The Use of MDEA and Mixtures of Amines for Bulk CO$_2$ Removal

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ABSTRACT

The use of MDEA and mixtures of amines for bulk CO2 removal was explored using three case studies. A process simulation program called TSWEET was used to study the effect of the amine used and the major operating parameters on the performance of MDEA solutions for bulk CO2 removal. The results showed that MDEA can be used quite advantageously for bulk CO2 removal and that the performance is often very sensitive to one or more of the operating parameters: liquid residence time on the trays, circulation rate and lean amine temperature. A good parametric analysis of the operating parameters should be performed in every case.

INTRODUCTION

In the past 10 years, numerous plants have been built or converted to methyldiethanolamine (MDEA) to take advantage of its selective absorption capability. In selective absorption, the H$_2$S is selectively absorbed from the gas leaving large amounts of CO$_2$ in the gas. The selective absorption characteristics of MDEA have been reported to a large degree in References 1-8. MDEA is well known for its relatively slow reaction rate for CO$_2$. As a result, MDEA is not usually associated with situations where the removal of large amounts of CO$_2$ is desired. However, MDEA has a number of properties which make it attractive for CO$_2$ removal:

1. High solution concentration (up to 50-55 wt%)
2. High acid gas loading
3. Low corrosion even at high solution loadings
4. Slow degradation rates
5. Lower heats of reaction
6. Low vapor pressure and solution losses.

The primary disadvantages are:

1. Slow reaction rate with CO$_2$

2. Tendency to foam at high concentration
3. Higher cost.

The disadvantage of slow reaction rate can usually be overcome by proper operating temperatures and the design of the trays in the absorber to give adequate liquid residence time. The slow reaction rate can also be overcome to a significant degree by adding one or two of the more reactive primary or secondary amines to form a mixture of amines in water. The primary or secondary amines are added in the amount of 5-10% of the total amine present.

If foaming occurs, it is often caused by some alien compound being introduced into the system such as a corrosion inhibitor being injected at the wellhead. If the cause cannot be found and eliminated, silicon based and a few other types of antifoam agents have been found to work reasonably well in many cases.

In most applications, considerably less MDEA is consumed or lost which assists in mitigating the higher costs. Thus the disadvantages associated with the use of MDEA and MDEA based mixtures of amines can usually be overcome to an acceptable level.

In this work, the use of MDEA and mixtures of amines for bulk removal of CO_2 are considered. The influence of the most important process parameters are investigated for three cases with CO_2 levels ranging from moderate to high. One case also uses H_2S and CO_2 in equal concentrations and involves a Claus plant and a tail gas cleanup unit.

PROCESS CHEMISTRY

The various reactions between MDEA and acid gases have been described in the References on numerous occasions[1,4,5,6,9]. In general, the H_2S is thought to react almost instantaneously with MDEA by proton transfer as is the case with primary and secondary amines.

$$H_2S + R_2NCH_3 \rightarrow R_2NCH_4^+ + HS^-$$
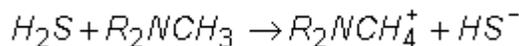
Since MDEA is a tertiary amine and does not have a hydrogen atom attached to the nitrogen, the CO_2 reaction can only occur after the CO_2 dissolves in the water to form a bicarbonate ion. The bicarbonate then undergoes an acid-base reaction with the amine to yield the overall CO_2 reaction:

$$CO_2 + H_2O + R_2NCH_3 \rightarrow R_2NCH_4^+ + HCO_3^-$$
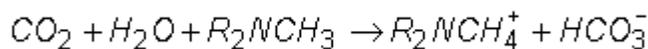
Since the CO_2 reaction with water to form bicarbonate is slow and the H_2S reaction is fast, it is generally assumed that the H_2S reaction with MDEA is gas phase limited while the CO_2 reaction is liquid phase limited[9]. Contrary to the case for selective absorption of H_2S, to effectively use MDEA for bulk CO_2 removal, the liquid phase residence time must be maintained sufficiently large for the CO_2 reaction to readily occur. Other operating parameters such as column temperature and solution loading must also be properly adjusted.

CONSIDERATION OF OPERATING PARAMETERS

The operating parameters for each application should be carefully examined. For the case of bulk CO_2 removal using MDEA and mixtures of amines, the most sensitive operating parameters include:

Liquid Residence Time on Tray:

Since the CO_2 reaction rate with MDEA is slow, the column diameter and weir height must be adjusted to give sufficient time for the reaction to occur. The usual range of weir heights are from 2"-4" resulting in residence times from about 2-5 sec.

Lean Amine Temperature:

Usually the only parameter available for control of the column temperature is the lean amine temperature. Since the CO_2 reaction with MDEA is kinetically controlled, the hotter the column the faster the reaction rate. However, once the lean amine temperature reaches about 135-140°F, the decrease in solubility of the CO_2 in the amine solution will usually become the overriding factor and the net CO_2 pickup will begin to decrease.

Circulation Rate:

As is the case for primary and secondary amines, when the circulation rate is increased for any given column, the CO_2 pickup will increase. This usually holds true for MDEA in a column of fixed diameter even though the liquid residence time on a tray will decrease with increased circulation.

Steam Stripping Rate:

For any given situation, as the steam stripping rate is increased, a leaner amine will be produced which will result in a higher CO_2 pickup.

Process Calculations:

To investigate the influence of the above operating parameters on the overall unit performance, a process simulation program called TSWEET® , developed by Bryan Research & Engineering, Inc., was used. With this program, the user can draw the process flow sheet on the computer screen and enter the process operating parameters on "pop-up" forms. The program can accommodate almost any conceivable flowsheet for amine units, Claus sulfur plants and amine tailgas cleanup units, either individually or as an integrated complex. Simultaneous distillation and chemical reaction calculations are performed rigorously to model the acid gas absorption and reaction with amines. The kinetic model is used to simulate the slow reaction of CO_2 with amines.

DISCUSSION

The use of MDEA and mixtures of amines for bulk CO_2 removal is explored using three cases with CO_2 levels ranging from about 3-15%. MDEA is compared to MEA, DEA, and DGA for a base set of conditions for bulk CO_2 removal. The effect of the most important operating parameters on the performance of a unit using MDEA based solvent is also explored.

Case 1 – Moderate CO_2:

The base conditions for Case 1 are from the data for the North Caroline Plant[6] in Alberta, Canada. The inlet gas was at 800 psia and contained 3.5% CO_2 and 60 ppm H_2S. The base operating conditions for this case were 33 wt% MDEA, 116 gpm circulation, 115°F lean amine temperature and 2.6 sec. liquid residence time on each tray. The flow arrangement was a standard sweetening unit with no flash tank on the rich amine.

The influence of the type of amine on the CO_2 overhead and various duties in the plant is shown in Table I. Typical solution concentrations and maximum rich loadings were chosen for DEA, DGA, and MEA as shown in Table I. Due to the limit on maximum allowable solution loading for DEA, DGA, and MEA, substantially higher

circulation rates and heat duties were required for these amines.

Table I. Effect of amine selection on CO_2 overhead, Case 1 (3.5% CO_2)						
Amine	GPM	CO2 Overhead	Loading	Condenser Duty	Reboiler Duty	Trim Duty
33% MDEA	116	1.09%	0.49	1.2	5.0	2.4
35% DEA	220	48 ppm	0.35	2.7	9.2	5.5
50% DGA	230	400 ppm	0.35	1.5	9.5	7.1
18% MEA	350	60 ppm	0.40	5.6	14.4	7.9

The effect of MDEA circulation rate, liquid residence time on tray, and lean amine temperature on the CO_2 and H_2S overhead from the absorber were explored as shown in Figures 1, 2 and 3.

Each of' these parameters were perturbed about the base conditions given above. As expected, the CO_2 and H_2S overhead continued to drop with increased circulation rate. Below 80 gpm, the CO_2 overhead rises very rapidly which would lead to good conditions for CO_2 rejection into the sweet gas. As shown in Figure 2 for the above stated operating conditions, the CO_2 overhead is quite sensitive to liquid residence time while the H_2S is not.
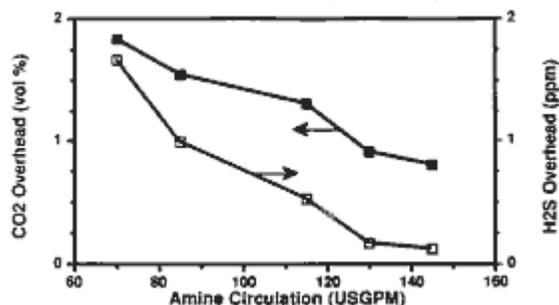
Figure 1. Effect of amine circulation on acid gas overhead: Case 1 (3.5% CO_2)
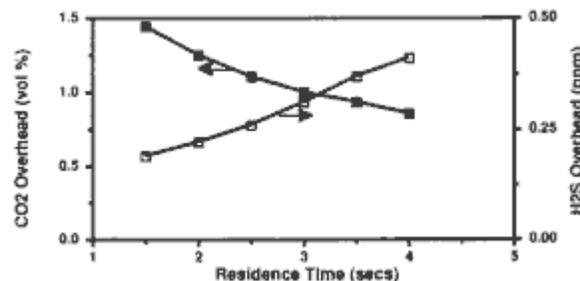
Figure 2. Effect of residence time on acid gas overhead: Case 1 (3.5% CO_2)
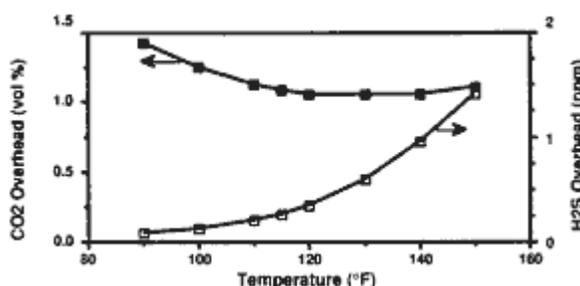
Figure 3. Effect of lean amine temperature on acid gas overhead: Case 1 (3.5% CO_2)

The competing effects of solubility and kinetic reaction rates are shown in Figure 3 where the CO_2 overhead goes through a minimum around 120-130°F lean amine temperature. Below about 110°F, the kinetic effects tend to dominate for this case while above about 140°F the solubility limitations start to control.

The addition of DEA to the MDEA solution will increase the CO_2 pickup for any given liquid residence time otherwise the trends discussed above for MDEA should hold.

Case 2 – High CO$_2$:

The inlet gas for this case was selected as 800 psia with 15% CO$_2$. The base operating conditions were selected to be 50 wt% MDEA, 350 gpm circulation, 115°F lean amine temperature and 2.5 sec liquid residence time on each tray. The flow arrangement was a standard sweetening unit with a flash tank operating at 60 psia on the rich amine.

An analysis similar to Case 1 was performed. As shown in Table II, the performance of the various amines is dramatically different due largely to the maximum allowable solution concentration and loading. Due to corrosion and solution degradation problems, these maximums cannot be ignored except for the loading on MDEA. If the CO$_2$ overhead specification was lower than 0.89%, the circulation rate for MDEA would have to be increased somewhat as shown in Figure 4. Once the MDEA circulation rate reaches about 380 gpm, the CO$_2$ is down to about 0.2%.

Table II. Effect of amine selection on CO$_2$ overhead, Case 2 (15% CO$_2$)						
Amine	GPM	CO2 Overhead	Loading	Condenser Duty	Reboiler Duty	Trim Duty
50% MDEA	350	0.89%	0.62	11.86	23.8	10.1
35% DEA	922	31 ppm	0.35	16.00	44.7	27.8
50% DGA	712	17 ppm	0.35	25.70	57.6	30.5
18% MEA	1460	56 ppm	0.40	20.70	60.7	38.7
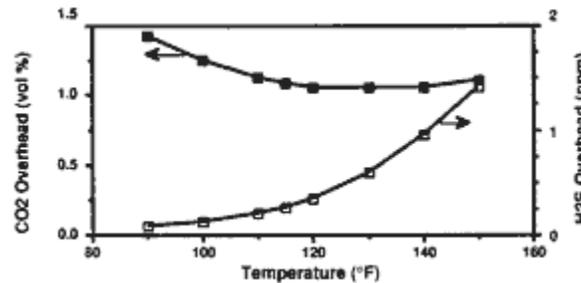
Figure 4. Effect of amine circulation rate on CO$_2$ overhead:

Case 2 (15% CO$_2$)

At a circulation rate of 350 gpm, the CO$_2$ overhead is only moderately sensitive to the liquid residence time as shown in Figure 5. Due to the high inlet CO$_2$ and resultant high solution loading, the solubility effects as depicted in Figure 6 become dominant at a much lower temperature than for Case 1.
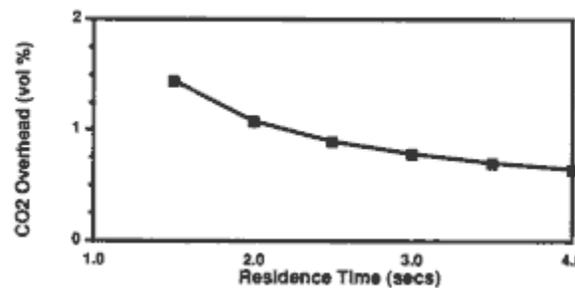
Figure 5. Effect of residence time on CO$_2$ overhead: Case 2 (15% CO$_2$)
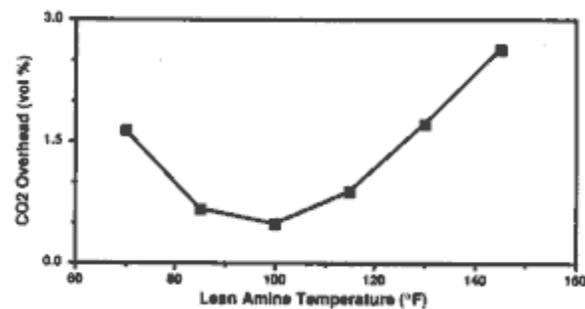
Figure 6. Effect of lean amine temperature on CO_2 overhead:

Case 2 (15% CO_2)

At the base conditions for this case, little advantage would be realized from the addition of a more reactive amine to form a mixture of amines.

Case 3 – Equal CO_2 and H_2S:

To provide an interesting contrast in CO_2 pickup and CO_2 rejection, an integrated complex consisting of a sweetening unit, Claus sulfur plant and amine tailgas cleanup unit (TGCU) as shown in Figure 7 was chosen for this case. The sour gas was 5% CO_2 and 5% H_2S at 210 psia. The base operating conditions for near complete CO_2 removal in the main absorber were 50 wt% MDEA, 200 gpm, 120°F lean amine temperature and a liquid residence time of 1.75 sec.
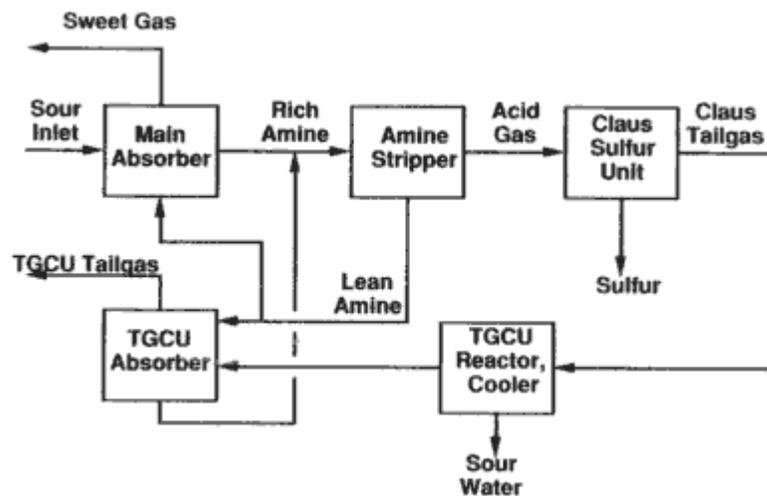
Figure 7. Schematic diagram of amine/Claus unit with tailgas cleanup unit.

An analysis of the influence of the operating parameters on the absorber performance was performed and the results are shown in Figures 8, 9 and 10. The parametric studies for this case were performed on the absorbers from the unit while holding all other parameters constant. In the integrated complex shown in Figure 7, the performance of the absorbers and the Claus unit are quite interdependent and a process simulation program such as TSWEET which can handle the complete integrated unit is needed. As can be seen from Figure 8, the CO_2 and H_2S overhead increase very rapidly as the circulation rate decreases from about 190 gpm. For the base operating conditions given above, this absorber could meet a 1/4 grain (3.5 ppm) H_2S specification with a circulation rate of 200 gpm.
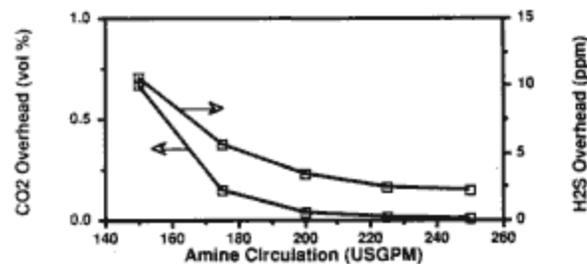
Figure 8. Effect of amine circulation on acid gas overhead: Case 3 (5% CO$_2$, 5% H$_2$S) Main Absorber

As shown in Figure 9, the CO$_2$ and H$_2$S are very responsive to changes in liquid residence times up to about 2 sec. for the base operating conditions. Once the lean amine temperature reaches 100°F, the CO$_2$ removal is not affected until it reaches about 180°F. However, as can be seen in Figure 10, the H$_2$S overhead increases significantly above a lean amine temperature of 120°F.
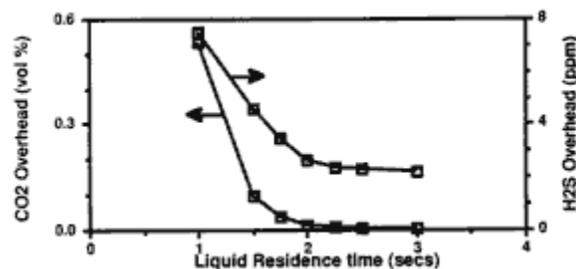
Figure 9. Effect of residence time on acid gas overhead: Case 3 (5% CO$_2$, 5% H$_2$S) Main Absorber
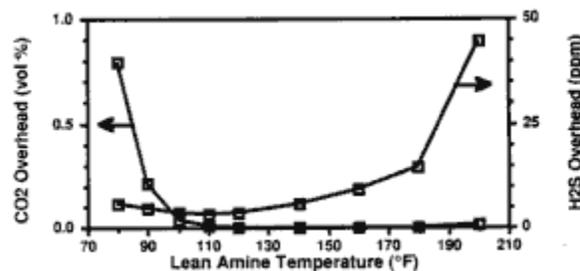
Figure 10. Effect of lean amine temperature on acid gas overhead: Case 3 (5% CO$_2$, 5% H$_2$S) Main Absorber

The response of the TGCU absorber used for selective absorption provides an interesting contrast to the previous bulk CO$_2$ removal cases. The gas to the absorber was 31.6% CO$_2$ and 0.8% H$_2$S at a pressure of 8 psig. The base operating conditions were 50 gpm, 120°F lean amine temperature and 1.75 sec. liquid residence time. As shown in Figure 11, the CO$_2$ overhead continues to decrease with circulation rate while the H$_2$S tends to level out at 250 ppm above 40 gpm. Figure 12 shows that the highest CO$_2$ overhead and lowest H$_2$S is obtained at the lowest liquid residence times. As expected, the CO$_2$ overhead decreases and the H$_2$S increases as the lean amine temperature increases as depicted in Figure 13.
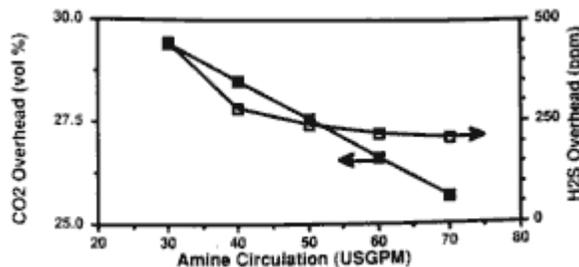
Figure 11. Effect of amine circulation on acid gas overhead: Case 3 (5% CO_2, 5% H_2S) TGCU Absorber
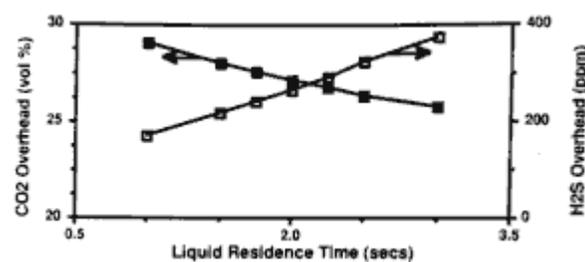
Figure 12. Effect of residence time on acid gas overhead: Case 3 (5% CO_2, 5% H_2S) TGCU Absorber
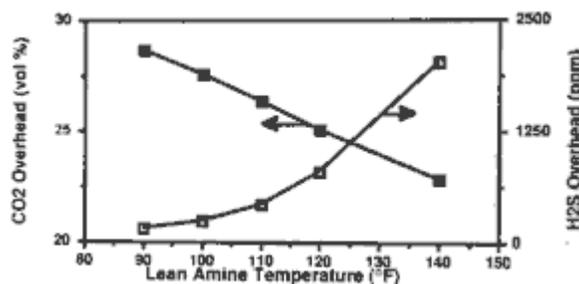
Figure 13. Effect of lean amine temperature on acid gas overhead: Case 3 (5% CO_2, 5% H_2S) TGCU Absorber

SUMMARY AND CONCLUSIONS

The use of MDEA and mixtures of amines for bulk CO_2 removal was explored for two cases with 3.5 and 15% CO_2 and one case with 5% CO_2 and 5% H_2S. The first two cases involved conventional flow schemes while the latter involved the main absorber and the tailgas absorber in an integrated sweetening, Claus plant and tailgas cleanup unit. A process simulation program called TSWEET was used to study the effect of the amine used and the important operating parameters on the performance of MDEA solutions for bulk CO_2 removal.

The results showed that MDEA can be used quite advantageously for bulk CO_2 removal as well as for selective absorption (CO_2 rejection). In general, CO_2 pickup can be achieved by longer liquid residence times on the trays, higher amine circulation rates and higher lean amine temperatures up to about 120 to 140°F. The results also showed that, when using MDEA or mixtures of amines for bulk CO_2 removal, the performance of the unit is often very sensitive to one or more of the operating parameters. Thus a good parametric analysis of the operating parameters should be performed in every case.

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