# CHAPTER IV
## RESULTS AND DISCUSSION

### 4.1 $CO_2$ Absorption by Amine–Based Solvent

In this research, the $CO_2$ absorption from flue gas by using amine-based solvent with various types of alkanolamines was investigated to obtain the high $CO_2$ absorption capacity.

#### 4.1.1 Effect of Absorption Time

Figure 4.1 shows the change in concentration in the outlet gas of $CO_2$, $O_2$ and $N_2$ with respect to absorption time by using the alkanolamines aqueous solutions with alkanolamines 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 $O_2$ and $N_2$ concentraions in the outlet gas remained almost invariant, whereas the $CO_2$ concentration strongly depended on the absorption time. The result clearly indicates that the MEA aqueous solution selectively absorbed $CO_2$ rather than DEA and TEA aqueous solutions. The absorption time of MEA aqueous solution required to reach a maximum $CO_2$ removal was in range of 40-80 minutes. At the MEA aqueous solution, the $CO_2$ concentration in the outlet gas reached a zero level which corresponds to 100 % $CO_2$ removal. It was also found that the high $CO_2$ removal efficiency at the MEA aqueous solution was maintained for a longer absorption time than the other alkanolamines. Figure 4.2 shows the change in concentration in the outlet gas of $CO_2$, $O_2$ and $N_2$ with respect to absorption time by using the alkanolamine aqueous solutions containing 5 wt.% of PZ in 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. Although the absorption time of MEA aqueous solution blended with PZ required to reach a maximum $CO_2$ removal was in range of 40-100 minutes that is more than the absorption time of MEA aqueous solution, the $O_2$ and $N_2$ concentrations have similar trend to the curve in Figure 4.1. The curves shown in Figure 4.1 and Figure 4.2 are

quite similar to the breakthrough curves reported in a previous research work (Choi et al,. 2009). The point, at which the outlet $CO_2$ concentration returns to become equal to the inlet $CO_2$ concentration, is considered to be the breakthrough point for the $CO_2$ absorption process. When the breakthrough point is reached, the $CO_2$ absorption can be no longer achieved. The time to reach the breakthrough point for each experiment in this research was different, depending on the amine solution.
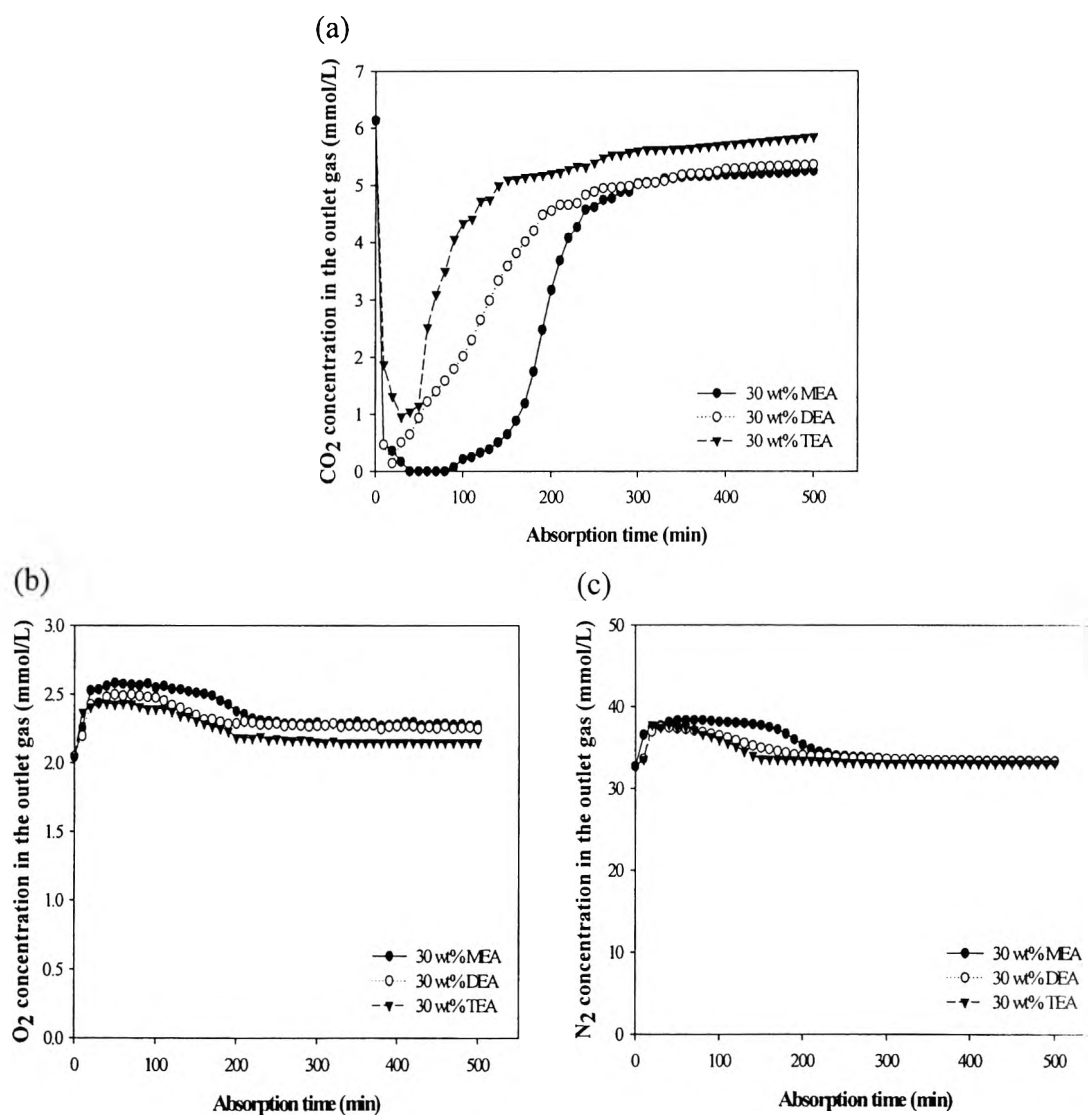
(a)

(b)                                    (c)

**Figure 4.1** Effect of absorption time on concentration in the outlet gas of (a) $CO_2$, (b) $O_2$ and (c) $N_2$ using the alkanolamines aqueous solutions with alkanolamines concentration of 30 wt.%. (Flue gas flow rate of 50 $cm^3$/min, inlet $CO_2$ concentration of 15 vol%, inlet $O_2$ concentration of 5 vol%, inlet $N_2$ concentration of 80 vol%, and initial absorption temperature of 25 °C).

The total $CO_2$ absorption can be calculated by the initial $CO_2$ concentration in the flue gas minus the $CO_2$ concentration in the outlet gas and the total quantity of the absorbed $CO_2$ was also calculated by area below the curves. The $CO_2$ absorption capacity expressed in mol $CO_2$/mol MEA. (or mol $CO_2$/mol amine in case of blended amines) was then obtained, as explained next.
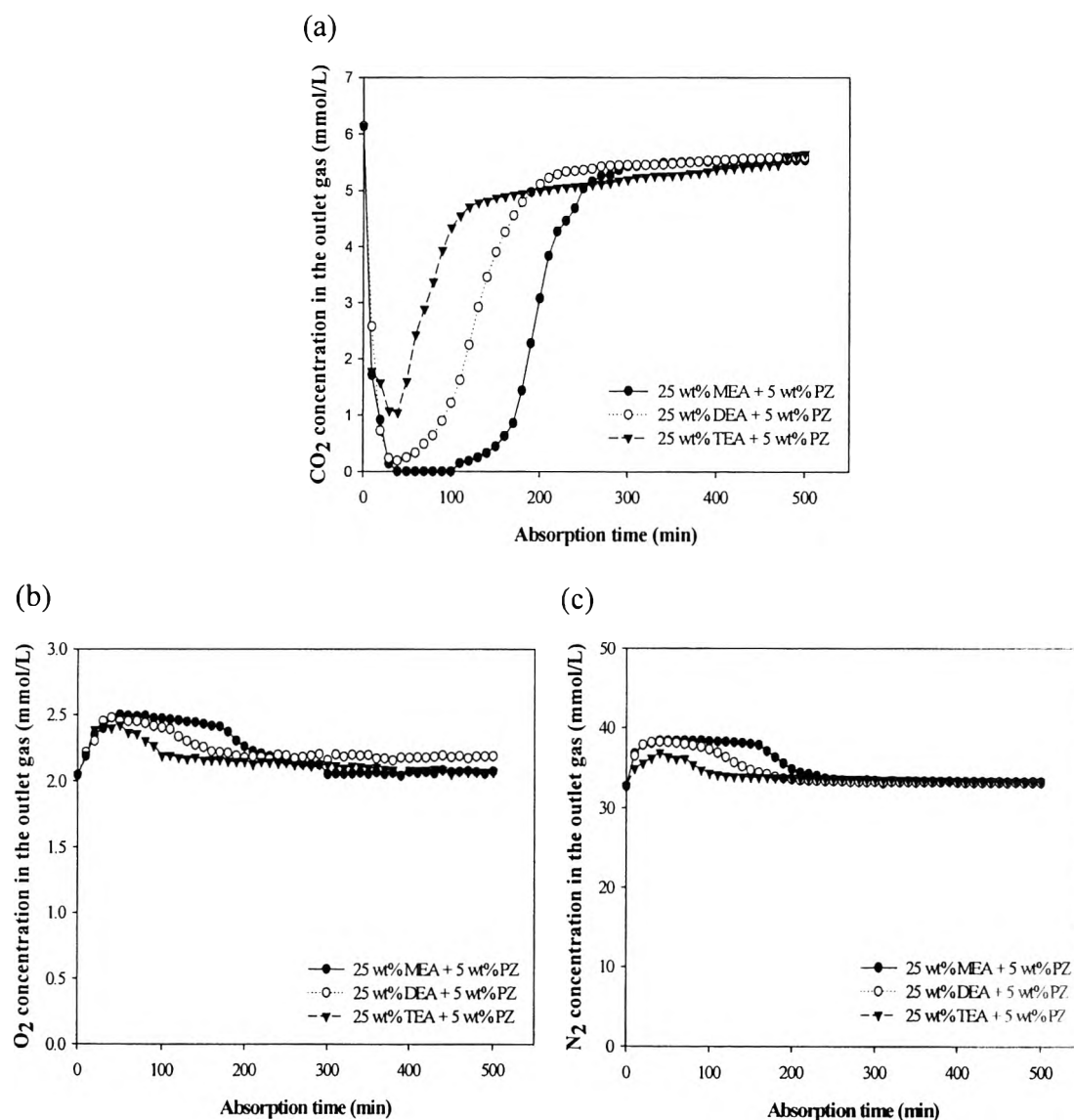
(a)

(b)                                                    (c)

**Figure 4.2** Effect of absorption time on concentration in the outlet gas of (a) $CO_2$, (b) $O_2$ and (c) $N_2$ using the alkanolamine aqueous solutions containing 5 wt.% of PZ in total amine concentration of 30 wt.%. (Flue gas flow rate of 50 $cm^3$/min, inlet $CO_2$ concentration of 15 vol%, inlet $O_2$ concentration of 5 vol%, inlet $N_2$ concentration of 80 vol% and initial temperature of 25 °C).

4.1.2 Effect of Types of Alkanolamines

Figure 4.3 shows the change in the total $CO_2$ absorption 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 data shows the result until the solvent cannot absorb $CO_2$ (The total $CO_2$ absorption equal to zero). It could be clearly seen that the MEA aqueous solution could be maintained for a longer absorption time than the other alkanolamines.
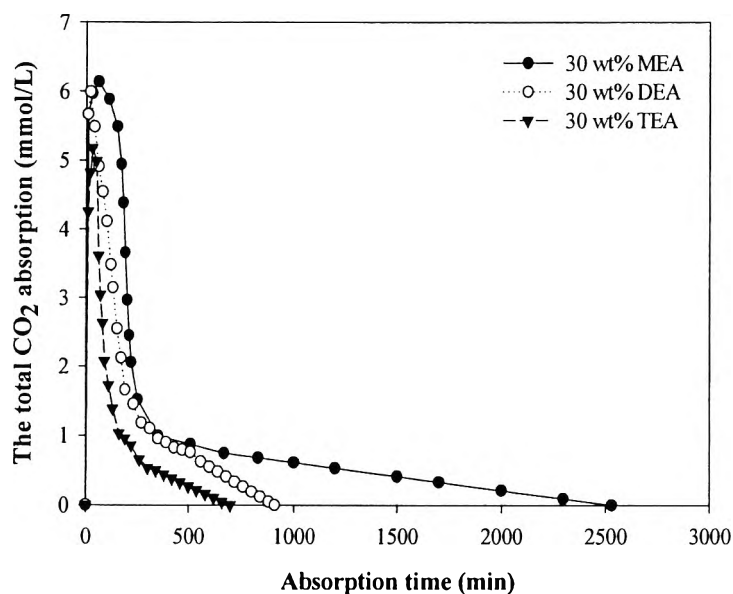


**Figure 4.3** Effect of types of alkanolamines on the total $CO_2$ absorption and time by using the alkanolamines aqueous solutions with alkanolamines concentration of 30 wt.%. (Flue gas flow rate of 50 $cm^3$/min, inlet $CO_2$ concentration of 15 vol%, inlet $O_2$ concentration of 5 vol%, inlet $N_2$ concentration of 80 vol% and initial temperature of 25 °C).

The $CO_2$ absorption capacity of the different alkanolamines in Figure 4.4 can be calculated by the area below the curve of Figure 4.3 divided by mol of amine. For $CO_2$ absorption capacity, MEA aqueous solution shows the highest capacity compared with DEA and TEA aqueous solutions. 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 confirmed that MEA follows the above trend for its loading capacity, but DEA and TEA failed to follow this pattern. As the structural bulkiness higher (DEA < TEA), loading capacity becomes lower.
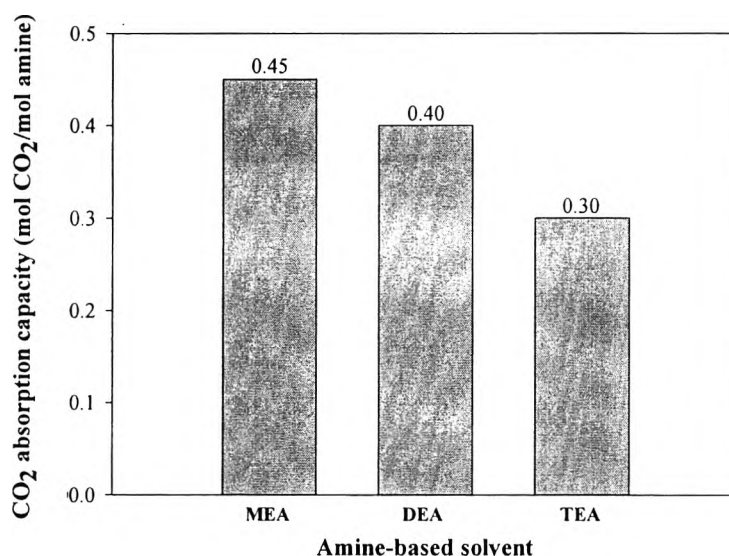


**Figure 4.4** Effect of types of alkanoamines on the $CO_2$ absorption capacity by using the alkanolamines aqueous solutions with alkanolamines concentration of 30 wt.% (Flue gas flow rate of 50 $cm^3/min$, inlet $CO_2$ concentration of 15 vol%, inlet $O_2$ concentration of 5 vol%, inlet $N_2$ concentration of 80 vol% and initial temperature of 25 °C).

### 4.1.3 Effect of Types of Alkanolamines Blended with Piperazine

Piperazine is a diamine that has the advantage of increasing the solvent capacity. To determine the influence of piperazine, the piperazine was blended with different alkanolamines. Figure 4.5 shows the total $CO_2$ absorption 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 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 4.6 shows the comparison between the $CO_2$ absorption capacities of the

different sole alkanolamines and the alkanolamines blended with piperazine. It could

be clearly seen that all the investigated alkanolamine blended with piperazine

increased the $CO_2$ absorption capacity. Particularly, PZ could significantly increase

the $CO_2$ absorption capacity because it possessed two amine groups with less

structural bulkiness as compared to the other investigated alkanolamines, as shown in

Figure 4.7. However, its limited solubility in an aqueous solution negatively makes it

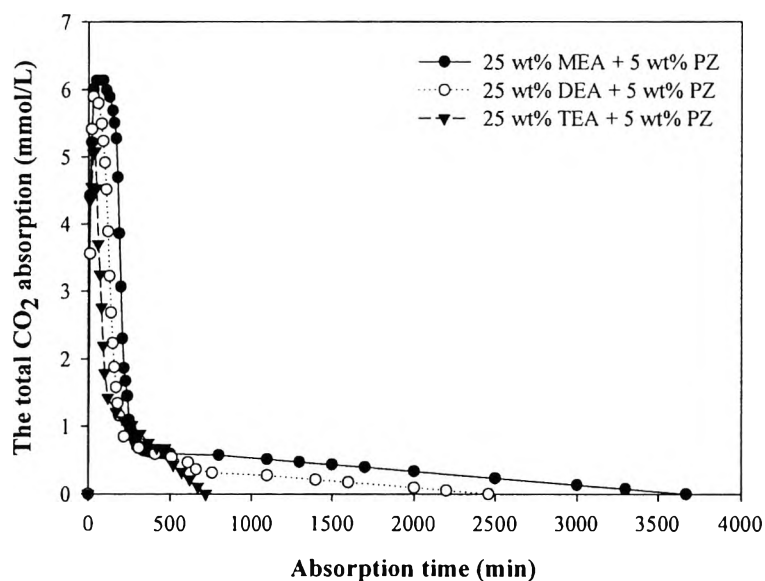unable to be employed at high concentration.



**Figure 4.5** Effect of types of alkanolamines on the total $CO_2$ absorption and time by

using containing 5 wt.% of PZ in total amine concentration of 30 wt.%. (Flue gas

flow rate of 50 $cm^3$/min, inlet $CO_2$ concentration of 15 vol%, inlet $O_2$ concentration

of 5 vol%, inlet $N_2$ concentration of 80 vol% and initial temperature of 25 °C).
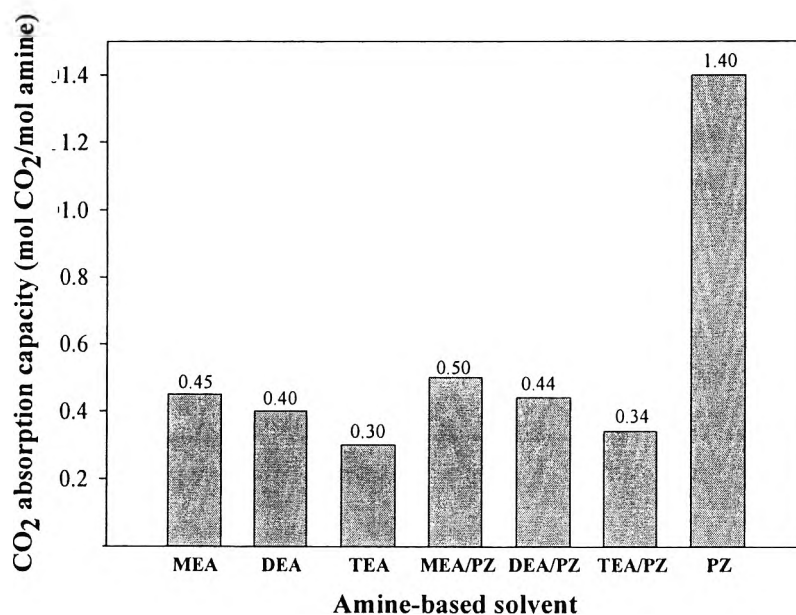
Figure 4.6 The comparison between the $CO_2$ absorption capacity of different sole alkanolamines and alkanolamines blended with piperazine. (Flue gas flow rate of 50 $cm^3/min$, inlet $CO_2$ concentration of 15 vol%, inlet $O_2$ concentration of 5 vol%, inlet $N_2$ concentration of 80 vol% and initial temperature of 25 °C).
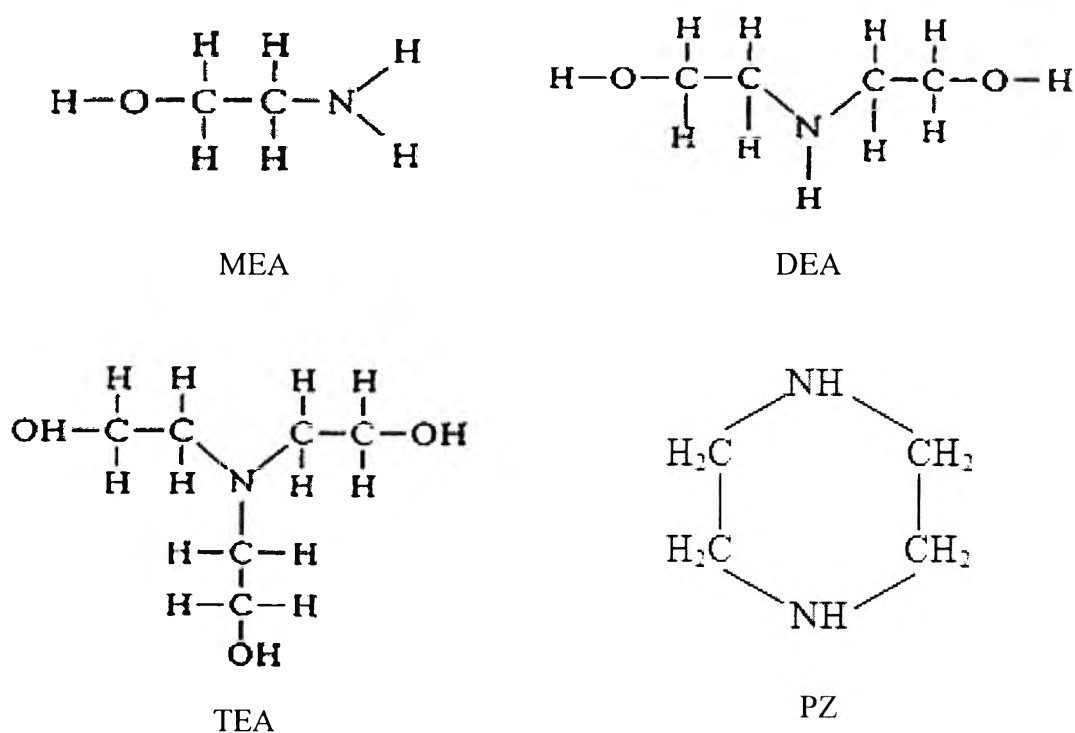


Figure 4.7 Molecular structures of MEA, DEA, TEA and PZ

## 4.2 Regeneration Temperature of Amine-Based Solvent

The effect of regeneration temperature on amine-based solvent was next investigated. The regeneration system was operated in two cycles at high temperature because it is an endothermic system. The regeneration temperature not too high for degradation of the solvent.

### 4.2.1 Effect of Regeneration Temperature on Regeneration Efficiency

The regeneration temperature was set at 80, 90 and 100 °C by heat treatment with a pure $N_2$ purge. The corresponding regeneration efficiency of different temperature for each amine-based solvent was presented in Figure 4.8. When compare the regeneration efficiency in each temperature, it was clearly seen that MEA gave the lowest regeneration efficiency and TEA offered the highest regeneration efficiency. 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. As expected, the regeneration efficiency increased with increasing temperature so the regeneration temperature of 100 °C gave higher regeneration efficiency than other temperatures. At regeneration temperature of 100 °C, MEA gave the lowest regeneration efficiency of 81.58 % in the first cycle, whereas, TEA offered the highest regeneration performance of 97.68 %. 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.

For the regeneration time, The regeneration time is the time that the solvent use to remove $CO_2$ out of it. The data shows the time for remove $CO_2$ until it cannot remove again. The corresponding regeneration time for each amine-based solvent is presented in Table 4.1. The result shows that at the regeneration temperature of 100 °C, the regeneration time is the shortest. The regeneration system is the endothermic reaction therefore the regeneration time decreased with increasing

the regeneration temperature. The regeneration time of TEA at 100 °C for the first and second cycle were 80 and 90 minutes, repectively. TEA was easily regenerated because it use the shortest time for regeneration. The first cycle of regeneration use the shorter regeneration time than the second cycle. At the first cycle, the solvent used for $CO_2$ absorption system only one time therefore it does not enough for the degradation of the solvent.
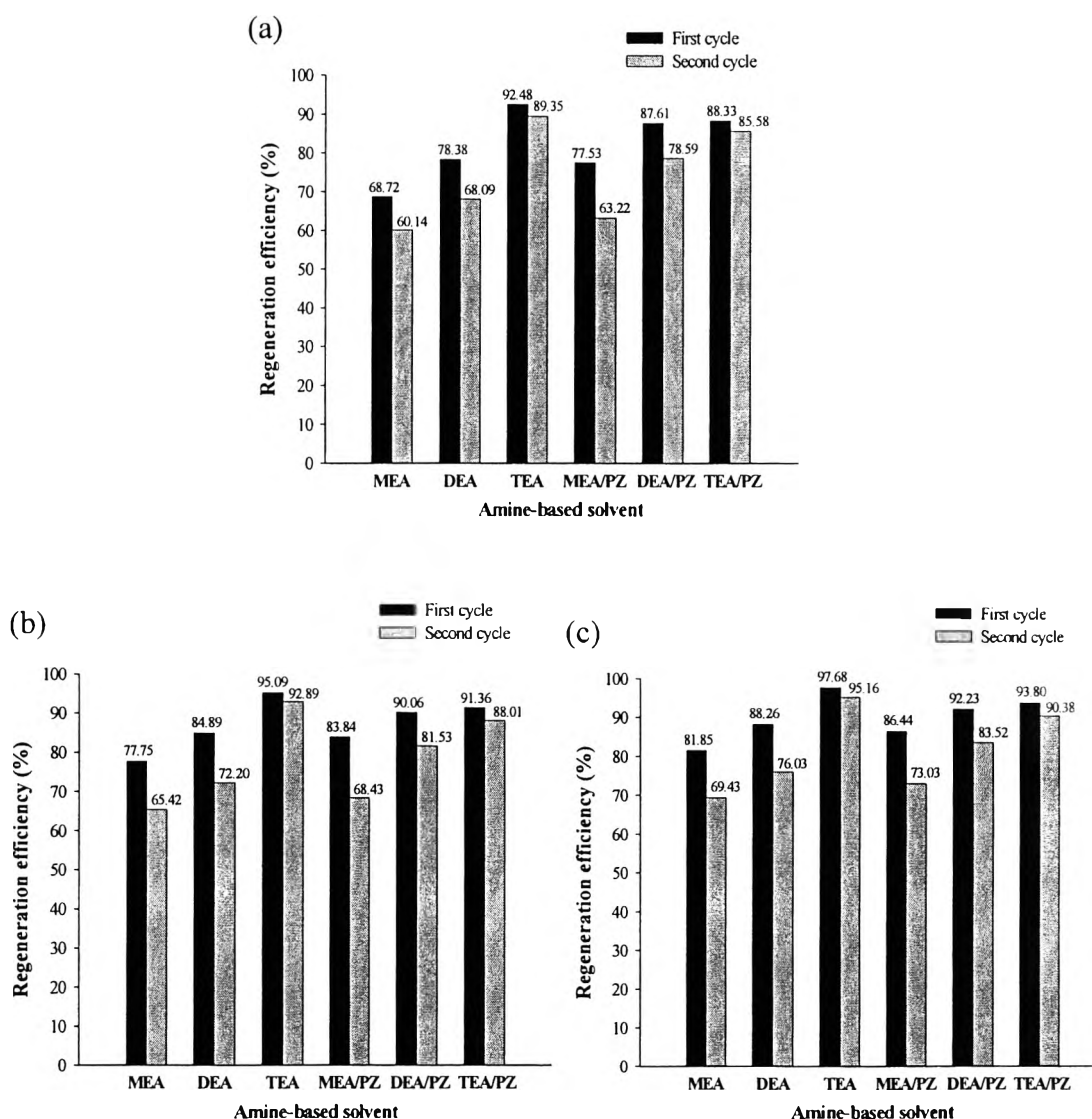


Figure. 4.8 The comparison of amine-based solvent regeneration efficiency in various regeneration temperature. (regeneration temperature of (a) 80 °C (b) 90 °C and (c) 100 °C).

**Table 4.1** Effect of regeneration temperature on the regeneration time of amine-based solvent

| solvent | regeneration time (min) | | | | | |
|---------|-------------|--------------|-------------|--------------|-------------|--------------|
| | 80 °C | | 90 °C | | 100 °C | |
| | first cycle | second cycle | first cycle | second cycle | first cycle | second cycle |
| MEA | 550 | 650 | 380 | 440 | 250 | 260 |
| DEA | 380 | 450 | 210 | 270 | 140 | 150 |
| TEA | 140 | 150 | 120 | 140 | 80 | 90 |
| MEA + PZ | 300 | 350 | 270 | 340 | 230 | 250 |
| DEA + PZ | 370 | 400 | 200 | 250 | 130 | 140 |
| TEA + PZ | 210 | 220 | 180 | 210 | 110 | 120 |

### 4.2.2 Effect of Regeneration Temperature on $CO_2$ Absorption Capacity

The $CO_2$ absorption capacity under the effect of regeneration temperature has been done for three times of absorption. The system starts with absorption, regeneration and then absorption again. It has been done step by step until two cycle of regeneration. Figure 4.9 shows the comparison between the $CO_2$ absorption capacity of different pure alkanolamines and alkanolamines blended with piperazine in various regeneration temperature. For absorption system was operated at an initial absorption temperature of 25 °C and a flue gas flow rate of 50 $cm^3$/min. For pure alkanolamines, using different sole alkanolamines aqueous solutions with alkanolamines concentration of 30 wt.%. For alkanolamines blended with piperazine, using alkanolamines aqueous solutions containing 5 wt.% of PZ in a total amine concentration of 30 wt.%. At the first time of $CO_2$ absorption, the $CO_2$ absorption capacity of the same amine-based solvent was the same in each regeneration temperature. In the second and third time of $CO_2$ absorption, it was clearly seen that at the regeneration temperature of 100 °C, the $CO_2$ absorption capacity of TEA is nearly to the $CO_2$ absorption capacity in the first time more other alkanolamines. MEA was low $CO_2$ absortpion capacity in the second and third time of $CO_2$ absorption at the regeneration temperature of 80 °C. It could be observed that with an increase in regeneration temperature, increasing the $CO_2$ absorption capacity. The

results corresponding to the regeneration efficiency in Figure 4.8. TEA has more regeneration efficiency than MEA therefore it has higher $CO_2$ absorption capacity than MEA in second and third cycle, respectively.
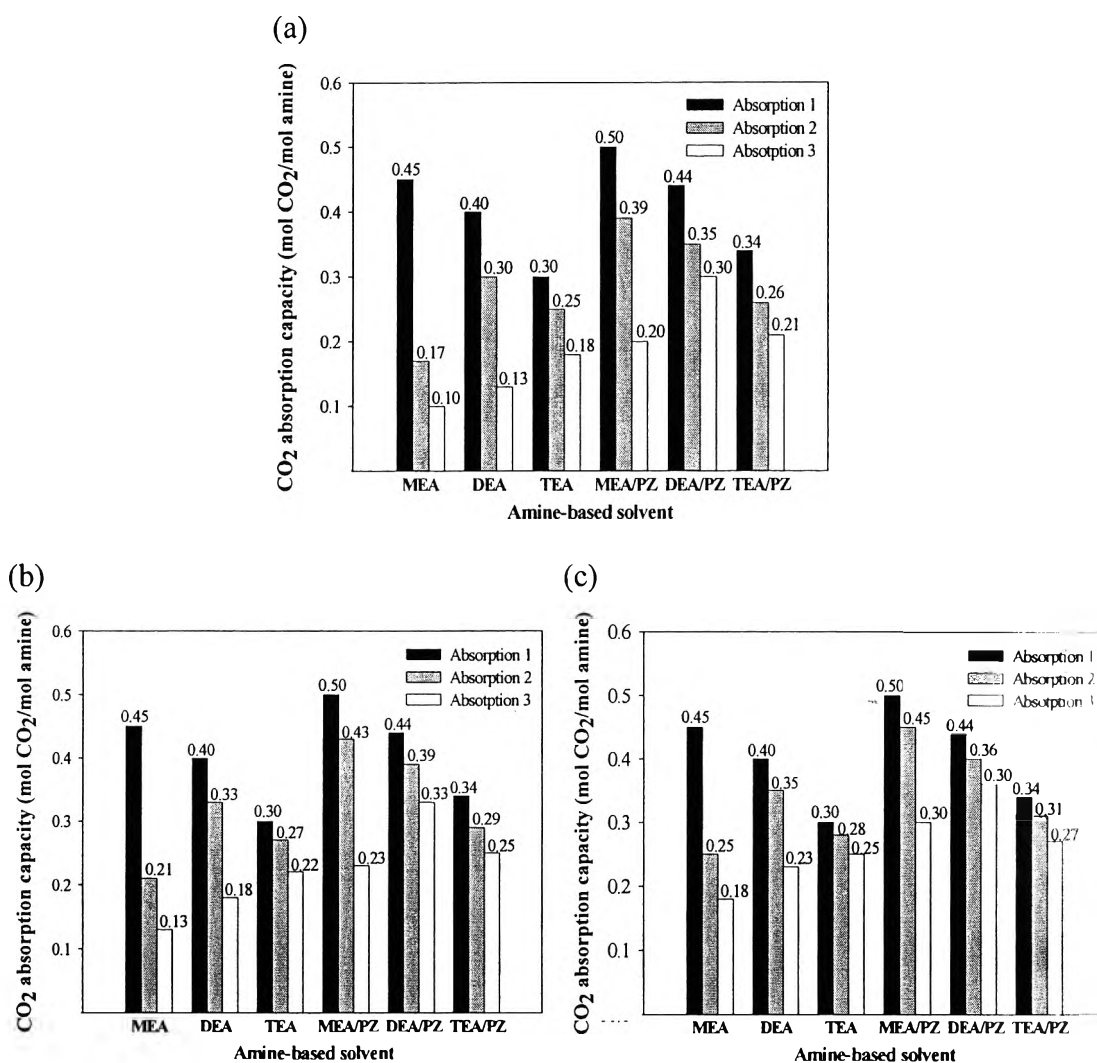


Figure 4.9 The comparison between the $CO_2$ absorption capacity of different sole alkanolamines and alkanolamines blended with piperazine in various regeneration temperature. (Flue gas flow rate of 50 $cm^3$/min, inlet $CO_2$ concentration of 15 vol%, inlet $O_2$ concentration of 5 vol%, inlet $N_2$ concentration of 80 vol% and initial temperature of 25 °C, regeneration temperature of (a) 80 °C (b) 90 °C and (c) 100 °C).