CO$_2$ Purification using an Aqueous Amine Absorbent in the Syngas

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Abstract:-- The acetic acid production using syngas in the BP chemical process showed superior performance compared to using rhodium-based catalyst. However, CO2 in the syngas causes poison of the promoted-iridium and the performance of the catalyst degrades. Therefore, CO2 must remain at extremely low concentration below 20 ppmv. In this study, we try to develop the new CO2 capturing absorbent for replacing with BASF a-MDEA (activated MDEA). The absorption performance of amine absorbents was evaluated to keep the CO2 concentration low and the applicability of the absorbent for acetic acid production process was evaluated. A continuously stirred-tank reactor and differential reaction calorimeter were used to measure the CO2 absorption capacity and heat of reaction, respectively.

As results among the amine absorbents, KIERSOL-N and KIERSOL-P showed better performance in both CO2 absorption capacity and heat of reaction than MEA's results and a- MDEA's results.

Index Terms— Acetic acid, Gas purification, CO2 control, amine absorbent.

I. INTRODUCTION

Acetic acid is used as a raw material for fine chemical products such as vinyl acetate and acetic acid ester. It is also a chemical substance widely used in such as terephthalic acid solution and dye [1]. A projected increase in the consumption of acetic acid has been reported at 4.0–4.5 % annually in China through 2020. China is expected to consume an average of 3–4 % of worldwide production [2]. The annual production of acetic acid is about 11.8 Mt/year, of which the production of acetic acid based on the methanol carbonylation technology is equivalent to about 80% [3],[4]. Processes for production of acetic acid using methanol carbonylation technology generally use noble metal catalysts such as iridium and ruthenium. The acetic acid production process based on ruthenium was widely used after being commercialized by Monsanto in 1970 [5]. In 1996, BP Chemical developed an improved methanol carbonylation process based on promoted iridium-iodide catalyst [6]. However, Bu4NI catalyst has the disadvantage that the iodide poisons the catalyzed reaction and reduces the reaction rate to 67% or less [7]. Therefore, many researchers have tried to improve the performance of catalyst using the iridium-complex [8],[9]. The annual production of acetic acid using iridium-complex catalyst was very high, but the problem of catalyst poisoning by CO2 occurred. Therefore, the use of CO2 capture technology was required to separate CO2 from the syngas.

A primary syngas manufactured through partial oxidation is commonly used to produce acetic acid [10]. The primary syngas is composed of CO (60–70 %), H2 (30–40 %), CO2 (1–5 %), along with CH4 and other impurities. The H2S present in the syngas was removed via desulfurizer, and the CO/H2 was separated by the pressure swing adsorption process (PSA). The CO2 in the syngas was removed by CO2 capture technology, and the remaining CO2 should be limited to less than 20 ppm to prevent poisoning of the catalyst. Thus, high-level purification of CO2 is very important for increasing efficiency in the acetic acid production process. The CO2 capture technology used in the petrochemical industry was developed for gas purification purposes. In particular, the gas purification method using amines has been widely used commercially since its development by R. Richards in 1930 [11]. The typical amine absorbents are monoethanolamine (MEA), diethanolamine (DEA), and N-methyldiethanolamine (MDEA) [12]. Amines are classified as primary, secondary, or tertiary amines depending on their structural characteristics. MEA is a primary amine, which has the advantages of low cost and high CO2 absorption rate, but the disadvantages of low CO2 capacity, thermal degradation, oxidative degradation, corrosion, etc [13]-[16]. DEA has a relatively lower CO2 absorption rate than MEA does. MDEA is an absorbent used in early 1950, and has the advantage of treating H2S and CO2 simultaneously

[17], but it has the disadvantage of a very low absorption rate [18]. In the 2000s, gas purification technology using amines was considered for application in carbon capture and storage (CCS) technology. The core technology of CCS is absorbents, and CO_2 capacity, absorption rate and regeneration energy for CO_2 capture process using a wet absorption method have been studied to evaluate the performance of absorbents. Recently, alternative absorbents in the form of cyclic amines such as piperazine (PZ) and 2-methylpiperazine (2MPZ) have been reported for use as commercial absorbents in power plants because of their advantages of low absorption heat, high CO_2 capacity and rapid reaction rate [19],[20]. In this study, various cyclic absorbents with potassium carbonate were evaluated to control CO_2 in an acetic acid production process, one of petrochemicals. The CO_2 absorption capacity and heat of reaction were measured and compared with MEA (30 wt%) and activated MDEA (α-MDEA; 40 wt% MDEA + 5 wt% PZ), in order to confirm the applicability of cyclic amines. When each absorbent was used, the concentration of emitted CO_2 was kept below 20 ppm.

II. EXPERIMENT

The CO_2 absorption capacity and heat of reaction were measured using a continuously stirred-tank reactor (CSTR) and differential reaction calorimeter (DRC), respectively. The mixed gases (3 vol% CO_2 / balanced N_2) used in the DRC experiment were purchased from Special Gas Co. in Korea. The CSTR experiments were conducted by mixing N_2 (99.9999%) and CO_2 (99.9999%) gas. MEA (2-aminoethanol; ≥99%), PZ (piperazine; 99.0%), and potassium carbonate (K_2CO_3; 99.5%) were from Samchun Chemicals. MDEA (N-methyldiethanolamine; ≥99.0) from Sigma Aldrich and 2MPZ (2-methylpiperazine; 98%) from Acros Organics were also used. The following four different absorbents mixed with deionized water were used for the experimental comparison of performance: 1) Commercially available and widely used aqueous 30 wt% MEA solution, 2) α-MDEA for simultaneous treatment of H_2S and CO_2, 3) KIERSOL-N (a brand of the Korea Institute of Energy Research) [21], and 4) KIERSOL-P (a brand used for petrochemical applications).

III. EXPERIMENTAL SETUP AND PROCEDURE

A. Continuously stirred-tank reactor (CSTR)
The experimental apparatus used in this study is shown in Fig. 1. The pressure in the CSTR was maintained at 9.50 to 9.52 bar to simulate the absorber of the CO_2 capture process. In the CO_2 absorption capacity experiment, the measurement was made by supplying 500 mL of absorbent to a reactor with an internal volume of 750 mL. The

reaction temperature
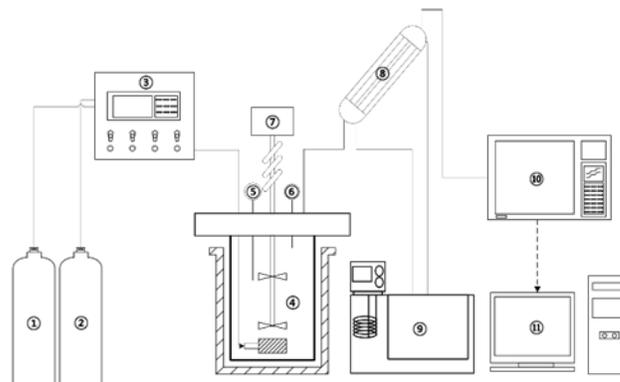
during the experiment was controlled by a water bath. CO_2 was supplied using a sparger to maximize contact with the surface of the absorbent; the stirring was done at a constant rate of 500 r min-1 during the reaction. CO_2 (3 vol%) was supplied at a constant concentration, in combination with nitrogen, using a mass flow controller. The gas supplied was injected into each reactor at a rate of 1,000 cm¬3 min-1. The concentration of CO_2 was inspected at five-minute intervals using GC (gas chromatography; Agilent Technologies, model 7890A).

B. Differential reaction calorimeter (DRC)
Fig. 2 shows the configuration for the differential reaction calorimeter (DRC) experiment. The reactor had a double jacket structure with an inner volume of 250 mL. A total of 150 mL of the absorbent was injected into each reactor. The temperature in the reactors was kept constant during the reaction time using a thermostat. Two types of reactors were used: a reference reactor and a measurement reactor. The gas injected into the reactor was 3 vol% CO_2 mixed gas. In order to maximize the reaction area of the absorbent, a sparger was used to give the injection a constant flow rate of 150 cm3 • min-1. The absorbent was stirred at a constant rate of 250 r • min-1 over the entire reaction time. Gas chromatography was used to analyze the concentration of CO_2 exhausted after reaction with the absorbent inside the reactor. The absorbent underwent an exothermic reaction as it reacted with CO_2; this reaction was measured in real time by the thermocouple located inside the reactor. Differences in the measured reaction heat were stored on the computer in real time. The details of the experimental procedure are available in a previous report [22].

IV. THEORETICAL FOUNDATIONS

A. Measurement of CO_2 capacity using CSTR
The moles of CO_2 absorbed by the absorbents (n_absorbed CO_2) at each measurement point was calculated using

Equation (1)-(3).
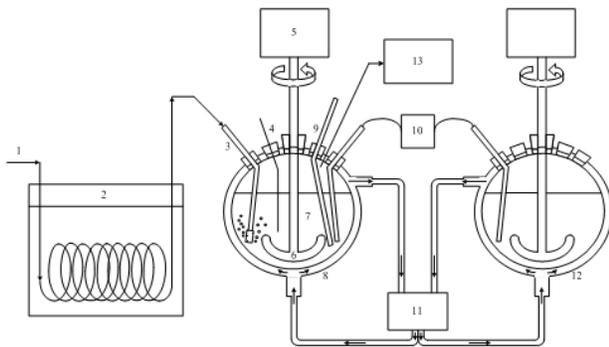
Figure 2. Schematic diagram of differential reaction calorimeter: 1) CO2 gas (3 vol% CO2 / balanced N2), 2) Water bath, 3) Inlet gas port, 4) Optional probe, 5) Motor, 6) impeller, 7) Absorbent, 8) Double jacketed reactor, 9) Calibration probe, 10) Temperatures and ΔT measurements, 11) Thermostat, 12) Reference reactor, 13) Gas chromatography.

$$n_{CO_2,out} = \frac{P_{CO_2,in} \times V_{CO_2,in}}{R \times T_{CO_2,in}} \qquad (1)$$

$$n_{CO_2,out} = \frac{P_{CO_2,out} \times V_{CO_2,out}}{R \times T_{CO_2,out}} \qquad (2)$$

$$n_{absorbed\ CO_2} = n_{CO_2,in} - n_{CO_2,out} \qquad (3)$$

$$n_{absorbed\ co_2} = \int_0^t n_{absorbed\ CO_2} t\,dt \qquad (4)$$

where PCO2 (atm), VCO2 (mol/min), and TCO2 (K) are the partial pressure, volume, and temperature of CO2, respectively. The subscripts, 'in' and 'out' indicate inlet and outlet. CO2 absorption capacity at saturated point was calculated using equation (4).

B. Measurement of the heat of reaction using DRC

]The measurement of the heat of reaction between the absorbent and CO2 was conducted three times: (1) calibration time before the CO2 reaction, (2) for the CO2 reaction, and (3) calibration time after the CO2 reaction. The heat of reaction is indicated by temperature changes per unit time in the reference reactor and the measurement reactor. As can be seen in equation (5), the heat of reaction calibration factor Q (kJ) can be calculated using the reaction-heat-transfer coefficient (UA; W• K-1) and the cumulative time changes (ΔT; K).

$$Q_{cal\ (1)} = UA_1 \times \int_{t_o}^{t_{end}} \Delta T\,dt \qquad (5)$$

The UA was calculated by injecting constant energy via the calibration probe; in this study, the measurement was made three times. The heat of reaction calibration after the reaction was calculated in the same way as the heat of reaction calibration before reaction. As shown in equation (6), the total heat of reaction calibration within the reactor

was calculated as the arithmetic mean of the heat of reaction calibration before the reaction and the heat of reaction calibration after the reaction.

$$UA_{average} = \frac{UV_1 + UV_2}{2}$$

In order to measure the heat of reaction between CO2 and absorbent, the enthalpy of the standard state was measured based on the heat of reaction per mole of CO2, and was found to be 40 °C.

V. RESULTS AND DISCUSSION
A. CO$_2$ absorption capacity

The CO$_2$ absorption capacity was expressed in mol of CO$_2$ dissolved in the absorbent per mol of absorbent (mol CO$_2$ • mol absorbents-1). Absorbents with high absorption capacity can dissolve large amounts of CO$_2$ in the CO$_2$ capture process and can thereby reduce operating cost.

The CO$_2$ absorption capacity was measured to evaluate the absorption performance of each absorbent. The breakthrough curve of CO$_2$ is shown in Fig. 3–5 at the reaction temperature of 40–80 °C. In this figure, the y-axis is the ratio of the concentration of injected CO$_2$ (C_i) to the concentration of
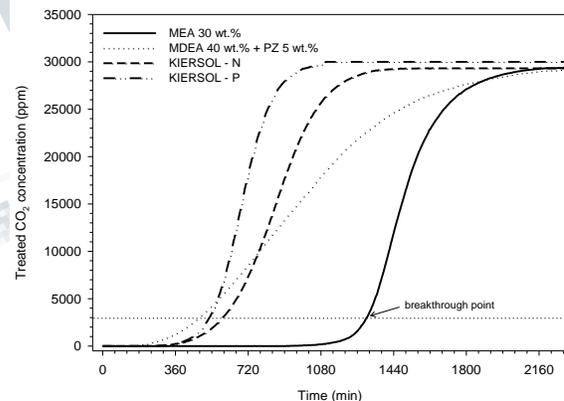
Figure 3. CO2 absorption curve of absorbents at 40 °C.
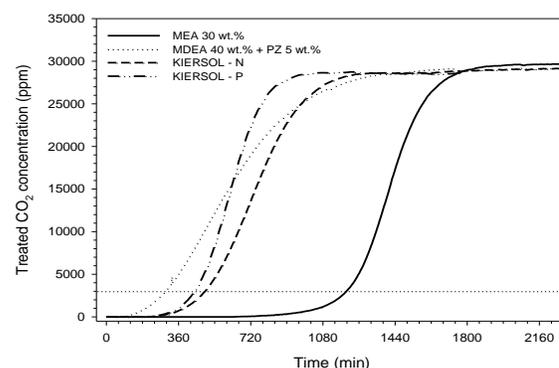
Figure 4. CO2 absorption curve of absorbents at 60 °C.
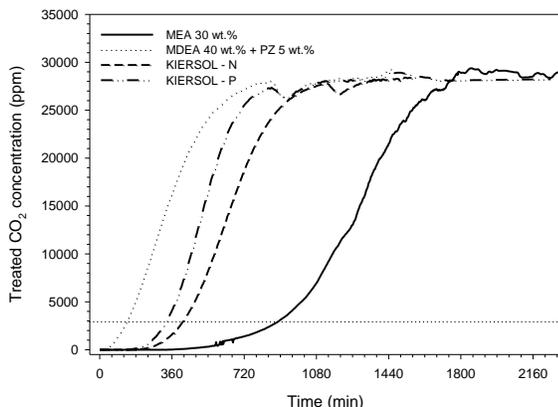
Figure 5. CO2 absorption curve of absorbents at 80 °C

emitted CO_2 (C_o), and the x-axis is the reaction time of the CO_2 and absorbent. In general, the point at which the outlet concentration is 10% of the inlet concentration is called the breakthrough point. As shown in Fig. 3–5, the breakthrough point is reached in a short time as the temperature increases. From these results, it can be shown that the amount of absorption of CO_2 depends on the reaction temperature. Table 1 shows the amount of absorbed CO_2 in each absorbent at different temperatures. The maximum CO_2 capacity of a primary amine such as MEA is generally limited to 0.5 mol $CO_2 \cdot$ mol amine^{-1} due to formation of MEA carbamate (MEACOO$^-$) and protonated MEA (MEAH$^+$). However, the absorption capacity of the MEA in this experiment was 0.74 mol $CO_2 \cdot$ mol amine^{-1}, which is higher than the theoretical value.

Table 1. CO2 absorption capacity of each absorbent at temperatures from 40 to 80 °C

Absorbents	CO₂ absorption capacity (mol $CO_2 \cdot$ mol absorbent^{-1})		
	40 °C	60 °C	80 °C
MEA	0.74	0.70	0.64
α-MDEA	0.63	0.38	0.23
KIERSOL-P	1.14	0.98	0.81
KIERSOL-N	1.17	1.00	0.84

These results were affected by the simulated pressure of the absorber (9.50–9.52 bar). The results for KIERSOL-P and KIERSOL-N at 40 °C were 1.14 and 1.17 mol $CO_2 \cdot$ mol absorbent^{-1}, respectively. KIERSOL-P showed 1.54 times greater CO_2 absorption than MEA and 1.81 times greater CO_2 absorption than a-MDEA. The difference in CO_2 absorption capacity at 60 °C was greater than at 40 °C. And, the difference in CO_2 absorption capacity at 60 °C was higher than at 40 °C. KIERSOL-P showed 1.40 times greater CO_2 absorption capacity than MEA, and 2.58 times greater CO_2 absorption capacity than a-MDEA. The

CO_2 concentration remains low (< 20 ppm) after the absorbent. The curve of CO_2 in a low range of concentration is shown in Fig. 6-8, and the time is shown in Table 2 until the concentration of CO_2 reaches 20 ppm.
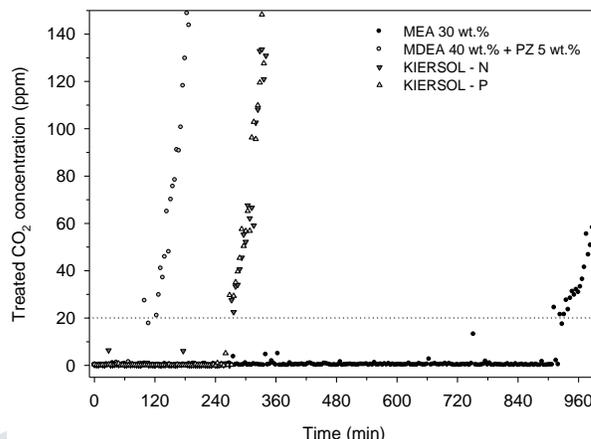
Figure 6. Initial CO2 concentration for CO2 absorption curve at 40 °C.
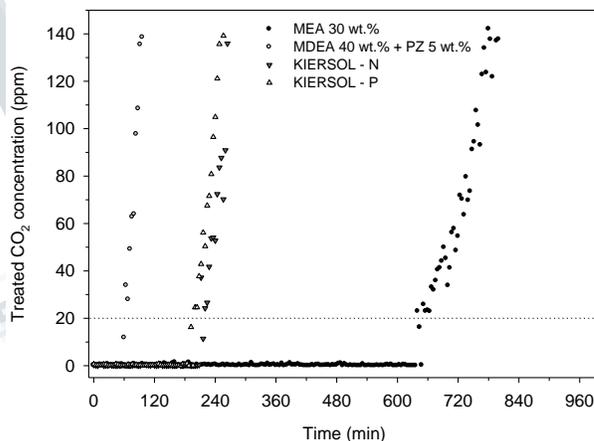
Figure 7. Initial CO2 concentration for CO2 absorption curve at 60 °C.
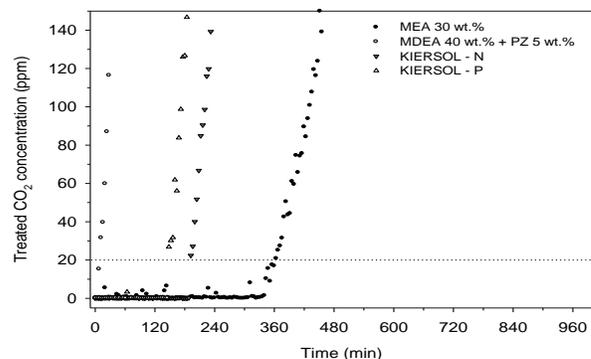
Figure 8. Initial CO2 concentration for CO2 absorption curve at 80 °C.

Table 2. Interval for absorbent to reach CO2 concentration of 20 ppm.

Temperature (°C)	Interval (min)			
	MEA	MDEA+PZ	KIERSOL-N	KIERSOL-P
40	912	100	272	268
60	640	64	212	200
80	364	12	192	148

MEA provided the highest absorbent concentration at which the concentration of CO2 was kept below 20 ppm. Interval of absorbents with a CO2 concentration of less than 20 ppm increased following the order MEA > MDEA > KIERSOl-N > KIERSOl-P.

A. Heat of reaction

High CO_2 absorption rate, high cyclic capacity and low reaction heat are required to reduce the energy requirement in the CO_2 capture process [23]. In general, the heat of reaction accounts for more than 50% of the total energy requirement and is an important indicator for evaluating the performance of the absorbent. As the reaction between CO_2 and absorbents is reversible reaction, it is possible to anticipate the heat of adsorption by measuring the heat of endothermic reaction produced during the reaction between CO_2 and absorbents. The heat of reaction is the energy (kJ • mol-1) that has increased through exothermic reaction per mol of CO_2 of each absorbent. Kim et al. found that when 30wt% MEA and CO_2 were made to react with each other at 40℃, the heat of reaction was 87.098 kJ • mol-1 [24], and Carson et al. reported that the reaction between 30 wt% MEA and CO_2 at 25 oC resulted in the heat of reaction 83.15kJ • mol-1 [24]. The results of this study showed that the heat of reaction of MEA was 96.00 kJ • mol-1, which was higher than previous report. Although preceding research was conducted using 10-30 vol% CO_2 based on flue gases of the power plant, this study used low concentration CO_2 (3 vol%) of petrochemical process. The heat of reaction of MEA was 96.00 kJ • mol-1 and that of a-MDEA was 68.22 kJ • mol-1. As a result of the experiment, while the heat of reaction of KIERSOL-N and P were similar to that of a-MDEA, it was 0.73-0.65 times lower than that of MEA. As a result of measuring the heat of reaction, it could be found that KIERSOL-N and P were better than MEA in the aspects of absorption capacity and heat of reaction.

Table 3. Heat of absorption of saturated CO_2 at 40 ℃

Absorbent	Absorbed CO_2 (mol)	CO_2 loading (CO_2 mol • absorbent mol-1)	Enthalpy ($\triangle H$: kJ • mol-1)
MEA	0.356	0.48	96.00
α-MDEA	0.145	0.25	68.22
KIERSOL-P	0.137	0.65	69.76
KIERSOL-N	0.160	0.59	62.83

VI. CONCLUSIONS

We assessed CO_2 absorption capacity, low concentration duration of CO_2, and the heat of reaction between absorbents and CO_2 in order to control 3vol.% CO_2 emitted during the acetic acid production process under ultra-low concentration 20ppm, As a result of the experiment, the absorption capacity of KIERSOL-N and KIERSOL-P at 40℃ was 1.14-1.17 mol CO2 • mol absorbent-1, which was rather higher than that of MEA (0.74 mol CO_2 • mol absorbent-1) or MDEA (0.63 mol CO_2 • mol absorbent-1). Although MEA kept the concentration of CO_2 under 20ppm longer than the others, KIERSOL-N and KIERSOL-P emitted low concentration CO_2 longer than MDEA. As for the heat of reaction, α-MDEA, KIERSOL-N and KIERSOL-P showed similar results, and MEA was found to have very high heat of reaction. The study results indicate that KIERSOL-N and KIERSO-P have high absorption capacity, low heat of reaction, and long low concentration carbon dioxide duration. Thus, KIERSOL-N and KIERSOL-P are expected to improve the efficiency of the acetic acid production process.

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