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Evaluation of carbon dioxide absorption by amine based absorbent

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Abstract

Toshiba has developed amine based aqueous solution (Toshiba solvent 1, TS-1) that can significantly reduce CO_2 regeneration energy compared with general 30 wt% monoethanolamine (MEA) aqueous solution and reported the results of the pilot plant of 10 t- CO_2 / day recovery from the flue gas of a coal-fired power plant. In order to reduce the CO_2 regeneration energy further, we have developed new hindered amine based absorbent, Absorbent-A.

In the present work, Absorbent-A was evaluated for CO_2 absorption properties by laboratory scale apparatus. Absorbent-A was found to have the high CO_2 absorption capacity and the low reaction heat. Furthermore, the CO_2 regeneration energy of Absorbent-A was 45% less than that of general 30 wt% MEA aqueous solution.

In future, we will additionally evaluate Absorbent-A in order to test in the pilot plant.

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Keywords**:** amine, CO_2 capture, vapor-liquid equilibrium, regeneration energy

1. Introduction

Carbon dioxide (CO_2) capture from the flue gas of thermal power plants is the easily applicable reduction method of CO_2 emissions from existing and future thermal power plants. Although chemical absorption using amine based absorbents is the closest to practical use, the more reduction of CO_2 regeneration energy is expected.

Toshiba has developed amine based aqueous solution (Toshiba solvent 1 and 2, TS-1 and TS-2) that can significantly reduce CO_2 regeneration energy compared with general 30 wt% monoethanolamine (MEA) aqueous solution and reported the results of the pilot plant of 10 ton-CO_2 / day recovery from the

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flue gas of a coal-fired power plant[1-2]. In addition, we have improved the system of the pilot plant using TS-1. As the result, we have confirmed the energy of 2.6GJ/t– CO_2 with exceeded values of 90% CO_2 capture ratio by using TS-1 [3].

On the other hand, in order to reduce CO_2 regeneration energy further, we have searched new amine based absorbents. As the basic properties of CO_2 absorbent, large absorption rate, high capacity of CO_2 and low reaction heat are required.

When we evaluated much amine solutions, it was found that the absorbent containing a cyclic tertiary amine has larger CO_2 absorption rate and lower reaction heat than those of TS-1. The amino group of cyclic tertiary amine is fixed by some bonds. It seems that molecular motion of amino group is low and the cyclic tertiary amine can easily react with CO_2. However, the CO_2 regeneration energy had not been improved as compared with TS-1.

Therefore, we made the search other amines considering molecular structure, we have developed the new hindered amine (Amine-A). It is considered that hindered amines require less reaction heat of CO_2 absorption than unhindered amines [4-5]. Amin-A has been improved the high CO_2 absorption capacity and low reaction heat. It is found that amine based absorbents (Absorbent-A) which is prepared from Amine-A shows good CO_2 absorption properties in comparison to TS-1 and the cyclic tertiary amine.

In this study, we present the evaluation of the CO_2 loading amount and the regeneration energy of Absorbent-A by laboratory scale apparatus.

2. Experimental

2.1. Vapor-liquid equilibrium

Vapor-liquid equilibrium at 40°C and 120°C were measured with an apparatus shown in Figure 1. CO_2 and N_2 gas mixed in prepared concentration by flow controllers were supplied to an absorbent in a reactor heated with an electric heater. When CO_2 concentration in outlet gas from a vapor-liquid separator was similar with CO_2 concentration in inlet gas, the equilibrium in the condition was determined. The absorbent was extracted from the reactor and the CO_2 loading in the absorbent was measured by gas chromatography.

For 40°C measurements, the apparatus shown in Figure 1 (1) was used and 1L absorbent was in the reactor at 40°C atmospheric pressure. We determined CO_2 partial pressure in the reactor from the water vapor partial pressure calculated from the amount of water in the absorbent and saturated water vapor pressure at 40°C.

For 120 °C measurements, the apparatus shown in Figure 1 (2) was used and 15L absorbent was in the reactor at 120 °C and 2 atm. Water containing the amine from the gas-liquid separator were returned to the reactor with automatically operated valve. In measuring the amount of water returned to the reactor with an integrating flow meter and calculating the amount of water vapor partial pressure in the reactor, CO_2 partial pressure was determined.

2-2 Reaction Heat

The reaction heats of CO_2 absorption was measured at 40°C with a calorimeter, DRC Evolution (SETARAM Instrumentation) connected to the CO_2 gas line and the CO_2 concentration meter.

2-3 Regeneration energy

The CO_2 regeneration energy was evaluated with the apparatus shown in Figure 1 (2) depending on

the heating energy to desorb CO_2 from the CO_2 loading absorbent. About 15 L absorbent in the reactor was mixed in the reactor with the liquid pump and heated with the electric heater from room temperature to about 120°C. As absorbent temperature rose with electric heater, CO_2 and vapor (mostly water) were desorbed from the absorbent. Flowing through a cooler, this mixed gas was separated to CO_2 and water with the gas-liquid separator. The amount of desorbed CO_2 was measured with the integrating gas flow meter. Therefore, the separated water returned into the reactor.

The CO_2 recovery energy in this apparatus was evaluated by the following formula.

$$Q_E = Q_H - Q_{rad} - Q_S - Q_{SAb}$$

Q_E: CO_2 recovery energy (kJ)
Q_H: Electric heater output
Q_{rad}: Heat radiation from the apparatus
Q_S: Heat storage of the apparatus
Q_{SAb}: Heat storage of the absorbent

The CO_2 recovery energy Q_E includes the water evaporation heat. The electric heater output Q_H was used as the integrated value after CO_2 desorbed from the absorbent. The amount of heat radiation Q_{rad} and heat storage Q_S of the apparatus were calculated from the equipment properties evaluated in advance. Also, heat storage of the absorbent Q_{SAb} was calculated from the specific heat and the temperature change of the absorbent. Then, we evaluated the CO_2 regeneration energies of each absorbent from the relation of Q_E and the amount of CO_2 desorption per unit time.
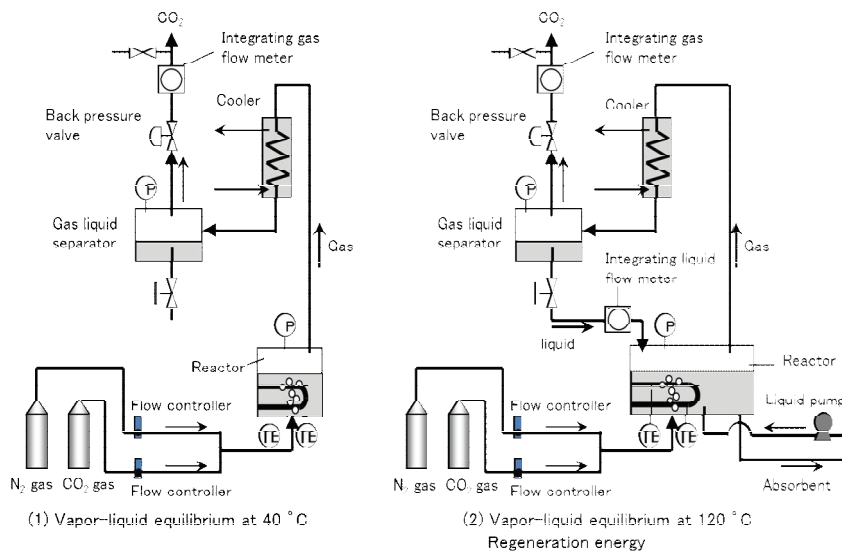

Figure1. Laboratory scale apparatus

3. Results

3.1. Vapor-liquid equilibrium

Figure 2 shows the vapor-liquid equilibrium for 30wt% MEA, Absorbent-A and Absorbent-C which contains a cyclic tertiary amine at 40 ℃ and 120 ℃.

At 40°C, the CO_2 loading of Absorbent-A was larger in high CO_2 partial pressure than that of 30wt% MEA and Absorbent-C. By contrast, in low CO_2 partial pressure (below about 3 kPa), it was smaller. On the other hand, Absorbent-A showed the small CO_2 loading at 120°C. In this paper, the effective CO_2 loading means the difference between absorption and desorption condition. Absorption condition is 40°C and CO_2 partial pressure 10 kPa, desorption condition is 120°C and CO_2 partial pressure 10 kPa. So, it turned out that, the effective CO_2 loading of Absorbent-A was larger than that of 30wt% MEA and Absorbent-C. In addition, it is expected that Absorbent-A is applicable to not only high CO_2 concentration flue gas of a coal fire power plant but also low CO_2 concentration (about 4 kPa) of a natural gas combined cycle power plant.
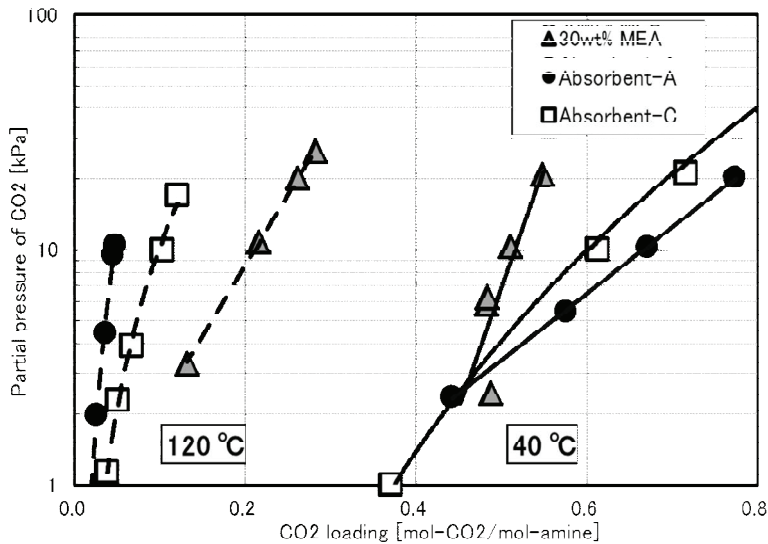

Figure2. Vapor-liquid equilibrium for 30wt% MEA, Absorbent-A and Absorbent-C

3.2. Reaction heat

Figure 3 shows the reaction heat at 40°C for 30wt% MEA, Absorbent-A and Absorbent-C at same CO_2 loading (0.45 mol-CO_2/mol-amine). Absorbent-A had low reaction heat as compared with MEA. MEA mainly forms the carbamate ion at CO_2 absorption reaction. In contrast, it is found that Absorbent-A forms the carbonate ion. Therefore, the reaction heat of Absorbent-A was low. On the other hand, the reaction heat of Absorbent-A was higher than Absorbent-C which contains the cyclic tertiary amine. It is considered that tertiary amines form the carbonate ion at CO_2 absorption reaction. This result indicates that the cyclic tertiary amine forms the carbonate ion as well as Amine-A.
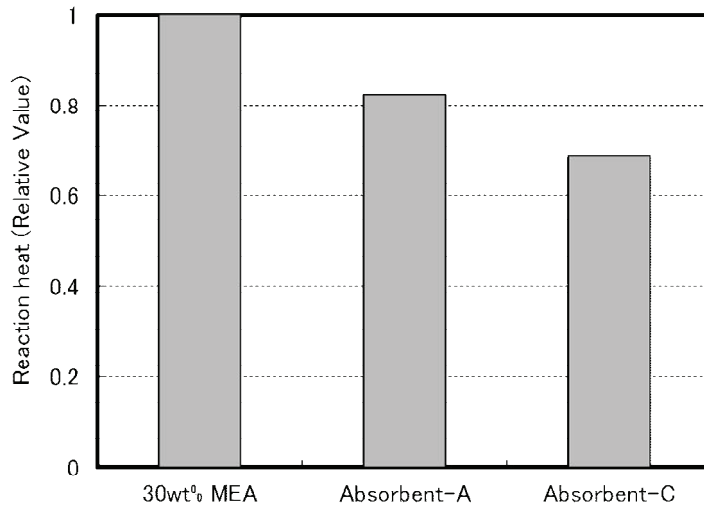
Figure3. Reaction heat for 30wt% MEA, Absorbent-A and Absorbent-C

3.3. Regeneration energy

Figure 4 presents the result of evaluated CO_2 recovery energy for 30wt% MEA, Absorbent-A, Absorbent-C.

For the calculation of the regeneration energy, the absorption condition was assumed to be 40°C and 10 kPa CO_2 and the desorption condition was assumed to be CO_2 loading at 120°C and 10 kPa CO_2. The CO_2 regeneration energy was integrated from the CO_2 recovery energy used between absorption and desorption condition
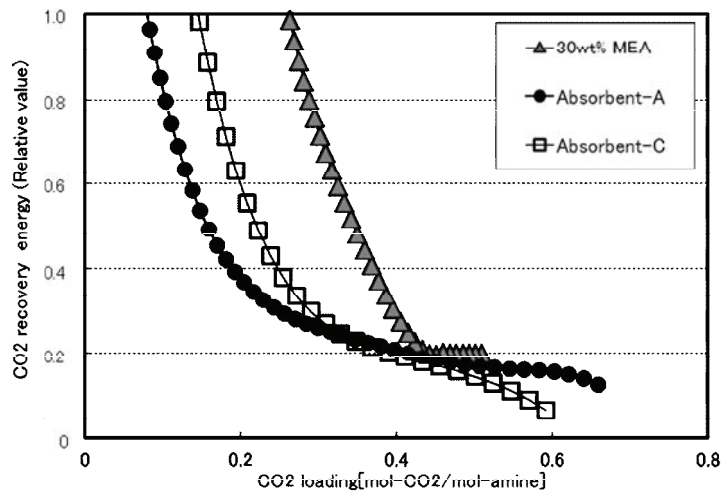

Figure4. CO_2 recovery energy for 30wt% MEA, Absorbent-A and Absorbent-C

The CO_2 regeneration energy was evaluated depending on the data in Fig.4. As shown in Fig.5, it was found that CO_2 regeneration energy of Absorbent-A is 45% less than that of MEA. Moreover, it was about 10% less than that of TS-1 which is our promising absorbent at present. The absorbent which has the high effective CO_2 loading and low reaction heat was confirmed to show low CO_2 regeneration energy.
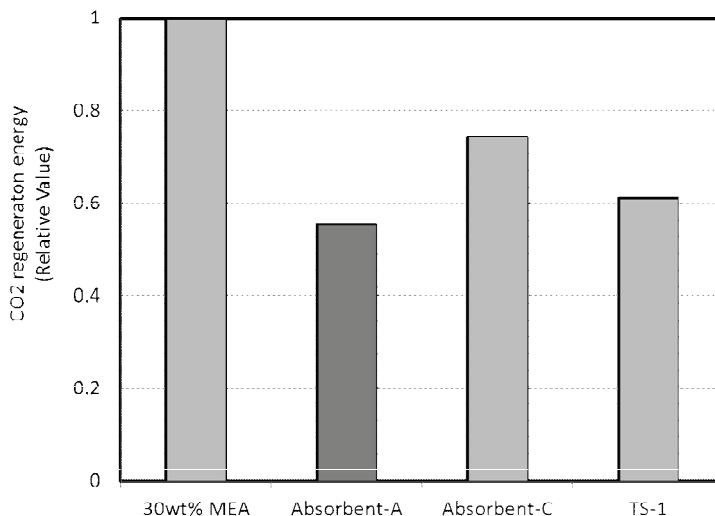

Figure5. CO_2 regeneration energy for 30wt% MEA, Absorbent-A, Absorbent-C and TS-1

4. Conclusions

We have developed a new promising amine which has improved the large CO_2 capacity and low reaction heat. It was found that amine based absorbents Absorbent-A prepared from it shows good CO_2 absorption properties at laboratory scale experiment in comparison to MEA and the cyclic tertiary amine. Furthermore, the CO_2 regeneration energy of Absorbent-A was found to be 45% less than that of MEA and about 10% less than that of TS-1. In future, we will evaluate not only the CO_2 regeneration energy but also the amine degradation and the amine emissions for Absorbent-A at the Mikawa pilot plant

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