Carbon Dioxide Removal from Flue Gas Using Amine-Based Hybrid Solvent Absorption

Supitcha Rinprasertmeechai, Sumaeth Chavadej, Pramoch Rangsunvigit, and Santi Kulprathipanja

Abstract—This study was to investigate the performance of hybrid solvents blended between primary, secondary, or tertiary amines and piperazine (PZ) for CO_2 removal from flue gas in terms of CO_2 absorption capacity and regeneration efficiency at 90 ^{o}C. Alkanolamines used in this work were monoethanolamine (MEA), diethanolamine (DEA), and triethanolamine (TEA). The CO_2 absorption was experimentally examined under atmospheric pressure and room temperature. The results show that MEA blend with PZ provided the maximum CO_2 absorption capacity of 0.50 mol CO_2/mol amine while TEA provided the minimum CO_2 absorption capacity of 0.30 mol CO_2/mol amine. TEA was easier to regenerate for both first cycle and second cycle with less loss of absorption capacity. The regeneration efficiency of TEA was 95.09 and 92.89 %, for the first and second generation cycles, respectively.

Keywords—CO_2 absorption capacity, regeneration efficiency, CO_2 removal, flue gas

I. INTRODUCTION

NORMALLY, flue gas released into the atmosphere from various industries, including petrochemical industry, contains approximately 80 % N_2, 15 % CO_2, and 5 % O_2, as well as 500 ppm SO_2, 100 ppm CO, and 50 ppm CH_4. Among of them, CO_2 has the most adverse impact, causing approximately 55 % of the currently observed global warming [1]. The increasingly accumulated CO_2 in the atmosphere has become a worldwide concern. The reduction of CO_2 emission is one of effective means to slow down the climate change. [2]-[3]. To reduce greenhouse gas emission, CO_2 separation and capture technologies are of growing importance. There are four main widely used commercial CO_2 removal processes; absorption, adsorption, membrane and cryogenic processes [4]. However the most important commercially applied technology for CO_2 removal is the absorption process, which can be called extraction process, by using a liquid solvent [5]-[10].

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Liquid solvents used in CO_2 absorption can be divided into two categories: chemical and physical solvents. The processes using amine-based solutions, such as alkanolamines, that chemically react with dissolved CO_2 are commonly used. One of the advantages of alkanolamines is that, structurally, they contain at least one hydroxyl group, which helps to reduce vapor pressure and also to increase their solubilities in aqueous solutions [11]. The amino group provides sufficient alkalinity to absorb CO_2. Monoethanolamine (MEA), diethanolamine (DEA), and methyldiethanolamine (MDEA) are some important amines [12]-[17]. Nowadays, the use of blends of alkanolamines, i.e. a solution of two or more amines with various compositions, is very interesting because it combines the desired characteristics of different solvents while suppressing their unfavorable characteristics [18]. Another important development in alkanolamines technology is the use of activated amine solutions which consist of a conventional amine doped with small amounts of an accelerator (activator) [19]. Piperazine (PZ) is one activator that has been considered as a promoter for amine systems to improve absorption kinetics such as MEA/PZ and MDEA/PZ blends, and to increase the concentration of PZ in solution which allows for increased solvent capacity and faster kineics [20]-[22].

The objective of this work was to investigate the performance of hybrid solvents blended between primary, secondary, or tertiary amines with PZ for CO_2 removal from flue gas in terms of CO_2 absorption capacity, and to examine the solvent regeneration at 90 ^{o}C to evaluate the solvent performance for reuse in CO_2 removal from flue gas.

II. EXPERIMENTAL

A. Materials

Simulated flue gas (15% CO_2, 5% O_2, and 80% N_2) and Nitrogen, used for this study were obtained from Thai Industrial Gas Co., Ltd. Monoethanolamine (99.0%), Diethanolamine (99.0%), Triethanolamine (99.0%), and Diethylenediamine were purchased from Italmar (Thailand) Co., Ltd.

B. Studied Conditions

The conditions for all studied parameters (MEA, DEA or TEA concentration, total feed flow rate, and diamine concentrations) were as follows:

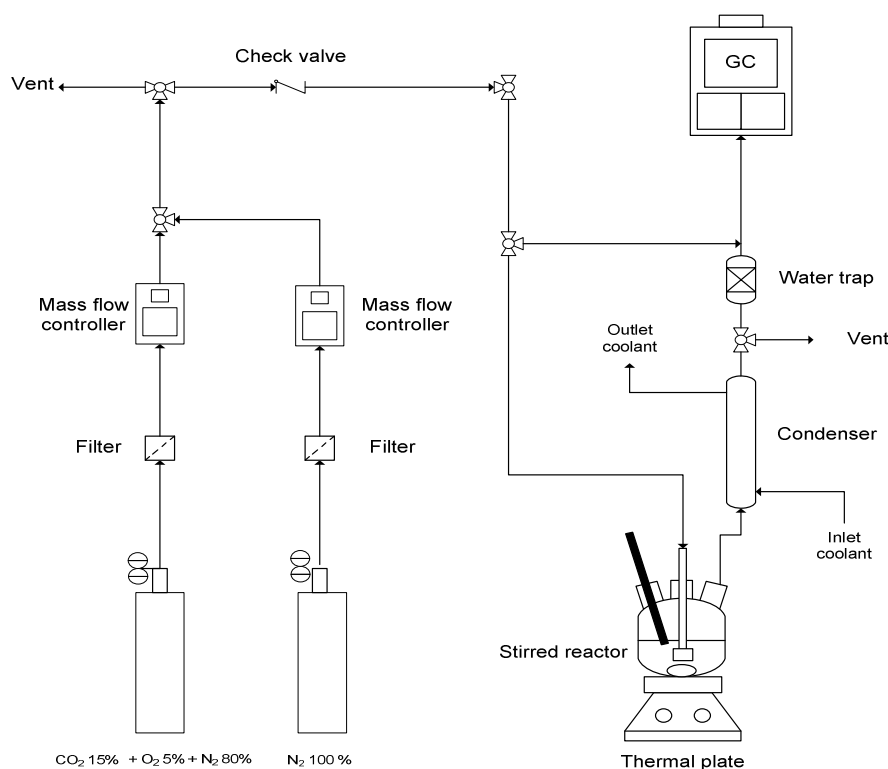|	
alkanolamine concentration	30 wt.%
total feed flow rate	50 cm^3/min
diamine concentration	5 wt.% of total amine

Fig. 1 Schematic of CO_2 absorption system

C. CO_2 absorption System

The schematic of the CO_2 absorption system used in this research is shown in Figure 1. There were 3 main sections in this system, including feed gas section, reactor section, and analytical section.

D. Feed Gas Section

A simulated flue gas, with compositions of 15 % CO_2, 5 % O_2, and 80 % N_2, was introduced into a stirred absorption reactor. The flow rate of the simulated flue gas passing through the reactor was regulated by a mass flow controller with a transducer. A stainless steel filter was placed upstream of the mass flow controller in order to trap any foreign solid particles in the simulated flue gas. A check valve was also be placed downstream of the mass flow controller to prevent any backflow. The pure N_2 gas was used to purge the reactor to remove air before the absorption experiments.

E. Reactor Section

The reactor had a total volume of 100 ml with a liquid holding volume of 50 ml. The flue gas was introduced into the reactor through a gas dispenser connected to one neck of the reactor, where the reactor contained a studied liquid solvent. During the absorption experiments, the reactor was continuously stirred by a magnetic stirrer. The reactor was placed in a temperature- controlling bath in order to maintain the temperature of the system at a desired value. The temperature of the solvent inside the reactor was monitored using a thermometer inserted through one neck of the reactor.

The gas exit at another neck of the reactor was connected to a condenser, which was connected to a cooling water bath, in order to condense any vaporized solvent to the reactor for preventing the solvent loss. The type and concentration of each studied solvent in an aqueous solution was comparatively investigated. The regeneration of each used solvent by heat treatment was performed at 90 °C with N_2 purge at a flow rate of 40 cm^3/min for 1 h to eliminate CO_2 bound to the solvent molecule. The regenerated solvent was reused for a next CO_2 absorption cycle to evaluate their reusability.

F. Analytical Section

The compositions of the feed flue gas and the outlet gas exiting the condenser were analyzed by an online gas chromatograph (GC) equipped with a thermal conductivity detector (TCD). For any studied conditions, the system was operated under an atmospheric pressure. An analysis of the outlet gas compositions was performed every 10 min until reaching absorption equilibrium. The CO_2 absorption capacity was then calculated. The experimental data taken after the complete absorption were be used to evaluate the performance of the studied solvents. The GC was operated under the following conditions:

TCD injection temperature	60 °C
Oven temperature	60 °C
Carrier gas	High purity argon

III. RESULTS AND DISCUSSION

A.Effect of Type of Alkanolamines

Figure 2a shows the change in the CO_2 concentration in with respect to absorption time of different alkanolamine aqueous solutions at an initial alkanolamine concentration of 30 wt.%. The absorption system was operated at an initial absorption temperature of 25 °C and a flue gas flow rate of 50 cm^3/min. The results clearly indicate that the MEA aqueous solution selectively absorbed CO_2 higher than the DEA and TEA aqueous solutions. The absorption time of MEA aqueous solution required to reach a complete CO_2 removal was in the range of 40-80 min showing that the high CO_2 removal efficiency of the MEA aqueous solution could be maintained for a longer absorption time than the other alkanolamines. The rate of CO_2 absorption can be calculated by the initial CO_2 concentration in the flue gas minus the outlet CO_2 concentration. The total quantity of the absorbed CO_2 was also calculated by the area below the graph of the CO_2 concentration difference versus time. The CO_2 absorption capacity expressed in mol CO_2/mol MEA. (or mol CO_2/mol amine in case of blended amines). Figure 2b shows the CO_2 absorption capacity of different alkanolamines. The order of CO_2 absorption capacity of the different alkanolamines was MEA > DEA > TEA. The results suggest that the increase in steric hinderence of the substituents bonded to nitrogen atom makes, in general, carbamate stability decrease and therefore, the loading capacity increases. However, the results confirm that MEA follows the above trend for its loading capacity, but DEA and TEA fail to follow this pattern. As the structural bulkiness is higher (DEA < TEA), the loading capacity becomes lower.

B. Effect of Type of Alkanolamines Blended with Piperazine

Piperazine is a diamine that has the advantage for increasing the solvent capacity. To determine the influence of piperazine, the piperazine was blended with different alkanolamines. Figure 3a shows the outlet amount of CO_2 with respect to absorption time by using different alkanolamine aqueous solutions containing 5 wt.% of PZ in a total amine concentration of 30 wt.%. The absorption system was operated at an initial absorption temperature of 25 °C and a flue gas flow rate of 50 cm^3/min. It can be clearly seen that the absorption time of the MEA aqueous solution blended with PZ required to reach a complete CO_2 removal was in the range of 40-100 min and this aqueous solution could absorb CO_2 up to 3670 min that was much longer than the sole MEA aqueous solution. Among these aqueous solutions, the CO_2 absorption capacity increased in the following order: TEA/PZ < DEA/PZ < MEA/PZ. Figure 3b shows the comparison between the CO_2 absorption capacities of the sole alkanolamines and the alkanolamines blended with piperazine. The CO_2 absorption capacity of any alkanolamine blended with piperazine was higher than that of any sole alkanolamine. The enhancement of the CO_2 absorption capacity of any alkanolamine by blending with PZ can be explained by the fact that PZ possesses two amine groups, resulting in increasing CO_2 absorption.

However, its limited solubility in an aqueous solution negatively makes it unable to be employed at high concentration.
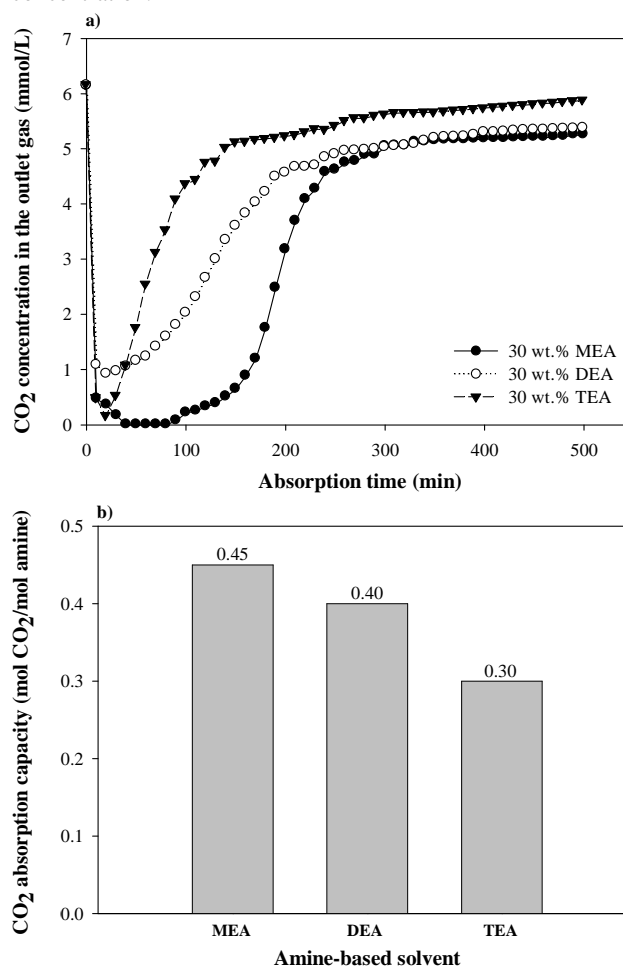

Fig. 2 (a) Effect of types of alkanolamines on outlet concentration of CO_2 at different absorption time (Absorption temperature of 25 °C and flue gas flow rate of 50 cm^3/min), (b) The CO_2 absorption capacity of different alkanolamines

C.Regeneration Efficiency of Different Amine-Based Solvents

The regeneration experiment was carried out at 90 °C with a pure N_2 purge. The corresponding regeneration efficiency for each amine-based solvent is presented in Figure 4. It was clearly seen that MEA gave the lowest regeneration efficiency of 75.75 % in the first cycle, whereas, TEA offered the highest regeneration performance of 95.09 %. The regeneration performance can be ranked in the following order: TEA > TEA/PZ > DEA/PZ > DEA > MEA/PZ > MEA. For any given solvent system, the second cycle showed a slightly lower regeneration efficiency as compared with that of the first cycle. TEA maintained the highest regeneration efficiency because TEA has the highest bulkiness molecular structure than MEA and DEA, which were easily regenerated and

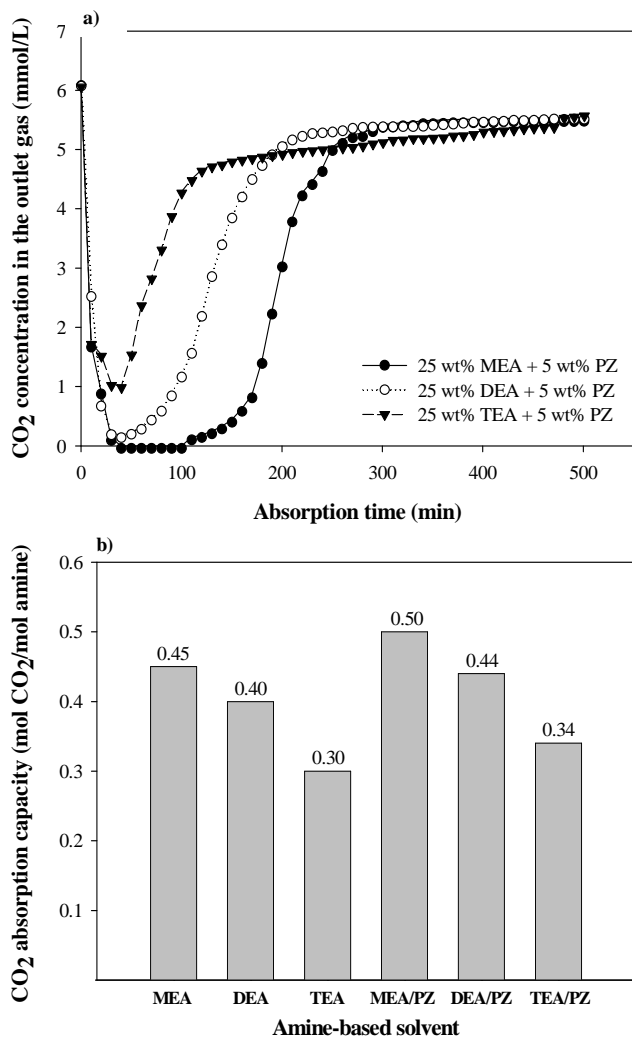introduced great degradation resistance, in comparison to other amine-based solvent.

Fig. 3 (a) Effect of type of alkanolamines blended with piperazine on outlet concentration of CO_2 at different absorption time (Absorption temperature of 25 °C and flue gas flow rate of 50 cm^3/min), (b) The comparison between the CO_2 absorption capacity of sole alkanolamines and alkanolamines blended with piperazine

IV. CONCLUSIONS

The aqueous solutions of different sole alkanolamines and alkanolamines blended with PZ were studied for CO_2 removal from flue gas via the absorption and regeneration steps. Under the experimental conditions, when PZ was used as an additive in the aqueous solutions of any alkanolamine showed the enhancement of CO_2 absorption capacity. MEA blended with PZ gave the highest CO_2 absorption capacity of 0.50 mol CO_2/mol amine. The order of CO_2 absorption capacity of different amines was MEA/PZ > MEA > DEA/PZ > DEA > TEA/PZ > TEA. Although the primary amine (MEA) had the highest CO_2 absorption capacity, the regeneration performance was the lowest. The regeneration of the 30 wt.% TEA aqueous

solution at 90 °C with a pure N_2 purge showed the best result. Over 90 % of the CO_2 contained in the solution could be desorbed, TEA had the highest regeneration efficiency of 95.1 % in the first cycle with a little decrease in the second cycle.
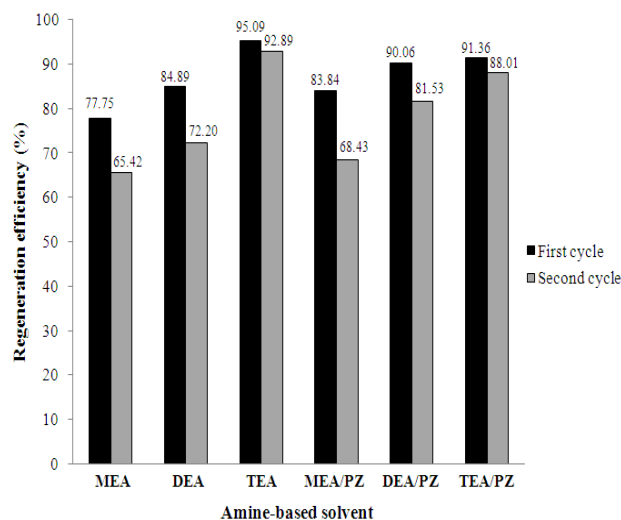

Fig. 4 Comparison of amine-based solvent regeneration efficiency

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