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Simultaneous Removal of CO_2 and H_2S from Biogas by Blending Amine Absorbents: A Performance Comparison Study

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ABSTRACT: Greenhouse gas treatment is urgently needed because of the impact of climate change caused by greenhouse gas emissions after global economic growth. In this study, postcombustion capture was carried out to screen absorbents for simultaneous absorption and regeneration of CO_2 and H_2S byproducts of biogas using *N*-methyldiethanolamine (MDEA)-based additives. Twelve different absorbents were selected and compared according to the types of the amine group and the alcohol group. The mixture gas of 35 vol % CH_4, 15 vol % CO_2, and 50 ppm H_2S balanced by N_2 was used for absorption and regeneration. Absorption and regeneration were carried out at 35 and 80 °C, respectively. The absorbent concentration was fixed at 4.5 wt % for MDEA and 0.5 wt % for additives. In the continuous absorption and regeneration experiments, rich loading, lean loading, cyclic loading, absorption rate, and desorption rate were measured according to the loading values of CO_2 and H_2S using MDEA/additive mixed absorbent. CO_2-rich loading was excellent in MDEA/diethylenetriamine (DETA), and CO_2 cyclic capacity was excellent in MDEA/bis(3-aminopropyl)amine (APA). H_2S-rich loading was superior in MDEA/APA, and H_2S cyclic capacity was superior in MDEA/DETA. The CO_2 absorption and regeneration rates were excellent in MDEA/piperazine (PZ), and the H_2S absorption and regeneration rates were excellent in MDEA/2-amino-2-methyl-1-propanol. MDEA-based blending absorbent showed better absorption and regeneration performance than MDEA, and MDEA/PZ showed good performance for CO_2 but very poor performance for H_2S. It was confirmed that MDEA/APA was superior for gas composition in the simultaneous absorption and regeneration of CO_2 and H_2S.

1. INTRODUCTION

As the demand for energy increases through the economic growth of all countries around the world, there is a need to develop new alternative energy because of energy depletion, rising oil prices, and rapid environmental pollution. The continuous increase in energy consumption (e.g., 2.3% increase in energy consumption in 2018) led to a sharp increase in the use of fossil fuels.[1] As an alternative fuel to rapidly growing fossil fuels, biogas is a clean and sustainable source of energy, which is a clean and accessible energy source and can be a potential solution to world's constant energy demands. It also helps to reduce the carbon footprint.[2] After separation, the methane (40−65 vol %) in biogas is used as an upgraded fuel. Biogas upgrading with absorption and removal of carbon dioxide (35−55 vol %) and hydrogen sulfide (0.1−3 vol %). The biogas absorption process must be developed as a sustainable energy source for greenhouse gas reduction and energy conversion. Application of biomethane (>90%) is expected to reduce greenhouse gas emissions by 60−80%, depending on the raw materials used compared to gasoline.[3]

All types of biomass can be used as substrates for biogas.[4] At the same time, as CO_2 recovery, H_2S must be removed from the biogas before it can be used as a combustion fuel.[5] Separated biomass energy serves a variety of purposes. In contrast to solar and wind, which are renewable energy such as cogeneration and electricity production or fuel in vehicles, bioenergy has proved competitively superior in terms of the costs of production and supply.[6] It is a fast-growing renewable energy that produces biodiesel, bioethanol, and biofuels through biogas purification, using technologies such as anaerobic digestion, carbonization, and gasification using bioresidues.[7]

Biogas upgrade technologies include water scrubbing, physical absorption with organic solvents and chemical absorption with amine solutions, pressure swing adsorption, membrane separation, cryogenic separation, and chemical hydrogenation process technologies.[8] In this study, we used a chemical amine absorption process that can simultaneously recover CH_4 and remove CO_2 and H_2S.[9] Conventional *N*-methyldiethanolamine (MDEA) has been widely used to absorb CO_2 and H_2S as a commercial amine.[15] MDEA/piperazine (PZ), a blended absorbent, shows excellent performance as a commercial absorbent for CO_2 absorption in the biogas treatment process. However, based on the research results, PZ is a new carcinogen. Formation of alternative materials is needed.[13] New blending absorbents have to be developed to remove acid gases as a substitute for MDEA/PZ.

Absorption of CO_2 and H_2S by aqueous solution in a packed column was experimentally investigated by the absorption process using amine solution. More than 90% CO_2 removal efficiency and CH_4 were separated and H_2S was removed to

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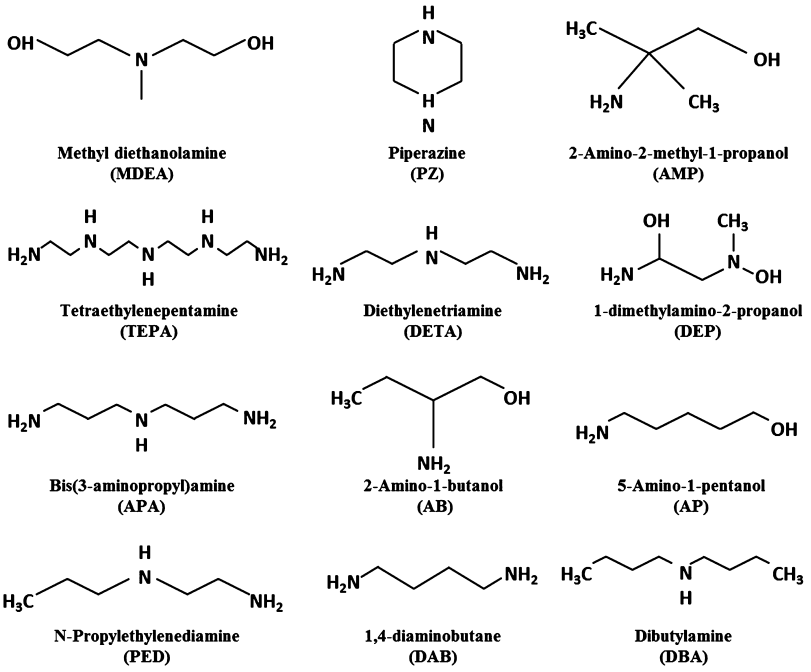

Figure 1. Materials used molecular formula.

ppb unit.[8] The absorption process has proven to be excellent for improving the quality of biogas when maintained continuously.[9] Conventional MDEA has been widely used to absorb CO_2 and H_2S as a commercial amine.[15] MDEA, a tertiary amine, has higher absorption capacity but relatively a slower absorption rate than primary amines.[16] PZ improves the absorption rate when used as an additive in blending absorbents, and MDEA/PZ has a shuttle effect, which is transferred to MDEA, the main absorbent, because of the influence of water, and improves the absorption capacity.[10] In order to measure the selective absorption of CO_2 and H_2S, the blending amine was studied.

Recently, by developing amino acid ionic liquids (AAILs)/MDEA as a CO_2 absorbent, it has been shown to be superior in improving the absorption rate, increasing the absorption capacity, and reducing the renewable energy compared to the existing MDEA absorbers.[11] In addition, the absorption rate and the desorption amount of H_2S at atmospheric pressure using the monoethanolamine/MDEA absorbent showed a 95% absorption performance.[12] AAIL/MDEA absorbents were used to test the absorption performance of H_2S to show superior commercial sorbents for desulfurization.[13] Based on the previous studies, the study of blending amine absorbents for simultaneous absorption and regeneration of CO_2 and H_2S is required.

In selecting the amine additives, the respective amines for the materials containing primary, secondary, and tertiary amines were selected, and the additives were selected based on the blending absorbent having high CO_2 absorption ability. The simultaneous absorption and desorption of acidic gases. CO_2 and H_2S in amine solvent were verified by absorption and regeneration experiments, and the stability of the solvent was confirmed by carrying out absorption and desorption experiments for multiple cycles using the same solvent.[14] The absorption was proceeded based on the temperature of the exhaust gas at 35 °C, and regeneration was carried out at 80 °C.[17] Twelve different amine solvents according to −NH functional groups and −OH functional groups were used as additives to select absorbents having excellent absorption and regeneration performance.[18−21]

In selecting additive materials, PZ, 2-amino-2-methyl-1-propanol (AMP), diethylenetriamine (DETA), tetraethylenepentamine (TEPA), bis(3-aminopropyl)amine (APA), and so forth have been proved as additives for MDEA because of their excellent kinetic rate constants for CO_2 absorption.[22,23,32,35] Simultaneous absorption and desorption experiments using MDEA-based additives were carried out, and CO_2 and H_2S absorption was studied for sterically hindered amine AMP.[24−29] In general, carbamate formation is faster than bicarbonate formation, so primary and secondary amines exhibit faster CO_2 absorption than tertiary amines.[27,30] When additives were added to MDEA, the main absorbent, H_2S absorption increased compared to MDEA only at atmospheric pressure.[13]

2. EXPERIMENTAL SECTION

2.1. Materials. The selected absorbent used the additive in Figure 1 based on MDEA (99%, Sigma-Aldrich). All materials were used without further purification. PZ (Sigma-Aldrich), AMP (99%, Sigma-Aldrich), TEPA (Sigma-Aldrich), DETA (Sigma-Aldrich), 1-dimethylamino-2-propanol (≥99%, Sigma-Aldrich), bis(3-aminopropyl) amine (98%, Sigma-Aldrich), 2-amino-1-butanol (97%, Sigma-Aldrich), 5-amino-1-pentanol (>95%, TCI), N- twelve amines of propylethylenediamine (99%, Sigma-Aldrich), 1,4-diaminobutane (99%, Sigma-Aldrich), and dibutylamine (≥99.5%, Sigma-Aldrich) were used. The gas used in the experiment was CO_2 (99.9%), N_2 (99.9%), and H_2S (100 ppm + N_2 balance) gas; all gas was purchased from Korea Nano Gas. The silicone oil used for the temperature control of absorption and regeneration was XIAMETER PMX-200 Dow Corning.[22−35]

2.2. Experimental Apparatus. The absorption and regeneration device used in the experiment is shown in Figure 2. The reactor consisted of a 250 mL jacketed reactor for absorption and regeneration temperatures. The absorbent (100 g) in the reactor was put into the experiment. The oil entering the reactor jacket to maintain the temperature in absorption and regeneration was

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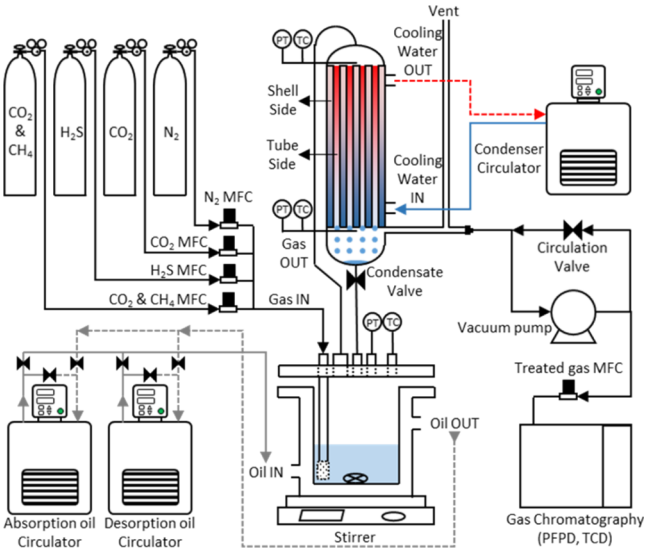

Figure 2. Schematic diagram of the experiment setup for simultaneous absorption and desorption CO_2 and H_2S.

maintained by using two RW-2025G products of JeioTech. In the initial condenser experiment of the basic experiment, it was found that a large amount of water volatilized upon regeneration. In order to solve this problem, a stainless steel condenser of a shell and tube type was manufactured instead of glass condenser. The fabricated shell and tube condenser showed an evaporation rate of 0.1−0.15 g/h in 20 consecutive experiments (for 120 h) of absorption (at 35 °C) and regeneration (at 80−105 °C). After the reaction in the reactor, the gas enters the top of the shell and tube condenser. Since the regeneration is performed at 80−105 °C, the condenser temperature was maintained at 2 °C condenser of heat duty more than condensation capacity was used. Condensation performance was confirmed by measuring the temperature at the top and bottom of the condenser, and the temperature inside the reactor during regeneration. In order to deliver a constant flow rate of gas after treatment into the gas chromatograph, it was injected using LABOPORT N86KT from KNF (Germany).[13,25,35]

2.3. Gas Analysis. After the absorption and regeneration experiment, the gas was sent to ±100 mL/min using a sampling pump to constantly send the gas to analysis equipment. After the rest of the treatment, the gas was vented. In order to maintain the same overall composition of the gas and the atmospheric pressure in the reactor, the valve was controlled by connecting the input and output of the vacuum pump, and a certain amount of concentration was sent to analysis equipment. For gas analysis, an Agilent 7890A GC(Gas Chromatography) pulsed flame photometric detector and a thermal conductivity detector were used. For CO_2, N_2, and CH_4 analysis, Supelco Analytical Porapak N column was used. For H_2S analysis, J&W GS-GasPro column 30 m × 0.32 mm × 7 in. was used. Analytik Jena total organic carbon was used for the CO_2 liquid phase analysis.

2.3.1. CO_2 and H_2S Absorption. The experimental conditions in this study were conducted to compare the absorption and regeneration performance of MDEA-based additives. When the acid gas of the amine absorbent was absorbed at 25, 35, and 45 °C intervals, it was confirmed that the absorption loading value at 25 °C was the highest. In general, the biogas production temperature is 35−42 °C, so it was set to 35 °C based on the biogas production temperature. The concentration setting of the absorbent is very important. The concentration of H_2S used in the experiment was in a ppm range, which is a small amount compared to the CO_2 concentration. If the absorbent concentration is high, the absorption capacity of CO_2 is available to compare, but it is difficult to confirm the tendency of H_2S. It has a very high solubility in water, so the absorption capacity of H_2S single gas is very high. Therefore, a low concentration (5 wt %) of amine was used to confirm the pronounced tendency of simultaneous absorption and regeneration of CO_2 and H_2S under the same conditions. The concentration of the total composition of the amine absorbent was fixed at 5 wt %, and the concentration was set to MDEA 4.5 wt % + additive 0.5 wt %. Under the experimental conditions of absorption, the reactor pressure was maintained at atmospheric pressure, the gas concentration was CO_2 (15 vol %) + N_2 balance, and the gas flow rate was 200 mL/min. When using mixture gas, CO_2 (30 vol %) + N_2 balance or CO_2 (30 vol %) + CH_4 (70 vol %) 100 mL/min, H_2S (100 ppm) + N_2 balance 100 mL/min, CO_2 (15 vol %), H_2S (50 ppm) to 200 mL/min. Gas was injected using stainless steel gas muffler for miscibility of gas flowing into the reactor. The amine solution was maintained at 500 rpm to maintain the temperature in the reactor. The treated gas after absorption was analyzed at GC.

If V is calculated by substituting 1 atm, T °C = (273.15 + T) K, and 1 mol from the ideal gas state equation PV = nRT,

$$V = nRT/P$$
$$= 1\ (\text{mol}) \times 0.08206\ (\text{atm·L/mol·K}) \times (273.15 + T)\ \text{K}/1\ \text{atm}$$
$$= 22.4\ \text{L (at 0 °C)}$$

$$CO_2\ \text{outlet gas} \times (1\ \text{mol}/22.4\ \text{L}) = CO_2\ \text{mol}$$

2.3.2. CO_2 and H_2S Desorption. In general, the biogas production temperature is from 35 to 42 °C, so it was set at 35 °C based on the biogas production temperature. The regeneration temperature was set to 80 °C using an absorbent in the absorption equilibrium state, where absorption was completed. Regeneration experiments 170 mL/min N_2 was injected to correct the concentration of CO_2 (15 vol %). The regeneration of the MDEA + additive absorbent at 80 °C was compared. Absorption and regeneration of the MDEA 5 wt % amine absorbent with CO_2 was completely regenerated at 105 °C, and four temperature-dependent experiments were performed at 80, 90, 95, and 105 °C.

2.4. Cyclic Capacity Measurement. Among the MDEA-based additives, an absorbent having excellent absorption and regeneration ability in simultaneous absorption of CO_2 and H_2S is selected. When absorption is completed, the absorption equilibrium is called rich loading, the regeneration equilibrium is called lean loading, and the difference is called cyclic capacity. Cyclic capacity was used to confirm the absorption and regeneration performance of absorbers.

$$\text{Cyclic capacity} = \text{rich loading}\ (\text{mol}_{\text{gas}}/\text{mol}_{\text{amine}}) - \text{lean loading}\ (\text{mol}_{\text{gas}}/\text{mol}_{\text{amine}})$$

2.5. Chemical Reactions. CO_2, H_2S, and CH_4 chemical absorption and separation reactions using amine-based absorbents in the biogas absorption and regeneration process are shown in the following equation. When CO_2 is absorbed into the aqueous solution in the secondary amine absorbent, the main reaction in which the reaction takes place is as follows, where R is alkyl and R′ is H for the primary amine and alkyl for the secondary amine.[9,20]

Carbamate formation

$$2RR'NH + CO_2 \leftrightarrow RR'NH_2^+ + RR'NCOO^- \quad (1)$$

Bicarbonate formation

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \quad (2)$$

$$H_2CO_3 \leftrightarrow HCO_3^- + H^+ \quad (3)$$

$$CO_2 + OH^- \leftrightarrow HCO_3^- \quad (4)$$

$$RR'NH_2 + HCO_3^- \leftrightarrow [RR'NH_2^+][HCO_3^-] \quad (5)$$

$$RR'NCOO^- + H_2O \leftrightarrow RR'NH + HCO_3^- \quad (6)$$

In addition to the formation of carbamate and bicarbonate, the zwitterion mechanism has been shown to form carbamate for primary

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and secondary amines, in which case it forms an intermediate mediator zwitterion ($RR'NH + COO^-$). The following zwitterion reactions indicate[9,23,32]

$$CO_2 + RR'NH \leftrightarrow RR'NH^+COO^- \quad (7)$$

$$RR'NH + COO^- + RR'NH \leftrightarrow RR'NCOO^- + RR'NH_2^+ \quad (8)$$

The reaction of the tertiary amine-absorber with CO_2 can be expressed as follows; it reacts like eq 9 without forming a carbamate and MDEA in the tertiary amine can be represented by the formula 10.[9]

$$R_3N + CO_2 + H_2O \leftrightarrow R_3NH^+ + HCO_3^- \quad (9)$$

$$R_2NCH_3 + CO_2 + H_2O \leftrightarrow R_2N + HCH_3 + HCO_3^- \quad (10)$$

AMP is a sterically hindered amine, reacts with CO_2 by the same reaction mechanism as the primary amine. For AMPs used as additives, faster absorption rates than tertiary amines are expected. PZ injected as an additive may react with the intermediate product R + $(NHCOO)_2$ generated by reacting with CO_2, as in 11 to rapidly react and regenerate, as in eq 12. R is (CH_3) $2CCH_2OH$ and R′ is $(CH_2)_4$ here.[23,32]

$$R'(NH)_2 + 2CO_2 \rightarrow R'(NHCOO)_2 \quad (11)$$

$$R'(NHCOO)_2 + 2RNH_2 \leftrightarrow R'(NH)_2 + 2RNH_2COO \quad (12)$$

Therefore, it can be predicted that the addition of PZ enables fast reaction and regeneration by eqs 11 and 12. As described above, the effect of the interaction that can occur when MDEA is added to AMP through the reaction of amine−amine can be predicted as follows.[9,23,24]

$$R_2NCH_3 + CO_2 \leftrightarrow R_2CH_3NCOO \quad (13)$$

$$R_2CH_3NCOO + RNH_2 \leftrightarrow R_2NCH_3 + RNHCOO^- \quad (14)$$

When absorbing H_2S by using the aqueous solution of primary and secondary amine-absorbents, it dissociates as shown in formulas 15 and 16; the main reaction is shown in 17.

$$H_2S \leftrightarrow H^+ + HS^- \quad (15)$$

$$HS^- \leftrightarrow H^+ + S^- \quad (16)$$

$$RR'NH + H_2S \leftrightarrow RR'NH_2^+ + HS^- \quad (17)$$

Even in the tertiary amine-absorbent aqueous solution, H_2S reacts as follows.[28]

$$R_3N + H_2S \leftrightarrow R_3NH^+ + HS^- \quad (18)$$

2.6. Gas Selectivity. The selectivity coefficients tend to have a higher selectivity of the amine solvent for H_2S in the liquid phase than the H_2S/CO_2 content in the gas phase. Selectivity coefficients are based on H_2S selectivity. The value of the selectivity coefficient is equal to the ratio of H_2S/CO_2 in the liquid phase and H_2S/CO_2 in the gas phase

$$S = \frac{x_{H_2S}/x_{CO_2}}{y_{H_2S}/y_{CO_2}}$$

The selectivity factor has no limit, and x is the mole fraction of component i in the liquid bulk.[15]

3. RESULTS AND DISCUSSION

3.1. Single Gas and Mixture Gas Absorption and Regeneration. In order to evaluate CO_2 absorption and regeneration capacity of bio byproduct gas, acidic CO_2 single gas, and CO_2 + H_2S mixture gas were absorbed and regenerated five times with MDEA 5 wt % absorbent, respectively. Blending absorbent using additives increases the reactivity to increase the absorption capacity. Simultaneous absorption and regeneration of CO_2 single gas and CO_2 + H_2S mixture gas was confirmed. Figure 3 shows the results of GC

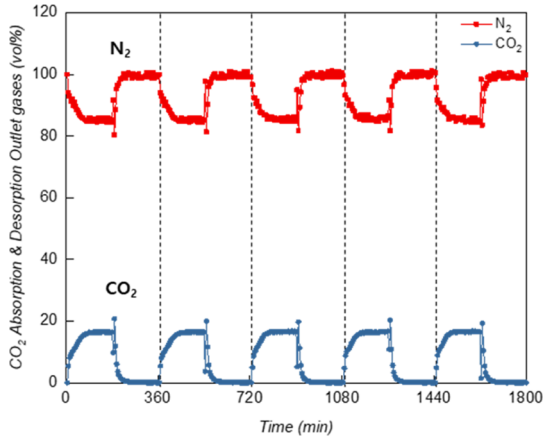

Figure 3. Absorption and regeneration five cycles of CO_2 (15 vol %) using MDEA 5 wt % absorbent outlet gas analysis results.

analysis on outlet gas in five experiments of CO_2 absorption and regeneration using MDEA 5 wt % absorbent. Absorption and regeneration were confirmed using CO_2 (15 vol %) and N_2 balance gas. In five consecutive experiments under the same conditions of absorption and regeneration, the CO_2 (15 vol %) absorption equilibrium and desorption equilibrium were identified.

Using the MDEA 5 wt % absorbent, CO_2 (15 vol %) and H_2S (50 ppm) + N_2 balance gas were used to confirm the results of analysis of CO_2 (15 vol %) and N_2 balance gas. The same trends were observed for CO_2 + H_2S mixture gas and for CO_2 single gas. Figure 4 shows the results of five consecutive

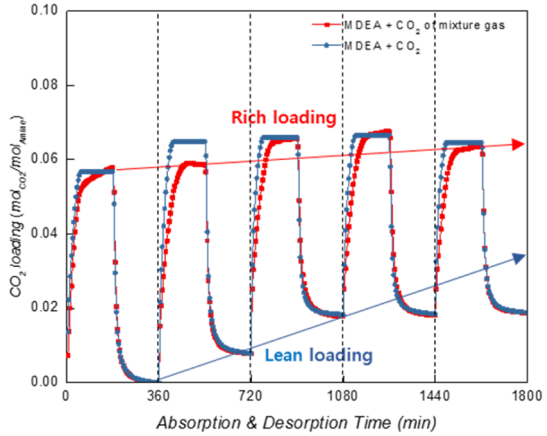

Figure 4. CO_2 (15 vol %) and CO_2 (15 vol %) + H_2S (50 ppm) mixture gas using MDEA 5 wt % analysis result of CO_2 outlet gas.

experiments of absorption and regeneration of CO_2 single gas and CO_2 (15 vol %) + H_2S (50 ppm) mixture gas using MDEA (5 wt %). When maintained the same at the absorption temperature of 35 °C and the regeneration temperature of 80 °C, the rich loading value due to the absorption temperature has the same loading value, but the base line rises because it is not completely regenerated because of the low regeneration temperature. As a result of regeneration temperature above three cycles, lean loading was constant. Rich loading was

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confirmed to be low because of evaporation of the absorbent and reduced performance of the absorbent. When comparing the outlet gas analysis results, the trend of CO_2 single gas and CO_2 + H_2S mixture gas was similar, but the absorption equilibrium was absorbed in the absorption experiment using MDEA 5 wt % absorbent of CO_2 + H_2S mixture gas. Seems to reach a difference. When comparing the loading values of absorption and regeneration of CO_2 (15 vol %) single gas and CO_2 (15 vol %) + H_2S (50 ppm), absorption and regeneration of CO_2 loading show the same loading values. In terms of absorption of CO_2 single gas and mixture gas, H_2S (50 ppm) had no effect of CO_2 (15 vol %).

3.2. Mixture Gas Absorption and Regeneration in MDEA. Simultaneous absorption and regeneration experiments were carried out using a mixed gas of five times CO_2 (15 vol %), H_2S (50 ppm), CH_4 (35 vol %), and N_2 balance composition using MDEA 5 wt % absorbent. Figure 5 shows

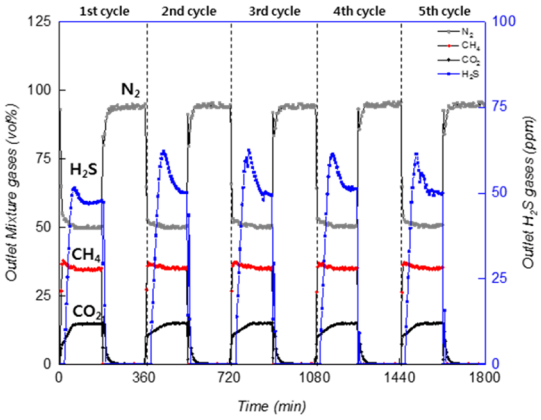

Figure 5. Analysis of five cycle absorption and regeneration of mixture gas using MDEA 5 wt % absorbent.

the results of GC analysis on the outlet gas after treat gas. CO_2 and H_2S have solubility in absorbents and are absorption and regeneration. CH_4 and N_2 are not bound to amine absorbents. CO_2 (15 vol %) and H_2S (50 ppm) equilibrium states after absorption and regeneration, and CH_4 (35 vol %) and N_2 were not absorbed and separated from the analysis results. The solubility of H_2S was higher than that of CO_2 at the same temperature pressure, and it took more time to reach the absorption equilibrium of H_2S even after CO_2 absorption. The absorbent performance in the mixture gas showed the same trend five times. Figure 6 shows the results of five consecutive absorption and regeneration of the mixture gas using MDEA 5 wt % absorbent. Because of the difference between rich loading and lean loading of CO_2, cyclic capacity was 0.04 mol_{CO_2}/mol_{amine}. Because of incomplete regeneration at relatively low regeneration temperatures of 80 °C, the base line for lean loading became increasingly high. At the same time, H_2S was also absorbable and renewable. H_2S also increased baseline because of incomplete regeneration at 80 °C. Cyclic capacity was confirmed by simultaneous absorption and regeneration of CO_2 and H_2S in the mixture gas.

3.3. Mixture Gas Absorption and Regeneration in MDEA + PZ. Comparison of the continuous absorption and regeneration of MDEA 5 wt % with CO_2 and H_2S, CO_2 (15 vol %), H_2S (50 ppm), CH_4 (35 vol %) was used with MDEA 4.5 wt %/PZ 0.5 wt %, using the N_2 balance gas was carried out five absorption and regeneration experiments. Figure 7 shows

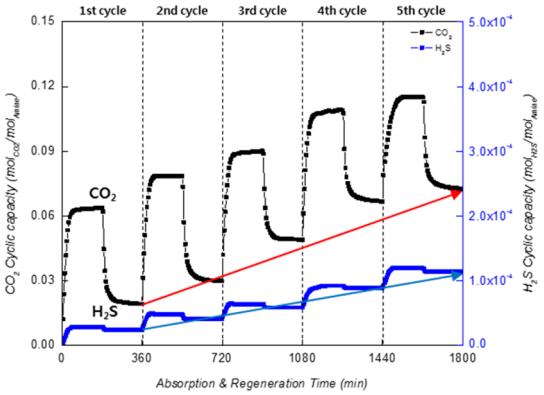

Figure 6. Five cycle absorption and regeneration analysis of MDEA 5 wt % absorbent using CO_2, H_2S of mixed gas.

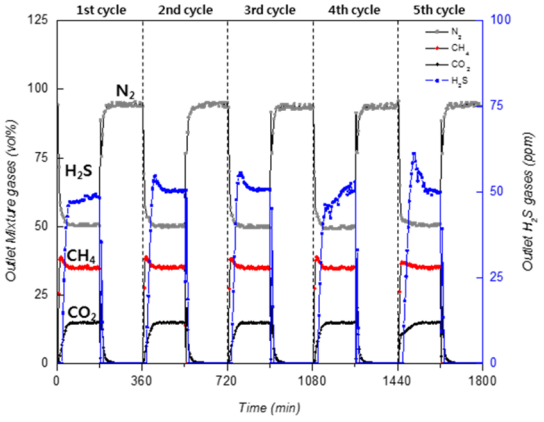

Figure 7. Analysis of five cycle absorption and regeneration of mixture gas using MDEA 4.5 wt % + PZ 0.5 wt % absorbent.

the GC analysis of the outlet gas after treatment. Absorption equilibrium and regeneration equilibrium were confirmed using a gas of the same composition as the MDEA 5 wt % absorbent. Absorption of CO_2 (15 vol %) and H_2S (50 ppm) composition was confirmed by an equilibrium analysis. In the case of CH_4 and N_2, it was confirmed that the absorbent is separated without being absorbed in Figure 8. The absorption and regeneration of MDEA/PZ was compared with MDEA in the same way as compared with MDEA 5 wt % absorbent. It was confirmed that the same absorption and regeneration occurred continuously. As a result of analysis, MDEA/PZ

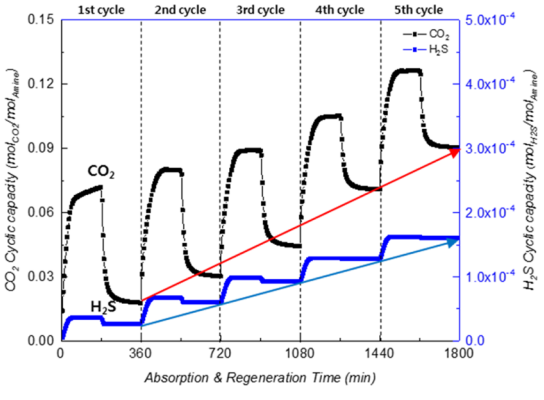

Figure 8. Five cycle absorption and regeneration analysis of MDEA 4.5 wt % + PZ 0.5 wt % absorbent using CO_2, H_2S of mixed gas.

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showed high CO_2 cyclic capacity of 0.01 mol_{CO_2}/mol_{amine} but low loading of H_2S. The absorption performance was higher when compared with MDEA 5 wt %, and the regeneration performance was lower based on the base line. This is seen as a difference in absorbent capacity and does not appear as a difference in absorbent performance depending on the regeneration temperature of the absorbent. However, it was found that CO_2 absorption and regeneration of single amine and mixed amine sorbents were different in low sorbents.

Desorption rate is important how easily desorbed gas from loaded amine. In order to confirm the regeneration performance according to the absorption temperature, as in Figure 9,

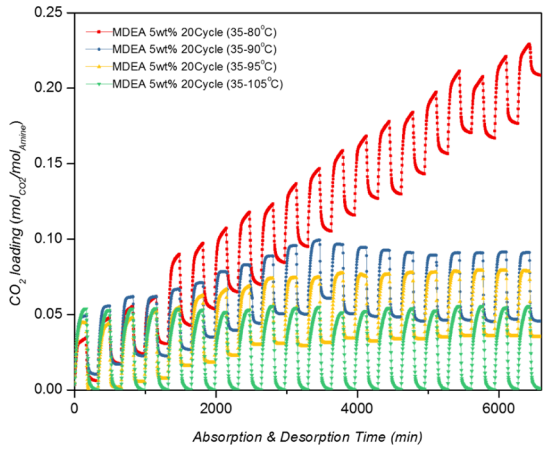

Figure 9. Depending on the regeneration temperature using MDEA 5 wt % 20 cycle CO_2 absorption and regeneration.

CO_2 single gas was absorbed at 35 °C continuously for 20 cycles using MDEA 5 wt % absorbent and regenerated at 80, 90, 95, and 105 °C. The lean loading part continued to rise because of the complete regeneration at 80 °C, and the regeneration equilibrium occurred after 10 times because of incomplete regeneration at 90 and 95 °C. This confirmed the absorbent performance for 20 cycles for the absorption and regeneration of the absorbent. For smooth regeneration, the regeneration temperature should be maintained above 100 °C because of the influence of water, the main substance of absorbent.

The baseline of lean loading increases because the absorbent cannot be completely regenerated, as shown in Figure 4 and 6, and Figures 8 and 9 show the base line for lean loading due to incomplete regeneration is increasing. Incomplete regeneration at temperatures below 100 °C also increases the base line and complete regeneration at temperatures above 105 °C. This is absorbed in a state that is not completely regenerated; the baseline gradually increased as the absorption and regeneration occurred continuously but appeared constant without increasing the baseline because of the performance of the absorbent. Because of the low concentration of the absorbent, complete regeneration was performed, and the reason why the regeneration experiment was carried out at temperature is to explain that incomplete regeneration and complete regeneration were performed.

3.4. Absorption and Regeneration Using Mixture Gas of MDEA + Additive. This is the result of the absorption and regeneration experiment of CO_2 (15 vol %) and H_2S (50 ppm) using blending absorbent with 12 additives of MDEA 4.5 wt % + additive 0.5 wt %. A comparison of absorption and regeneration rates was also made, which is an important factor reflecting the reactivity of each amine system or blend.

3.4.1. CO_2 Absorption and Desorption. Simultaneous absorption was performed using a mixture gas of CO_2 (15 vol %) and H_2S (50 ppm) using the MDEA + additive blending absorbent. Figure 10 shows the results of CO_2

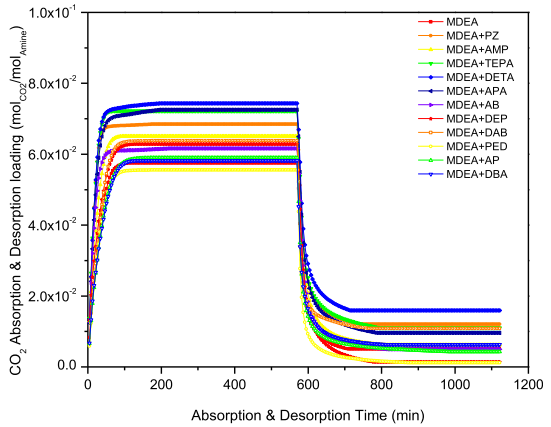

Figure 10. Measurement of CO_2 cyclic capacity in mixture gas using MDEA + additive blending absorbents with time.

absorption and regeneration using MDEA + additive blending absorbents over time. The CO_2 absorption and regeneration performance by the characteristics of the blended amine were compared, and the absorption rate and regeneration rate were confirmed. The higher the absorption rate and the regeneration rate, the better the loading value.

Figure 11 shows the rich loading, lean loading, and cyclic loading of each additive to select absorbents with excellent

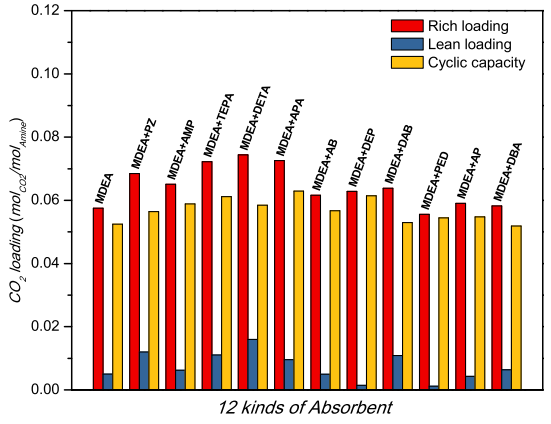

Figure 11. Cyclic capacity according to CO_2 rich loading and lean loading for each absorbent in mixture gas.

CO_2 absorption and regeneration ability in the mixture gas. CO_2 rich loading by blending absorbents was excellent in DETA, TEPA, APA, PZ, and AMP. The blending absorbent enhanced the reactivity as an activator of the MDEA absorption capacity by the shuttle effect. As a result of CO_2 rich loading for each additive, DETA, TEPA, and APA were secondary amines. MDEA/PZ, a commercial absorbent, shows higher CO_2 absorption than MDEA, and CO_2 rich loading is also an excellent sterically hindered amine in AMP. Additives with good circulation capacity of CO_2 absorption and regeneration according to additives of absorbents using a

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mixture of CO_2 and H_2S are represented as follows: APA > DEP > TEPA > AMP > DETA > AB > PZ > AP > PED > DAB > MDEA > DBA. As experiment result, the additive was excellent as an active agent, but in the case of PED it was confirmed that the performance as a CO_2 absorbent additive. As a result of lean loading, DEP, PED seemed to be low, but APA was the highest because of the difference in absorption and regeneration results.

3.4.2. H_2S Absorption and Desorption. Simultaneous absorption was performed using a mixture gas of CO_2 (15 vol %) and H_2S (50 ppm) using MDEA + additive blending absorbent. Figure 12 shows the results of H_2S absorption and

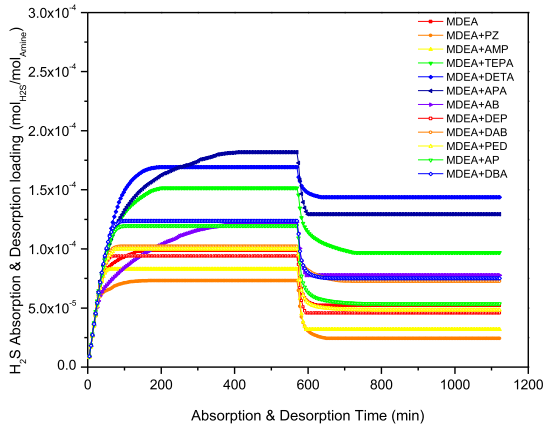

Figure 12. Measurement of H_2S cyclic capacity in mixture gas using MDEA + additive blending absorbents with time.

regeneration using MDEA + additive blending absorbents over time. Simultaneous absorption and regeneration experiments showed that CO_2 (15 vol %) and H_2S (50 ppm) were simultaneously absorbed. H_2S has a long absorption time unlike CO_2. In the case of H_2S, the solubility in water is high, but the loading value is different according to the additive under the same conditions. DEP, AMP, and PZ based on MDEA 5 wt % showed higher CO_2 absorption than MDEA 5 wt %, while H_2S absorption was lower.

Figure 13 shows the rich loading, lean loading, and cyclic loading of each additive in order to select an absorbent with good absorption and regeneration of H_2S in the mixture gas. TEPA, DETA, and APA with excellent CO_2 absorption capacity showed higher H_2S absorption loading values in the

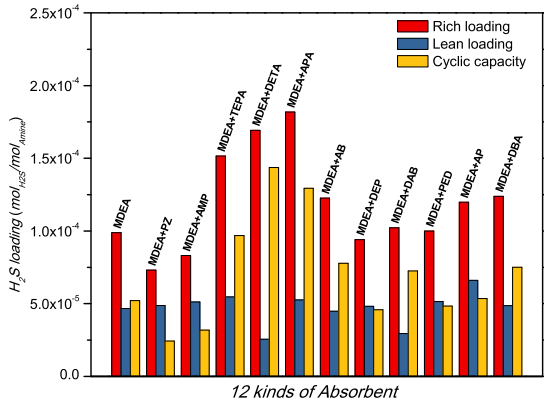

Figure 13. Cyclic capacity according to H_2S rich loading and lean loading for each absorbent in mixture gas.

order of APA > DETA > TEPA. However, PZ and AMP, which have high CO_2 absorption capacity, have low H_2S absorption capacity. Additives with good circulating capacity of H_2S absorption and regeneration according to additives of absorbents using a mixture of CO_2 and H_2S are expressed as follows: DETA > APA > TEPA > AB > DBA > DAB > AP > MDEA > PED > DEP > AMP > PZ. As shown in Figure 13, APA additive showed the highest rich loading. DETA and DAB had the lowest lean loading. Therefore, DETA showed the highest circulation capacity. The additives of APA, DETA, and TEPA are relatively low in CO_2 absorption ability such as PZ and AMP, and anti-H_2S bond is expected to interfere with the formation of carbamate and bicarbonate formed by reacting with CO_2. This can be seen as the result of absorption and regeneration of single gas of CO_2 single gas and H_2S single gas and selective absorption in mixture gas.

3.5. Absorption and Regeneration Rates of CO_2 and H_2S Using MDEA + Additive. *3.5.1. CO_2 Absorption and Desorption Rates Using Mixture Gas.* The absorption rate and the regeneration rate are important with regard to contact time and energy, as well as the loading capacity of the additive-specific absorbent whose primary absorbent is MDEA. Figure 14 shows that PZ was the most absorbed per hour, and AMP

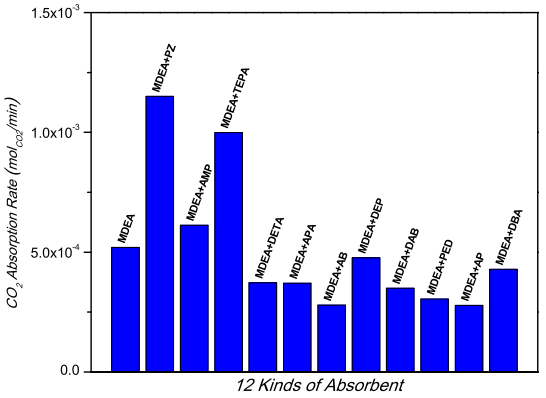

Figure 14. Absorption rate of CO_2 by absorbent in mixture gas.

and TEPA were also superior to MDEA when comparing the apparent velocity of each absorbent using the mixture gas. CO_2 loading was better than MDEA, but all the additives except PZ, TEPA and AMP showed low absorption rates in apparent absorption rates.

The regeneration rate of the absorbent is an important factor for the regenerative heat energy. This is because the lean loading from the continuous circulation process is recycled to the absorption tower. Figure 15 shows the apparent regeneration rate of loaded CO_2 by additive. The fast absorption rate PZ shows excellent regeneration performance compared to other additives at 80 °C regeneration. With the formation of the carbamate, the CO_2 desorption rate is excellent because of the fast absorption rate.

3.5.2. H_2S Absorption and Desorption Rate Using Mixture Gas. The simultaneous absorption and regeneration rate of H_2S in the mixture gas was compared for each additive. Figure 16 shows the absorption rate of H_2S in mixture gas. Additives AMP and DEP showed lower H_2S absorption capacity than MDEA single absorbent, but the absorption rate was faster. Additives TEPA, DETA, and APA showed high absorption capacity at the same time, but the absorption rate was similar to that of MDEA.

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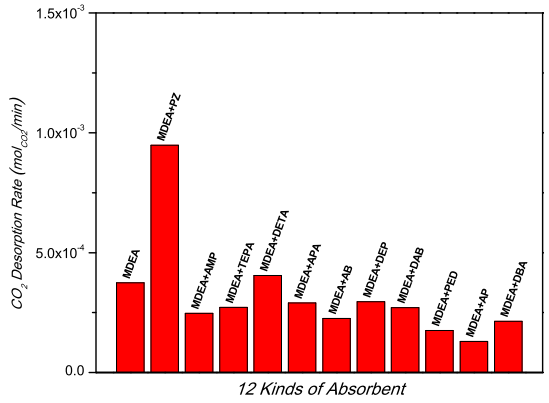

Figure 15. CO_2 regeneration rate by absorbent in mixture gas.

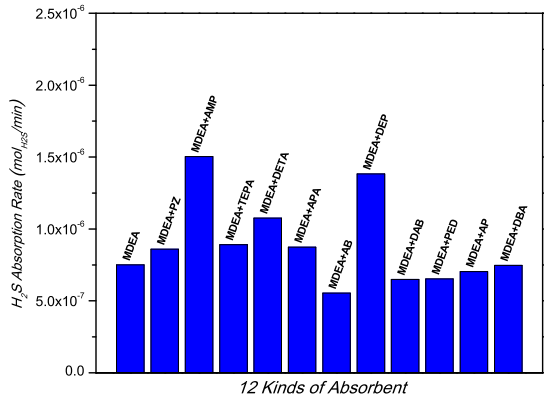

Figure 16. H_2S absorption rate by absorbent in mixture gas.

Figure 17 shows the regeneration rate of H_2S by absorbent additive in the mixture gas. AMP, APA, AB, and DEP showed

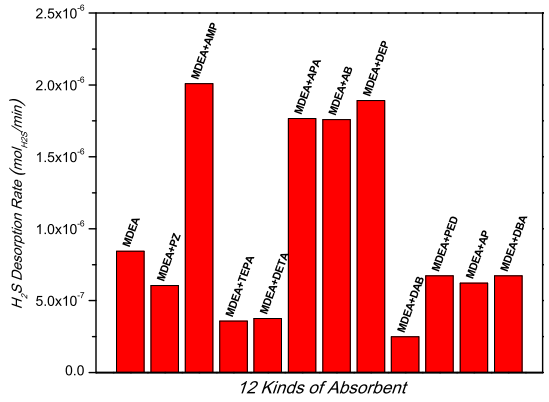

Figure 17. H_2S regeneration rate by absorbent in mixture gas.

faster regeneration performance than MDEA single absorbent, which is different from the CO_2 regeneration rate.

4. CONCLUSIONS

Simultaneous absorption of CO_2 and H_2S was carried out using MDEA blended with 12 different additives. As an alternative to commercial sorbents of MDEA/PZ mixture, it has an excellent loading value and was selected by comparing the optimal sorbents by measuring the regeneration efficiency, absorption rate, and regeneration rate using low energy.

- The CO_2 absorption capacity of the mixed gas was the highest in the MDEA/DETA among the absorbents, but the circulation capacity was the highest in the MDEA/APA. The H_2S absorption capacity was highest in MDEA/APA, but the cyclic capacity was highest in MDEA/DETA.

- The apparent absorption rate of CO_2 in mixed gas is the fastest in MDEA/PZ, and also, the apparent regeneration rate is fastest in the MDEA/PZ. The apparent absorption rate of H_2S is the highest in MDEA/AMP and also the apparent regeneration rate is fastest in MDEA/AMP.

- MDEA/PZ and MDEA/AMP were superior in the apparent absorption rate and the apparent regeneration rate in CO_2 and H_2S, respectively. This indicates that the combination of PZ and AMP with acid gas shows excellent desorption performance for structural reasons.

MDEA was mixed with 0.5 wt % of additives based on 4.5 wt % of concentration. MDEA/TEPA and MDEA/DETA had high loading values because of the large number of amino groups, but in the MDEA/APA mixed absorbents, they had three amine groups and showed excellent performance in the simultaneous absorption capacity of CO_2 and H_2S. This study confirms the superior CO_2 absorption and regeneration capacity of MDEA/APA as an alternative absorbent, and the superiority of absorption and regeneration of H_2S and CO_2 for reusability as an absorbent through continuous experiments.

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Notes

The authors declare no competing financial interest.

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