

Using Mixed Amine Solutions for Gas Sweetening

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ABSTRACT

The use of amine mixtures employing methyldiethanolamine (MDEA), monoethanolamine (MEA), and diethanolamine (DEA) have been investigated for a variety of cases using a process simulation program called TSWEET . The results show that, at high pressures, amine mixtures have little or no advantage in the cases studied. As the pressure is lowered, it becomes more difficult for MDEA to meet residual gas requirements and mixtures can usually improve plant performance.

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INTRODUCTION

In the past few years, mixed amine solvents for the removal of acid gases have received increased attention. In most cases, the mixtures contain MDEA as the base amine with the addition of one or two more reactive amines such as MEA or DEA. These amine mixtures have been called a variety of names including formulated amines and MDEA based amines.

Historically, MDEA has been recognized primarily for its ability to selectively absorb H_2S from a gas while leaving large amounts of CO_2 in the gas. The selective absorption characteristics of MDEA have been widely reported in the literature.¹⁻⁹ MDEA's selective absorption ability is due to its relatively slow reaction rate with CO_2 . Until the last few years, MDEA has not been associated with cases where the removal of large amounts of CO_2 is desired.

As reported in the literature, MDEA has a number of properties which make it desirable for broader application:⁹

- High solution concentration (up 50 to 55 wt %)
- High acid gas loading
- Low corrosion
- Slow degradation rates
- Lower heats of reaction
- Low vapor pressure and solution losses

Due to the above advantages, MDEA is the most desirable amine to use even in cases where large amounts of CO_2 must be removed. In cases where a large degree of CO_2 removal is necessary, the relatively slow CO_2 -MDEA reaction rate must be overcome by the proper design of the absorber and amine system. The CO_2 reaction

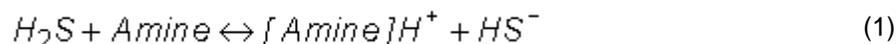
rate can be significantly increased by a combination of the following:

1. Selection of proper operating temperatures in the absorber.
2. Proper design of the absorber trays to give adequate liquid residence times.
3. Addition of one or two more reactive primary or secondary amines to form a mixture of amines in water.

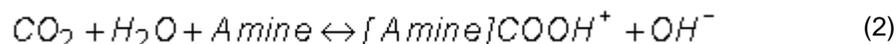
The primary or secondary amines are usually added in the amount of 5 to 10% of the total amine present. In this work, the use of mixed amine solutions for gas sweetening is addressed. The influence of amine mix along with several of the other important process parameters are investigated for several case studies.

PROCESS CHEMISTRY

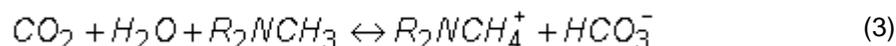
The various reactions between amines and acid gases have been described on numerous occasions.^{1,4,5,6,9,10} In general, the H₂S is thought to react almost instantaneously with the amines by proton transfer.



CO₂ is thought to react with primary and secondary amines to form a carbamate.



Since MDEA is a tertiary amine and does not have a hydrogen attached to the nitrogen, the CO₂ reaction can only occur after the CO₂ dissolves in the water to form a bicarbonate ion. The bicarbonate ion then undergoes an acid-base reaction with the amine to yield the overall CO₂ reaction:



Since the CO₂ reaction with the amines is relatively slow and the H₂S reaction is fast, the H₂S absorption is generally assumed to be gas phase limited while the CO₂ absorption is liquid phase limited.¹⁰ Since the CO₂ reaction rate with the primary and secondary amines is much faster than with MDEA, the addition of small amounts of primary or secondary amines to an MDEA based solution should greatly improve the overall reaction rate of CO₂ with the amine solution.

PROCESS OPERATING PARAMETERS

Several operating parameters must be carefully examined to yield the optimum design for each application. Of course, the sweet gas requirements will strongly influence the operating parameters. These may easily range, for H₂S, from 3.5 ppm pipeline specification to higher values in fuel gas systems or hydrocracker recycles and, for CO₂, from 2% for pipeline specification down to less than 100 ppm for feed to some LP-gas separation facilities. Depending on the feed gas composition, temperature and pressure along with the sweet gas requirements, the most sensitive operating parameters include:

Liquid Residence Time on Tray

Since the CO₂ 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 to 4 in. resulting in residence times from about 2 to 5 sec.

Lean Amine Temperature

Usually the only parameter available for control of the column temperature is the lean amine temperature. Since the CO₂ reaction with MDEA is kinetically controlled, a hotter column increases the reaction rate. However, once the lean amine temperature reaches about 135 to 140°F, the decrease in solubility of the CO₂ in the amine solution will usually become the overriding factor and the net CO₂ pickup will begin to decrease.

Circulation Rate

When the circulation rate is increased for any given column, the CO₂ pickup will increase. This usually holds true for MDEA in a column of fixed diameter even through 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 lower H₂S and CO₂ in the sweet gas.

PROCESS CALCULATIONS

To analyze the use of mixed amine solutions for gas sweetening, the NRTL equation of state was added to a process simulation program called TSWEET to predict the vapor-liquid equilibria for mixed amine systems. TSWEET was developed by Bryan Research & Engineering, Inc. for amine units, sulfur recovery, and amine tailgas cleanup units, either individually or as an integrated complex.¹¹ With this program, the user can draw the process flowsheet on the computer screen and enter the process operating parameters on pop-up forms. The program has great flexibility and can accommodate almost any conceivable flowsheet. 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 CO₂ reaction with amines.

DISCUSSION

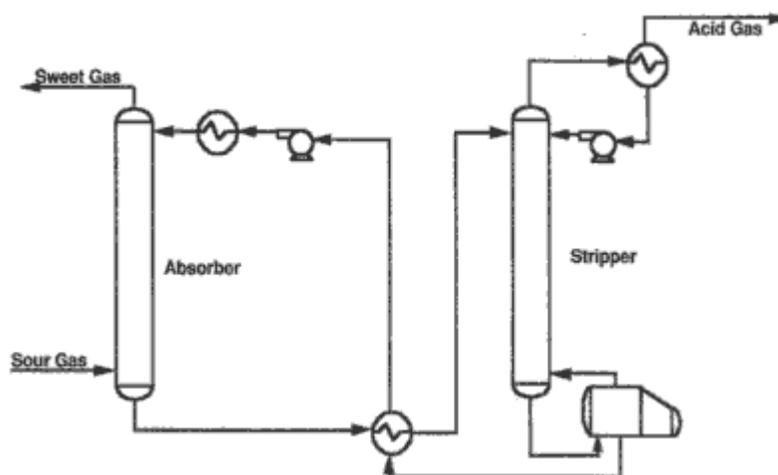


Figure 1. Process flow sheet for a common gas sweetening plant.

The use of mixed amine solutions for gas sweetening was investigated using a variety of cases in a standard amine unit as shown in Figure 1. As shown in Table 1, the cases involve gas pressures of 200 and 800 psia and several acid gas concentrations. These cases were chosen to demonstrate the influence of adding small amounts of a primary or secondary amine to an MDEA solution. Since the solution circulation rate dictates, to a large degree, the plant size and duty, the results are presented in the form of residual acid gas concentrations as a function of circulation rate for selected amine mixtures.

Table 1. Identification of case studies.				
Case	Blend	psia	H ₂ S mol%	CO ₂ mol%
1	MDEA/MEA	200	0.1	5.0
2	MDEA/MEA	200	1.0	5.0
3	MDEA/MEA	200	0.1	10.0
4	MDEA/MEA	200	1.0	10.0
5	MDEA/MEA	800	0.1	5.0
6	MDEA/MEA	800	1.0	5.0
7	MDEA/DEA	800	1.0	10.0

In an effort to more clearly demonstrate the influence of the amine mixture, all operating parameters were held constant in all runs except for amine mixture and circulation rate. This includes the sour gas feed rate, liquid residence time on the trays in the absorber, and the steam rate to the reboiler. In all cases, a 50 wt % total amines in water was used with the base case as 50 wt % MDEA.

When reviewing the results for the various cases, the fact that the best amine solution mix will often depend on the residual acid gas requirements should be kept in mind. In all of the following cases, the results for MEA alone (15 wt %) and DEA alone (30 wt %) using maximum acid gas loadings of 0.3 mol/mol were also compared to the results presented below. In all cases, the required circulation rates for MEA and DEA alone were far higher than for MDEA and MDEA based mixtures and, thus, these results have not been included in the presentation.

Case 1: 5% CO₂, 0.1% H₂S, 200 psia

The results for this case are presented in Figure 2. The residual H₂S and CO₂ concentrations are shown as a function of circulation rate for amine solutions of 50/0, 48/2, 45/5 wt % MDEA/wt % MEA. The results show that in the lower circulation range of 60 to 80 gpm, the addition of MEA causes the residual H₂S to increase. This phenomenon will be addressed in Case 2.

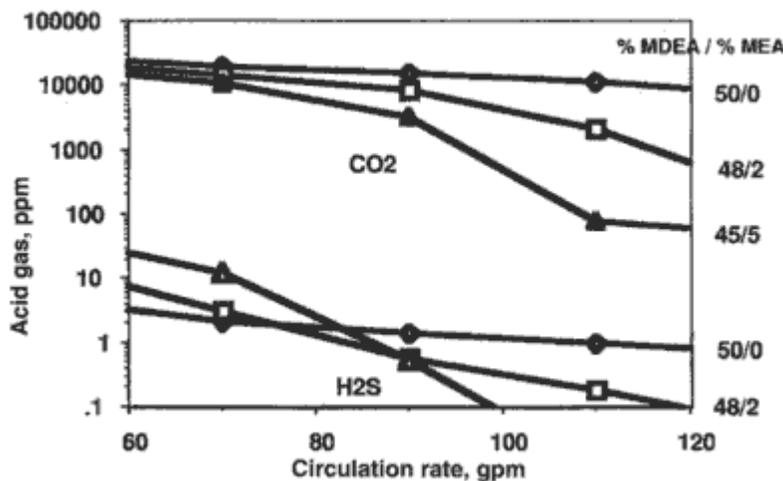


Figure 2. Effect of amine mixture on residual acid gas Case 1 (5% CO₂, 0.1% H₂S, 200psia)

As mentioned previously the best amine mix depends on the residual acid gas requirements. For example, if the requirements are 8.5 ppm H₂S and 3.0% CO₂, then 50 wt % MDEA at 60 gpm is the solution of choice. If the requirements are 3.5 ppm H₂S and 2.0 % CO₂, both 50/0 and 48/2 wt % MDEA/wt % MEA would meet the requirements at a circulation rate slightly above 70 gpm. Thus, 50% MDEA would be preferred since the problems of maintaining the proper amine mixture would be avoided. If the requirements are 3.5 ppm H₂S and 1% CO₂, an amine mixture containing about 2% MEA would be preferred. The circulation rate for the mixture would be about 80 gpm compared to about 120 gpm for 50 wt % MDEA. As can be seen from Figure 2, for all requirements of CO₂ below 1%, amine mixtures would produce substantial savings in plant size and operating cost. The results for Case 1 are also representative for cases where no H₂S is present in the feed gas. Thus, for bulk CO₂ removal at pressures on the order of 200 psia, the addition of MEA is clearly very advantageous.

Case 2: 5% CO₂, 1% H₂S, 200 psia

As shown in Figure 3, the results for this case show trends similar to Case 1. However, at the higher inlet H₂S, MDEA alone will have great difficulty meeting a 3.5 ppm H₂S specification. The amine mixtures will meet 3.5 ppm H₂S at about 100 gpm compared to 150 gpm or greater for MDEA alone. This case shows that the addition of MEA would be most advantageous.

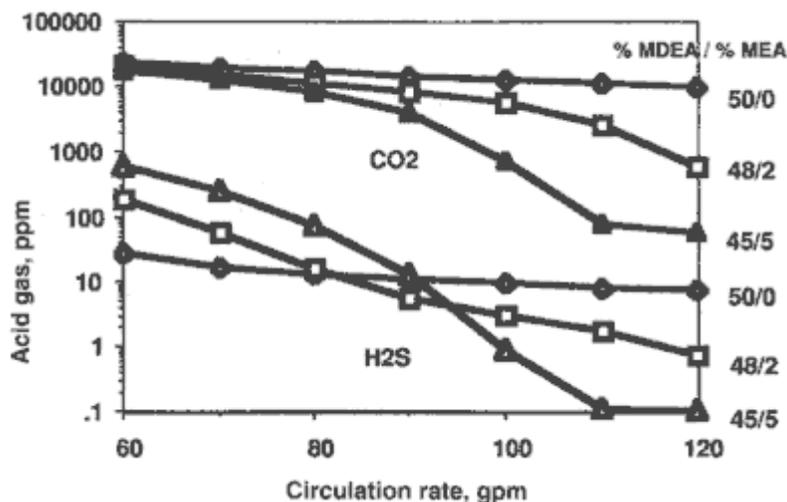


Figure 3. Effect of amine mixture on residual acid gas Case 2 (5% CO₂, 1% H₂S, 200psia)

The results for this case were also studied to determine why the addition of MEA causes the residual H₂S to increase at circulation rates below about 80 to 90 gpm. A comparison of the temperature profiles in the absorber were made for circulation rates of 70 and 100 gpm as shown in Figures 4 and 5. The profiles in Figure 4 along with the concentrations from Figure 3 show that the addition of MEA caused the CO₂ to be absorbed more strongly in the upper portion of the column than for MDEA alone. This higher CO₂ absorption raises the residual H₂S dramatically due to the combined effort of high CO₂ loading and high temperature in the upper portion of the column. This problem tends to become compounding since high temperatures at the top cause the CO₂ to react faster which in turn heats the solution. In the 70 gpm case much of the heat generated in the absorber is carried out of the column overhead.

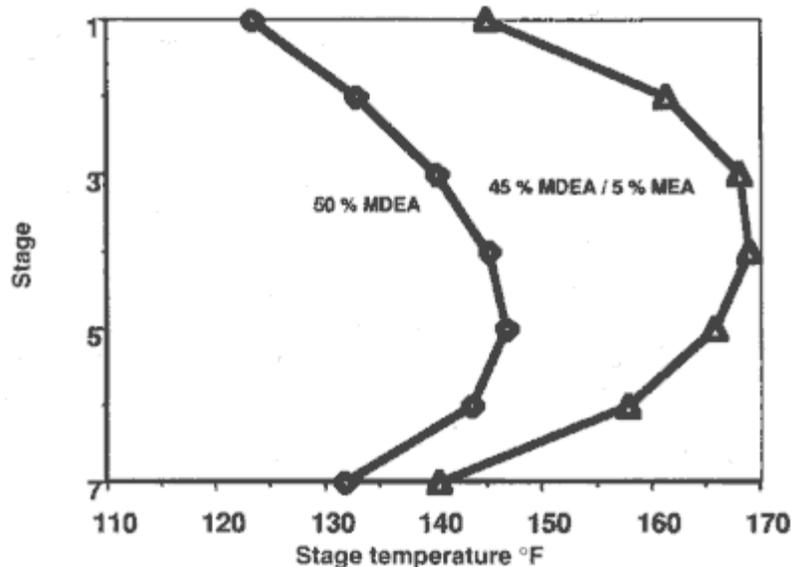


Figure 4. Absorber temperature profile for Case 2 at 70 gpm (5% CO₂, 1% H₂S, 200psia)

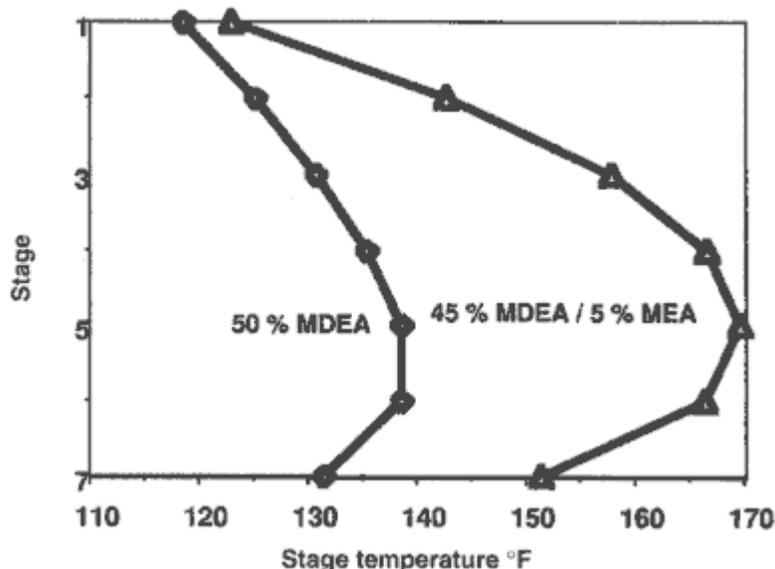


Figure 5. Absorber temperature profile for Case 2 at 100 gpm (5% CO₂, 1% H₂S, 200psia)

On the other hand, raising the circulation rate to 100 gpm, CO₂ is almost completely absorbed in the lower portion of the column. This is sufficient to cause nearly all of the heat to be carried out of the absorber at the bottom. In this case, the addition of MEA causes the CO₂ to be almost completely absorbed in the lower portion of the column. Thus, the top of the column is operating at the lean amine temperature with a reactive, unloaded primary amine present which readily absorbs the H₂S to low levels.

This behavior has been previously documented for the North Carolina plant in Alberta. Prior to switching to MDEA, this plant used DEA. With DEA, the plant was marginally producing 3.5 ppm H₂S gas during normal operations. The plant had one well connected to it which would produce an occasional spike of H₂S. These spikes caused the sweet gas to rise above 3.5 ppm. When the plant was converted to MDEA, the H₂S was lowered to less than 1.0 ppm during normal operation and it stayed below 3.5 ppm during the spikes. This type of operation between DEA and MDEA is very analogous to the situation at hand where the addition of MEA or DEA actually

raises the residual H₂S. A comparison of the temperature profiles for DEA and MDEA for the North Carolina plant are shown in Figure 6. The MDEA profile was verified with actual measurements from the absorber. These profiles illustrate the reaction zones which are occurring in the absorber.

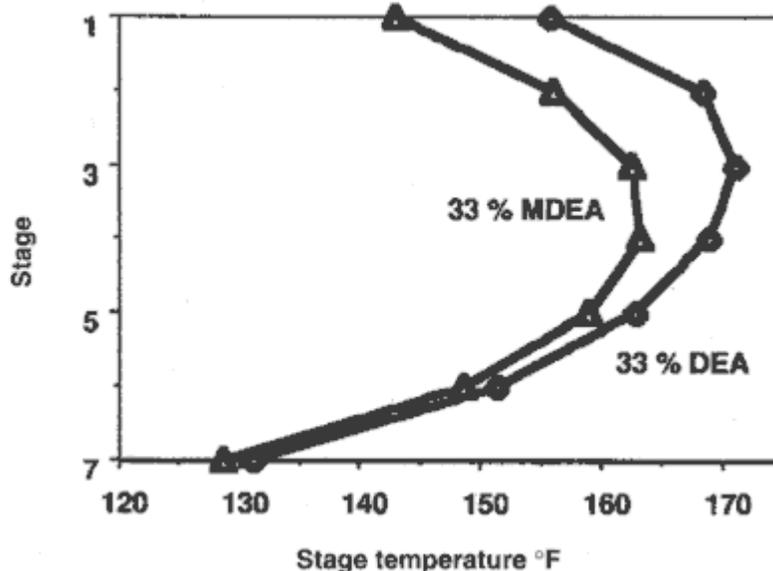


Figure 6. Absorber temperature profile for North Carolina plant (3.6% CO₂, 700ppm, H₂S, 800psia)

Case 3: 10% CO₂, 0.1% H₂S, 200 psia

For high levels of CO₂, MDEA alone has no problem achieving H₂S below 3.5 ppm at all reasonable circulation rates as shown in Figure 7. The results also show that to obtain CO₂ residuals down to 2%, no particular advantage is gained by adding MEA. However, below 2% residual CO₂, a mixture would be preferred.

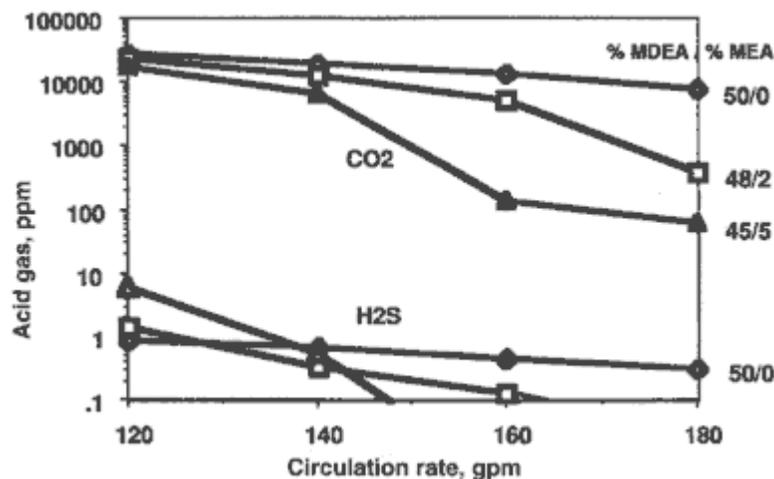


Figure 7. Effect of amine mixture on residual acid gas Case 3 (10% CO₂, 0.1% H₂S, 200psia)

Case 4: 10% CO₂, 1.0% H₂S, 200 psia

As shown in Figure 8, the increased H₂S creates considerable difficulty for MDEA alone in meeting a 3.5 ppm specification and would require a circulation rate well above 180 gpm. The addition of 2 or 5% MEA would yield

3.5 ppm H₂S at about 150 gpm. Thus, the use of an amine mixture would clearly be desirable in this case.

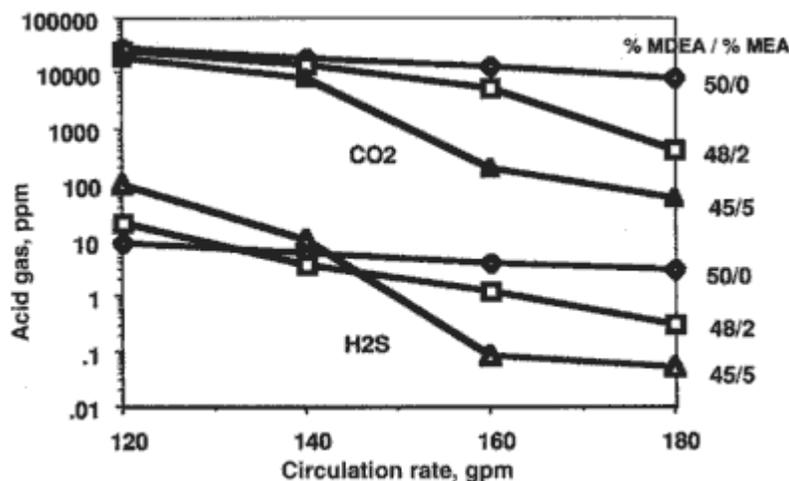


Figure 8. Effect of amine mixture on residual acid gas Case 4 (10% CO₂, 1% H₂S, 200psia)

Case 5: 5% CO₂, 0.1% H₂S, 800 psia

High absorber pressures tend to overcome the slow CO₂-MDEA reaction rates as presented in Figure 9. In this case, the addition of MEA would actually create problems and would not be recommended.

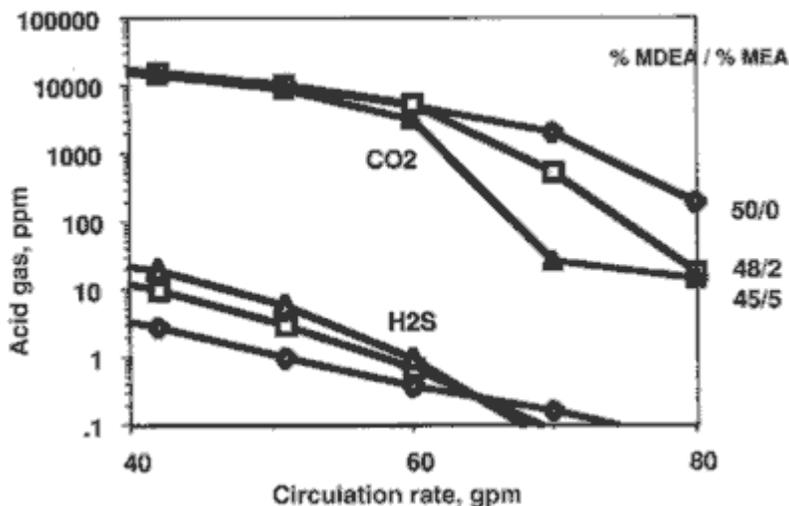


Figure 9. Effect of amine mixture on residual acid gas Case 5 (5% CO₂, 0.1% H₂S, 800psia)

Case 6: 5% CO₂, 1% H₂S, 800 psia

The increased H₂S in this case would require moderate increases in circulation rate as shown in Figure 10. The fact that MDEA alone and with 2 and 5% MEA, all tend to meet 8.5 ppm H₂S at about 65 to 70 gpm is very interesting. Again, there is no advantage in using a mixture.

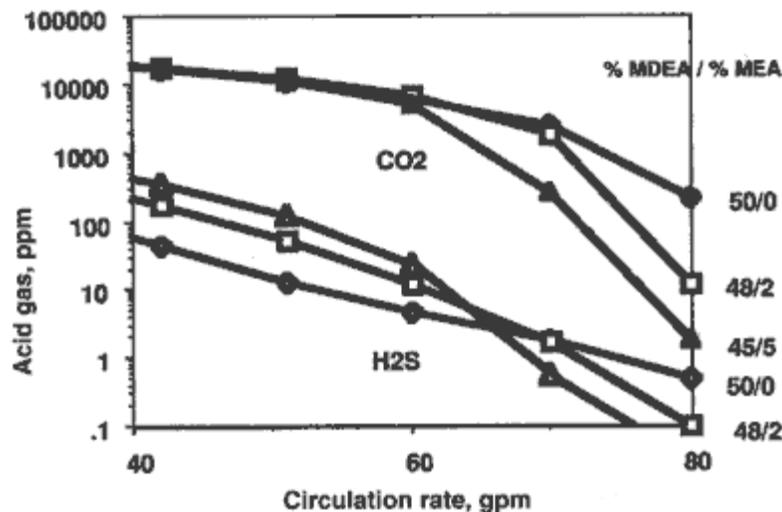


Figure 10. Effect of amine mixture on residual acid gas Case 6 (5% CO₂, 1% H₂S, 800psia)

Case 7: DEA, 10% CO₂, 1% H₂S, 200 psia

In general, the trends for the addition of DEA were very similar to those for MEA. Thus, only one case for DEA is included for comparison. The effect of adding secondary vs. primary amine can be seen by comparing Figures 3 and 11. These figures show that DEA does not cause as much increase in the residual H₂S as MEA at low circulation rates and that DEA does not increase the CO₂ absorption as dramatically as MEA. Due to the above and the better stability of DEA, it would likely be preferred in many applications over MEA for an amine mixture.

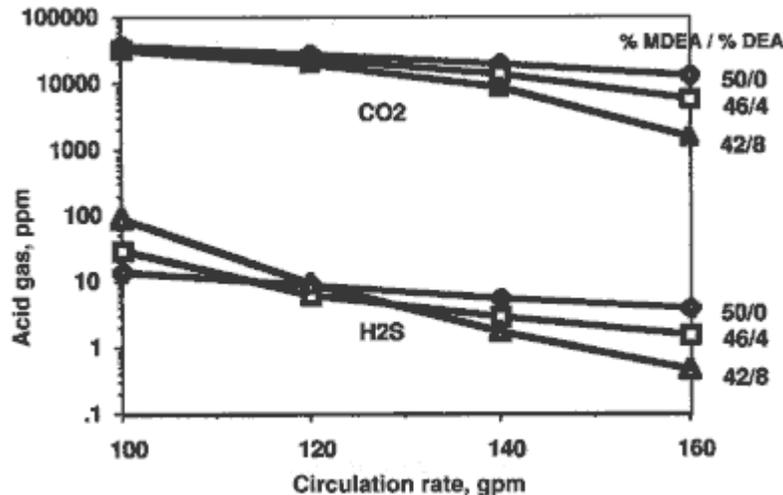


Figure 11. Effect of amine mixture on residual acid gas Case 7 (DEA, 10% CO₂, 1% H₂S, 200psia)

SUMMARY AND CONCLUSIONS

The use of mixed amine solvents for gas sweetening has been investigated using a process simulation program called TSWEET. A variety of cases with inlet gas conditions of 200 psia and 800 psia with 5 to 10% CO₂ and 0.1 to 1.0% H₂S were studied. In all cases, a 50 wt % total amines in water was used with the base case as 50 wt % MDEA. MEA and DEA were used as additives to form the mixture.

The results show that, at high pressures, amine mixtures have little or no advantage in the cases studied. As the pressure is lowered, MDEA becomes less capable of picking up sufficient CO₂ to meet pipeline specification. When large amounts of CO₂ are being passed through to the sweet gas at relatively low pressures, it becomes difficult for MDEA to reach pipeline specification for H₂S if the inlet gas contains more than about 1000 ppm H₂S. At these lower pressures, the addition of a more reactive amine clearly enhances the solution ability to remove CO₂. Thus, in areas where MDEA cannot meet the residual gas requirements, the use of amine mixtures can usually improve the plant performance.

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