have high permeability and selectivity of CH_4-CO_2 as compared with inorganic type membranes, but they are characterized by high cost, heavy and difficult formability [3].

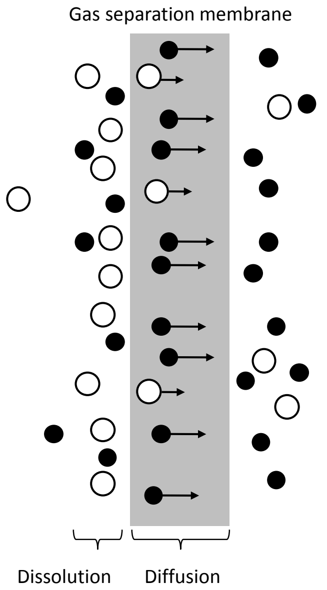
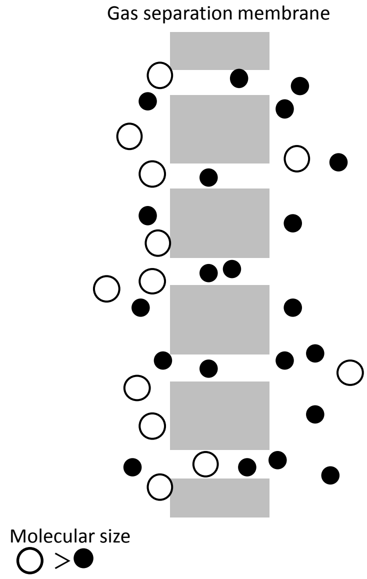
Types of membranes	Organic Non-porous	Inorganic Porous
Structures	Follow fiber	Monolith
Mechanism of permeation	Dissolution and Diffusion	Molecular sieving
Images of permeation		

Fig.2 Principal of CH_4-CO_2 separation.

Left; organic and non-porous type membranes

Right; inorganic and porous type membranes

2.2.2. Properties of the membrane separators for this study

Modularized organic type membranes as shown in Fig. 3 are used for this study. Two types of commercialized membrane separators, polyimide follow fiber membrane and polysulfone follow fiber membrane, are selected.

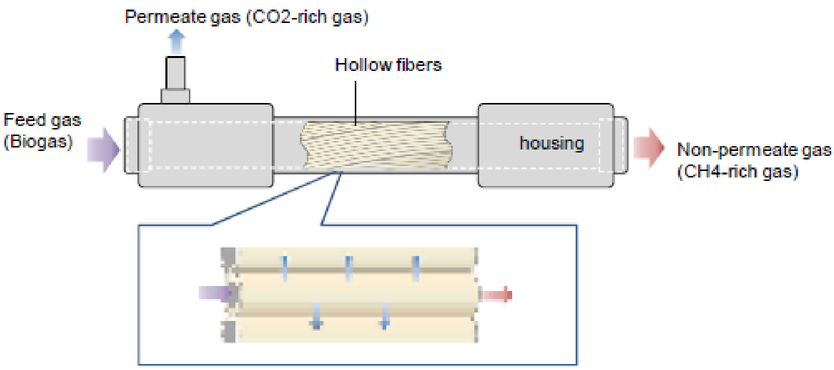


Fig. 3 Structure of the organic type membrane separators for gas separation.

Gas separation takes place due to the difference of permeability through membranes which depend on gaseous species. In the case of CH_4 and CO_2, CO_2 has high permeability through membranes. Then, CO_2 is concentrated in the permeate gas and CH_4 is concentrated in the non-permeate gas, which is passed through inside the follow membranes. The non-permeate gas are extracted as upgraded gas and the permeate gas are offgas. The permeate volume of CO_2 is adjusted by controlling the feed gas pressure, the flow rate of biogas and the heating temperature. Two membrane separator modules are connected in series in order to increase CH_4 concentration from 60% to 98% by feeding non-permeate gas of the first membrane to the second membrane.

The specs and characteristics of polyimide follow fiber membrane and polysulfone follow fiber membrane are listed in Table 2. The properties of these membranes are not published, however they are known to have good chemical resistance to acids and alkalis in general, and they are practically used for air separation and so on.

In this study, the membrane separators for biogas upgrading are selected with the simulation results which are optimized by membrane suppliers. It is expected that the relationship between separation capabilities and properties of each membranes is investigated by finding the optimum conditions for upgrading biogas to achieve the target level.

Table 2 Spec and characteristics of two type membranes.

Characteristics	Unit A	Unit B
Materials	Polyimide	Porisurphone
Structure	Follow fibers	Follow fibers
Using temperature	5 - 60℃	15-55℃
Using pressure	0.3 – 1.0 MPaG	0.4 – 2.5 MPaG

2.3. Experimental

2.3.1. Process of the biogas upgrading system

Raw digestion gas generated from a sewage treatment plant in Yokohama-city is used for the experiment and feed gas is separated to CH_4 and CO_2 in a biogas upgrading system. Fig.4 shows the flow diagram of biogas upgrading system. After the desulfurization, the biogas is stored in a low-pressure gas holder. The low-pressure biogas is compressed at 0.6MPaG and stored in a medium-pressure gas holder. Some part of biogas from the medium-pressure gas holder is introduced to the test unit and then treated with a siloxane remover before pressured at less than 1.0MPaG with a compressor (2BSN-P3.7, MIKUNI KIKAI KOGYO CO., LTD, JAPAN). The pressurized gas passes through a desulfurization unit and heated at 30°C with a ribbon heater. Then, the pressurized and heated biogas is fed to the follow membranes to separate to permeate gas which mainly contains CO_2 and non-permeate gas which mainly contains CH_4. The gas compositions of the permeate gas and the non-permeate gas are measured with infrared gas analyzer (CGT-7000, SHIMADZU CORPORATION, JAPAN) to obtain the CH_4 concentration of the upgraded gas. The flow rates of each gas are measured with mass flow meters. The CH_4 recovery rate is calculated from with the measured results of the flow rates and gas compositions.

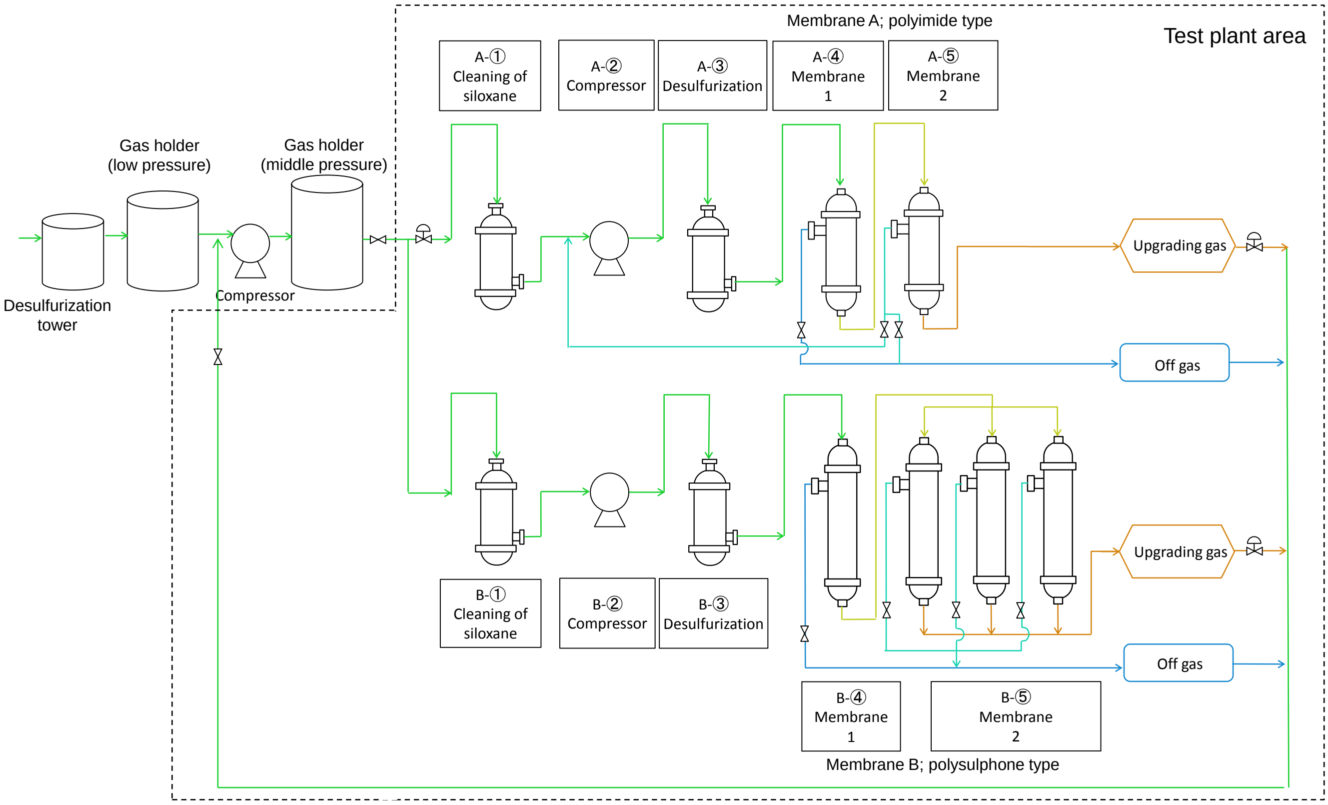


Fig.4 Flow diagram of biogas upgrading units.

Ground plan of the pilot scale biogas upgrading units is shown in Fig.5 and their appearances are shown in Fig.6. These units are operated for 24 consecutive hours. The experiment has been performed from March 2014 and will continue until March 2015.

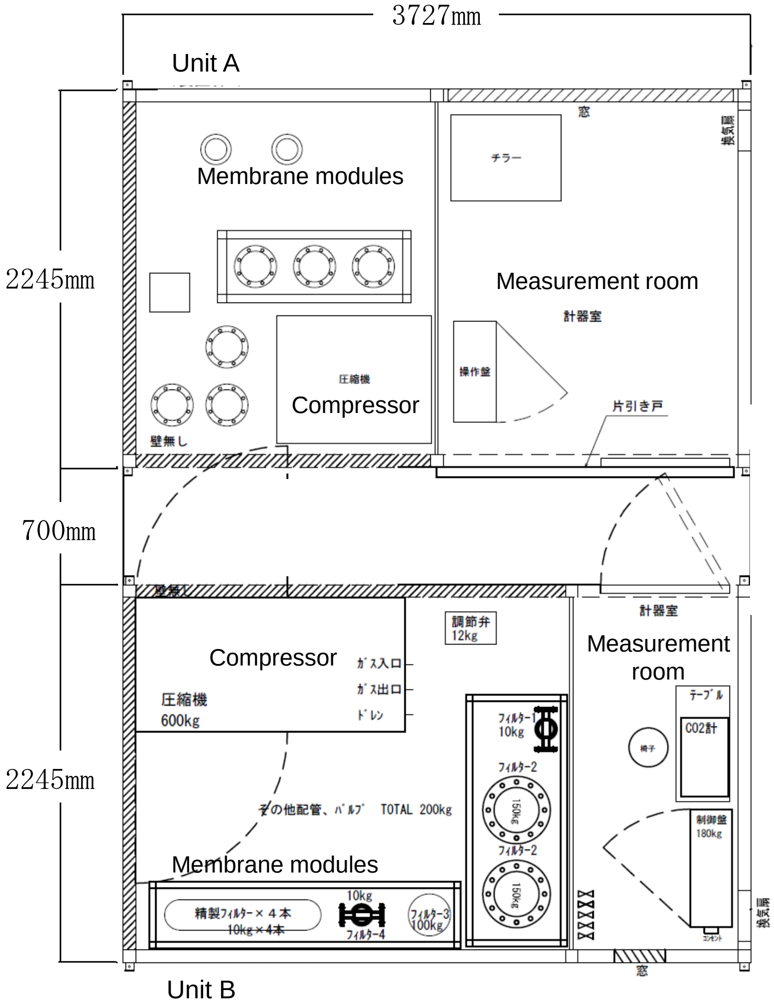


Fig.5 Ground plan of biogas upgrading test units.

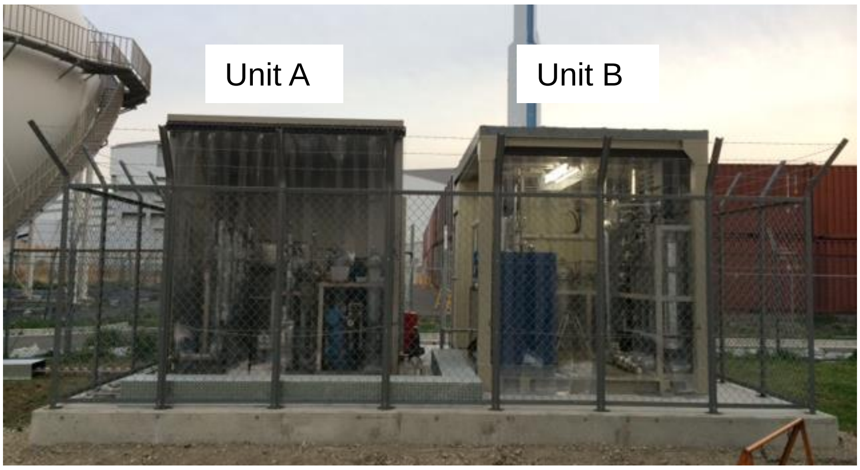


Fig.6 Appearances of .test units of biogas upgrading.

2.3.2. Confirmation of separation capability of the membranes

(A) Properties of membranes

The target level of CH_4 concentration of upgraded gas is set at 98% and CH_4 recovery rate is set at higher than 90%. Operational conditions such as feed gas pressure, temperature and flow rate is not yet found to satisfy the target level. Therefore, the experiments are being performed to find the relationships between operational conditions and separation capability with membrane separators.

(B)Capability of gas separation with membrane separators

The capability of gas separation with membrane separators are evaluated with CH_4 concentration of upgrading gas and CH_4 recovery rate. CH_4 recovery rate indicates how much CH_4 can be collected from digestion gas. It is calculated according to the following equations.

$$CH_4 \text{ recovery } (\%) = (C_u \times F_u) / (C_f \times F_f)$$

C_u (%); CH_4 concentration of upgrading gas
C_f (%); CH_4 concentration of feed gas
F_u (NL/min); Flow rate of upgrading gas
F_f (NL/min); Flow rate of feed gas

The upgrading conditions to increase CH4 recovery rate as high as possible are investigated in this experiment.

2.3.4. Durability evaluation of the membrane separators

The capability of separation with the membrane separators without removing impurities in biogas will be examined. After the experiments described above are finished, the siloxane remover and the desulfurization unit are by-passed, and then the separation test will be performed with biogas containing trace impurities. The concentrations of the impurities such as H_2S, NH_3, siloxane and so on will be measured at the desulfurization unit inlet and outlet, the medium-pressure gas holder inlet and the membrane separators inlet and outlet. The dew points of the permeated and non-permeated gas are measured too, and the properties of separation of the impurities with the membrane separators are evaluated. The tests are performed in conditions similar to the method described on (B) previously. Also, the effects on CO_2 separation by long term upgrading of the biogas containing impurities are confirmed, and the presence or absence of the membrane corrosion is determined with the observation of the membrane surface after the experiments.

The data obtained from the durability evaluation is applied to the determination of need for the removal devices of the impurities, the projection of replacement cycle for the membrane separators and the estimation of capital and operation costs.

2.4. Future plan of this study

The schedule of this study is shown in Table 3.

Table 3 Schedule of this study.

Year	2014												2015		
Month	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3
Confermation of separation capability with the membranes				←	—	—	—	—	—	→					
Preparing (get off the filters)								←	→						
Durability evaluation of the membrane separators									←	—	—	—	—	→	
Estimation for effective utilization of biogas upgrading system				←	—	—	—	—	—	—	—	—	—	—	→

Utilizing excess biogas with common city gas appliances and its effects will be investigated as following.

- The effect of utilizing gas cogeneration system will be assessed.
- CHP, gas turbine and fuel cell are intended for the gas cogeneration system. Restriction for each appliance to utilize excess biogas will be validated.
- It is assumed that the waste heat from cogeneration system is used for heating of digestion tank when this system is installed in a sludge treatment plant.

The upgrading system with the membrane separators will be compared with PSA method and pressurized water scrubbing method at various scales of biogas generation plants. In addition, the costs of integrating biogas upgrading system and biogas utilization in various schemes will be estimated. The adoption of biogas utilization in sewage sludge treatment plant in Yokohama-city will be evaluated at the end of this study.

3. Acknowledgement

This study has collaborated with City of YOKOHAMA, Environmental Planning department. The authors are grateful to officials for continuing interest and valuable advices for this study.

4. References

[1] S. Heile, S. Rosenberger, A. Parker, B. Jefferson, E.J. McAdam, Establishing the stability of symmetric ultrathin wall polydimethylsiloxane hollow-fiber membrane contractors for enhanced CO_2 separation during biogas upgrading, Journal of Membrane Science, 452 (2014) 37-45.

[2] B. Ozturk, F. Demirciyava, Comparison of biogas upgrading performances of different mixed matrix membranes, Chemical Engineering Journal, 222 (2013) 209-217.

[3] S. Basu, A. L. Khan, A. Cano-Odena, C. Liu, Ivo F. J. Vankelecom, Membrane-based technologies for biogas separations, Chemical Society Reviews, 39 (2010) 750-768.

5. List Tables

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