International Gas Union Research Conference 2011

Development of innovative technologies for biogas production and purification

S. Osumi

T. Kume

J.Tsubota

H. Sakamoto

Energy Engineering Dept.

Osaka Gas Co., Ltd.

Japan

ABSTRACT

Energy industries in Japan such as electric power, gas delivering, or petroleum are required by law to make effort to increase the renewable energy use. One of the most synergetic renewable energy for gas companies is baiogas, so Osaka Gas Co., Ltd. is developing the technologies from the biogas production to purification as bio-methane and transportation through the gas pipeline.

In order to use biogas, various kinds of technologies such as production, utilization, purification, storage, and transportation of biogas are necessary. We are developing technologies for all of above five fields. We describe the especially state-of-the-art approach such as high performance biogas production system, expanding the field to apply UASB (upflow anaerobic sludge blanket) process, and biogas purchase through gas pipeline.

<u>TABLE OF CONTENTS</u>

INTRODUCTION

The expansion of the renewable energy (RE) use is very important issue in Japan and one of the most synergetic RE for gas companies is biomethane. So Osaka Gas Co., Ltd. is developing the technologies from biomethane production, usage, purification, storage, to transportation.

There are two methods to produce biomethane. One is methane fermentation and another one is UASB (upflow anaerobic sludge blanket) process.

The accumulation of ammonia, high cost of the treatment of wastewater from the methane fermentation, and the high disposal cost of the methane fermentation residue are the main problems which prevent to make methane fermentation popular. In order to improve these problems, we have developed the hyper-thermophilic hydrolysis technology. This is the system which integrate the high temperature (55 degree-C) methane fermentation and the hyper thermophilic hydrolysis under 80 degree-C in which the high molecular weight organic substances are converted into smaller molecular weight ones. Because of the hyper thermophilic hydrolysis, the degradation rate of organic substances increase and the amount of residue decrease. Additionally the ammonia including in the system is vaporized in the hyper thermophilic tank because of its high temperature, so the accumulation of ammonia is avoidable and the wastewater can be reused as dilution water attributing the reduction of wastewater from the system.

Osaka Gas is developing so-called "Biogas production system from whole garbage (garbage bag and kitchen garbage) ", by which the collected kitchen garbage put in the plastic garbage bag can be converted into biogas without removing the plastic bag. In order to complete this system, we have developed the plastic bag made of PLA (poly lactic acid) which is biodegradable material. PLA is degraded very slowly under anaerobic condition but we found that PLA is solubilized quickly under hyper thermophilic condition and have succeeded in establish the system to produce biogas from PLA plastic bag by integrating the hyper thermophilic hydrolysis and methane fermentation. Additionally PLA plastic had been difficult being used as garbage bag because of its less stretchablity, but we have succeeded to develop the PLA plastic garbage bag by the optimization of the additives into PLA. Because of these technologies, we can expect to complete the "Biogas production system from whole garbage " and we are going ahead the development.

UASB (upflow anaerobic sludge blanket) is one of the biomethane production technologies which is expected to become popular. Wastewater is treated in a reactor filled by granule of anaerobic bacteria and its degradation speed is much faster than conventional methane fermenter. So UASB is widely used in the beer industry etc. But the expansion of the field of UASB application is required because it had almost introduced to the factories it can be applied easily, for example beer industry.

Osaka Gas has succeeded in establish the biogas production system from the soap factory's effluent which had been thought to be difficult to apply UASB treatment because of its high salinity and high alkaline.

In the case the location of the supply and demand of biogas is far away, it is difficult to use biogas. In such case, it works on to transport the excess biogas from supply site to demand site through existing gas pipeline. One of the examples where huge amount of excess biogas in Japan is produced is sewage-treatment plant (STP). Osaka Gas started a business to purchase biogas from STP in Kobe city through our gas pipeline.

In Japan, most of the city gas is imported as LNG and originally includes very less amount of impurities, so very strict standard is decided. Therefore, in order to inject biogas into the pipeline, standards showed in below table, for example, should be abided. Osaka Gas established the technologies to satisfy all of these standards and has started to inject biogas into our pipeline.

HIGH PERFORMANCE ANAEROBIC DIGESTER

Continuous feed bench-scale digester test

Continuous feed bench-scale (3 liter) digester study was done for months under following settings and conditions (Figure1). Each tank is lined with 6mm inlet silicon tube. Minced municipal solid waste (MSW) get easily blocked in the tube. In order to avoid this block, smashed and sieved dog food was used. Control test was also done without hyper thermal hydrolyzing tank. With data of produced biogas volume, methane and carbon dioxide concentration, and residue VS, COD balance was calculated and compared with normal thermal digester without hyper thermal hydrolyzing process.

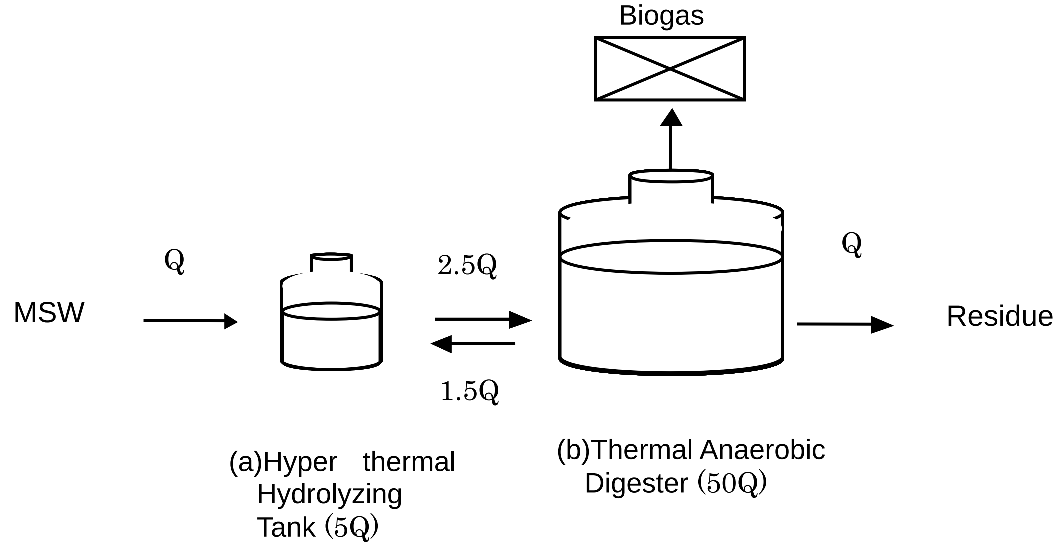

Fig. 1 Settings and conditions of continuous feed bench-scale digester.

Figure 2,3 and 4 shows the results of continuous feed bench-scale digester study. The methane yields increased by 27% and the amount of residue was reduced by 57%. COD balance shows that this study was done with certain accuracy. We have already showed that under hyper thermal hydrolysis condition (80 degrees Celsius and pH 7.5), ammonia easily evaporates. Hence anaerobic digester can be operated without fear of ammonia inhibition (Anaerobic Digestion 2004, Montreal).

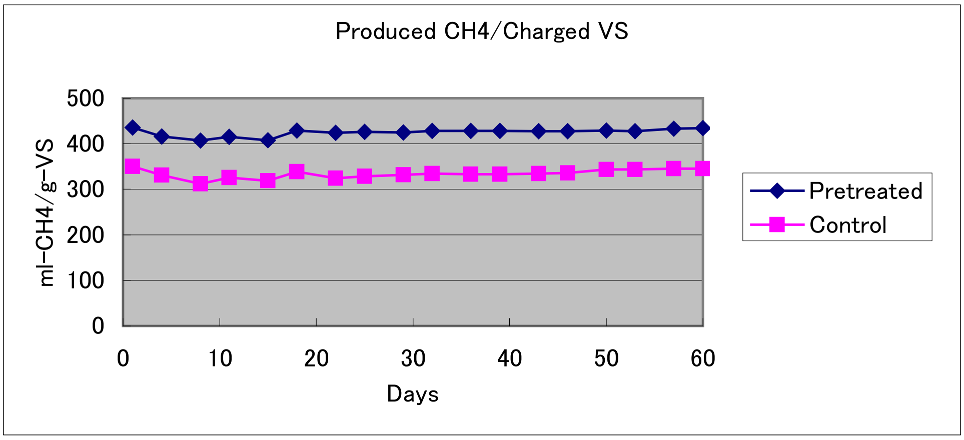

Fig. 2 Comparison of methane yields

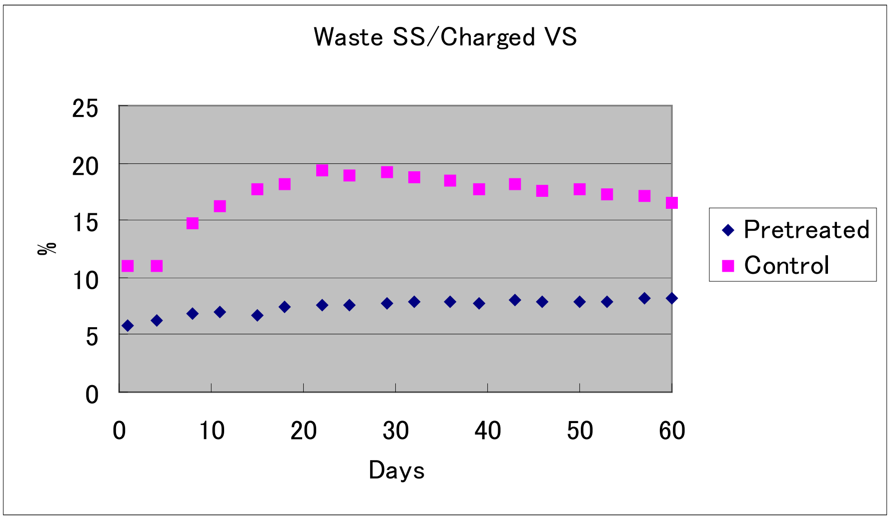

Fig. 3 Comparison of Waste SS versus Charged VS

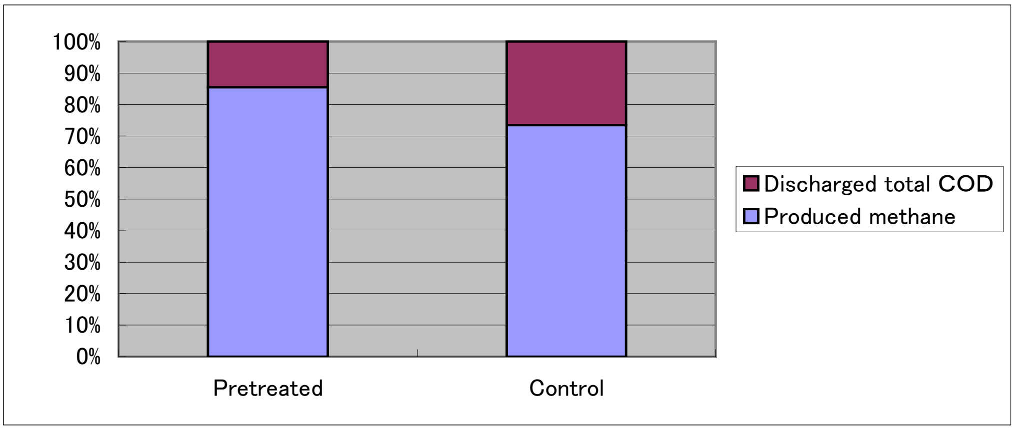

Fig. 4 Comparison of COD balance

Hyper-thermophilic pre-treatment of biodegradable plastics

There are series of biodegradable plastics, but most of them are not easily degraded under anaerobic digestion (AD) condition. We have tested hydrolysis rate and efficiency of these plastics under thermal and hyper thermal condition (Table1).

In normal, organic matter ratio of municipal solid waste organic fraction (MSWOF) is 50 kg garbage per 1m3 digester. This garbage contains 5% garbage bag, therefore 2.5kg plastics have to be hydrolysed in 1m3 digester a day. AD process could not digest more than 0.57kg plastics/m3-day, which was less than 20% of input. In contrast, under hyper-thermophilic hydrolysis condition, 5 kinds of plastics hydrolysed more than 2.5kg plastics/m3-day. Plastic A, C, D and E are mainly composed of polylactide, where Plastic B of polybutylensucinate.

Table 1 Degradation of bio-degradable plastic under AD and Hyper-thermophilic hydrolysis condition

	AD	Hyper-thermophilic hydrolysis
Plastic A	0.49 kg/m3-day	2.8 kg/m3-day
Plastic B	0.11 kg/m3-day	0.2 kg/m3-day
Plastic C	0.57 kg/m3-day	2.5 kg/m3-day
Plastic D	0.33 kg/m3-day	2.6 kg/m3-day
Plastic E	0.49 kg/m3-day	2.6 kg/m3-day

Figure 5 shows possible scheme of AD in urban area. MSWOF is separately collected using plant-based (polylactide) garbage bag. Garbage and garbage bag is put into hyper-thermophilic hydrolysis reactor altogether, mixed with effluent of dehydrator which contains hyper-thermophilic bacteria in anaerobic digester. During HRT of hyper-thermophilic hydrolysis reactor 24-48 hours at 80 degree, MSWSOF is highly hydrolysed by hyper-thermophilic bacteria, and almost all the polylactide of garbage bag is also hydrolyed. Pre-treated MSWOF is then put into anaerobic digester and converted to methane. Residue of anaerobic digester contains less plastics and easily process to fertilizer.

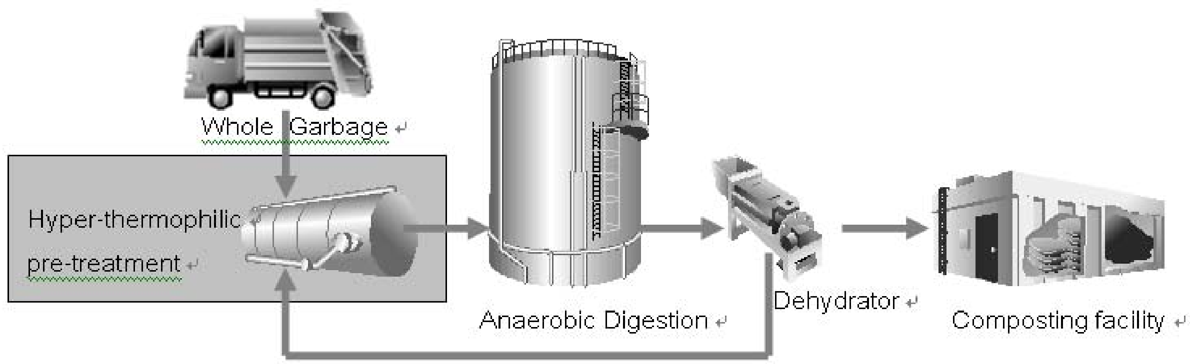

Fig. 5 Whole Garbage (Plant-based Garbage Bag and MSWOF) pre-treatment for high-efficiency AD

Biomethane production from wastewater at factory - the technology to expand the field of UASB application

Continuous feed bench-scale reactor test

In order to apply UASB process into a chemical factory's effluent including high salinity and high alkaline, we have devised such process as shown in Fig. 6. In the process, the effluent is diluted by industrial water at first, and then is fermented into organic acid such as acetic acid and so on in acid fermentation tank by microorganism. In this acid fermentation process, pH of the solution decreases into less than 6. After that alkaline agent is added and neutralize into the pH around 7 in the regulation tank. Then the organic matter in the solution is converted into methane and carbon dioxide in UASB tank.

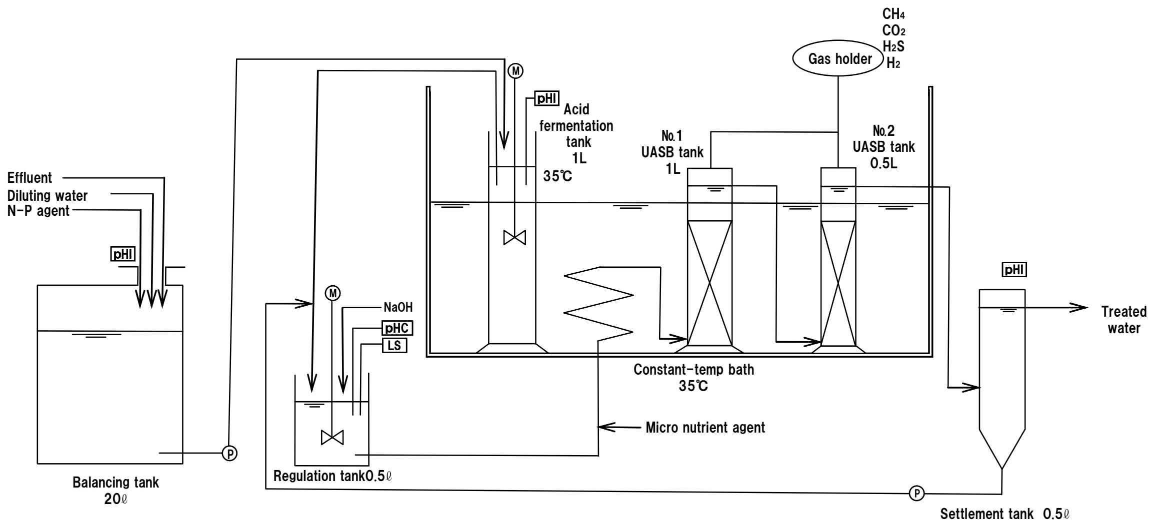

Fig. 6 Flowchart of continuous UASB treatment experiment

Table 2 shows the composition of the chemical factory's effluent. The effluent includes 120,000 mg/L of COD. And its pH is very high, 12.7, and includes 55,000 mg/L of Na+ which is also very high concentration. We use this effluent for our experiments diluted by tap water.

Item (unit)	Conc.
pH	12.7
BOD (mg/L)	3,800
COD (mg/L)	120,000
CL (mg/L)	18,000
Na (mg/L)	55,000

Table 2 Composition of chemnical factory's effluent

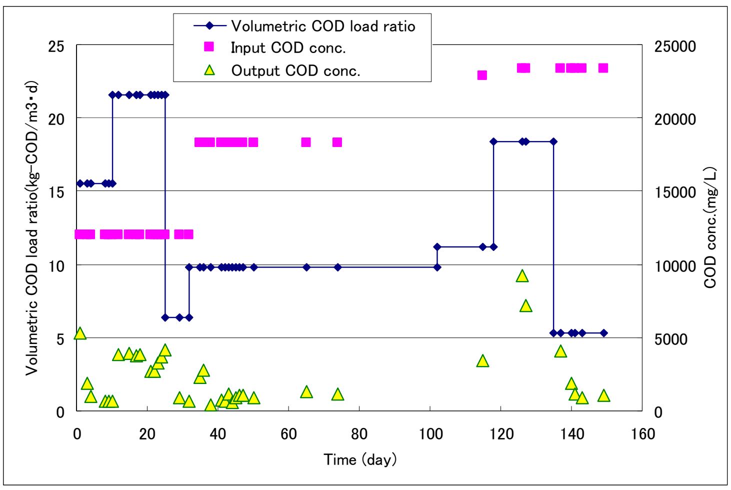

Fig.7 Results of continuous UASB treatment experiment

When the experiment started, the granule which used to be used for sugar contained wastewater treatment was filled in the UASB tank. After cultivation under low volumetric load ratio with 10-fold diluted effluent for about six weeks, the experiments started at the load ratio of 15.5kg-COD/m3/d. Under the dilution ratio of 5.0, 6.7, 10.0 respectively, the removal ratio of organic carbon is measured in changing the volumetric load ratio.

The results are shown in Fig. 7. We can continue the UASB treatment of soap factory's effluent changing the volumetric load ratio for about 5 months. Fig. 8 shows the relation between volumetric load ratio and COD removal ratio, and Fig. 9 shows the relation between Na+ concentration and the volumetric load ratio in order to achieve 90% of COD removal (VL90). We found that VL90 correlate linearly with Na+ concentration. It means the more the dilution ratio is, the smaller the reactor become.

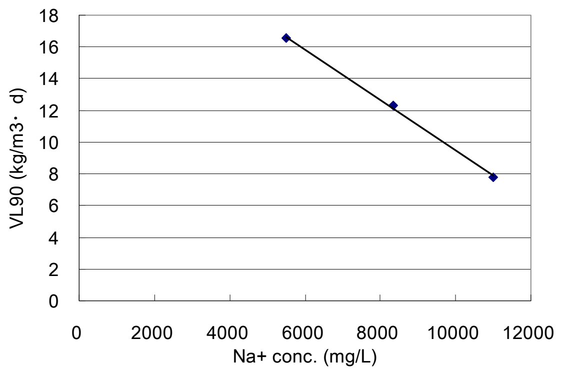

Fig. 8 Correlation between Na+ conc. and VL90

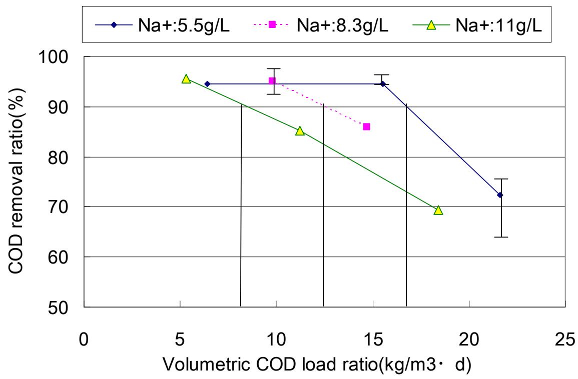

Fig.9 Correlation between volumetric COD load ratio and COD

Through this research, we can establish the process to convert the soap factory's effluent into biogas steadily and are planning to build the plant which produces 355,000 m3N/y (as 45.0MJ-HHV/m3N of city gas) of biogas.

Transportation technology of biomethane through gas pipeline

We considered to transport the residual biomethane being produced at a sewage-treatment plant (STP) at Kobe City in Japan through Osaka Gas's pipeline. The biomethane from this STP was used for NGV and so on after purified by high pressure water wash. So most of the CO2 and H2S were already removed from the biomthane. But in order to inject biogas into our pipeline, the purification level was not enough, because Osaka Gas has a strict standard for the city gas as shown in Table 3. Then the process to meet the biomethane composition to Osaka Gas's standard had been developed.

Component	Standards
CO_2 (vol%)	<0.5
H_2S (mg/m^{3}N)	<1.0
O_2 (vol%)	<0.01
Calorie (MJ/m^{3}N)	44.2-46.0
Odrant (mg/m^{3}N)	12-16

Table 3 Osaka Gas's standard for injection into pipeline

In order to meet the biomethane composition to Osaka Gas's standard, we established the process shown in Fig. 10. In this process, oxygen is removed by catalytic conversion into water adding hydrogen at first. Secondly CO2 and water are removed by pressure swing adsorption system. Third the calorie is adjusted by adding LPG, and forth odorant agent is added. After monitoring the composition, biomethane is injected into Osaka Gas's pipeline. The data monitored is transmitted to Osaka Gas's control center. At the border between purification plant and pipeline, there are two shutoff valves and they can be shut off automatically or by remote control in case the biomethane composition departs from the standard.

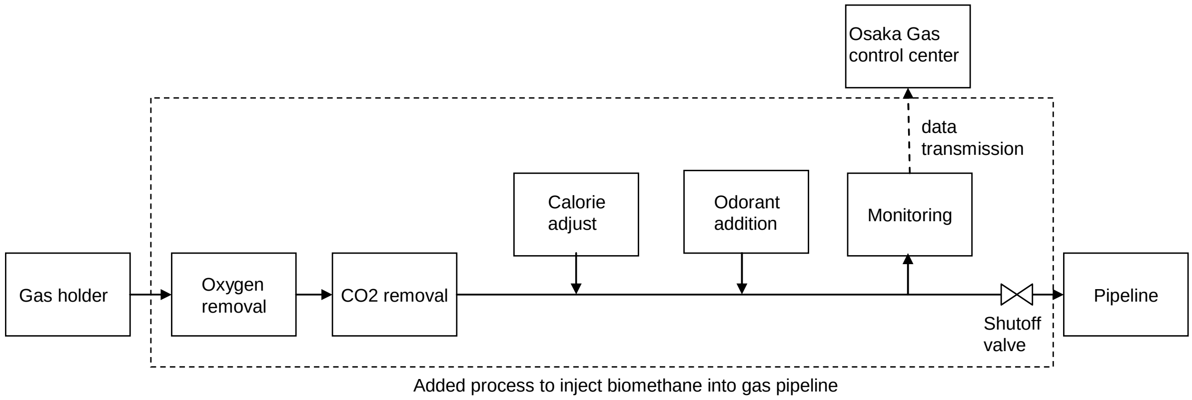

Fig.10 Biomethane composition adjustment system

It has recognized that above system work appropriately and the transportation of the purified biomethene through Osaka Gas's pipeline began in Sep. 2010. 790,000 m3N a year of biomethane will be transported through pipeline, according to the plan.

SUMMARY

Osaka Gas Co., Ltd. has developed high performance biomethane production system which integrate the high temperature (55 degree-C) methane fermentation and the hyper thermophilic hydrolysis under 80 degree-C in which the high molecular weight organic substances are converted into smaller molecular weight ones. We recognized that the biomethane yield increased by 27% and the amount of residue was reduced by 57%. We also developed biodegradable plastic bag which can be hydrolysed more than 2.5 kg plastics/m3-day under hyper-thermophilic condition, whereas only 0.57 kg plastics/m3-day can be hydrolysed under normal anaerobic condition. And as the results of these developments, we created a new scheme to use MSWOF in which MSWOF collected using biodegradable plastic bag is treaded anaerobically without removal of the plastic bag. This scheme will make MSWOF use easy.

We also developed a UASB based technology to produce biomethane from a chemical factory's effluent which includes high concentration alkaline materials and salinity. After dilution by tap water, acid fermentation, and neutralization, the effluent could be converted into biomethane. Applying this process, 355,000 m3N (as 45.0MJ-HHV/m3N of city gas) a year would be produced and can contribute to CO2 reduction.

The transportation of residual biomethane from a sewage-treatment plant through Osaka Gas's pipeline has begun in Sep. 2010. In order to meet to Osaka Gas's standard, a biomethane compositon adjustment process including oxygen removal, CO2 and water removal, calorie adjust, odorant addition, monitoring and data transmission has been established. 790,000 m3N a year of biomethane is planned to be transported through pipeline.

REFERENCES

J. Tsubota , T. Tsubone and H. Tsuno (2004). Use of thermophilic anaerobic microbes for municipal solid waste hyfrolysis and its utilization to methanogenesis. Anaerobic Digestion 2004 Proceedings, 3, 1702-1706.