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An analysis of CH_4/N_2 rich biogas production, fuel treatment process and microturbine application

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Abstract−Biogas usually contains CH_4 and CO_2 as main components with the ratio of 6 : 4, and its composition varies with wide range depending on digester conditions. In addition to concentration change of each constituent, biogas composition could be changed due to the variations in the organic matter treatment process. The aim of the study is to analyze the production and application to a microturbine system of CH_4/N_2 rich biogas produced from Gong-Ju wastewater treatment plant. CH_4/N_2 rich biogas is produced due to the internal wastewater recirculation. The internal wastewater recirculation is intended to enhance NO_3^- removal without additional carbon source input. As a result, the digester was shown to be the highest contributor for nitrogen removal and average CH_4 concentration was lowered compared to the typical biogas composition. Nitrate removal rate was influenced by the internal recirculation ratio. Content of N_2 has no effect on biogas clean-up system performance. Besides, adaptability of CH_4/N_2 rich biogas to microturbine was satisfactory with very low NOx and SO_2 concentration in microturbine exhaust gas. Influence of high N_2 concentration of biogas on NOx concentration was limited due to the low combustion temperature.

Key words: Biogas, Anaerobic Digestion, Microturbine, Livestock Wastewater, Wastewater Recirculation

INTRODUCTION

Among different options for wastewater treatment, anaerobic digestion is recently favored in many countries since it decomposes organic matters while producing energy containing biogas and mitigating greenhouse gas emission. Demand for anaerobic digestion will be increased since sea dumping of wastewater is about to be prohibited.

Although anaerobic digestion is one of the best alternatives for decomposition of high strength organic carbon compounds, it is incapable for nitrogen removal. Especially, the nitrogen oxidized form could pose a threat to human health and cause eutrophication of the natural water resource [1]. Therefore, the nitrogen removal process should be coupled with the anaerobic digestion process. Due to the insufficient C/N ratio for anaerobic digestion and denitrification process, additional carbon source should be supplied. To reduce additional carbon source supply for denitrification, the recirculation of the NO_3^- rich supernatant from the nitrification reactor to the anaerobic digester was proposed and has been studied extensively [2,3]. The adaptation of nitrified effluent recirculation results not only in a reduction of additional carbon source supply but also in a change in the produced biogas composition. Increase of recirculation ratio results in lower CH_4 concentration and higher N_2 concentration [4]. Internal wastewater recirculation results in CH_4/N_2 rich biogas composition and it differs from typical biogas composition with the concentration of 50-60% CH_4 and 40-50% CO_2. High N_2 concentration of over 50% comes from the denitrification reaction in the anaerobic digester.

Report on the utilization of CH_4/N_2 rich biogas has been limited. In the combustion science area, however, dilution effect to conventional gaseous fuel such as CH_4 and C_3H_8 has been studied extensively and the studies are deeply related with biogas combustion and utilization. CO_2 dilution is related with the FGR (flue gas recirculation) scheme to reduce NOx emission [5,6]. CH_4 flame with N_2 dilution affects flame stabilization conditions [7]. CH_4/N_2 rich biogas contains fewer greenhouse gas components and is obviously expected to reduce greenhouse gas emission and N_2 content will affect NOx emission level [8]. N_2 dilution of fuel will reduce NOx emission due to decrease of the flame temperature [9]. Low combustion temperature effect is dominant compared to higher chances of N_2 oxidation. However, for utilization of CH_4/N_2 rich biogas with real prime movers, the situation will be different since prime movers tend to maintain its design temperature in the combustor.

Despite many small scale and separate studies about the wastewater recirculation process for enhanced denitrification and dilution effect of N_2, there is a need for large scale analysis on anaerobic digestion with waste recirculation and energy conversion of CH_4/N_2 rich biogas. Therefore, the focus of this work was to analyze CH_4/N_2 rich biogas production from GWTP (Gong-Ju Wastewater Treatment Plant) and evaluate CH_4/N_2 rich biogas application to a microturbine system combined with biogas clean-up in terms of operation stability and emission.

CH_4/N_2 RICH BIOGAS PRODUCTION AND BIOGAS-MICROTURBINE CHP SYSTEM

1. Livestock Wastewater Treatment Process

GWTP (capacity: 250 m^3/day) is located in the city of Gong-Ju, Republic of Korea. GWTP is in charge of the nutrient removal of

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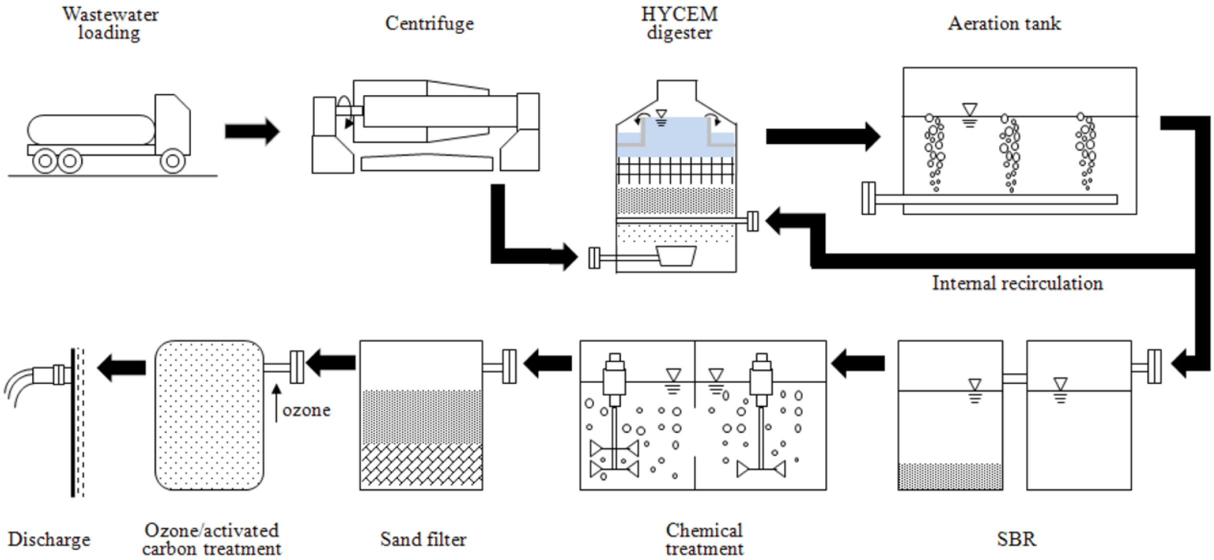

Fig. 1. Flow diagram of wastewater treatment process of GWTP.

Table 1. Summary of the facilities and treatment methods of GWTP

Facilities or methods	Characteristics
Capacity of treatment	250 m^3/day
Method of treatment	HYCEM (USAB+AF, Ceramic media)
Pre-treatment equipments	Drum screen, Centrifuge and Sand basin
Primary treatment process	Storage tank, HYCEM anaerobic digester, Nitrification aeration tank, and Sedimentation basin
Secondary treatment process	SBR
Tertiary treatment process	Chemical condensation, Sand filteration, Ozone contact chamber, and Activated carbon filtration
Method of deodorization	Ozone deodorization

livestock wastewater produced by local farmers and its final effluent is discharged into the river nearby. The plant treats livestock wastewater with the pre-treatment, anaerobic digestion, nitrification reactor, sedimentation tank, SBR, chemical flocculation and other treatment processes. The facility components of the treatment process and treatment flow diagram are shown in Table 1 and Fig. 1, respectively.

For anaerobic digestion, the HYCEM (Highly effective hybrid wastewater treatment system with ceramic media) process has been adopted. HYCEM process is a kind of hybrid UASB/AF process with ceramic porous media. The UASB (upflow anaerobic sludge blanket) process is a highly efficient system which forms granular sludge so that high concentration of microorganisms can be maintained in the reactor [10]. UASB and AF (anaerobic filter) are combined and designed to maintain more active microorganisms in the reactor [11]. Capacity of the anaerobic digester is 1,800 m^3, and floating porous ceramic media is installed at the top of digester to maintain high concentration of anaerobic microorganisms. Also, for optimal organic material decomposition, the temperature of the mesophilic digester has been maintained at 35 °C.

After the anaerobic digestion process, treated wastewater is transferred to the nitrification tank where further decomposition of organic material (to CO_2 and H_2O) and nitrification reaction (conversion of NH_4^+ to NO_3^- via NO_2^-) take place. The biological nitrification process is combined with NO_3^- rich supernatants recirculation. As a result of the recirculation, denitrification (conversion of NO_3^- to N_2) and methane fermentation happen simultaneously in an anaerobic digester. The amount of wastewater recirculation ratio has been controlled for optimal nutrient removal performance and the recirculation ratio varied between 1.8 and 3.8.

The SBR (sequencing batch reactor) is followed by the nitrification process and its main functions are phosphorous removal and denitrification. A portion of NO_3^- rich supernatants from nitrification reactor recycle to the anaerobic digester. Remainder of nutrient in the stream is removed by the following chemical flocculation using alum, anion polymer and ferrous salts. Further, treatment process, sand filtration, ozonation and activated carbon filtration are utilized to remove refractory organics and particles. Then the final effluent is discharged to the river. The complicated post-digestion process steps are essential to meet relevant regulations.

2. Biogas-microturbine Power Generation System

GWTP previously flared the produced biogas. To reduce GWTP energy consumption, a biogas-microturbine power generation system was designed and installed. A schematic diagram of the biogas-microturbine system is shown in Fig. 2. The biogas-microturbine system consists of two sub-systems: biogas pre-treatment and microturbine.

As a prime mover for energy conversion of CH_4/N_2 rich biogas, the microturbine is selected with a consideration of low CH_4 production rate, low CH_4 concentration and environmental merits. Although microturbines' electrical efficiency is around 30% based on state-of the-art technology [12], microturbines have some merits such as higher reliability, lower maintenance needs and low NOx emission

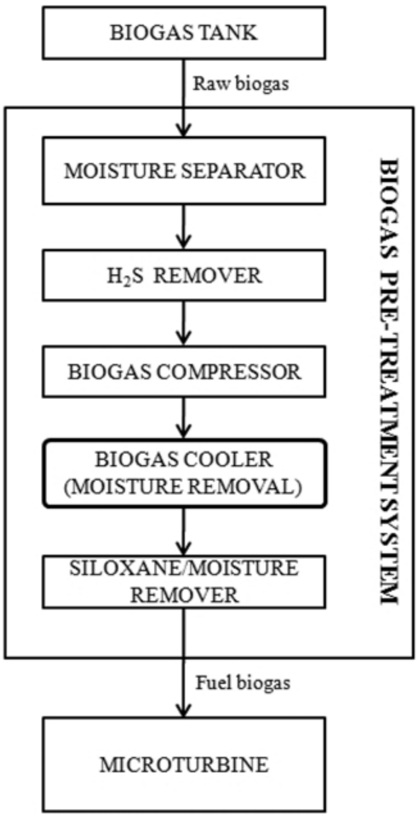

Fig. 2. Schematic diagram of biogas-microturbine power generation system at GWTP.

Table 2. Performance specification of CR-30 microturbine (Capstone)

Electrical power output	30 kW	at ISO conditions
Electrical efficiency, LHV	26%	at ISO conditions
Fuel flow HHV	415,000 kJ/hr	Full load
Exhaust gas flow	0.31 kg/s	275 °C

Table 3. Fuel biogas quality requirement of the CH_4/N_2 rich biogas-microturbine system

Condition	Requirement
CH_4 concentration	Over 35%
Fuel pressure	345-552 kPa (depends of calorific value)
Fuel temperature	Less than 50 °C and 20 °C above the fuel dew point temp. (at the fuel supply pressure)
H_2S concentration	Less than 200 ppm
NH_3 concentration	Less than 50 ppm
Siloxane concentration	Less than 5 ppb
Moisture content	No liquid water Gas temperature should be at least 20 °C higher than gas dew point temperature

[13]. Table 2 summarizes the characteristics of 30 kW class microturbine manufactured by Capstone Turbine Corporation. The microturbine's low power generation efficiency can be compensated if exhaust gas heat is recovered for digester heating.

The quality of biogas heavily affects the feasibility, stability and economics of a biogas utilization system. Calorific value or CH_4 concentration is related to flame stability in the turbine combustor since it influences the flow rate to achieve the same thermal output [14]. H_2S is corrosive and leads to wear of compressor and turbine parts [15]. Combustion of ammonia results in NO formation, and NO can react to produce other oxides of nitrogen in the atmosphere [16]. Siloxane containing biogas can cause problems such as fouling of a heat exchanger and abrasion of the gas engine surface [17]. Moisture fosters a corrosive environment and liquid water inlet into the microturbine could damage turbine blades.

The biogas pre-treatment system converts raw biogas to fuel biogas by removing harmful contaminants such as H_2S, NH_3, siloxane and moisture. Sometimes a higher degree of pre-treatment includes

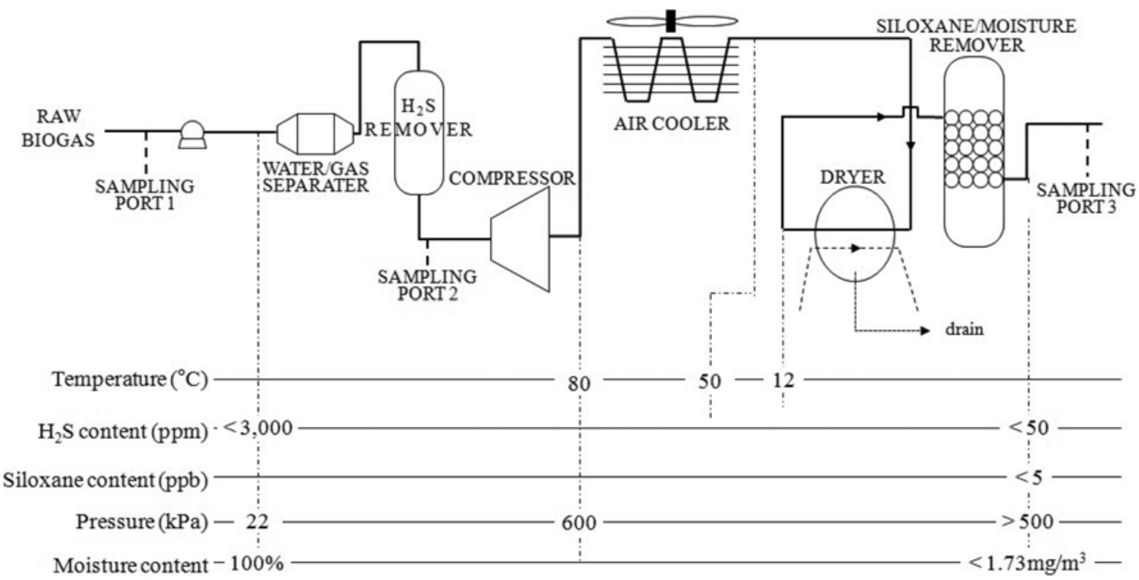

Fig. 3. Process diagram and design data of Biogas pre-treatment system.

a CH_4 enrichment step. Since biogas pre-treatment is mainly intended to protect system components, specification of each component determines the system fuel requirement. Table 3 summarizes the biogas-microturbine fuel requirement.

Based on the system fuel requirement, a biogas pre-treatment system was designed as shown in Fig. 3. The pre-treatment system consists of water separator, H_2S dry scrubber, fuel gas compressor with air-gas cooler, refrigerated gas dryer with heat exchanger for moisture condensation and removal, and siloxane/moisture remover. The water separator consists of inlet diffuser, outlet nozzle, and PVC fillers which separate liquid water molecular with collision and absorption of its momentum. The adsorption material in the H_2S scrubber is activated carbon and iron sponge. Reciprocating gas compressor compresses biogas to 0.6 MPa. In the refrigerated gas dryer, cooling water of 5 °C decreases the temperature of the compressed biogas (from 80 °C to 12 °C) and water vapor is condensed and removed. The last stage of biogas pre-treatment is siloxane/moisture removal by silica gel and activated carbon.

EXPERIMENT AND MEASUREMENT METHOD

1. Measurement of Physio-chemical Characteristics of Wastewater

To evaluate the HYCEM process with the internal recirculation of NO_3^- rich supernatants, BOD, SS, TN and TP were sampled at four different process steps: upstream, centrifuge outlet, HYCEM digester outlet, and SBR outlet. Sampled wastewater was measured by standard method. On a monthly basis, sampling and analysis was conducted for more than three years.

2. Measurement for Biogas Composition and Property

Biogas analysis was conducted on a weekly basis. To evaluate the performance of the biogas pre-treatment system, biogas was sampled at three different locations as shown in Fig. 3: blower inlet (sampling port 1), H_2S remover outlet (sampling port 2), microturbine inlet (sampling port 3). Biogas composition was analyzed with gas chromatography (GC-14A, Shimadzu), GC/MS (HP 5890+5972MSD), gas detection tube (No. 2H, No. 31B, No. 4H, etc) and NDIR/electro-chemical sensor gas analyser (AEMS with GEM- 2000, CES-Landtec). Siloxane content was analyzed by normal hexane impinge sampling method and GC/MS analysis using the standard materials for hexamethyldisiloxane, octamethylrisiloxane, octamethylcyclotetrasiloxane, and decamethylcyclopentasilxane. Besides, the dew point of biogas at the final stage of the pre-treatment system was also measured with a dew point sensor of aluminium oxide type.

3. Experiment for CH_4/N_2 Rich Biogas Emission Characteristics on Microturbine Operation

Test operation of CH_4/N_2 biogas-microturbine CHP system was conducted. The test was conducted on a daily basis depending on biogas production condition. During the tests, biogas composition was analyzed with the biogas analyzer above mentioned for continuous biogas analysis. Emission characteristics of CH_4/N_2 rich biogas on microturbine application were also analyzed with Testo-350 for evaluating environmental influence.

To evaluate the effect of microturbine load, which affects to its operational stability, exhaust gas sampling was done with different microturbine load: 15, 20, 25 and 30 kW. However, due to higher ambient temperature compared to 15 °C, ISO standard, actual turbine output for 30 kW load was reduced under 28 kW.

RESULTS AND DISCUSSION

1. Analysis HYCEM Digester Performance and Biogas Composition

Concentration variations of BOD, SS, TN, and TP by treatment steps are shown in Fig. 4 and Fig. 5. Removal efficiencies of them

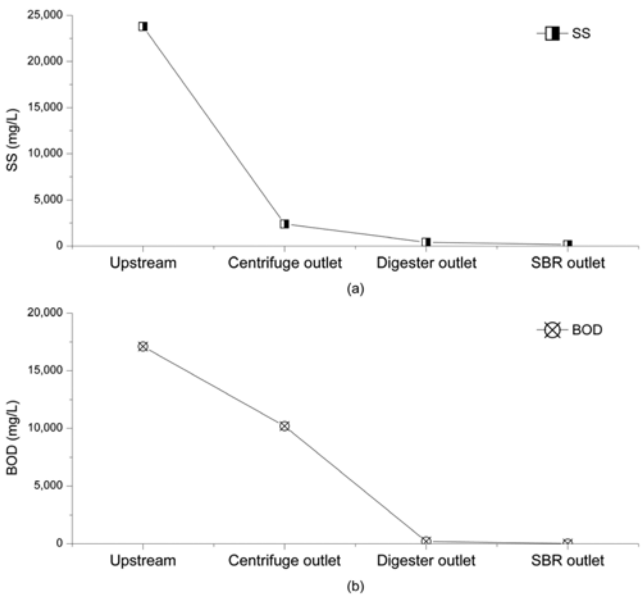

Fig. 4. Concentration variations at different treatment steps (mg/L, 36 months average value). (a) SS concentration (b) BOD concentration.

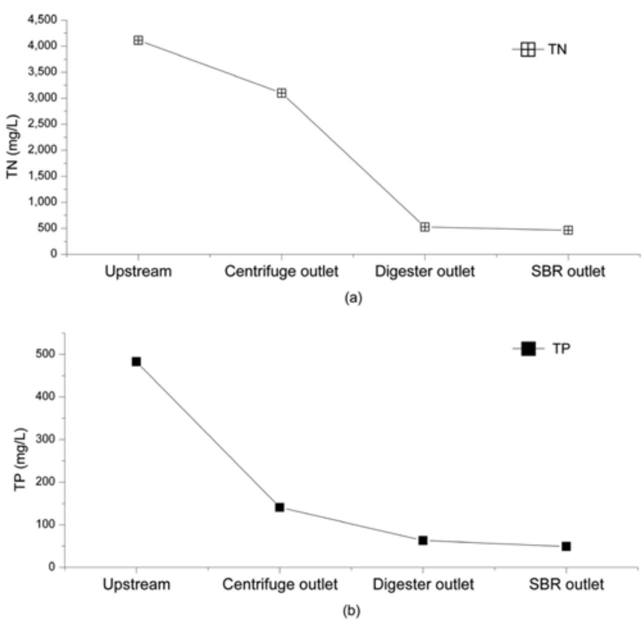

Fig. 5. Concentration variations at different treatment steps (mg/L, 36 months average value). (a) TN concentration, (b) TP concentration.

Table 4. Contribution and efficiency of HYCEM digester on total removal performance

	BOD	SS	TN	TP
Removal contribution (%)	59.5	8.5	70.3	17.1
Removal efficiency (%)	97.7	81.5	82.8	50.8

to the removal of 59.5% of BOD, 8.5% of SS, 70.3% of TN and 17.1% of TP. Also, the removal efficiency of the digester is 97.7%, 81.5%, 82.8% and 50.8%, respectively.

The highest contributor of TN removal was found to be the HYCEM digester rather than the aeration tank or SBR. This shows significant amount of biological carbon source was consumed for denitrification as shown in the general biological denitrification equation [18]:

$$NO_3^-\text{+Carbon Source} \rightarrow N_2\text{+}CO_2\text{+}H_2O\text{+}OH^-\text{+Cell} \quad (1)$$

Fig. 6(a) shows NO_3^- removal rate in the anaerobic digester with full organic loading rate range. It can be seen the rate was increased with higher recirculation ratio and it directly supports the occurrence of the denitrification process in the digester. The correlation between NO_3^- removal rate and recirculation ratio was found to be strong from regression analysis (the coefficient of correlation ≒0.82). With sufficient carbon input and high NO_2^- and/or NO_3^- concentration, organic matters are consumed firstly as electron donor for denitrification process and N_2 concentration increases with higher NO_2^- and/or NO_3^- concentration [19]. Fig. 6(b) shows NO_3^- removal rates in the anaerobic digester with different organic loading rate ranges. With lower organic loading rate range, the correlation coefficient and slope became smaller. This means that the effect of recirculation ratio became weaker with sufficient input of organics and it coincides with the fact that nitrification is influenced negatively by the presence of organic matter which promotes the growth of heterotrophs [2].

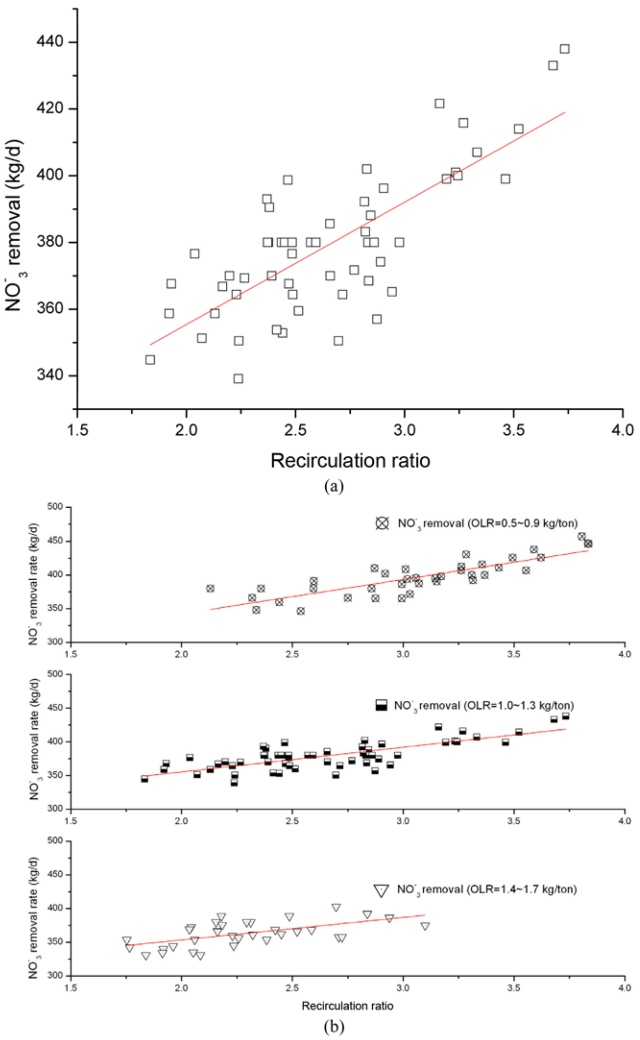

Fig. 6. Nitrate removal in the anaerobic digester. (a) With full range of organic loading ratio, (b) with divided ranges of organic loading ratio.

Biogas was collected in a collecting bag. Biogas production rate was estimated as 248-803 m^3/day. The wide range of biogas production is due to the variation of operating conditions like organic loading rate and hydraulic retention time. As summarized in Table 5, biogas composition also varied with wide range. CH_4 concentration was between 31.1% and 51.1% with average value of 40.7%. N_2 was a balance gas with high concentration and it resulted from denitrification taking place in the HYCEM digester. Overall CH_4 and N_2 concentration was more than 95%. Fig. 7 shows CH_4 concentration in the biogas. A weak correlation between CH_4 concentration and recirculation ratio was found (the coefficient of correlation <0.5) and it is contrary to other research results which show strong

Table 5. Summary of raw biogas composition analysis result

Components	Max. value	Min. value	Avg. value
CH_4 (%)	51.09	31.05	40.66
NH_3 (ppm)	150	3	36.16
H_2S (ppm)	3000	285	759.26
CO_2 (%)	3.00	0.96	1.75
O_2	3.8	0.1	0.74
N_2 (%)		Balance gas	

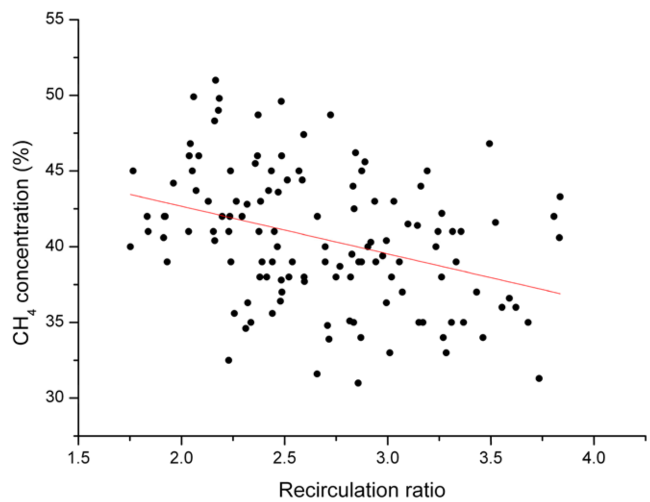

Fig. 7. Relationship between CH_4 concentration and recirculation ratio.

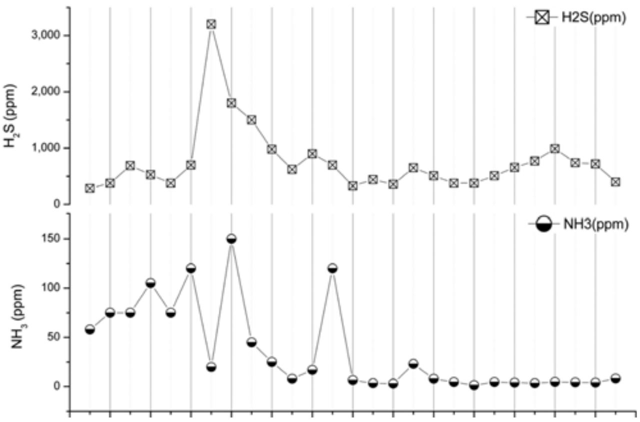

Fig. 8. Concentrations of H_2S and NH_3 in raw biogas.

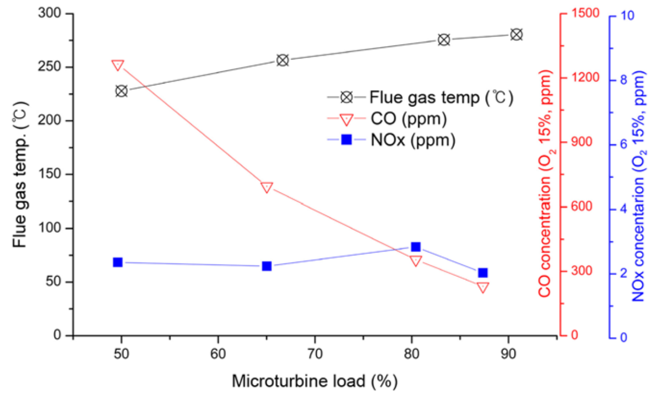

Fig. 9. NOx and CO emission and exhaust gas temperature with different microturbine load conditions.

relations between two factors [2,4]. It was thought that the weak correlation was due to the effect of other factors such as hydraulic retention time, organic loading ratio and input wastewater composition. CH_4 concentration was mostly over 35%, the CH_4 concentration limit for normal microturbine operation. Biogas contained an average of 759 ppm of H_2S (285-3,000 ppm) and 36 ppm of NH_3 (3-150 ppm) as shown in Fig. 8. Though siloxane detection analysis focused on four siloxane compounds, no siloxane compound was detected. The result seems to be consistent with the fact that livestock wastewater contains extremely low siloxane source such as shampoo and cosmetics.

As a result of internal recirculation for simultaneous methanogenesis and denitrification process, 70.3% of TN was removed by the digester and its TN removal efficiency reached to 82.8%. Also the effect of recirculation ratio on nitrate removal was found.

2. Performance of Biogas Pre-treatment System

Table 6 shows the test results of biogas pre-treatment performance. The tests were performed by collecting biogas samples from the different locations of biogas pre-treatment system and measured with gas chromatography. H_2S and NH_3 concentration was not detected at the outlet of the H_2S scrubber.

CH_4 concentration decreased along the pre-treatment system slightly. Decrease of CH_4 by H_2S scrubber (1.37%) was higher than across the siloxane/moisture remover (1.21%). Activated carbon absorbs CH_4 like other gases and the amount of absorption depends on temperature and pressure [20]. Although the absorption reaction is enhanced with higher pressure and lower temperature, more CH_4 was absorbed in the H_2S scrubber with lower pressure and higher temperature than in the siloxane/moisture remover. It was thought that the short residence time caused by high pressure decreased absolute amount of CH_4 absorbed in the remover.

It could be concluded that the biogas pre-treatment system performance for the elimination of impurities satisfied the biogas quality goal shown in Table 3.

Table 6. Variation in biogas composition by measuring points

Concentration	Upstream	After H_2S scrubber	After siloxane remover
CH_4 (%)	40.06	38.69	37.48
H_2S (ppm)	759.26	9.28	0.82
NH_3 (ppm)	36.16	1.52	0.29

3. Emission and Operation Characteristics of Microturbine with CH_4/N_2 Rich Biogas Application

Turbine operation was stable with the CH_4 concentration as low as 32%. However, for lower CH_4 concentration, turbine operation was extremely unstable, resulting in an increase of operable minimum turbine load, small tolerance of load change. For example, the load input should be over 20 kW and load change should be less than 3 kW for CH_4 content less than 40%.

Fig. 9 summarizes the result of test operations. Measured NOx emission level was maintained below 3 ppm for all microturbine load conditions. Compared to the manufacturer's specification, 9 ppm, the emission level is very low. The NOx measurement is consistent with other work [21]. The result suggests that the contribution of N_2 in fuel gas to NOx formation is negligible. It can be thought that low combustion temperature of microturbine prevents the oxidation of N_2 in the combustion air. Considering high combustion temperature of commercial mid and large scale gas turbines and gas engines, in terms of NOx emission, a microturbine is suitable for utilization of CH_4/N_2 rich biogas since the turbine inlet temperature of the microturbine is around 800-900 °C. Low NOx emission is one of representative characteristics of the microturbine due to its low turbine inlet temperature.

SO_2 was not detected at all for all tested load levels. CO concentration was increased with load level from 230 ppm at 90.8% load to 1,265 ppm at 50% load. On the contrary, flue gas temperature was decreased with load level decrease. CO emission is higher than the specification of the manufacturer for all tested loads. Similar trend of increased CO emission level with microturine load increase was found in natural gas fuelled microturbine system which shows 36 ppm at full power to 500 ppm level at around 70% load [21]. However, there was a huge difference in the absolute emission level (230 ppm v.s. 50 ppm at 90% load condition). High CO emission resulted from the increased combustion instability and decreased residence time due to low CH_4 concentration.

Microturbine operation with CH_4/N_2 rich fuel seems to be technically feasible unless CH_4 concentration is above 32%. NOx and SOx emission level was satisfactory while CO emission level was relatively higher compared to natural gas fuelled microturbine system. Detail investigation on NOx, SOx and CO emission covering wide range of CH_4 concentration and microturbine load should be executed.

CONCLUSIONS

With the analysis of CH_4/N_2 rich biogas production and application to microturbine on commercial scale wastewater treatment facility and pilot scale biogas-microturbine system, the following conclusions were drawn:

1. CH_4/N_2 rich biogas was produced due to simultaneous methanogenesis and denitrification. Denitrification was increased with internal recirculation ratio and TN removal contribution rate and efficiency of HYCEM digester was 70.3% and 82.8%, respectively.

2. The performance of the pre-treatment system was confirmed to satisfy all fuel requirements such as H_2S, NH_3, siloxane and moisture content. Removal of hydrogen sulphide and ammonia is successful with 99.9% and 90.2% of removal efficiency, respectively.

3. High N_2 concentration in biogas and microturbine load change did not affect NOx emission. Low combustion temperature of microturbine was thought to prevent high N_2 concentration from increasing NOx emission level.

4. CO emission was increased from 114 ppm to 310 ppm with decrease of microturbine load from 90.2% to 66.7% and the emission level was always higher than microturbine specification.

5. As the next step in this field of study, the emission level with a wide range of CH_4 concentration and isolated effect of recirculation ratio on CH_4 concentration and CH_4 production rate should be investigated in detail.

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