Structure and Activity Relationships for CO_2 Regeneration from Aqueous Amine Based Absorbents

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Abstract

A study to determine the structure and activity relationships of various amine based CO_2 absorbents was performed in which, the desorption of CO_2 from saturated absorbent at 80 ^{o}C and atmospheric pressure was measured to assess the initial desorption rate and desorption capacities at pseudo equilibrium. Evaluation of desorption capacity at 80 ^{o}C will give a better understanding for more energy efficient and lower circulation rate absorbent for CO_2 absorption process. Results showed that an increase in chain length between the amine and different functional groups in the absorbent structure up to four carbon, result in an increase in initial desorption rate, also increase in the desorption capacity at pseudo equilibrium in most absorbents. Steric hindrance effect was noticed when side chain with an alkyl group was present at α –carbon to amine group in the structure. Increase in the number of amine group in absorbent structure, results in higher desorption capacity that reaches up to 75 % of CO_2 is desorbed. Aromatic amines substituted with an amine group by a side chain at the cyclic ring shows an increase in desorption capacity at pseudo equilibrium.

1. Introduction

Although the absorption of acid gases such as CO_2 in aqueous amine solutions like e.g. MEA (monoethanolamine) from natural gas concerns proven technology, the removal of CO_2 from flue gases is not as straightforward as it could be expected. In these currently used systems a major part of the operational costs is caused by the solvent regeneration (up to 40%). In industrial processes, very high temperatures (>100 ^{o}C) are used to regenerate MEA solutions. Usually high pressure steam is applied, which provides the heat of reaction and enables the transport of CO_2 out of the reactor. The regeneration process is usually done at the temperature in excess of the boiling temperature, as the chemical kinetics of regeneration increases with temperature. The energy consumption in the stripper reboiler is estimated to be 15-30% of the net power production of a coal-fired power plant. The development of an improved absorbents with lower regeneration energy requirement is identified as the highest priority research and development objective for amine based CO_2 capture systems. Such improvements are needed to reduce the large energy requirement of current systems, which is the major contributor to the relatively high cost of this technology.

A complete and rigorous (rate based) model of chemical absorption- desorption process requires a large number of physico-chemical data (solvent viscosity, density, diffusivities, kinetics data, equilibrium model). To characterize a large number of solvent systems with all this information is tedious task and could not be performed for more than a few solvents in a short time. Also studies devoted to desorption are not as numerous as those concerning absorption. More specifically, the relationship of structure and regeneration characteristics of various amines based absorbent for CO_2 is hardly studied. Therefore, a screening method has been developed for the desorption of CO_2 from various loaded amine based aqueous absorbents. It is aimed that in this investigation, screening of various solvents on their regeneration at low temperature, atmospheric pressure with rapid regeneration rate and low evaporation solution loss especially. Desorption of CO_2 from various amine based absorbents was measured to assess the amount of CO_2 desorbed and the overall rate of desorption at 80 ^{o}C. In this study the effects which were investigated are the chain length, number of functional groups, different functional groups substitution at the α-carbon to the amine group, cyclic amine, substituted cyclic amines etc. and compared with MEA base case. Based on the results a better understanding of the structural effect on CO_2 desorption will be developed. This study will be advantageous in the development of an improved efficiency of an amine based CO_2 absorbent.

2. Experiment

The various amine based absorbents were tested in a screening apparatus (see Figure 1), where the relative rates of desorption and desorption capacity at pseudo equilibrium can be measured and compared to the MEA default case. The apparatus is designed to operate at atmospheric pressure and temperature up to 80 ^{o}C. In a typical experiment first the solvent was degassed for sufficient time and then saturated with pure CO_2 for approx. one hour. This saturation of solvent was performed at 30 ^{o}C and at atmospheric pressure. Once the solvent is completely saturated, a sample is taken to determine the total CO_2 loading in the solvent by desorption/titration procedure as described by Blawuhoff et al (1984). Once the total CO_2 loading is determined the known volume of a saturated amine sample of 40 ml is taken from the absorption column and is transferred into the desorption vessel. The temperature of the desorption vessel was maintained at 80 +/- 0.5 °C. To ensure that the temperature in the solution during desorption remained constant, the solution is stirred continuously with a constant speed in every experiment. Saturated solution reached 80 ^{o}C within approximate 2.5 minute.

The carbon dioxide released during this heating time is measured by a gas burette connected to desorption vessel. Once the temp is reached to 80 ^{o}C the valve of gas burette is closed and CO_2 is being measured by inline CO_2 IR detector. At this time pure N_2 gas is bubbled through the saturated absorbent to increase the interfacial area for CO_2 desorption. The vapour leaving the desorption vessel containing the CO_2 and N_2 passed into a vertical condenser. The condenser was at a temperature of 20 °C. The gas leaving the top of the condenser was at 25 +/- 1 °C and thus contained only about 3% of water vapour. Further in this outlet stream the N_2 gas is added for dilution. This diluted stream is passed through an ice trap with a temp of approximate 4 °C to remove the remaining amount of water vapour from the stream.

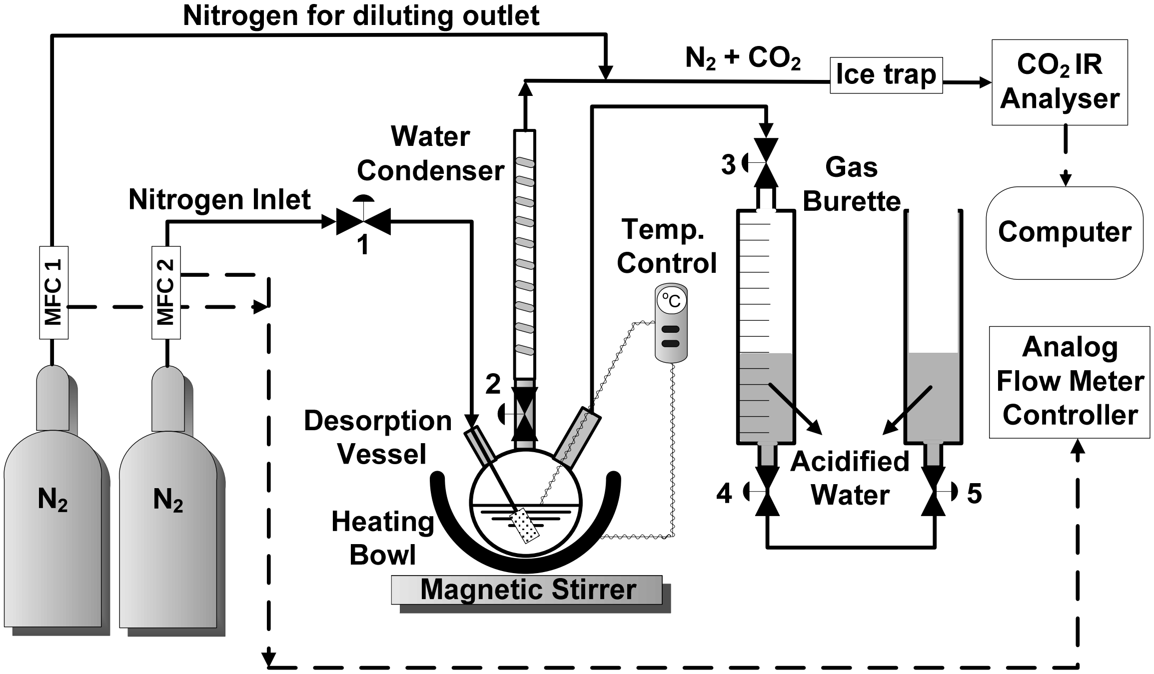


Figure 1, Schematic diagram of the experimental set-up for determining the desorption capacity of various amine based absorbents.

Then this stream is send to CO_2 IR detector where the amount of CO_2 in the stream is measured. To ensure that there was no significant depletion on the partial pressure of CO_2 during desorption experiment, the flow of N_2 gas is kept very low in the saturated absorbent. Hence the effect on CO_2 partial pressure was negligible in the desorption experiment. Therefore, whole desorption experiment was at prevailing atmospheric pressure, as the pressure-drop being very small. The N_2 flow in absorbent and for dilution is kept constant in every experiment. After a certain time in this desorption experiment when pseudo equilibrium is reached, the total CO_2 loading in the desorbed absorbent is determined by desorption/titration procedure as described by Blauwhoff et al (1984). The time for each desorption experiment is kept constant. The amine concentration in the solution could vary with the type of compound only to e.g. molecular weight and solubility. As default MEA was chosen for comparison with a concentration of 2.5 moles/litre.

3. Results and discussion

Examination of the desorption from a saturated amine based absorbent with pure CO_2, where desorption was reached for all absorbents within the experimental time frame, allows for a comparison of the initial desorption rates and desorption capacity defined as the amount of CO_2 that remains at experimental condition at the end of the experiment. From the initial desorption rate an indication can be obtained about the reactivity of various amine based absorbents. It must be noticed, however, that due to the mass transfer effects e.g. interfacial area and enhancement factor, that are contractor specific, no quantitative conclusions can be presented. However, the stirring speed of the absorbents was same, so differences would arise mainly due to the variations in physical properties, like e.g. interfacial tension, density, viscosity and heat of absorption, these are characteristics for each compound. The solvents with the lower desorption capacities are more suitable as they will decrease the solvent circulation rate in the CO_2 capture process. Hence, that will be economically beneficial for the whole CO_2 absorption process. Also the evaluation of the desorption rate at 80 ^{o}C will give the indication of more energy efficient absorbent, that might result in a decrease in energy cost for the CO_2 absorption process.

3.1 Effect of chain length in alkanolamine

In Figure 2 (a), 2 (b) and Table 1, the effect of an increase in the chain length between the amine and hydroxyl group on the desorption rate and capacity of an alkanolamine based absorbents is shown. In these experiments the chain length varied from two carbon chain (MEA) up to five (5-amino-1-pentanol) respectively. Figure 2 (a) shows the detailed overview of the desorption trend of CO_2 from aq. MEA. As it can be seen from the Figure 2 (a) that in the beginning from time 0 to 2.5 minute the desorption rate is influenced with an increasing temperature from that is starting from 30 ^{o}C and reaches up to 80 ^{o}C. The desorption rate is increasing with increase in temperature. Hence, in this region of the desorption is affected by combination of phenomenon; lower physical solubility, changing thermodynamics and increasing kinetics with temperature. It is clear that neither qualitative nor quantitative conclusions can be presented during this period of experiments.

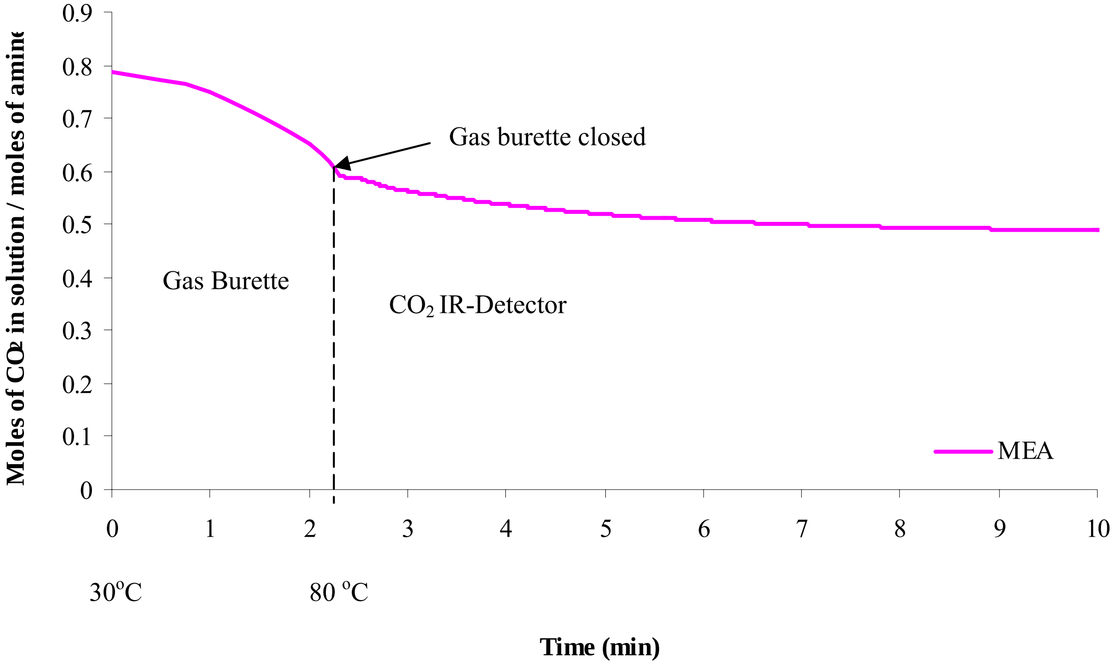


Figure 2 (a), Detailed overview on desorption of CO_2 from aq. MEA.

Once the temperature is reached at 80 °C the desorption rate would be more effected by chemical desorption. Therefore, the evaluation of initial desorption rate was done once the temperature in the absorbent was reached at 80 °C and remained constant. It should be noticed that the slope value of initial desorption rate was taken from the CO_2 concentration in moles/m3 sec unit. Due to the lower concentration of some absorbents results in the lower concentration of CO_2 in moles/m3. Hence, this might result in lower slope value of initial desorption rate in some absorbents.

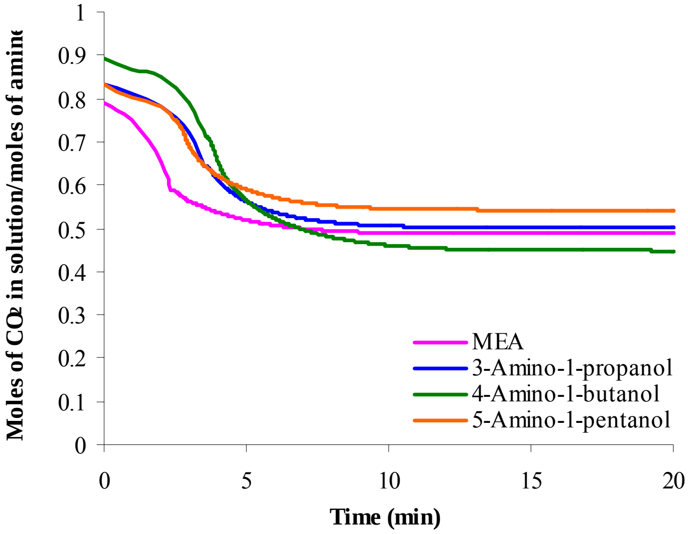
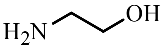
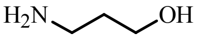
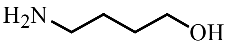
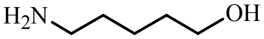


Figure 2 (b), Influence of the chain length in aq. alkanolamine based absorbent for the desorption of CO_2 .

Table 1, Capacity of aq. alkanolamine based absorbents; Absorption: A (moles CO_2 / moles amine)**, Desorption: B** (moles CO_2 / moles amine), **Slope value of initial desorption rate: C** (mole/m3 sec)**.**

Aqueous Absorbent	**CO_2 loading**		
	A	**B**	**C**
 Monoethanolamine	0.79	0.49	2.61E-2
 3-Amino-1-propanol	0.83	0.45	5.96E-2
 4-Amino-1-butanol	0.89	0.44	1.02E-1
 5-Amino-1-pentanol	0.83	0.54	4.08E-2

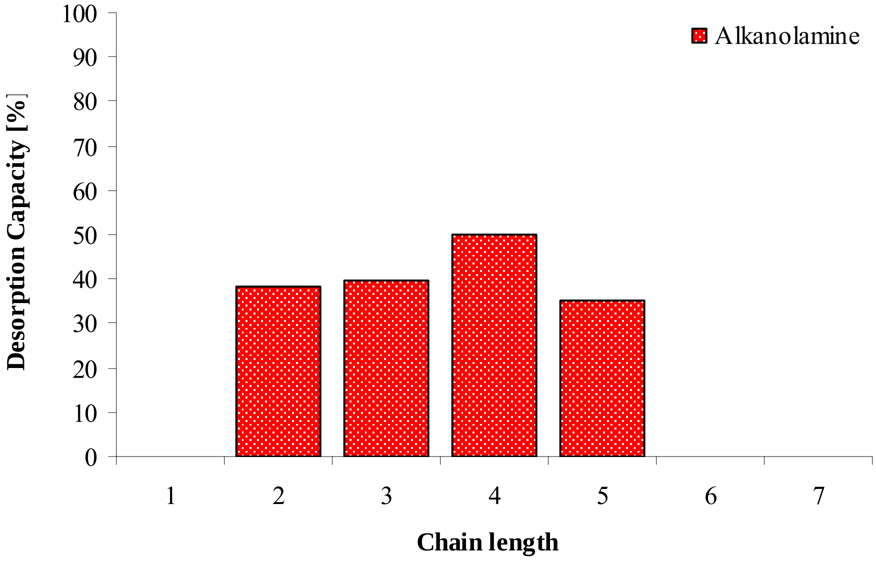


Figure 3, Influence of the chain length in aq. alkanolamine based absorbents on desorption capacity [%] of CO_2 at pseudo-equilibrium.

In Figure 2 (b), the overall results are presented. It must be noticed that the concentration of all alkanolamine was kept to 2.5 moles/litre. In MEA carbamate is the main product in CO_2 absorption, while bicarbonate and carbonate are present in very small quantities. The high loading in MEA of 0.79 moles of CO_2 / moles of amine occurred due to the conversion of the carbamate to bicarbonate and hence results in an increase in mole faction of CO_2 that is a result of physical absorption. The MEA absorption loading is in comparison with the results presented in literature Keh-Perng Shen et al. (1992). The effect of an increase in chain length on the initial desorption rate for alkanolamine is clearly shown in Figure 2 (b). It can be noticed that chain length up to 4 carbon (4-Amino-1-butanol) (see Table 1) showed an increase in initial desorption rate. Further increase in chain length decrease the initial desorption rate. At this stage no further qualitative analysis will be presented on the initial desorption rate. As the desorption rate is a complex interaction between mass transfer, kinetics and equilibrium. The interpretation is not as straight forward as was expected before hand.

Increase in the chain length results in a slight increase in CO_2 desorption capacity till four carbon up to 0.44 moles of CO_2 / moles of amine that is approximate 49 % of CO_2 is desorbed (see Figure 3 and Table 1). Further increase in chain length results in a decrease in desorption capacity. Hence, overall in alkanolamine the desorption capacity increases up to four carbon chain length also the initial desorption rate is increased.

3.2 Effect of chain length in alkylamines

In the experiment with alkylamine based solvents the chain length varied from two carbon chain (Ethylamine) up to six (Hexylamine) respectively. In Figure 4, the overall results are presented. It must be noticed that the concentration of alkylamine up to five carbon chain (N-pentylamine) was kept to 2.5 moles/litre. Due to the low solubility in water the concentration of six carbon chain (Hexylamine) was kept at 0.1 moles/litre. The influence of the chain length in alkylamines is shown in Figure 4, 5 and Table 2. Result shows that an initial desorption rate in alkyl amine increases gradually with an increase in chain length up to four carbon. Interestingly, the six carbon chain length absorbent (Hexylamine) was found to have a very fast desorption rate in the heating up period, as the most of the CO_2 is desorbed until temperature is reached to 80 ^{o}C. However, slope value of initial desorption rate is low (see Table 2) that cold be due to the lower concentration of hexylamine solution being used in the experiment. Hence, that results in lower concentration of CO_2 present in the absorbent in mole/m^3 sec unit. Still when comparing the initial desorption rate from Figure 4 in Hexylamine in CO_2 is fast to the others.

There can be two possible explanations for this behaviour, either the stability of hexylamine carbamate is very low, or there is hardly any formation of the carbamate in the solution, results into a higher concentration of bicarbonate and hence, generate faster CO_2 during desorption. From Figure 5 and Table 2, results shows that an increase in chain length from two carbon chain (Ethylamine) to three carbon chain (Propylamine) the CO_2 desorption capacity remains the same that is 30% of CO_2 is desorbed.

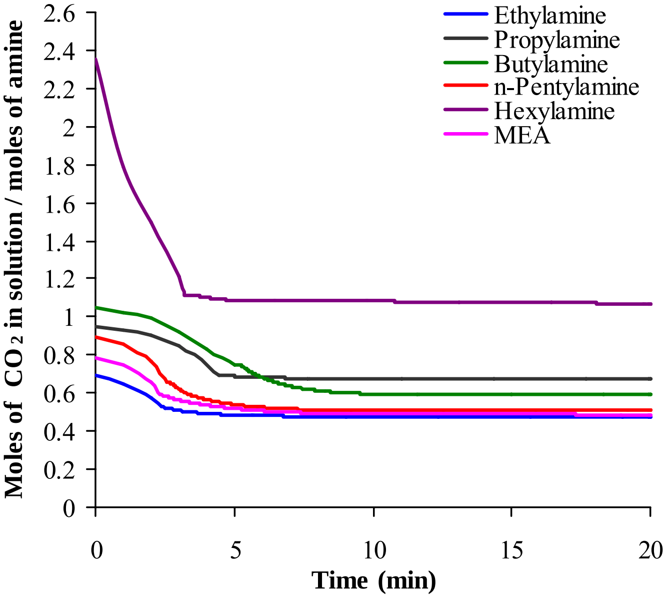
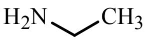
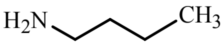
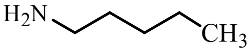
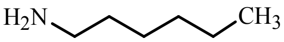
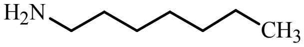


Figure 4, Influence of the chain length in aq. alkylamine based absorbent for the desorption of CO_2.

Table 2, Capacity of aq. alkylamine based absorbents; Absorption: A (moles CO_2 / moles amine)**, Desorption: B** (moles CO_2 / moles amine), **Slope value of initial desorption rate**: C (moles/m3 sec**.**

Aqueous Absorbent	**CO_2 loading**		
	A	**B**	**C**
 Ethylamine	0.69	0.48	2.94E-2
 Propylamine	0.97	0.68	1.46E-1
 Butylamine	1.07	0.59	1.44E-1
 N-pentylamine	0.90	0.51	3.16E-2
 Hexylamine	2.36	1.07	2.45E-2

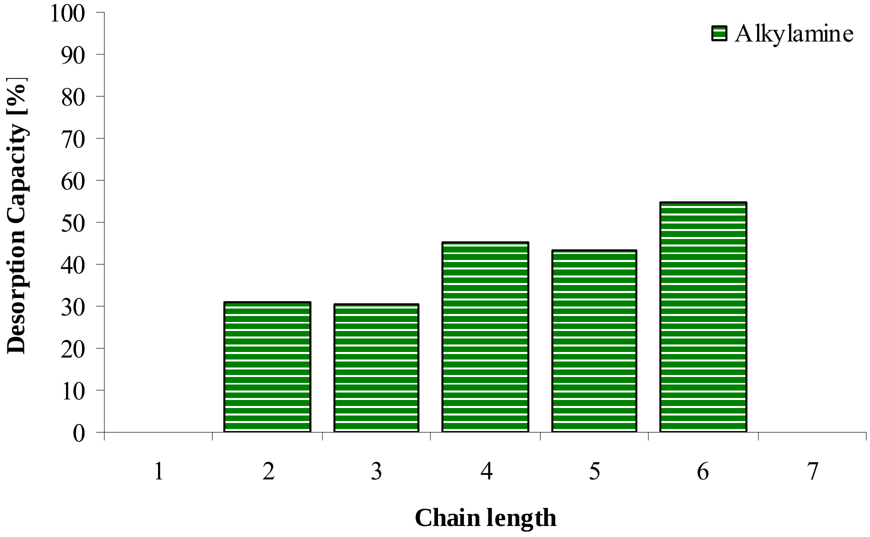


Figure 5, Influence of the chain length in aq. Alkanolamine based absorbents on desorption capacity [%] of CO_2 at pseudo-equilibrium.

Further increase in chain length desorption capacity is increased as in four carbon chain (Butylamine) in which 45% of CO_2 is desorbed. Whereas, with six carbon chain length (hexylamine) the desorption capacity is highest up to 1.07 moles of CO_2 / moles of amine that is 54% CO_2 is desorbed.

3.3 Effect of chain length in diamines

In the diamine experiments the chain length varied from two carbon chain (Ethylenediamine) up to seven (1, 7-Diaminoheptane) respectively. In Figure 6 the overall results are presented. It must be noticed that the concentration of diamine up to six carbon chain (Hexadimethylenediamine) was kept to 2.5 moles/litre. Due to the low solubility in water the concentration of seven carbon chain length absorbent (1, 7-Diaminoheptane) was kept at 1.5 moles/litre. Figure 6, 7 and Table 3, shows that an increase in chain length decreases the initial desorption rate in diamines up to three carbon chain length (1,3-Diaminopropane).

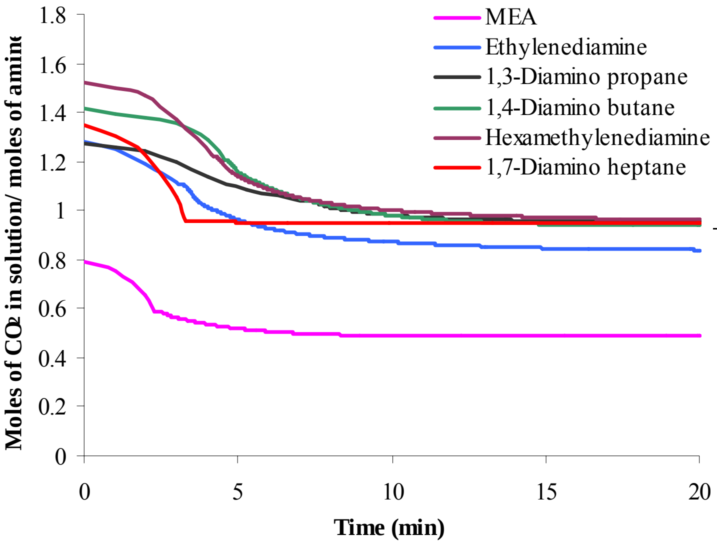
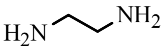
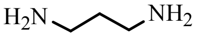
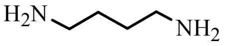
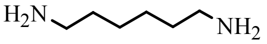
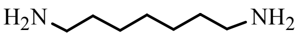


Figure 6, Influence of the chain length in aq. diamine based absorbent for the desorption of CO_2.

Table 3, Capacity of aq. diamine based absorbents; Absorption: A (moles CO_2 / moles amine)**, Desorption: B** (moles CO_2 / moles amine), **Slope value of initial desorption rate: C** (mole/ m^3 sec)**.**

Aqueous Absorbent	**CO_2 loading**		
	A	**B**	**C**
 Ethylenediamine	1.28	0.84	8.51E-2
 1,3-Diamino propane	1.27	0.94	5.38E-2
 1,4-Diaminobutane	1.42	0.94	9.20E-2
 Hexadimethylenediamine	1.52	0.95	9.66E-2
 1,7-Diaminoheptane	1.35	0.95	6.80E-3

However, further increase in chain length from four (1,4-Diamino butane) up to six carbon (Hexadimethylenediamine) results in an increase in initial desorption rate (see Table 3). Higher chain length with seven carbon results in a decreased initial desorption rate (1,7-Diaminoheptane). Hence, from these results it can be noticed that the Ethylenediamine and Hexadimethylenediamine could thus have a greater potential for CO_2 desorption as they have showed the higher initial desorption rate.

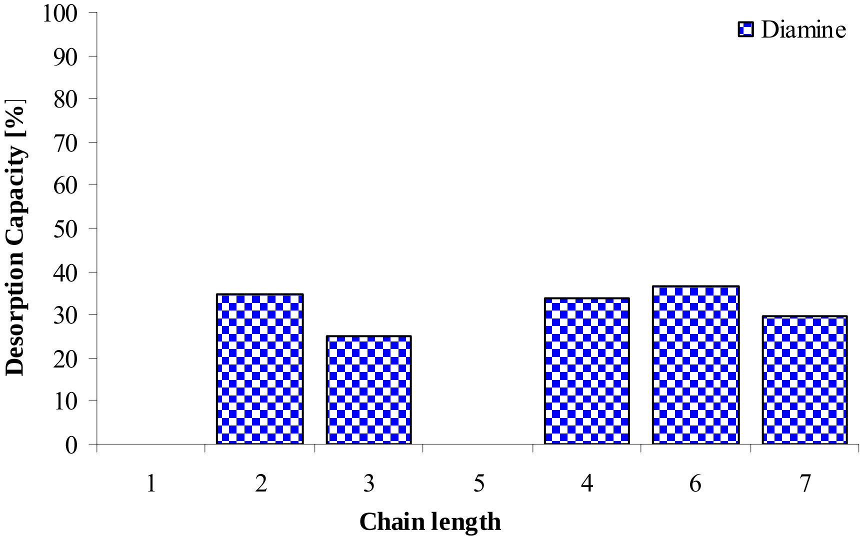


Figure 7, Influence of the chain length in aq. diamine on desorption capacity [%] of CO_2 at pseudo-equilibrium.

An increase in the chain length in diamine based absorbent results in an increase in desorption capacity as can be noticed in Hexadimethylenediamine is up to 0.95 moles CO_2 / moles diamine that is approximate 36 % of CO_2 is desorbed (see Figure 7 and Table 3). This might be very well caused by the decrease in the stability of the carbamate with an increase in the chain length. Therefore, the bicarbonate concentration is higher and hence, higher amount of CO_2 is released.

Interesting comparison could be made on the effect of an increase in chain length in alkanolamine, alkylamine and diamine from Figure 3, 5 and 7. It can be noticed that in alkanolamine the desorption capacity is increased up to more than 50% of CO_2 is desorbed, when chain length is increased up to 4 carbon (4-Amino-1-butanol). Whereas in alkylamines the CO_2 desorption capacity is highest with six carbon chain length (Hexylamine) up to 50% of CO_2 is desorbed. In diamine based absorbents there is a slight increase in desorption capacity up to six carbon chain length (Hexadimethylenediamine) with a desorption capacity of around 40% CO_2 is desorbed. Overall comparison shows that alkanolamine with four carbon chain length and alkylamine with six carbon chain length has the highest CO_2 desorption capacity. Therefore, from these results it is clear that the structural effect is important in the behaviour of amine based absorbents for CO_2 desorption.

3.4 Effect of side chain

The position of different functional groups in the structure of various amine based absorbents is an important factor. In Figure 8, 9 and Table 4 the effect of the position of substituted hydroxyl group is compared. It should be noticed that the concentration for 3-Amino-1-propanol, and 2-Amino 1-butanol was kept at 2.5 moles/litre, whereas concentration used for 1-Amino 2-propanol was 0.5 moles/litre.

In these experiments the hydroxyl group is positioned at α-carbon (1-Amino 2-propanol) and β-carbon (2-Amino 1-butanol) to the amine group in the absorbent structure is investigated.

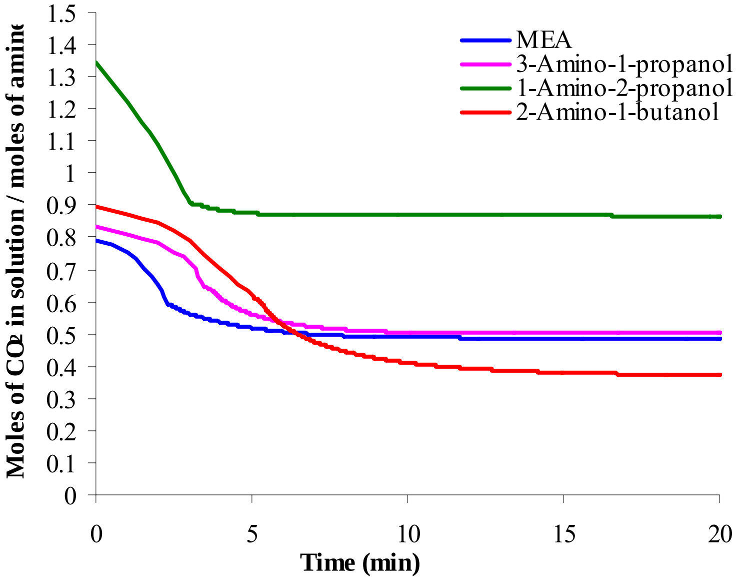
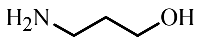
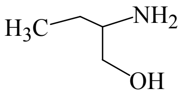
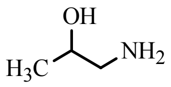


Figure 8, Influence of the hydroxyl group position in aq. alkanolamine based absorbent for the desorption of CO_2.

Table 4, Capacity of aq. alkanolamine based absorbents; Absorption: A (moles CO_2 / moles amine)**, Desorption: B** (moles CO_2 / moles amine), **Slope value of initial desorption rate: C** (mole/m^3 sec)**.**

Aqueous Absorbent	**CO_2 loading**		
	A	**B**	**C**
 3-Amino-1-propanol	0.83	0.50	5.96E-2
 1-Amino-2-propanol	1.34	0.86	1.35E-1
 2-Amino-1-butanol	0.89	0.37	5.30E-2

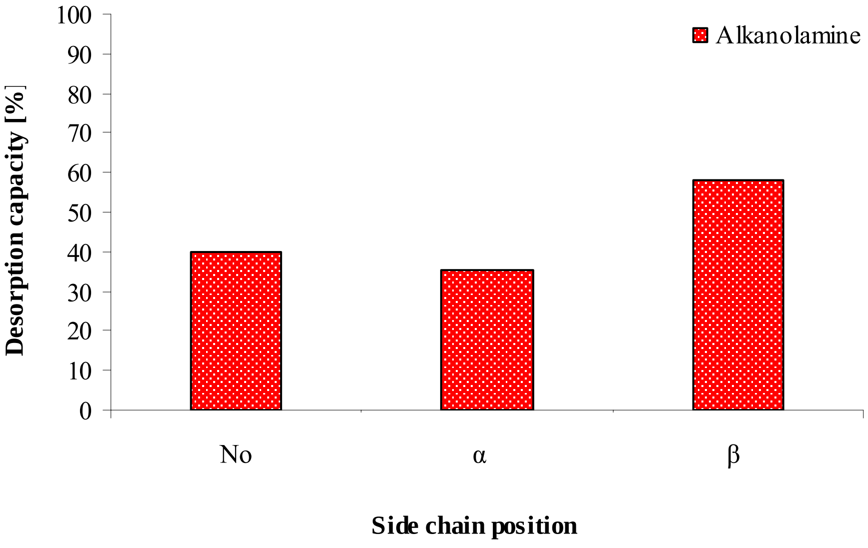


Figure 9, Influence of the hydroxyl group position in aq. alkanolamine on desorption capacity [%] of CO_2 at pseudo-equilibrium.

Figure 8, shows that the hydroxyl group substitution on α-carbon (1-Amino 2-propanol) to the amine group an increase in initial desorption rate when compared with hydroxyl group substitution on β-carbon (2-Amino-1-butanol) (see Table 4). These results explain the effect of steric hindrance caused at the amine group. At this stage no further qualitative analysis will be presented on the initial desorption rate. As the desorption rate is a complex interaction between mass transfer, kinetics and equilibrium. The interpretation is not as straight forward as was expected before hand.From Figure 8 and 9 it must be noticed that a substitution of a hydroxyl group on the β-carbon (1-Amino-2-propanol) to the amine group increases the desorption capacity up to 0.37 moles CO_2/moles amine that is approximate 58 % of CO_2 is desorbed when compared with the hydroxyl group substitution on α-carbon (2-Amino-1-butanol) which has desorption capacity of 0.86 moles CO_2/moles amine (see Table 4) that is 35 % of CO_2 is desorbed. It is clear from these results that the hydroxyl group substitution at β-carbon (1-Amino 2-propanol) to the amine group shows an increase in desorption capacity.

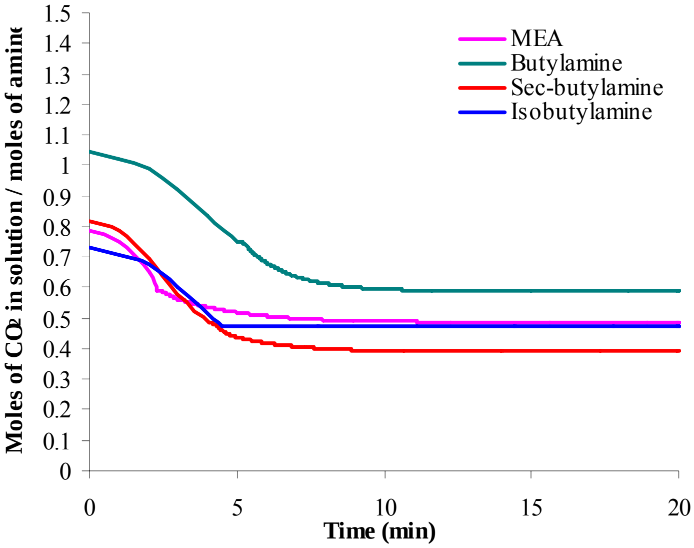
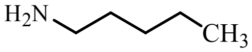
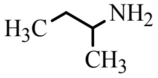
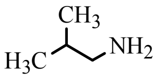


Figure 10, Influence of a methyl group position in aq. alkylamine based absorbent for the desorption of CO_2.

Table 5, Capacity of aq. alkylamine based absorbents; Absorption: A (moles CO_2 / moles amine)**, Desorption: B** (moles CO_2 / moles amine), **Slope value of initial desorption rate: C** (mole/m^3 sec)**.**

Aqueous Absorbent	**CO_2 loading**		
	A	**B**	**C**
 Butylamine	1.07	0.59	1.44E-1
 Sec-butylamine	0.85	0.39	1.04E-1
 Isobutylamine	0.73	0.47	1.90E-3

Furthermore the effect of methyl group substitution at the α or β-carbon to amine group in alkylamine were also investigated (see Figure 10, 11 and Table 5). The concentration of Butylamine, Sec-butylamine and Isobutylamine used in these experiment was 2.5 moles/litre. Figure 10, shows the effect of alkyl group substitution on initial desorption rate. Results shows that the alkyl group substitution on α-carbon (Sec-butylamine) to amine group is having higher initial desorption rate when compared with alkyl group substituted at β-carbon to amine group (Isobutylamine). The higher initial desorption rate in Sec-butylamine might be caused by the effect of steric hinderance at the amine group that causes the faster breaking of the C-N bond and results in an increases of the initial desorption rate. Figure 10 and 11 shows the overall results from alkyl substituted absorbents. It can be noticed that the substitution of alkyl group at α-carbon (Sec-butylamine) to amine group increases the desorption capacity upto 0.39 moles CO_2/moles amine that is 54 % of CO_2 is desorbed, when compared with alkyl group substitution on β carbon to amine group (Isobutylamine) which has the desorption loading of 0.47 moles CO_2/moles amine (see Table 5) in which only 35 % of CO_2 is desorbed (see Figure 11).

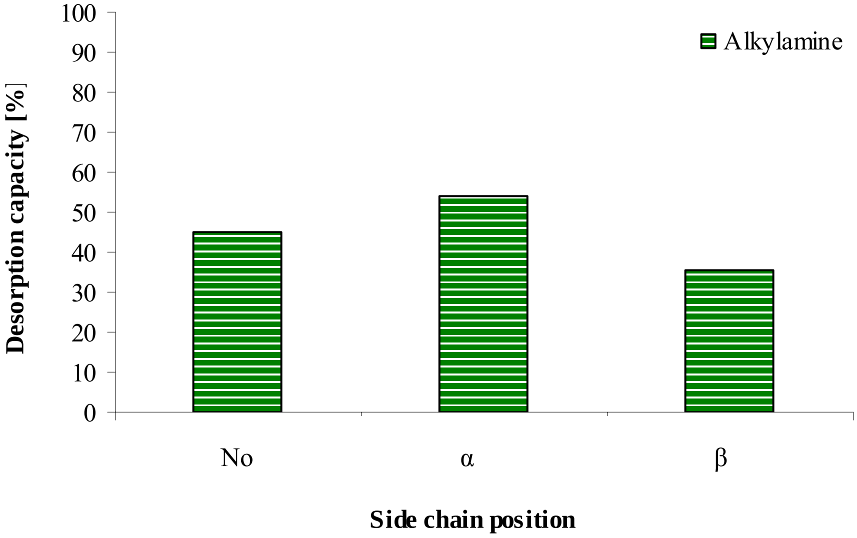


Figure 11, Influence of the alkyl group position in aq. alkylamine on desorption capacity [%] of CO_2 at pseudo-equilibrium.

This effect might be due to the fact that the alkyl group substitution at the α-carbon to the amine group creates steric hindrance at the reaction site and thus lowers the stability of carbamate. That can cause enhanced hydrolysis of carbamate and hence, driving equilibrium towards bicarbonate. Therefore, higher amount of bicarbonate present in the system causes higher amount of CO_2 release during desorption.

Influence of amine group substitution by side chain in diamine based absorbents is also investigated. Figure 12 shows the overall desorption results. It should be noticed that the concentration of 1,2-Diamino propane and 1,3-Diamino propane was kept at 2.5 moles/litre. The results from Figure 12 shows that there is a slight decrease in an initial desorption rate when amine group is substituted at the β-carbon to amine group (1, 2-Diamino propane) in structure (see Table 6).

Figure 12 and 13 it can be noticed that the amine group substitution at the β-carbon to amine group (1,2-Diamino propane) in the structure cause an increase in desorption capacity up to 0.74 moles CO_2/moles amine that is approximate 33 % CO_2 is desorbed when compared with the non-substituted (1, 3-Diamino propane) with desorption capacity of 0.91 moles CO_2/moles amine (see Table 6) that is only 25 % CO_2 is desorbed. Hence, amine group substitution on β-carbon to amine group by side chain in the structure results in an increase in desorption capacity whereas desorption rate is slightly decreased.

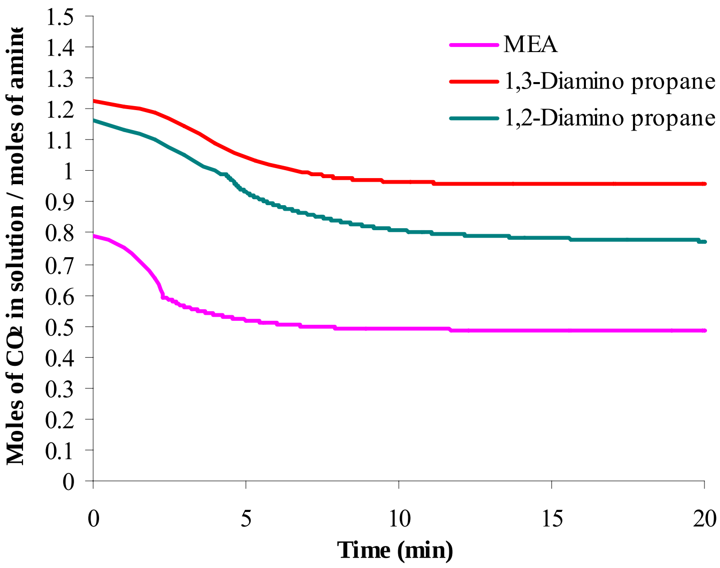
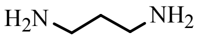
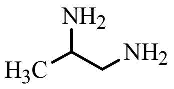


Figure 12, Influence of amine group position in aq. diamine based absorbent for the desorption of CO_2.

Table 6, Capacity of aq. diamine based absorbents; Absorption: A (moles CO_2 / moles amine)**, Desorption: B** (moles CO_2 / moles amine), **Slope value of initial desorption rate: C** (mole/m^3 sec)**.**

Aqueous Absorbent	**CO_2 loading**		
	A	**B**	**C**
 1,3-Diamino propane	1.27	0.91	5.38E-2
 1,2-Diamino propane	1.16	0.74	9.54E-3

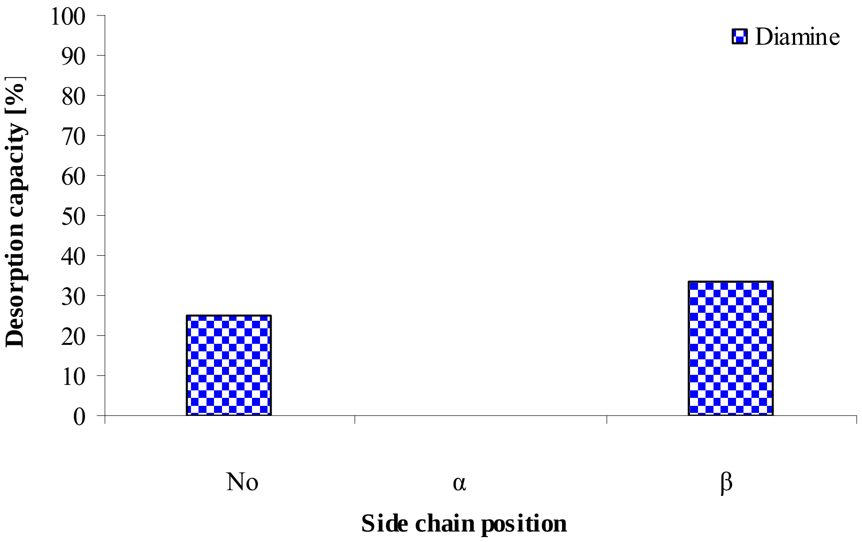


Figure 13, Influence of the amine group position in aq. diamine on desorption capacity [%] of CO_2 at pseudo-equilibrium.

The results from Figure 9, 11 and 13 was compared to investigate the effect of position of various functional group by side chain in amine based absorbents. It can be noticed from these results that substitution of an alkyl group with side chain at α-carbon to the amine group in structure results in an increase in desorption capacity whereas in alkanolamine and diamine substitution of a hydroxyl and amine group respectively by side chain at the β-carbon to amine group results in an increase in desorption capacity. However hydroxyl group substitution at the β-carbon to amine group (2-amino 1-butanol), is having the highest desorption capacity around 60% of CO_2 is desorbed.

3.5 Effect of number of functional groups

The effect of an increase in the number of amine group was investigated. It should be noticed that the concentration of Ethylenediamine, Diethylenetriamine and Trietheylenetetramine was kept at 2.5 moles/litre. Whereas due to high viscosity of Tetraethylenepentamine, the concentration used for this absorbent was kept at 0.5 moles/litre. Figure 14, 15 and Table 7, shows the result from the effect of an increase in number of amine group in the absorbent structure. Results from Figure 14 shows that an increase in the number of amine groups increases the initial desorption rate (see Table 7). This might be caused by increase in number of amine group creates more reaction sites available for the reaction with CO_2. Therefore more CO_2 could be present in bicarbonate form and increases in faster release of CO_2 in desorption. Still when compared the initial desorption rate of 4 and 5 amine group in the structure there is no further enhancement of the initial desorption rate.

Results from Figure 14 and 15 shows that an increase in number of amine groups from 2 (Ethylenediamine) up to 5 (Tetraethylenepentamine) shows an increase in desorption capacity.

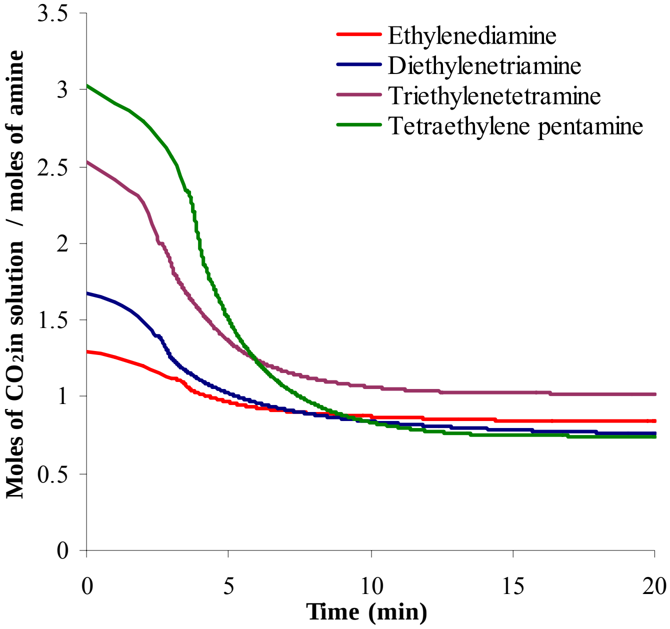
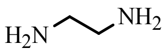
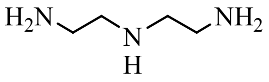
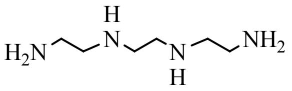
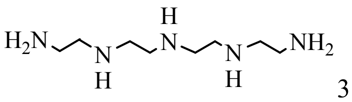


Figure 14, Influence of the number of amine groups in aq. amine based absorbent for the desorption of CO_2.

Table 7, Capacity of aq. amine based absorbents; Absorption: A (moles CO_2 / moles amine)**, Desorption: B** (moles CO_2 / moles amine), **Slope value of initial desorption rate: C** (mole/m^3 sec)**.**

Aqueous Absorbent	**CO_2 loading**		
	A	**B**	**C**
 Ethylenediamine	1.08	0.84	8.51E-2
 Diethylenetriamine	1.83	0.76	1.54E-1
 Trietheylenetetramine	2.51	1.02	3.67E-1
 Tetraethylenepentamine	3.03	0.74	3.18E-1

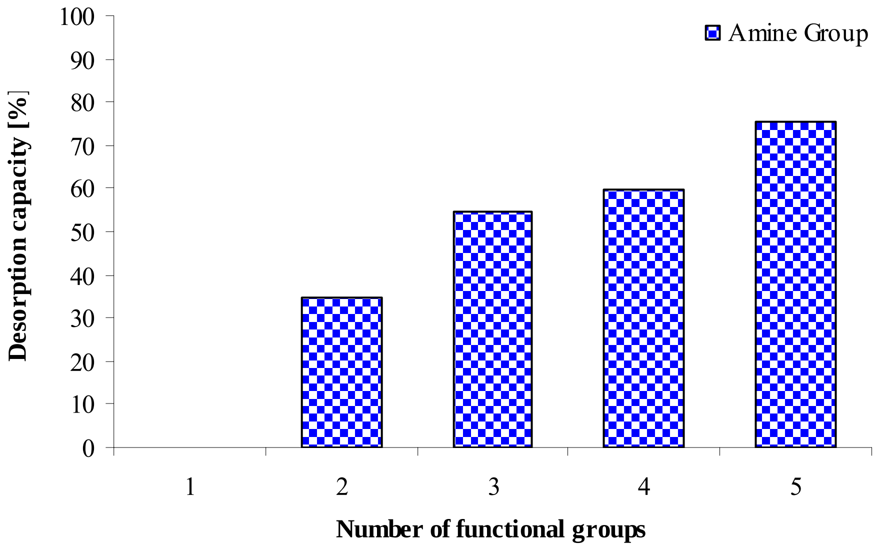


Figure 15, Influence of the number of amine groups in aq. amine based for the desorption capacity [%] of CO_2 at pseudo-equilibrium.

In Tetraethylenepentamine desorption capacity reaches up to 0.74 moles CO_2/moles amine that is approximate 75 % of CO_2 is desorbed. Hence, higher number of amine group present in absorbent structure results in an increase in desorption capacity.

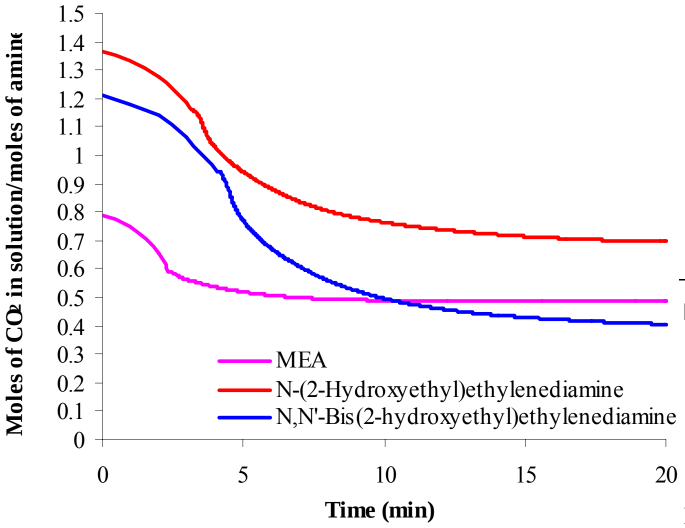
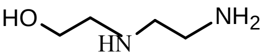
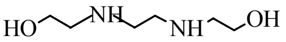


Figure 16, Influence of the number of OH group in aq. diamine based absorbent for the desorption of CO_2 .

Table 8, Capacity of aq. diamine based absorbents; Absorption: A (moles CO_2 / moles amine)**, Desorption: B** (moles CO_2 / moles amine), **Slope value of initial desorption rate: C** (mole/m^3 sec)**.**

Aqueous Absorbent	**CO_2 loading**		
	A	**B**	**C**
 N-(2-Hydroxyethyl) ethylenediamine	1.36	0.70	1.20E-1
 N,N'-Bis(2-hydroxyethyl) ethylenediamine	1.21	0.41	1.94E-1

The effect of increase in number of hydroxyl group was also investigated. It should be noticed that the concentration of N-(2-hydroxyethyl) Ethylenediamine and N,N'-Bis (2-hydroxyethyl) ethylenediamine) is kept at 2.5 moles /litre. Results from diamine based alkanolamine absorbent with one (N-(2-Hydroxyethyl) ethylenediamine) and two hydroxyl groups (N,N'-Bis (2-hydroxyethyl) ethylenediamine) is presented in Figure 16, 17 and Table 8. When compared the initial desorption rate of one and two hydroxyl group diamine absorbent the absorbent with two hydroxyl group present in structure is having slightly higher initial desorption rate. This increase in initial desorption rate could be caused by the effect of steric hinderance at the reaction site that is created by hydroxyl group results in faster release of CO_2.

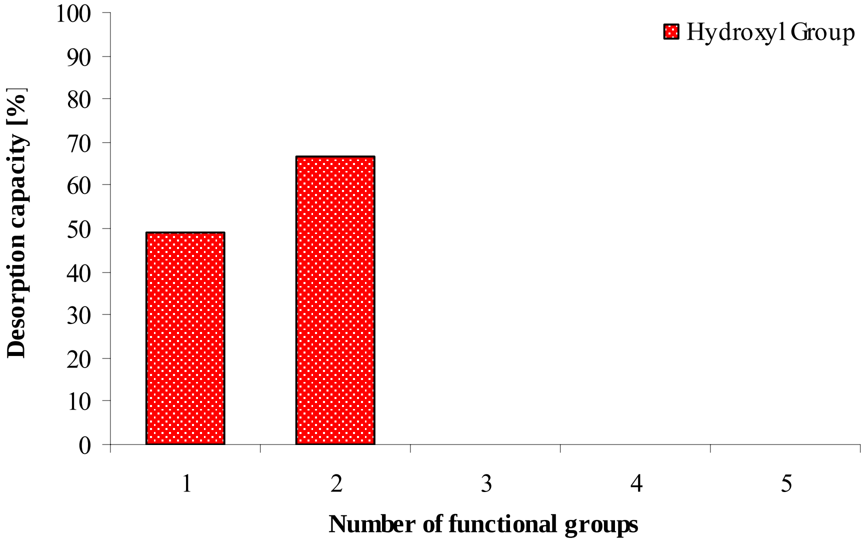


Figure 17, Influence of the number of amine groups in aq. amine based absorbent for the desorption capacity [%] of CO_2 at pseudo-equilibrium.

Figure 17 shows that increase in number of hydroxyl group in diamine absorbent increases desorption capacity as in (N,N'-Bis(2-hydroxyethyl)ethylenediamine) desorption loading is reached upto 0.41 moles CO_2/moles amine that is approximate 66 % of CO_2 is desorbed. This might be caused by the presence of steric hindrance effect around both amine group when two hydroxyl groups are present (N,N'-Bis(2-hydroxyethyl)ethylenediamine). Hence, results in an increased amount of CO_2 released in desorption.

While comparing the effect of increase in number of different function group on their the desorption capacity from Figure 14 and 17, absorbent with five amine group present in structure is having the highest desorption capacity of around 75 % where as absorbent with two hydroxyl group desorption capacity is close to 66 %. Therefore from these results it can be noticed that an increase in number of amine group and hydroxyl group enhances the desorption capacity of CO_2 in amine based absorbents.

3.3 Effect of functional groups in cyclic amines

Cyclic amines are potential absorbents for CO_2 absorption due to their fast absorption rate and higher absorption capacity. Therefore, the effect of different substituted saturated and unsaturated cyclic amines was investigated. In Figure 18, 19 (a), 19 (b) and Table 9 the comparison between saturated monoamine and similar compounds, substituted with an alkyl and amine groups is presented.

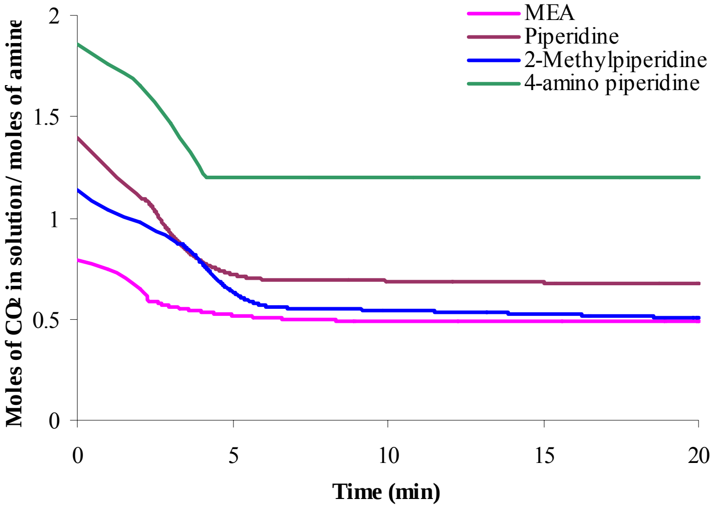
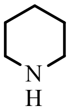
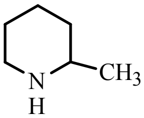
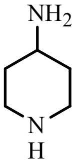


Figure 18, Influence of a substitution on aq. saturated cyclic monoamines for the desorption of CO_2.

Table 9, Capacity of aq. saturated cyclic monoamine based absorbents; Absorption: A (moles CO_2 / moles amine)**, Desorption: B** (moles CO_2 / moles amine), **Slope value of initial desorption rate: C** (mole/m^3 sec)**.**

Aqueous Absorbent	**CO_2 loading**		
	A	**B**	**C**
 Piperidine	1.40	0.67	4.57E-1
 2-Methylpiperidine	1.14	0.50	3.01E-1
 4-Aminopiperidine	1.90	1.20	7.39E-1

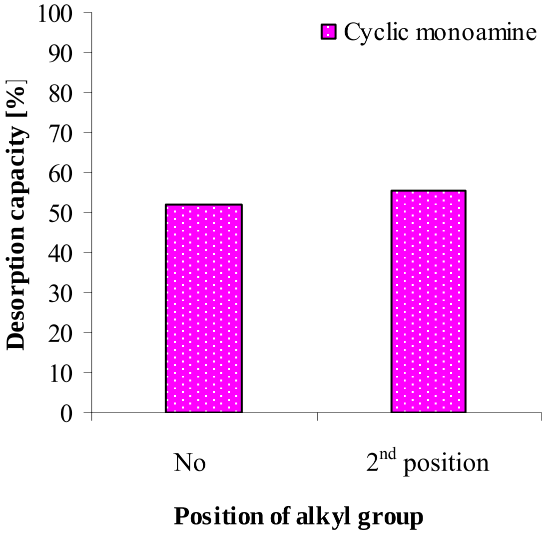


Figure 19 (a), Influence of alkyl group substitution in aq. saturated cyclic monoamine on desorption capacity [%] of CO_2 at pseudo-equilibrium.

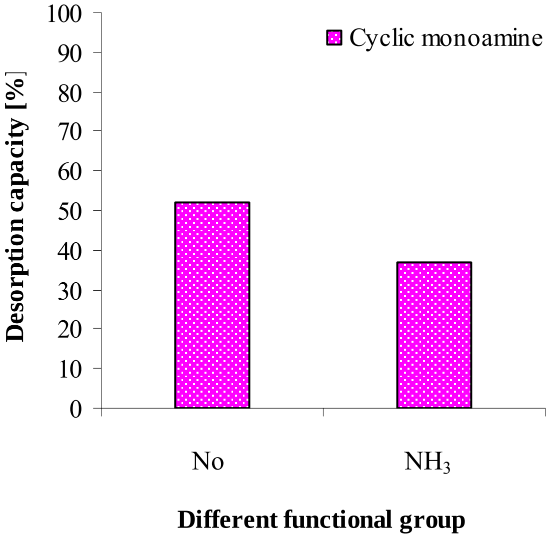


Figure 19 (b), Influence of amine group substitution in aq. saturated cyclic monoamine on desorption capacity [%] of CO_2 at pseudo-equilibrium.

It must be noticed that the concentration of Piperidine and 2-Methylpiperidine and 4-Amino piperidine was kept to be at 0.5 mole/litre. From the results in Figure 18 and Table 9 it can be noticed that the initial desorption rate is increased with a substitution of an amine group at the saturated ring (4-Amino piperidine). This could be caused by the effect of amine group substitution at saturated cyclic ring increase the formation of carbonate in the solution and hence, results in faster initial desorption rate. Whereas, substitution of methyl group at the second position in the saturated ring (2-Methyl piperidine) results in a slight decrease in initial desorption rate.

Results from Figure 18 and 19 (a) and 19 (b) shows that the substitution of methyl group at the second position in the saturated ring (2-Methyl piperidine) slightly increases the desorption capacity 0.50 moles of CO_2/moles of amine (see Table 9), that is approximate 55% of CO_2 is desorbed. Where as substitution of an amine group by side chain at the saturated ring (4-Amino piperidine) decreases the desorption capacity 1.20 moles of CO_2/moles of amine (see Table 9) that is 37 % of CO_2 is desorbed.

In Figure 20, 21 and Table 10 the effect of a methyl group substitution on saturated cyclic diamines is presented. It should be noticed that the concentration of Piperazine, 2-Methylpiperazine and Trans piperazine, 2,5-Dimethyl was kept to be at 0.5 moles/liter in these experiment. From Figure 20, it can be noticed that the initial desorption rate of Trans piperazine, 2,5-Dimethyl is slightly higher than 2-Methyl piperazine.

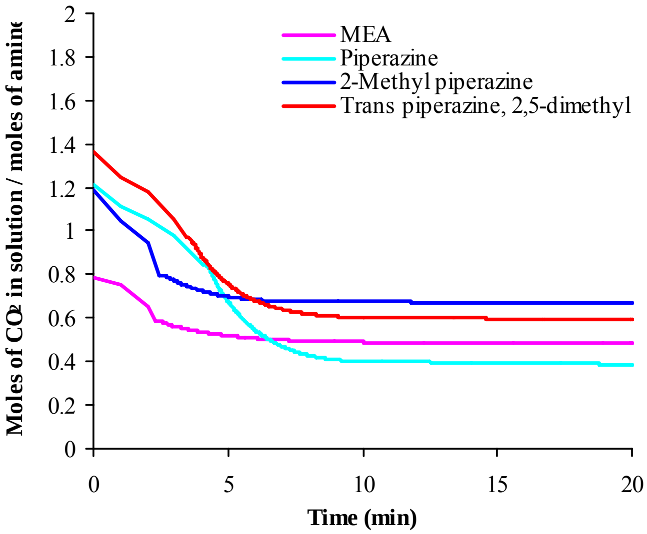
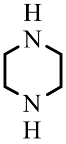
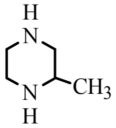
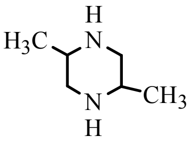


Figure 20, Influence of a alkyl group substitution on aq. saturated cyclic diamine based absorbent for the desorption of CO_2.

Table 10, Capacity of aq. saturated cyclic diamine based absorbents; Absorption: A (moles CO_2 / moles amine)**, Desorption: B** (moles CO_2 / moles amine), **Slope value of initial desorption rate: C** (mole/m^3 sec)**.**

Aqueous Absorbent	**CO_2 loading**		
	A	**B**	**C**
 Piperazine	1.30	0.40	6.08E-2
 2-Methyl piperazine	1.19	0.67	1.30E-2
 Trans piperazine, 2,5-dimethyl	1.36	0.59	4.08E-2

This could be caused due to the substituted two methyl groups has a highly electronegative function. That can favour the accessibility of the lone-pair electrons of the amine group for CO_2. Hence, higher carbonate present in the system that cause faster CO_2 desorption. Still nonsubstituted cyclic diamine was noticed to have high initial desorption rate (see Table 10). Results from Figure 20, 21 and Table 10 shows that a substitution of one methyl group in the saturated ring at 2nd carbon position (2-Methyl piperazine) decreases the desorption capacity upto 0.67 moles of CO_2/moles of amine that is approximate 43 % of CO_2 is desorbed, whereas when compared with two methyl group substitution on 2nd and 5th position in the saturated ring (Trans piperazine, 2,5-dimethyl) upto 0.59 moles of CO_2/moles of amine that is 56% of CO_2 is desorbed. It was also noticed that the nonsubstituted saturated amine (Piperazine) has the highest desorption capacity compared to substituted saturated cyclic amine that reaches upto 0.40 moles of CO_2 /moles of amine that is approximate 70% of CO_2 is desorbed.

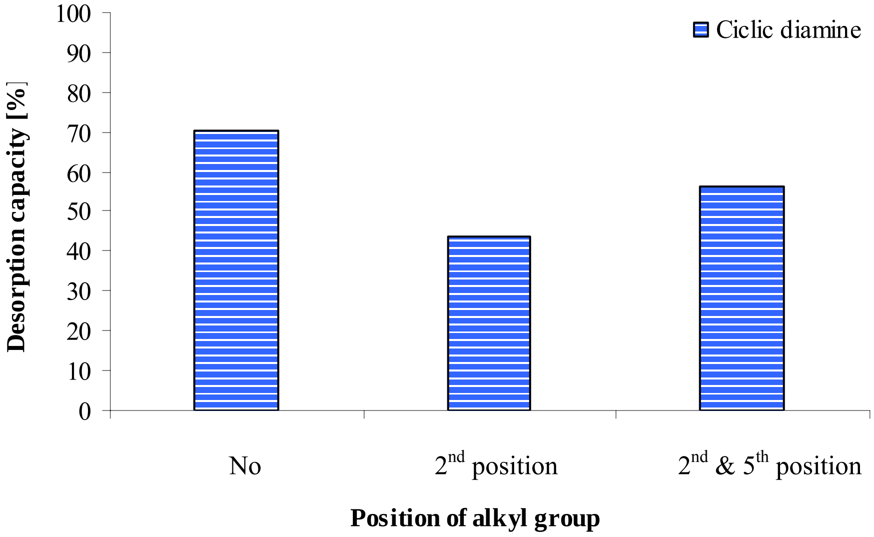


Figure 21, Influence of the position of alkyl group in aq. saturated cyclic diamine based absorbent on desorption capacity [%] of CO_2 at pseudo-equilibrium.

The effect of different functional groups in aromatic diamines was also investigated. Figure 22, 23 and Table 11 shows the effect of substitution of amine, alkyl and hydroxyl group at the saturated cyclic diamine compound. It should be noticed that the concentration of N-ethylpiperazine, 2-(1-Piperazinyl) ethylamine and 2-(1-Piperazinyl) ethanolamine was kept to be 1 moles/litre.

Results from Figure 22 and Table 11 shows that the substitution of amine group in saturated cyclic diamine increases the initial desorption rate. The desorption loading of the saturated cyclic diamines substituted with an amine, alkyl or hydroxyl group were 0.69, 0.65 and 0.38 moles CO_2 / moles amine, respectively (see Table 11). From these results it is clear that an amine group (2-(1-Piperazinyl)ethylamine) and hydroxyl group (2-(1-Piperazinyl)ethanol) substitution in saturated cyclic diamine is having higher desorption capacity of approximate 66 % and 58 % of CO_2 is desorbed compared to alkyl group substituted saturated cyclic diamine (N-ethyl piperazine) in which 51% of CO_2 is desorbed (see Figure 23).

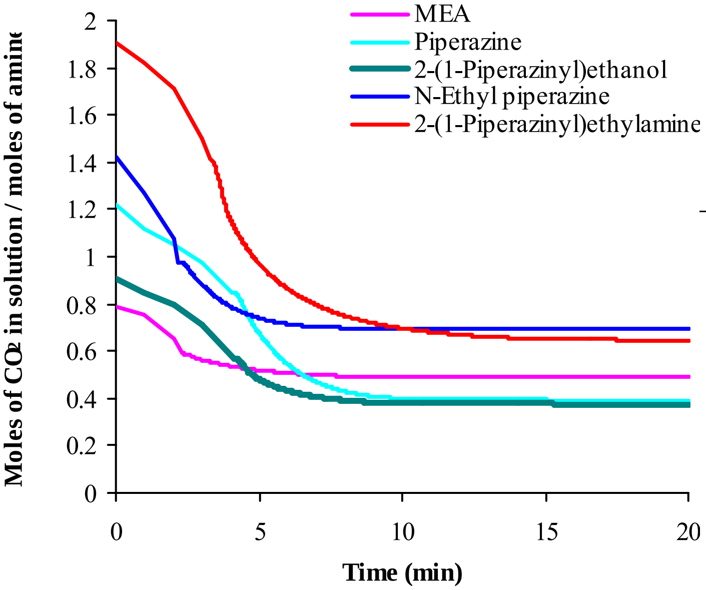
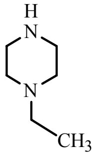
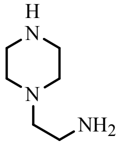
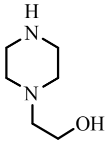


Figure 22, Influence of a side chain on aq. saturated cyclic diamine based absorbent for the desorption of CO_2.

Table 11, Capacity of aq. saturated cyclic diamine based absorbents; Absorption: A (moles CO_2 / moles amine)**, Desorption: B** (moles CO_2 / moles amine), **Slope value of initial desorption rate: C** (mole/m^3 sec)**.**

Aqueous Absorbent	**CO_2 loading**		
	A	**B**	**C**
 N-ethylpiperazine	1.43	0.69	5.01E-2
 2-(1-Piperazinyl) ethylamine	1.90	0.65	1.20E-1
 2-(1-Piperazinyl)ethanol	0.90	0.38	5.69E-2

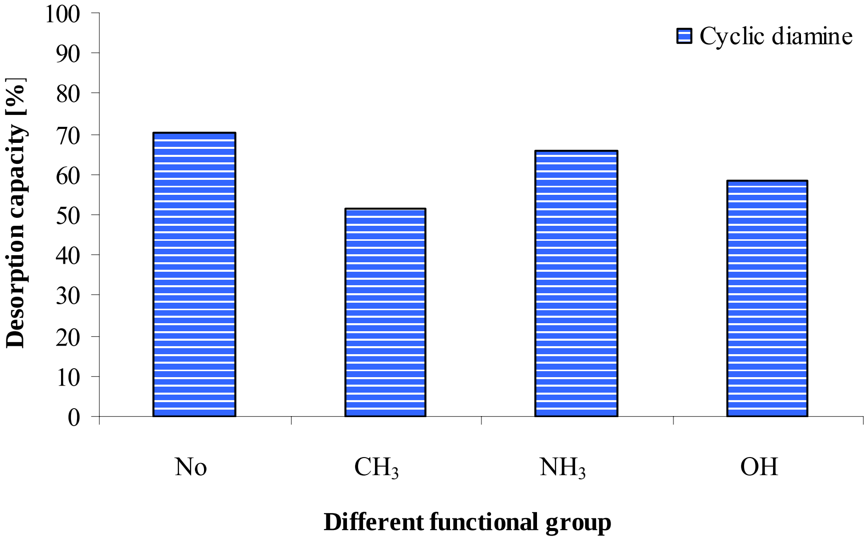


Figure 23, Influence of the different functional groups substitution on saturated cyclic diamine on desorption capacity [%] of CO_2 at pseudo-equilibrium.

Hence, amine group is more suitable substituted functional groups to enhance the initial desorption rate. Still nonsubstituted saturated diamine is having the higher desorption capacity. Whereas with hydroxyl and alkyl group substitution results in a slight decrease in the initial desorption rate (see Table 11). Comparision could be made from the results for mono, di saturated cyclic amine and similar compounds substituted with different functional groups from Figure 21 and 23. Results shows that the nonsubstituted saturated diamine absorbent is having the highest desorption capacity.

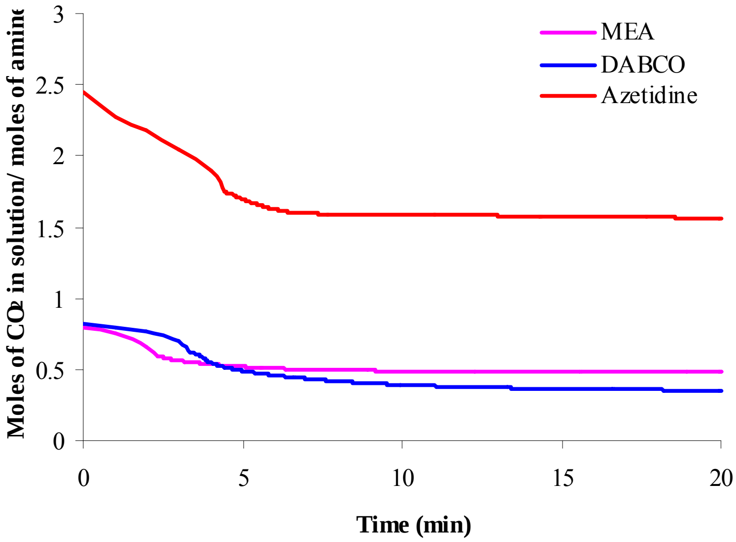
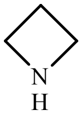
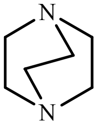


Figure 24, Comparison of various ring shape structure for the desorption of CO_2 in aq. absorbents.

Table 12, Capacity of various shape absorbent; Absorption: A (moles CO_2 / moles amine)**, Desorption: B** (moles CO_2 / moles amine), **Slope value of initial desorption rate: C** (mole/m^3 sec)**.**

Aqueous Absorbent		**CO_2 loading**		
		A	**B**	**C**
	Azetidine	2.45	1.56	1.80E-2
	DABCO Or 1,4-Diazabicyclo [2.2.2]octane	0.83	0.35	5.95E-2

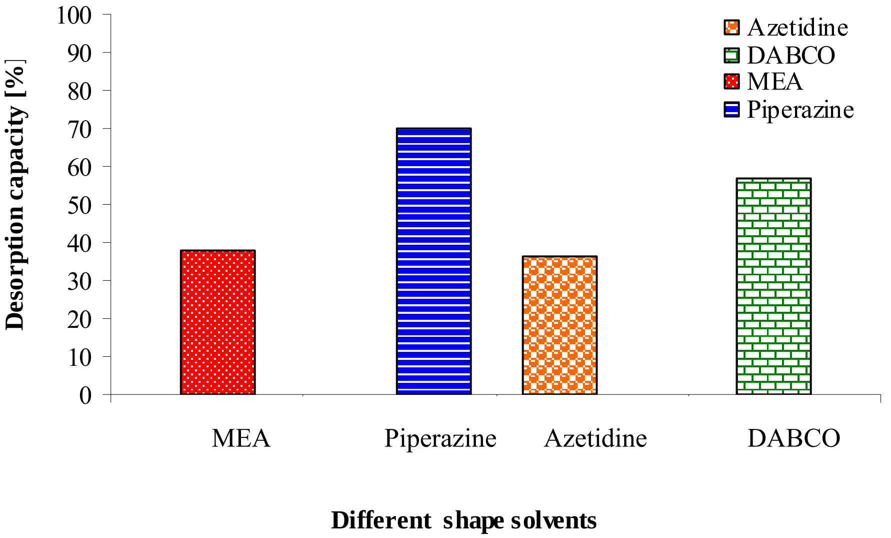


Figure 25, Comparison of various shape absorbent on desorption capacity [%] of CO_2 at pseudo-equilibrium.

Finally, the effect of different ring shapes was investigated. Figure 24, 25 and Table 12 shows the results from Azetidine and DABCO desorption. The concentration of Azetidine and DABCO was kept to be 0.24 moles/litre and 2.5 moles/litre respectively in these experiments. Figure 24, shows that DABCO has a slightly higher initial desorption rate compared to Azetidine (see Table 12).

Results shows that the DABCO is having the higher desorption capacity reaches upto 0.35 moles CO_2 / moles amine (see Table 12) that is 57 % of CO_2 is desorbed where as in Azetidine that has a small ring shape structure was noticed to be having lower desorption capacity that is 36 % of CO_2 is desorbed.

4. Conclusion

The present study revealed some of the structural effects of various amine based absorbent on their initial CO_2 desorption rate and desorption capacities at pseudo-equilibrium. In alkyl and diamine based absorbents chain length of six carbon between amine and functional group is found to be high in CO_2 desorption capacity. Whereas in alkanolamine chain length of four carbon is having higher desorption capacity that reaches up to 49% of CO_2 is desorbed at pseudo-equilibrium. In alkyl and alkanolamine based absorbents the initial desorption rate was found to be high with four carbon chain length. In diamine based absorbent chain length with six carbon was noticed to be in an increase in initial desorption rate. Alkyl group substitution at the α-carbon to the amine group results in an enhanced desorption capacity. This shows the effect of steric hinderance that enhances the desorption capacity. Substitution of different functional group at β-carbon to amine groups decreases the initial desorption rate. Increase in the amine group in absorbent structure shows an increase in desorption capacity e.g with five amine group desorption capacity reaches up to 70% of CO_2 is desorbed. It is also noticed that the increase in number of amine group up to four results in an increase in initial desorption rate. Presence of two hydroxyl group in diamine based absorbent shows an increase in desorption capacity up to 60% of CO_2 is desorbed at pseudo-equilibrium. Nonsubstituted saturated cyclic diamine has showed the higher desorption capacity of around 70% of CO_2 is desorbed when compared to the substituted saturated cyclic diamine based absorbent. In saturated cyclic monoamine desorption capacity is slightly increased with the substitution of an alkyl group at the cyclic ring, reaches up to 55% of CO_2 is desorbed. In both saturated cyclic mono and diamine amine group substitution with side chain at the ring enhances the initial desorption rate. Hence, these results could be an advantage in the development of an improved amine based CO_2 absorbent, which will lead to a better approach for development of new technologies in the CO_2 capture area.

5. Acknowledgement

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