

Performance comparison of aqueous MEA and AMP solutions for biogas upgrading

Young Cheol Park*, Jong-Seop Lee*, Jong-Ho Moon*, Byoung-Moo Min*[†], Dong-Min Shim**, and Hyun-Je Sung**

*Korea Institute of Energy Research, 152 Gajeong-ro, Yuseong-gu, Daejeon 34129, Korea

**Hansol EME, 55 Bundang-ro, Bundang-gu, Seongnam-si, Gyeonggi-do 13591, Korea

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Abstract—Two different aqueous amine solutions were applied to CO₂ removal from simulated biogas in a lab.-scale continuous absorption process that can handle 5 Nm³/hr of gas treatment. The effects of the gas-to-liquid ratio in the absorber and of the temperature of the reboiler on the CO₂ removal were analyzed in aqueous MEA and AMP solutions. Since the CO₂ loading ratio of AMP solutions is larger than that of MEA solutions for the same absorbent concentration, the AMP solutions have higher CO₂ removal efficiency than that of MEA solutions for the same gas-to-liquid ratio and reboiler temperature. Also, the 30 wt% MEA solution has a higher CO₂ removal efficiency than that of the 20 wt% MEA solution at the same gas-to-liquid ratio and reboiler temperature. To evaluate the feasibility of biogas upgrading, a commercial simulator, Aspen Plus[®], was used to analyze the effects of absorbent concentration, absorbent flow rate at the absorption column, and absorber height on CO₂ removal and CH₄ purity; the regeneration energy was also evaluated. The results were applied to the design of a pilot-scale biogas upgrading plant that can handle 10,000 Nm³/day of biogas treatment.

Keywords: Biogas, CO₂ Removal, Amine Solutions, Gas-to-liquid Ratio, Reboiler Temperature

INTRODUCTION

Biogas derived from organic material decomposition with anaerobic conditions has become a medium-energy fuel [1] that could be a source of bio-methane (CH₄) when the quality of the biogas has been sufficiently improved by reducing CO₂ content. To separate CO₂ from biogas, absorption by chemical and physical absorbents, cryogenic separation, and membrane separation have been developed [2-5].

One promising existing option for biogas upgrading by reducing CO₂ content in raw biogas is based on chemical absorbents such as mono-, di-, and tri-alkanol amine solutions [6]. Already, these separation processes have been applied to petrochemical processes for a long period and have had technical reliability confirmed. Recently, CO₂ separation processes have been highlighted to reduce greenhouse gas from all kinds of emission sources, including those in the energy field. Among the CO₂ separation processes, the mono-alkanolamine process has been widely applied to commercial CO₂ separation and is assumed as a reference (base line) process because it has seen considerable use in engineering and operation experience. Even though that process has been widely applied to the flue gas condition, there has been little attention to the gas condition with higher CO₂ concentration such as biogas at the continuous experimental unit.

Although the monoethanolamine (MEA) process has a fast reaction rate compared to those of other amines, it requires high energy

consumption during the regeneration of the absorbent and requires a high absorbent circulating rate to increase the working capacity. Also, there are material corrosion problems due to the strong alkalinity when the absorbent concentration is increased. In general, the steric hindrance of the amine structure can improve the above issues, by inducing weak chemical bonding and allowing the stoichiometric limitations in the acidic gases-amines to be overcome [7]. Thus, a sterically hindered amine process such as 2-amino-2-methyl-1-propanol (AMP) process could be applied to emission sources that have high CO₂ content. Compared to MEA, AMP, one of the sterically hindered amines, has higher loading capacity, lower regeneration energy, and lower degradation rate [8]. In the biogas upgrading process, the sterically hindered amine (AMP) process is well suited to effect CO₂ removal because raw biogas is composed of around 40% CO₂ and 1,500 ppm of H₂S content.

We compared the performance of aqueous MEA and AMP solutions in a lab-scale continuous CO₂ separation unit to obtain experimental data at the condition of high CO₂ concentration in the simulated biogas. The effects of the gas-to-liquid (G/L) ratio in the absorber and of the temperature of the reboiler in the stripper on the CO₂ removal performance were analyzed. In these experiments, the CO₂ removal performance of the AMP solutions was found to be higher than that of the MEA solutions at the same absorbent concentration (30 wt%) and at the same gas-to-liquid ratio and reboiler temperature. Also, under the same operational conditions, the CO₂ removal performance of the MEA solution moved to a higher level with increasing of the MEA concentration in aqueous solution. The effects of the absorbent concentration, the feed rate of absorbent to the absorber, and the height of the absorber on CO₂ removal behavior and CH₄ purity, as well as the regeneration energy, were analyzed with a commercial simulator, Aspen Plus[®]. The results of the simulation were applied to the design of a pilot-scale biogas

[†]To whom correspondence should be addressed.

E-mail: bmmin@kier.re.kr

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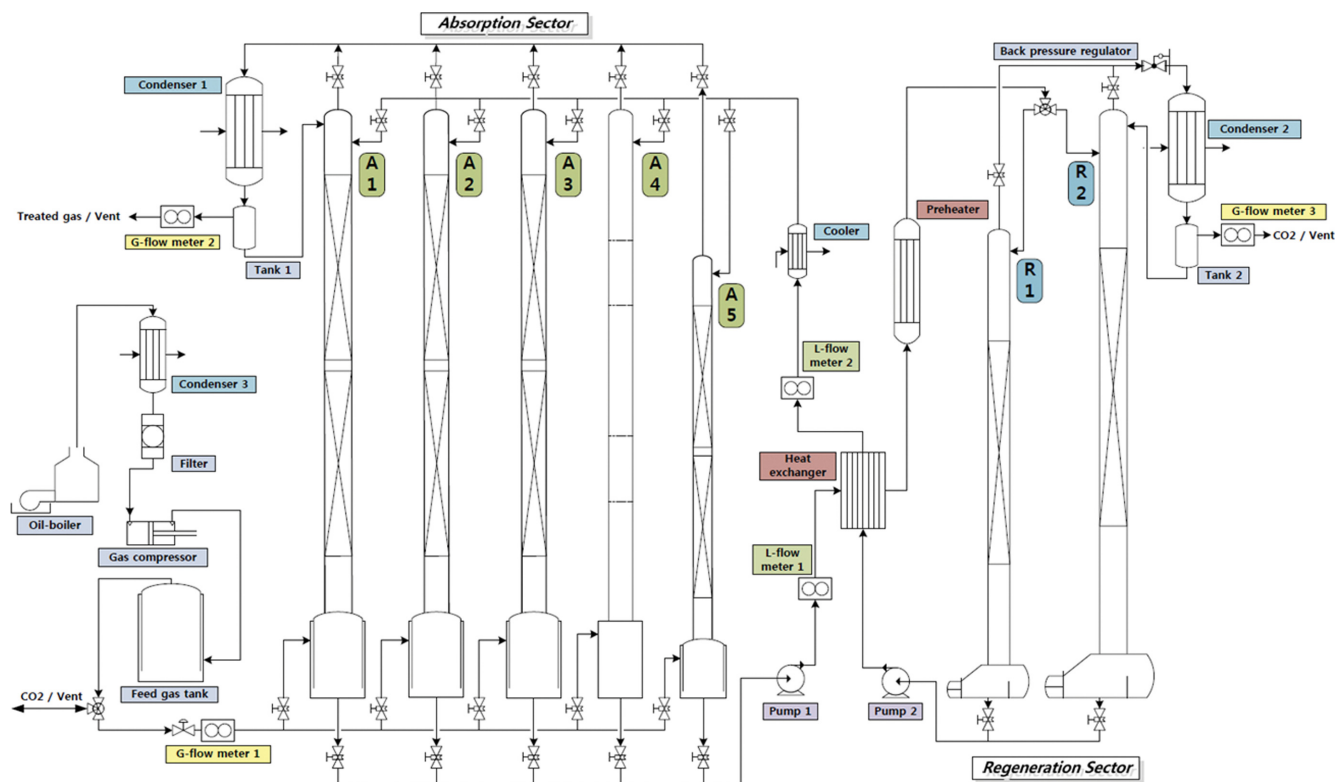


Fig. 1. Schematic diagram of a lab.-scale CO₂ separation unit.

- A. Absorber
 A1. ID 134, H 2,000 mm (Acirle/Random packed)
 A2. ID 94, H 2,000 mm (Acirle/Structure packed)
 A4. ID 94, H 2,000 mm (Glass/Tray column)

- R. Regenerator
 R1. ID 75, H 1,800 mm (Glass/Random packed)
 R2. ID 81, H 2,392 mm (SS/Random packed)
- G-flow. Gas flow
 L-flow. Liquid flow
 A5. ID 75, H 1,000 mm (Glass/Random packed)

upgrading facility that can treat 10,000 Nm³/day of raw biogas from waste sludge anaerobic digestion.

EXPERIMENTAL

1. Experimental Apparatus

Fig. 1 shows a schematic diagram of a lab.-scale CO₂ separation unit that can handle 5 Nm³/hr of gas treatment. This unit consists of five different-size and -packing absorption columns (absorber), and two different-size regeneration columns (stripper); it also has a heat exchanger, condensers, reboilers, absorbent circulating pumps, and measuring and control system, all of which are shown in detail. The system has an oil-fired boiler to supply feed gas and a cooling system to provide additional control of the temperature of the gases and liquids. In this unit, it was possible to connect the entire apparatuses of the absorber and the stripper at a ratio of 1 : 1 by changing the valve positions individually according to the experimental conditions. In this study, absorber A3 (i.d.: 94 mm, height: 2,000 mm) and stripper R2 (i.d.: 81 mm, height: 2,392 mm) were connected and other absorbers and strippers were disconnected by controlling of the valve positions. The A3 absorber and R2 stripper were packed with 1/4 inch Propak[®] and 1/2 inch Pall Ring[®], respectively. Three dry gas meters were installed to measure the gas volume of each gas stream; it was possible to convert the measured gas volumes to the corresponding gas flowrates by using the oper-

ating times at steady state. Also, thermocouples and low pressure gauges were installed at each gas meter to correct the gas flowrates of the standard state. The circulating flow rate of absorbent (maximum, 4.0 liter/min) was controlled by manipulating the rotating speed of the motor in the pump. The volume of the reboiler was 7.5 liters; its temperature was controlled in a range from 85 to 130 °C using an immersed electric heater of 4.5 kW with a PID controller; a back pressure regulator was installed at the end of the regeneration column to maintain the temperature of the absorbent at a level above 100 °C in the reboiler.

The pilot-scale biogas upgrading facility was constructed at a waste sludge treatment site in Busan. This facility is composed of a moisture and sulfur removal pretreatment unit, a CO₂ separation unit, a heating value adjusting unit, and a unit to connect the plant to the city gas supply network. The process of the CO₂ separation unit is very similar to the lab.-scale or amine-based commercial CO₂ separation processes. The inside diameter of the absorber and regeneration column is 0.6 m; the heights of the absorber and the regeneration column are 14 and 13 m, respectively.

2. Experimental Conditions and Methods

In this experiment, the main operational variables were the kinds and concentrations of the absorbent (amine), the gas and absorbent flow rates in the absorber, and the temperature of the reboiler. The amine solutions, utilized as CO₂ absorbent, were 20 and 30 wt% MEA and 30 wt% AMP aqueous solutions; these were pre-

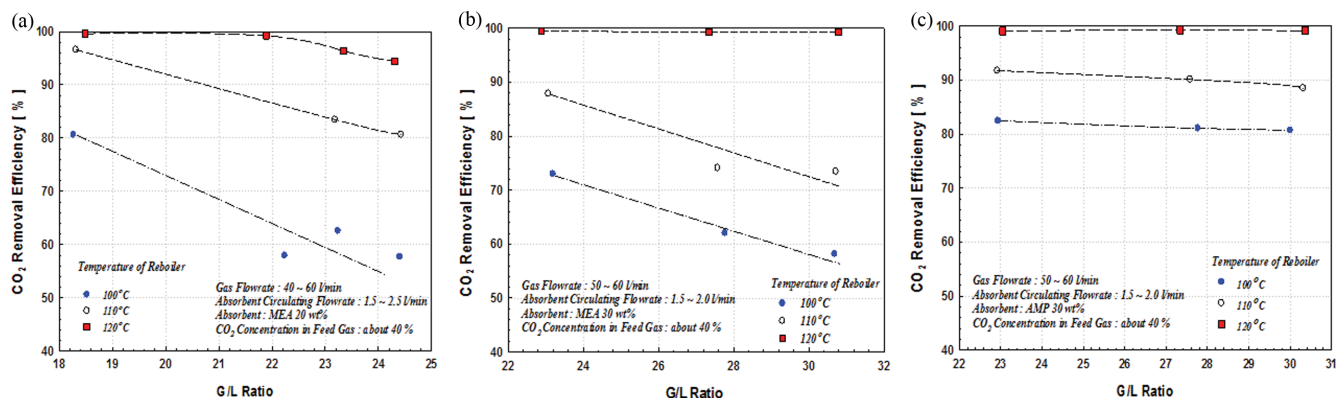


Fig. 2. Effects of G/L ratio and temperature of reboiler on CO₂ removal efficiency. (a) MEA 20 wt% solution, (b) MEA 30 wt% solution, (c) AMP 30 wt% solution

pared from reagent grade amines (Aldrich Co.) and distilled water. To adjust the G/L ratio, which is the ratio of the gas and liquid flow rates in the absorber, feed gas and absorbent circulating flow rate were varied within ranges of 40 to 60 and 1.5 to 2.0 liter/min, respectively. The CO₂ concentration of the feed gas was kept in a range of 40–42 vol%; this range is similar to that of biogas formed by the addition of pure CO₂ gas to flue gas from a light oil-fired boiler. The compositions of O₂, N₂, and CO₂ of each gas stream were analyzed with gas-chromatography.

The temperature of the feed absorbent was controlled at 15 °C with a condenser (heat exchanger) that was connected to the water chiller. Depending on the experimental conditions, the reboiler temperature was kept in a range of 100–120 °C. The pressure in the regeneration column was controlled to keep under the maximum value of 2.5 kg/cm² gauge; this was done to increase the reboiler temperatures to values over 100 °C. The performance of given experimental conditions was analyzed using steady-state operational data maintained for more than 1 hour. Using the ideal gas law, the effects of the G/L ratio, the reboiler temperature, and the absorbents on the CO₂ removal efficiency were calculated based on the mass balance of CO₂.

RESULTS AND DISCUSSION

1. Experimental Results

G/L is defined as the ratio of the biogas flow rate to the liquid (absorbent) flow rate, so this value can be used indirectly to describe the gas-liquid contact phenomena in the absorber. At identical liquid circulating flow rates, increasing the G/L ratio reduces the contact time of the gas and reduces the removal efficiency. When the gas flow rate is over the maximum allowed value, the removal efficiency suddenly drops due to flooding effects in the absorber. In this experiment, flooding phenomena appeared at 2.0 l/min of absorbent circulating flow rate; the superficial velocities in the absorber were over 13 cm/sec.

The reboiler temperature affects the regeneration level of the absorbent, such that higher reboiler temperatures lead to higher regeneration levels, which are closely related to the cyclic loading of absorbent. To maximize the performance of the absorption process, the temperature in the reboiler must be maintained at a sufficiently

high level, and the absorption temperature must be adjusted to the exact temperature. However, unexpected optimum temperature conditions can lead to large energy waste sources in this process.

Fig. 2 shows the CO₂ removal efficiency in relation with the G/L ratio for each reboiler temperature. At the reboiler temperature of 100 °C, the CO₂ removal efficiency when using MEA solutions remained at the 80% level or less for low G/L ratio of 18.3 at 20 wt% MEA solution and 23.2 at 30 wt% MEA solution; this removal efficiency fell to a 60% level at higher G/L ratio. However, when using the AMP solution, the removal efficiency dropped only slightly as the G/L ratio increased. At a reboiler temperature of 110 °C, the CO₂ removal efficiency when with the MEA solution decreased as the G/L ratio increased by a certain value of G/L ratio; the removal efficiency then remained above that value, while the removal efficiency when using the AMP solution dropped slightly as the G/L ratio increased. At a reboiler temperature of 120 °C, the CO₂ removal efficiency maintained a value above 99% at high G/L ratio when using 30 wt% MEA solution and 30 wt% AMP solution; however, this removal efficiency fell to a 94% level at high G/L ratio when using 20 wt% MEA solution. At the same G/L ratio, the 30 wt% AMP solution showed the highest CO₂ removal efficiency among the three different aqueous amine solutions. It is obvious that AMP shows better performance than that of MEA at the same concentration in the solution because the CO₂ loading of aqueous AMP is better than that of MEA under the same conditions [9].

Fig. 3 shows the solubility of CO₂ in aqueous amine solutions such as 20 wt% MEA solution and 29.2 wt% AMP solution at the temperatures of 50 °C and 130 °C. The AMP solution shows a higher CO₂ loading than the MEA solution at the absorption temperature of 50 °C; the AMP solution shows a lower CO₂ loading at the regeneration temperature of 130 °C. As can be seen in Fig. 3, the AMP solution shows a higher difference of loading ratio between the absorption and regeneration temperatures at the same partial pressure of CO₂ than does the MEA solution. From these results, the AMP solution is expected to improve the CO₂ removal efficiency; the AMP solution is therefore suitable for CO₂ recovery in systems such as this one.

Fig. 4 shows the cyclic CO₂ loading and recovery rates of three different aqueous amine solutions with respect to the reboiler temperature of the lab-scale unit. As expected, the cyclic CO₂ loading

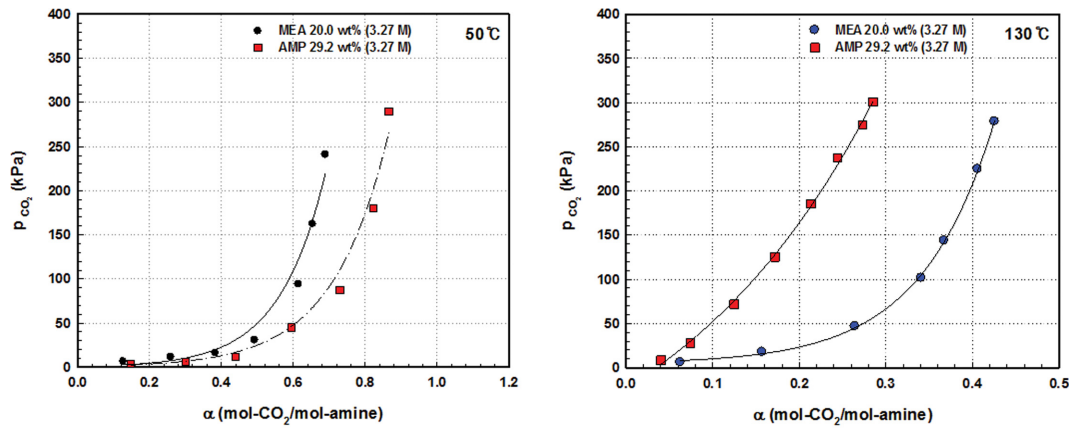


Fig. 3. Loading ratio of CO₂ in absorbents at 50 and 130 °C.

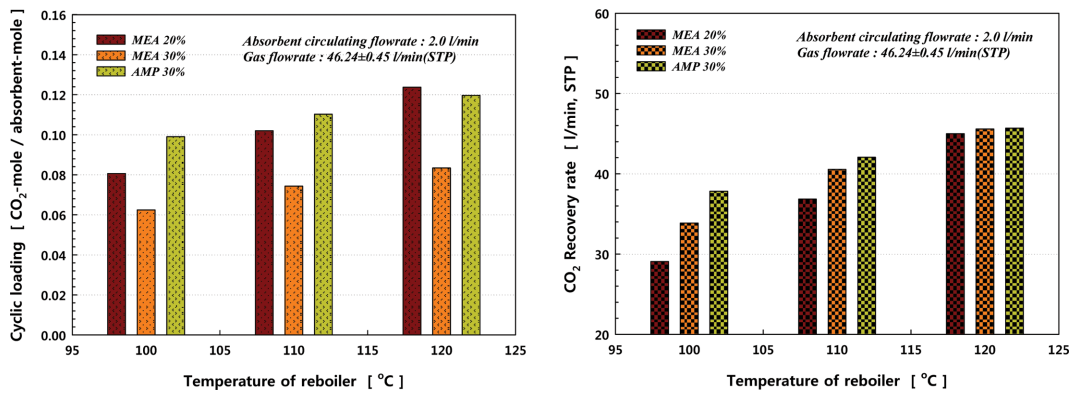


Fig. 4. Effect of temperature of reboiler on cyclic loading and recovery rate by absorbents.

of the AMP solution shows a higher value than those of the MEA solutions; however, that of the MEA 20 wt% solution is similar to that of the AMP 30 wt%. Even though the 20 wt% MEA solution shows cyclic CO₂ loading higher than that of the 30 wt% MEA solution, it shows lower CO₂ removal efficiency at the same G/L ratio, and so the cyclic loading can be seen to be inversely proportional to the molar number of the absorbent at the same CO₂ recovery rate, which is defined as separated CO₂ flow rate in this system. As shown in Fig. 4, the increasing of the reboiler temperature has an

effect on the regeneration level of the absorbent, enhancing the CO₂ removal efficiency at the same levels of absorbent and the same concentrations. At 120 °C of the reboiler, the CO₂ recovery rates were maximized, except for the case of the MEA 20 wt% solution in this system, which means that all of the CO₂ in the feed gas was totally recovered with the MEA 30 wt% and AMP 30 wt% solutions.

2. Simulation Results

To design the pilot-scale facility (10,000 Nm³/day of biogas treat-

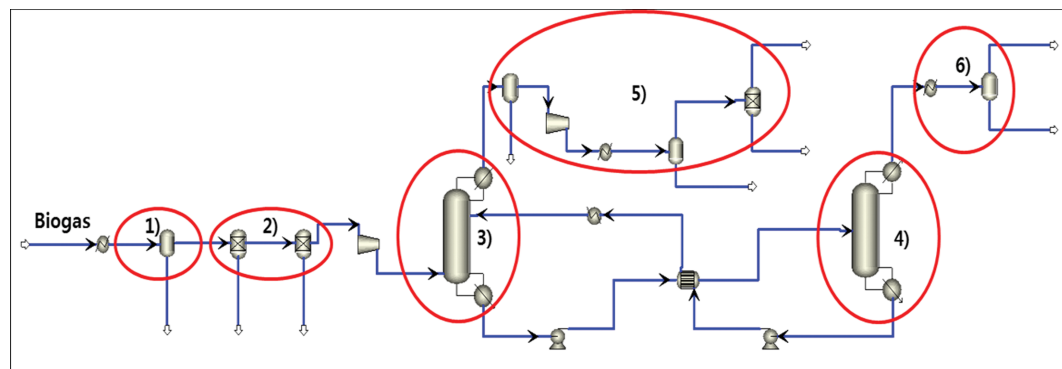


Fig. 5. Process flow diagram for pilot-scale biogas upgrading simulation.

- 1) H₂S removal unit
- 2) Siloxane removal unit
- 3) CO₂ absorption column
- 4) Stripping column
- 5) Bio-methane conditioning unit
- 6) High-concentrated CO₂ conditioning unit

ment), a commercial simulator, Aspen Plus[®], was used. Fig. 5 shows the pilot-scale facility, which mainly consists of 1) an H₂S removal unit, 2) a siloxane removal unit, 3) a CO₂ absorption column, 4) a stripping column, 5) bio-methane conditioning units, and 6) highly-concentrated CO₂ conditioning units. To analyze the CO₂ removal efficiency of the amine-based absorbents, the CO₂ absorption column and the stripping column were simulated using MEA- and AMP-based data packages supplied by Aspen Plus[®].

For simulation of this system, the biogas conditions were as follows: 1) biogas treatment: 10,000 Nm³/day; 2) biogas composition: CH₄ 60 vol%, CO₂ 40 vol%, H₂S 2,000 ppmv (dry basis), and moisture content 51.1 g/m³; 3) temperature: 35-40 °C; 4) pressure: 20 mbar. After the H₂S was removed to the 10 ppmv level, the biogas was introduced into the CO₂ absorption column. The performance targets of the process are as follows: 1) methane recovery rate: above 99%; 2) bio-methane purity: above 97%; and 3) CO₂ removal efficiency: above 95%. The typical characteristics of the feed gas are as

Table 1. Typical characteristics of biogas

CH ₄	CO ₂	H ₂ S	O ₂	N ₂	Temperature
65.0%	33.5%	10 ppm (2,000 ppm)*	0.2%	1.3%	40.0 °C

*Concentration of H₂S in biogas before sulfur removal unit

Table 2. Simulation conditions of the biogas upgrading process

Methane recovery (%)	CO ₂ concentration in bio-methane (vol%)	Methane concentration in bio-methane (vol%)	H ₂ S concentration in biogas introducing amine process (ppmv)	Temperature (°C)	
				Absorption column	Stripping column
>95.0	<2.0	>97.0	<10.0	40	120

summarized in Table 1. The simulation conditions which include design specifications and unit efficiencies are listed in Table 2.

From the simulation results, the process flow diagram of the whole biogas upgrading process was derived and is shown in Fig. 6; this system was connected to the city gas supply network and included the amine (MEA 20.0 wt%) based CO₂ recovery system. These PDFs were applied to the pilot plant for biogas purification; the properties of each stream are shown in Fig. 6. From this simulation results, the methane concentration increased to 93.9% from 53.7% at the end of absorber; finally, methane was supplied to the city gas network at a concentration of 99.2% after passing through the methane conditioning unit. When CO₂ in the feed gas was perfectly recovered at the out stream of the stripper, the concentration of methane in the end was 97%. These results can be seen to have satisfied the performance targets, which were mentioned above and in Table 2 and were applied to this pilot scale design.

Fig. 7 shows the bio-methane purity, CO₂ removal efficiency, and equilibrium CO₂ loading of the CO₂ absorption column with respect to the flow rate and the amine concentration in the lean amine solution. In Fig. 7(a), both the bio-methane purity and CO₂ removal efficiency can be seen to decrease as the lean amine solution flow rate decreases under fixed MEA concentration of 20 wt%. Also, these values decrease as the MEA concentration in the lean amine solution flow decreases under fixed lean amine solution flow rate

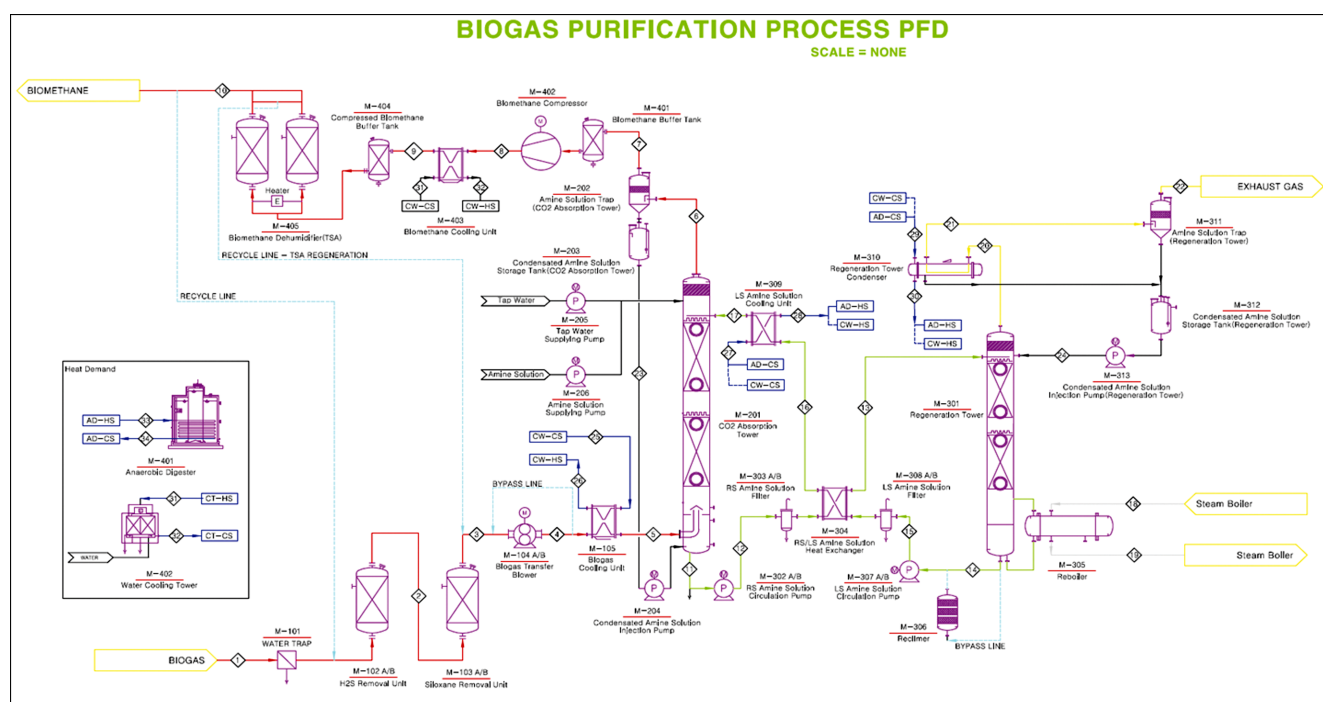


Fig. 6. PFD of biogas upgrading pilot facility in MEA-based CO₂ recovery system.

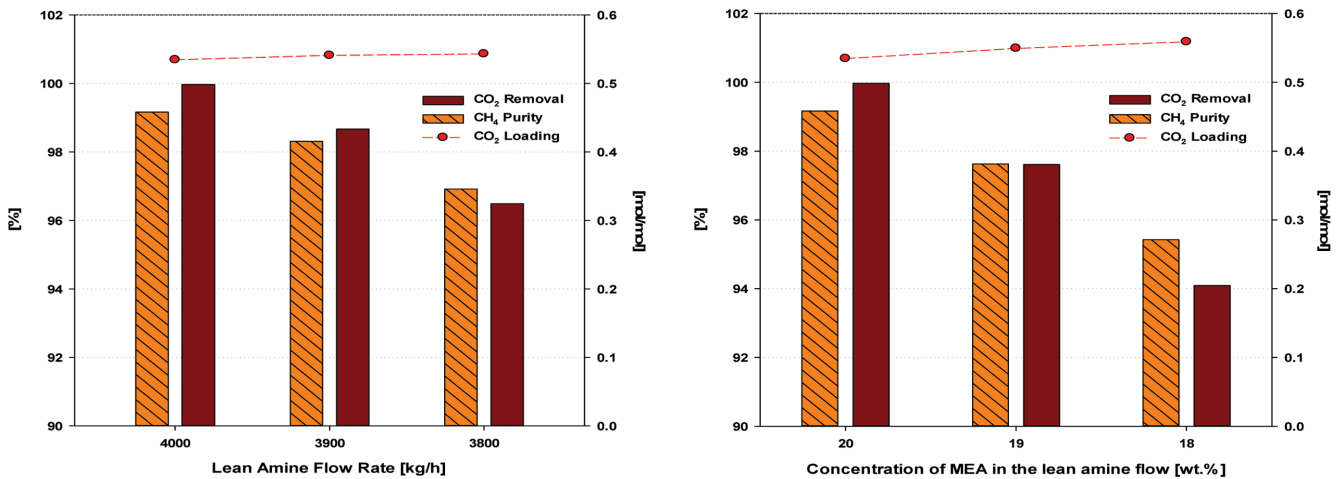


Fig. 7. Effects of MEA concentration and circulating rate on the performance of this system.

(a) MEA concentration: 20 wt%, (b) Amine circulating flow rate: 4,000 kg/h

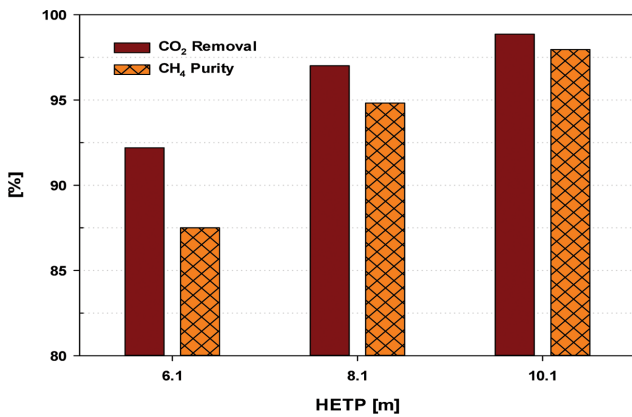


Fig. 8. Effect of HETP on CO₂ removal and CH₄ purity.

MEA concentration: 20.0 wt%, circulation flow rate: 4,000 kg/h

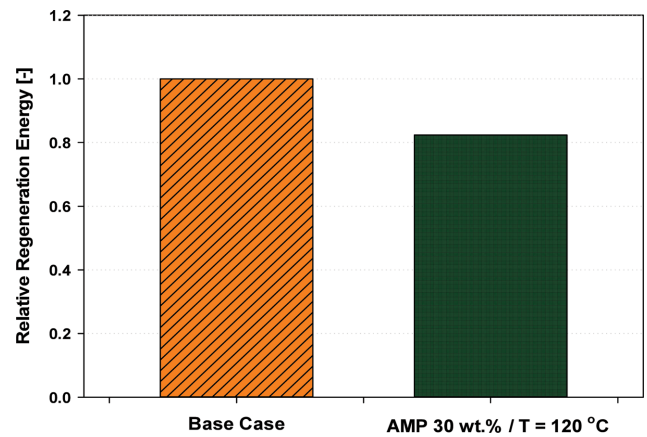


Fig. 9. Comparison of relative regeneration energy of absorbents (base case: MEA 20 wt%).

of 4,000 kg/h, as shown in Fig. 7(b). To meet the performance target, either the lean amine solution flow rate should be greater than 3,800 kg/h, with an MEA concentration of 20 wt%, or the MEA concentration in the lean amine flow should be greater than 19 wt%, with a lean amine solution flow rate of 4,000 kg/h. These results are similar to the experimental results derived using the lab-scale CO₂ separation unit that was mentioned above. The equilibrium CO₂ loading of the CO₂ absorption column has been approximately 0.55 level in the simulation and it shows a similar result compared with the experimental results in Fig. 3 and the U.E. Aronu et al. [10].

Fig. 8 shows the bio-methane purity and CO₂ removal efficiency with respect to the height equivalent of a theoretical plate (HETP) in the CO₂ absorption column when using the 20 wt% MEA solution. To analyze the effect of HETP on CO₂ removal, the rate-based model was used. In this sensitivity analysis, the bio-methane purity reached a value above 97 vol% at the HETP of 10.1 m. As the HETP in the CO₂ absorption column decreased, both the CO₂ removal efficiency and the bio-methane purity decreased.

Both 30 wt% MEA and 30 wt% AMP solutions were used in order to allow a comparison of the regeneration energy with respect to the reboiler temperature of the stripping column. Fig. 9 shows the

relative regeneration energy compared with the base case, for which the amine is an MEA and the reboiler temperature is 120 °C. The reasons for this comparison of the relative regeneration energy are as follows: The absolute regeneration energy using the same amine solutions can be different for different simulation models, thermodynamic models, various simulation techniques, etc., and MEA is an important material in the process of CO₂ capture using amine solutions, so the relative difference according to concentration of MEA can be used to analyze the performance of a given amine solution. The regeneration energy when using AMP solution drops to a level of approximately 80% compared with the base case because of the high cyclic CO₂ loading of AMP solutions; this causes a low lean amine solution flow rate and low energy requirement for heating of the amine solution in the stripping column.

CONCLUSIONS

We used a commercial simulator to compare the performance of MEA and AMP solutions in a laboratory-scale continuous process of CO₂ capture from simulated biogas and analyzed the effects

of absorbent concentration, absorbent flow rate at the absorption column, and absorber height on CO₂ removal and CH₄ purity; the regeneration energy was also evaluated.

(1) At the same G/L ratio, the 30 wt% AMP solution showed the highest CO₂ removal efficiency among the three different aqueous amine solutions in the laboratory-scale CO₂ capture process.

(2) Compared to the MEA solution at the same absorbent molar concentration, the AMP solution had a larger absorption capacity in the absorption column and higher cyclic CO₂ loading between the absorption column and the stripping column.

(3) By process simulation using the MEA data package in Aspen Plus[®], the CO₂ loading remained constant at the same MEA concentration in the lean amine flow; however, the CO₂ loading slightly increased as the MEA concentration in the lean amine flow decreased.

(4) By process simulation using both the MEA and AMP data packages in Aspen Plus[®], the regeneration energy when using AMP solution, because of this solution's high cyclic CO₂ loading, dropped to a level of approximately 80% compared with the base case.

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