Optimization of Amine Sweetening Units

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ABSTRACT

The dramatic increase in the use of selective amines for gas sweetening has resulted from the inherent economic benefits including smaller equipment sizes, lower circulation rates, and higher overall amine concentration. Selective amines absorb H2S in the presence of CO2, either from thermodynamic solubility or kinetic effects. Mixtures containing selective amines can be formulated to allow a certain amount of CO2 to remain in the processed gas. Units designed with selective amines often have little margin for error with respect to plant capacity. Unfortunately, increases in the acid gas concentration or increases in throughput exceeding design can result in sweet gas which does not meet the CO2 specification. Since adding additional equipment can be very expensive, variables such as increasing the amine concentration, using mixtures of amines, and varying the lean amine temperature affect amine sweetening were studied. These variables require little or no additional capital expenditure relative to other alternatives such as adding reboiler area or pumping capacity.

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INTRODUCTION

The optimization of amine units has been discussed thoroughly in the literature. Authors have discussed amine selection (Polasek and Bullin, 1984), plant configuration (Polasek *et al*., 1983) and mixtures of amines with water or other physical solvents (Polasek *et al*. 1992; Okimoto, 1993). In these papers, the authors recognize the importance of selective amines in the gas sweetening industry.

Selective amines absorb H_2S preferentially to CO_2. Many authors have concluded that this preference results from differences in solubility, rates of reaction, or a combination of the two (Barth *et al*., 1981, Cornelissen, 1982, and Danckwerts, 1979). Although all amines show some degree of selectivity based on kinetic effects (Bullin *et al.*, 1982), the rate of reaction for CO_2 decreases with the substitution on the nitrogen group such that primary amines react faster than secondary and tertiary amines. The rate of reaction for H_2S is so fast that equilibrium is effectively reached for all of the amines. Designing a selective commercial sweetening unit with primary amines is thus not feasible since the CO_2-amine reaction rate is so fast; however, selective units incorporating secondary and tertiary amines are routinely designed to exploit this capability.

The development of selective amine treating units has resulted in an increase in plant efficiency. The industry has been quick to embrace this new technology because of its economic advantages. The primary amines methanolamine (MEA) and diglycolamine, (DGA) offer no selectivity in normal operating units, absorbing CO_2 as completely as H_2S. The secondary and tertiary amines diethanolamine (DEA), diisopropanolamine, (DIPA), and methyldiethanolamine (MDEA) are selective amines and are most effective for high pressure applications (> 300 psi, 20 kPa). Trying to improve the efficiency with selective amines, researchers have studied some low molecular weight sterically hindered amines with advantages similar to MDEA regarding selectivity (Sartori and Savage, 1983).

Benefits of using selective amines include smaller equipment sizing and circulation rates. Recently, Denny Law (1994) described how using MDEA mixtures decreased the number of theoretical trays for a particular acid gas specification. Furthermore, additional trays may actually increase H_2S concentration in the sweetened gas due to CO_2 absorption. Apparently, adding more stages allows more CO_2 to be absorbed which tends to displace the H_2S. Since heats of reaction for the selective amines are less than non-selective amines (Kohl and Reisenfeld, 1985), regeneration requires less energy and smaller reboilers. Selective amines also tend not to form corrosive salts.

The use of selective amines, and MDEA in particular, has evolved into a new industry utilizing "specialty" amines. BASF, Betz Chemical, Dow, Huntsman Chemical, Shell, Union Carbide and other companies offer MDEA based specialty amines to enhance or to "customize" the sweetening capability of the amine solution. Shell incorporates a physical solvent, sulfolane, with MDEA or DIPA to form the Sulfinol solvent which increases the mercaptan and COS removal (Okimoto, 1993). Improving the performance of these "specialty" amine units has also been reported in the literature. Huffmaster and Nasir (1995) discuss optimizing both amine and Sulfinol plants by comparing circulation rate and steam consumption.

Concern over efficient operation of amine units has prompted numerous workshops and publications. Keller *et al.* (1995) describes an industry symposium which discussed amine process operations, the most common problems encountered, and some solutions to these problems. This survey reports that amine losses, solution contamination, and off-specification products were the primary reasons for inefficient units based on cost of operation. Surprisingly, with data from MEA, DEA, and MDEA units, the amine type was not a factor with regard to efficiency and ease of operation.

Abry and Dupart (1995) offer excellent guidelines for optimizing an amine plant based on historical plant data. The authors report how this process information is designed to circumvent upsets and to facilitate control. The authors also show how this plant data can be used to optimize the facility if operated away from design conditions. The optimization presented in this reference considered a decrease in inlet gas flow rate with the same concentration of acid gas components. Since operating companies usually exceed design inlet gas flow rates with higher concentration of acid gas components, their analysis was somewhat unrealistic and perhaps overly optimistic.

With the concern over efficient amine unit operation, most of the recent literature addresses using plant data, or proprietary "specialty" amines to solve the problem. This is very important and valuable information yet somewhat incomplete. Very few of these recent studies mention process simulators in amine unit optimization. This is a somewhat disturbing trend as simulators for the amine sweetening process are becoming increasingly accurate. Engineers can use these tools to supplement plant data to determine optimum operating conditions. An optimization analysis may include looking at alternative amines, mixtures of amines, number of equilibrium stages in the absorber, or the regenerator reboiler duty. Unfortunately, obtaining plant information for other amines, or more equilibrium stages is next to impossible in an operating facility. However, these conditions can be easily studied via process simulation.

The process simulator TSWEET® was used for this study. The accuracy of this program has been well documented for single amines (MacKenzie *et al.*, 1987) as well as mixtures of amines (Spears *et al.*, 1996). The program supports both the Kent and Eisenberg (1976) and NRTL (Chen and Evans, 1986) acid gas models. The NRTL model was used for all of the simulations and calculations reported in this paper. Details of the program's calculation methods can be found in other sources (Bullin *et al.*, 1981).

BASIC AMINE UNIT OPERATION

Although there are many different types of amines and different configurations for an amine sweetening facility, the fundamental process is the same in nearly all cases. Some complex facilities may include series and parallel configurations for economic advantages.

Figure 1 represents a simple amine treating facility. Sour gas is introduced in the absorber where it contacts lean amine solution traveling down the column. The acid gas components, H_2S and CO_2, are absorbed by the amine solution and the sweet gas leaves the absorber for further processing. The rich amine is sent to a flash tank and absorbed hydrocarbons exit as the flash-tank vapor. The rich amine flows through the lean/rich exchanger increasing the temperature to about 377.7K (220°F). The hot rich amine is stripped at low pressure removing the absorbed acid gases, dissolved hydrocarbons, and some water. The energy required to strip the amine is the sum of the sensible heat required to raise the solution temperature, the energy of absorption, and latent heats. Stripping columns should be operated at as high a pressure as possible to increase the reboiler temperature for optimum stripping (Kohl and Riesenfeld, 1985). However, the amine degradation temperature should not be exceeded. The stripped or lean amine is sent back through the lean/rich exchanger decreasing its temperature. A pump boosts the pressure such that it is greater than the absorber column. Finally, a heat exchanger cools the lean solution before completing the loop back to the absorber. The lean amine entering the absorber is usually 322.2K (120°F).

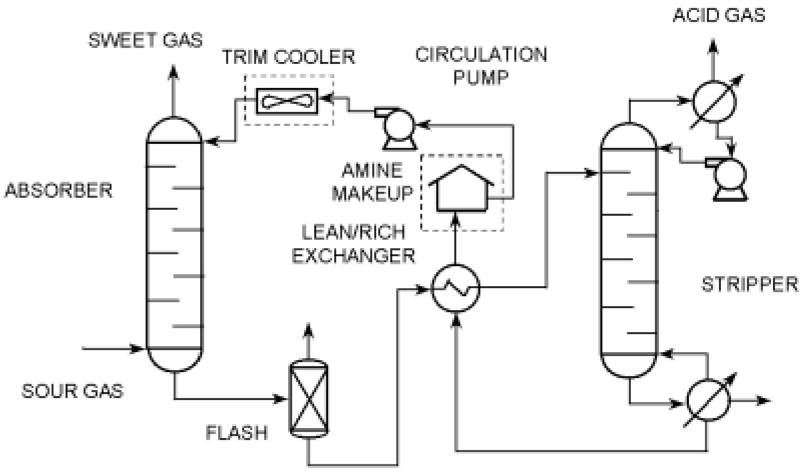

Fig. 1. Schematic of simple amine sweetening plant.

EXAMPLE FACILITY

Table 1. Design and Operation Conditions of the Bryan Gas Plant, 1994

		Inlet Gas		Sweet Gas	
	Flow Rate MMSCFD	H_2S ppm	CO_2 mole %	H_2S ppm	CO_2 mole %
Design	35	0.1	2.91	nil	0.35
Operating	26	7	3.50	nil	0.42

Table 1 shows the design and current operating conditions of the example facility. The operators were concerned that the sweet gas exceeded CO_2 specification and changes were made to alleviate this problem. Spears *et al.* (1996) further describes the facility and discusses how the process simulator TSWEET accurately matches the plant data for both DEA and a mixture of MDEA and DEA. The design specification is 0.35 mole % CO_2. Figure 2 shows simulation results versus plant data for both a 32 wt % DEA solution and a mixture of 32 wt % DEA and 13 wt % MDEA. This figure establishes a reference point for the accuracy of the simulation.

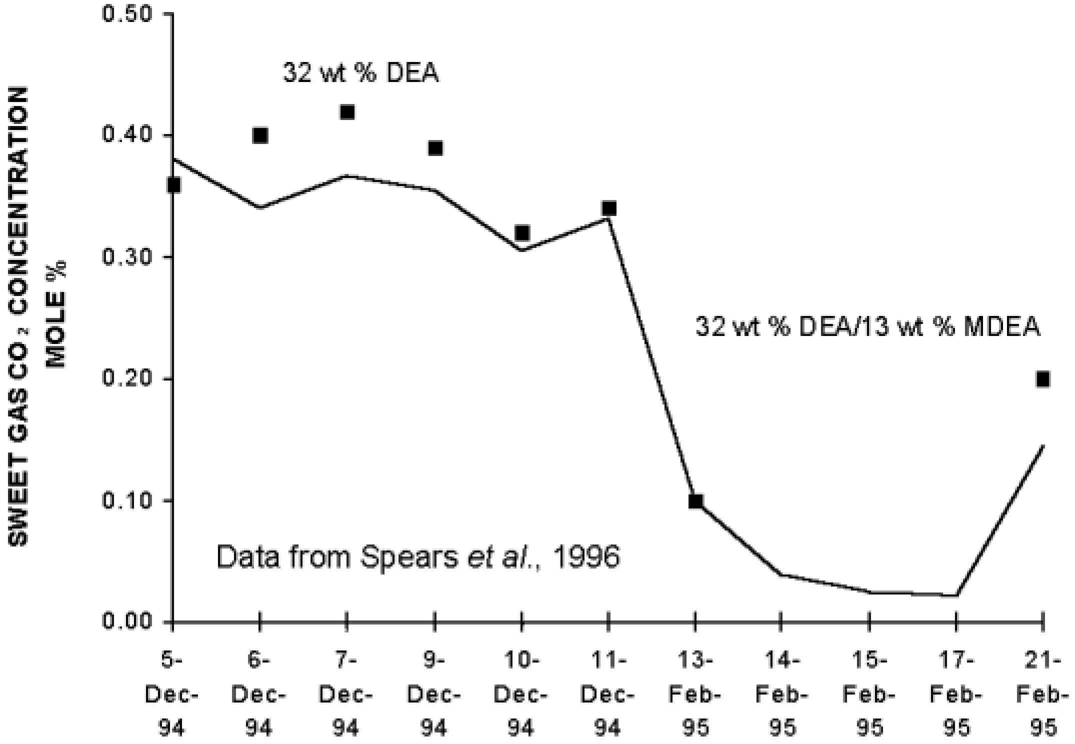

Fig. 2. Comparison between plant data and TSWEET results for CO_2 concentration in the sweet gas for a single amine and a mixture of amines.

Using the simulator, the amine concentration, use of a mixed amine system, and lean amine temperature were studied. These variables can be altered without having to increase existing equipment or purchase new capital equipment. Increasing circulation rates, stripping steam, or increasing the number of equilibrium stages all may require some capital investment if the plant is currently running at capacity.

Bullin *et al.* (1989) discuss the effect of lean amine temperature on CO_2 removal using MDEA. This paper analyzes an inlet gas stream with both low and high concentrations of CO_2. In both cases, increasing the trim cooler temperature within the range of 311 to 328K (100 to 130°F) increased the amount of CO_2 absorbed. Exceeding this upper temperature results in a decrease in the CO_2 absorbed because of the decrease in solubility. However, the maximum temperature appears to be a function of amine concentration, inlet acid gas concentration, and amount of acid gas absorbed in the contactor. Unfortunately, no data were available for comparison at the time.

The example facility discussed here should not be thought of as being representative of general conditions since, in gas processing, there really is no "general case." Each case must be considered on an individual basis due to a wide range of conditions and requirements for gas processing units. The engineer may not have control over some variables such as inlet gas flow rate and composition. Moreover, the objective of each sweetening unit may be different depending of the ultimate destination of the sweetened gas. For example, two facilities may use the exact same inlet gas composition and flow rate. One facility may be able to slip as much CO_2 as possible while the other facility may have strict limitations on sweet gas CO_2 concentration. In either case, the H_2S must be achieved. Each of these facilities should be designed differently to achieve the objective as optimally as possible.

Amine Concentration

The simplest variable to explore is increasing the amine concentration. However, this is not always feasible because of corrosion. High primary and secondary amine concentrations result in rich acid gas loadings which are high enough to cause severe corrosion problems in the lean/rich exchanger and reboiler. Figure 3 shows the sweet gas CO_2 and H_2S concentration as a function of wt % amine. DEA, DIPA, and MDEA were studied while holding the other process variables constant.

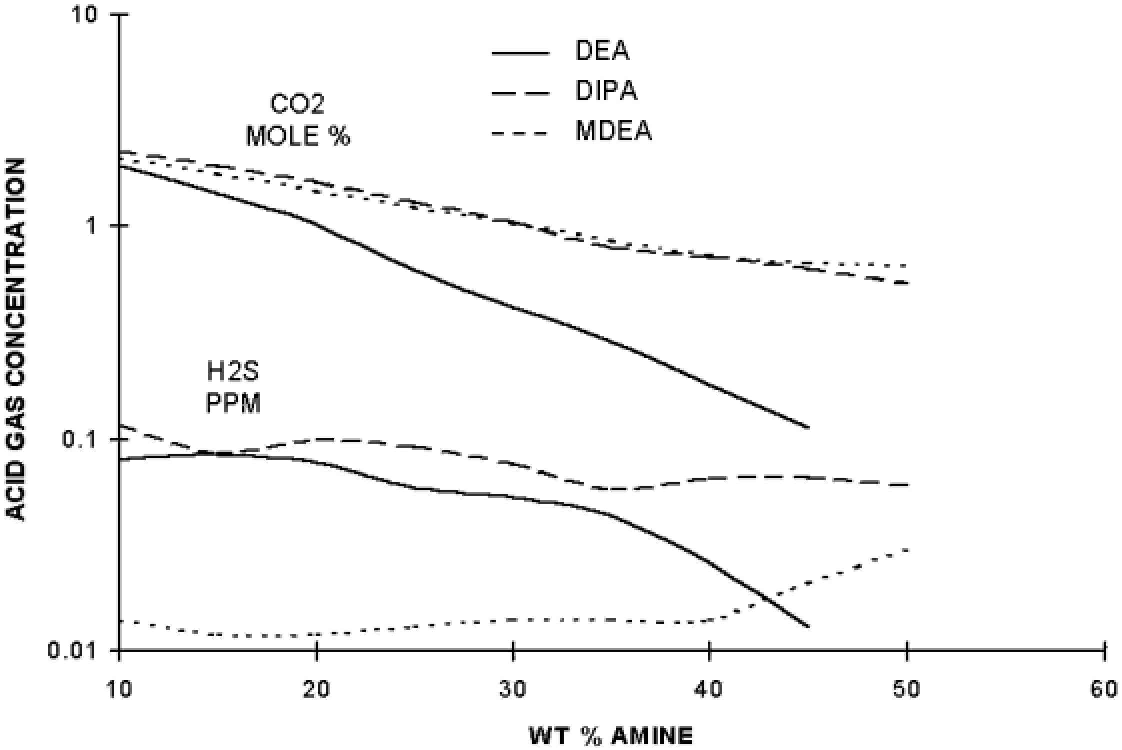

Fig. 3. Calculated results for CO_2 and H_2S concentration in the sweet gas for DEA, DIPA, and MDEA as a function of weight percent amine.

For DEA, both CO_2 and H_2S concentrations decreased with increasing amine concentration. For DIPA and MDEA, CO_2 concentrations decreased but H_2S concentrations remained relatively unchanged with increasing amine concentration. The additional CO_2 absorbed by these amines tends to displace the H_2S. For this case, the H_2S concentration was always well within specification for all amines studied.

Based on Figure 3, DEA at 40 wt % or greater is required to achieve the specified acid gas removal. At that concentration DEA tends to pick up a large amount of acid gases and may cause corrosive conditions. In this particular case, increasing the amine concentration is not a viable option.

Amine Mixtures

Since the CO_2 specification was not achieved with increasing concentration for a single amine, the possibility of amine mixtures was explored. Figure 4 shows the CO_2 concentration in the sweet gas as a function of wt % MDEA added to a 30 wt % DEA solution. H_2S concentrations are not shown since these were well below specification. The circulation rates and all other process variables were held constant. Since highly loaded MDEA is not nearly as corrosive as DEA, higher amine concentrations can be used. With the addition of 5 % MDEA, the facility was within specification; 10 % MDEA allowed the facility to operate within a safety margin. It may seem ironic that adding an amine known for slipping CO_2 would tend to increase the pickup of CO_2. However, adding

MDEA increases the *total* amine concentration.

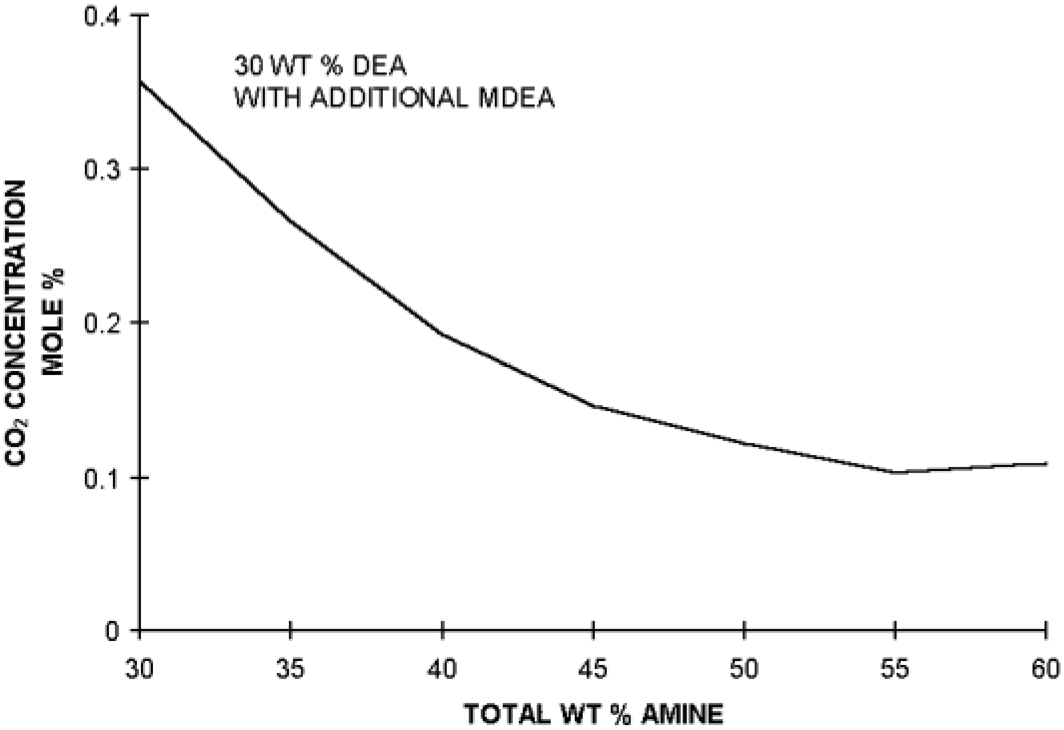

Fig. 4. Calculated results for CO_2 concentration in the sweet gas for DEA/MDEA mixture.

Figure 5 compares the sweet gas CO_2 concentration for DEA and a DEA/MDEA mixture. The solid line represents DEA at the 12/94 inlet conditions of the operating facility and the dashed line represents the DEA/MDEA mixture at the 2/95 inlet conditions. Since the slope of the pure DEA line is greater than that of the MDEA/DEA mixture, this suggests that the DEA alone has a greater affinity to absorb CO_2 than MDEA in the mixture. Using MDEA is advantageous only to the extent that it increases the amine concentration and decreases the mixture's heat of absorption while being much less corrosive.

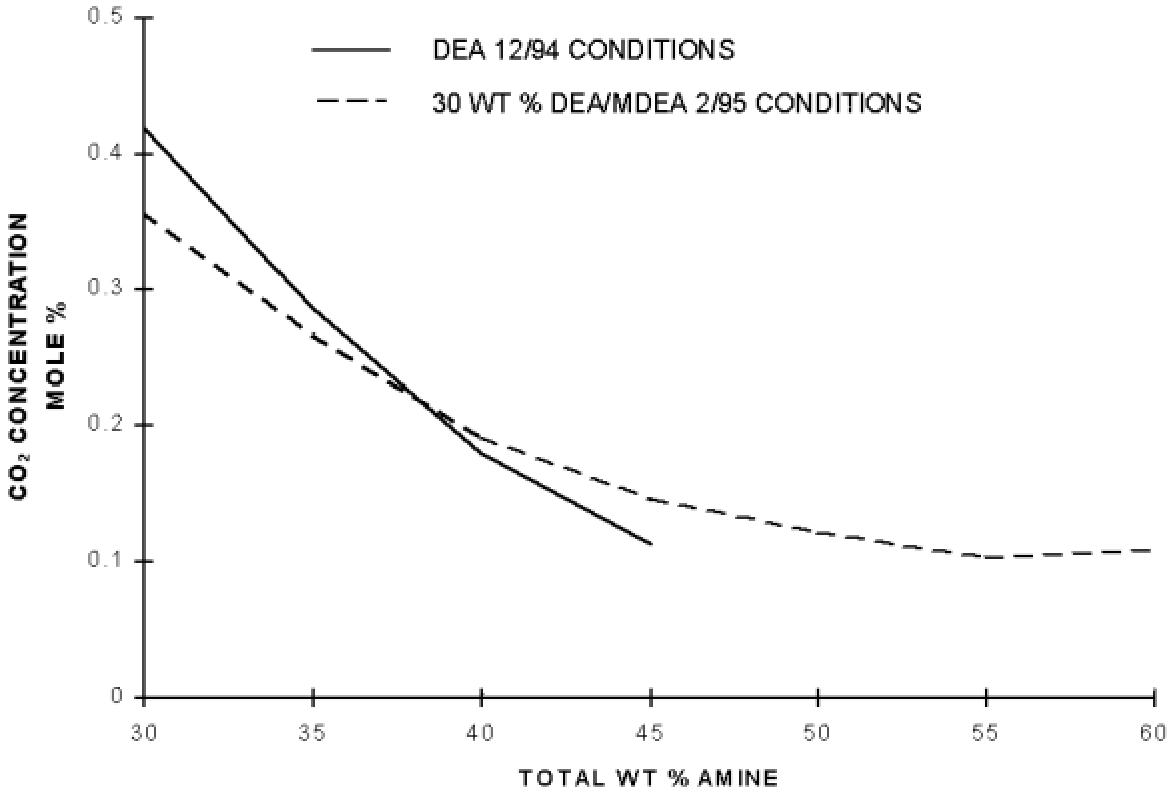

Fig. 5. Comparison between calculated results for CO2 concentration in the sweet gas for DEA and DEA/MDEA mixture.

Trim Cooler Temperature

For selective amine sweetening, the competition between thermodynamic equilibrium and kinetically limited absorption may be exploited. Temperature variation of the lean amine appears to have an effect on the amount of CO_2 absorbed. This may be important for removing significant amounts of CO_2 from the inlet stream.

Figure 6 shows the Bryan gas plant data as a function of lean amine temperature.

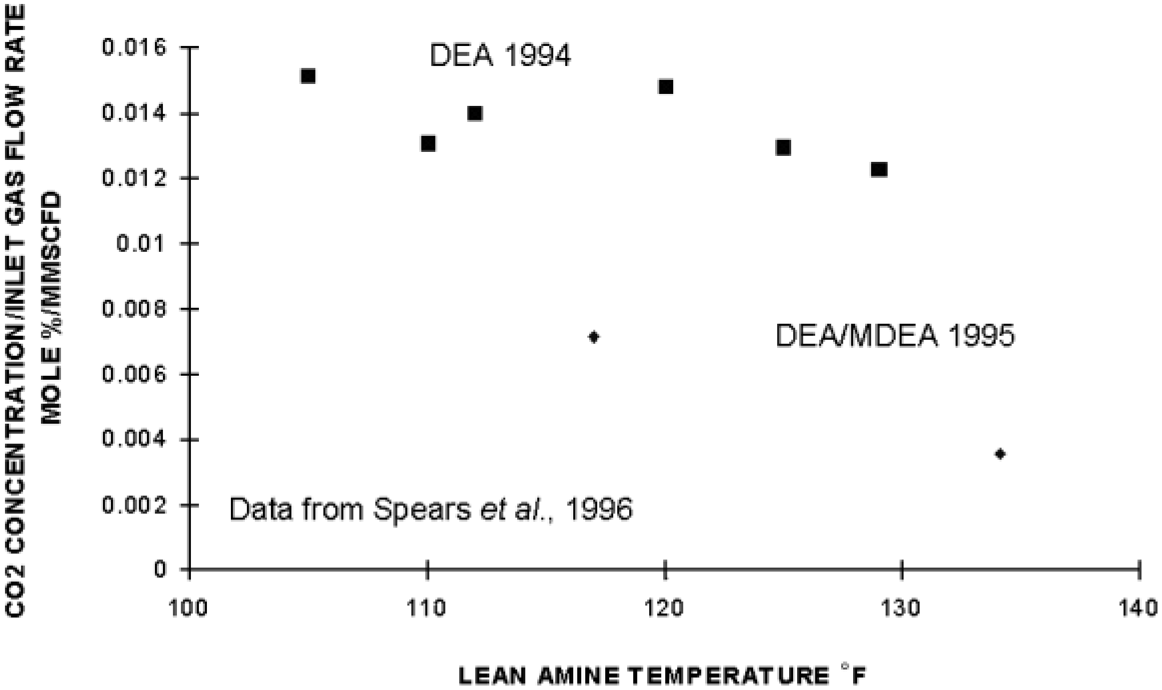

Fig. 6. CO_2 concentration in the sweet gas per unit volumetric flow rate of inlet gas as a function of lean amine temperature for a single amine and mixtures of amines.

Since the inlet gas flow rate varied slightly while the acid gas composition and all other process variables remained the same, Figure 6 shows CO_2 concentration in the sweet gas on a per volume inlet gas flow rate basis. The limited data suggests that trim cooler temperature does affect CO_2 absorption using selective amines. Furthermore, for the temperatures from 314 to 331K (105 to 135°F), as the lean temperature increases, the CO_2 concentration in the sweet gas decreases.

Again, the simulator was used to study how lean amine temperature affects the CO_2 composition of the sweet gas while holding all other process variables constant. Obviously, the duty in the lean amine cooler and the amine and water makeup are adjusted to account for increases in lean amine temperature.

Figure 7 shows the acid gas concentration in the sweet gas as a function of lean amine temperature for 32 wt % DEA. For this system, the concentration of H_2S increases monotonically with trim cooler temperature due to decreasing solubility. Even with lean amine temperatures of 336K (145°F), the H_2S specification is met. The sweet gas CO_2 concentration exhibits a minimum at a lean amine temperature of 322K (120°F). The higher temperature increases the kinetic effect to a greater extent relative to the decrease in solubility. However, after a certain temperature, the solubility dominates the kinetics. Note that the CO_2 concentration is never below the specification of 0.35 mole %.

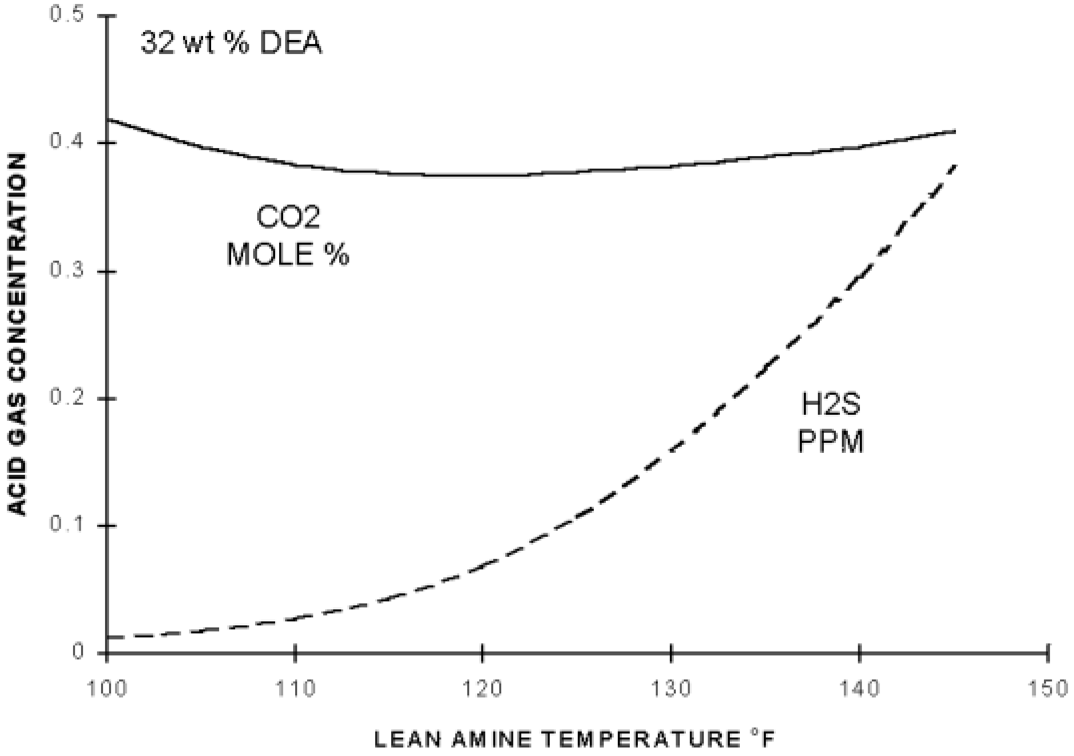

Fig. 7. Calculated CO_2 and H_2S concentrations in the sweet gas as a function of lean amine temperature for 32 wt % DEA.

Figure 8 compares DEA, DIPA, and MDEA at 32 wt % for lean amine temperatures from 311 to 336K (100 to 145° F). DIPA and MDEA show more dramatic effects than DEA since DIPA and MDEA are more selective or kinetically controlled. MDEA shows a 40 % decrease in the CO_2 concentration in the sweet gas from 311 to 327K (100 to 130°F). It is worth noting that the 32 wt % DIPA and MDEA cross at approximately 322K (120°F). For the same wt % amine, DIPA absorbs more CO_2 than MDEA at lower temperatures but absorbs less than MDEA at higher temperatures. However, neither MDEA nor DIPA at 32 wt % concentration absorb enough CO_2 to meet the specification.

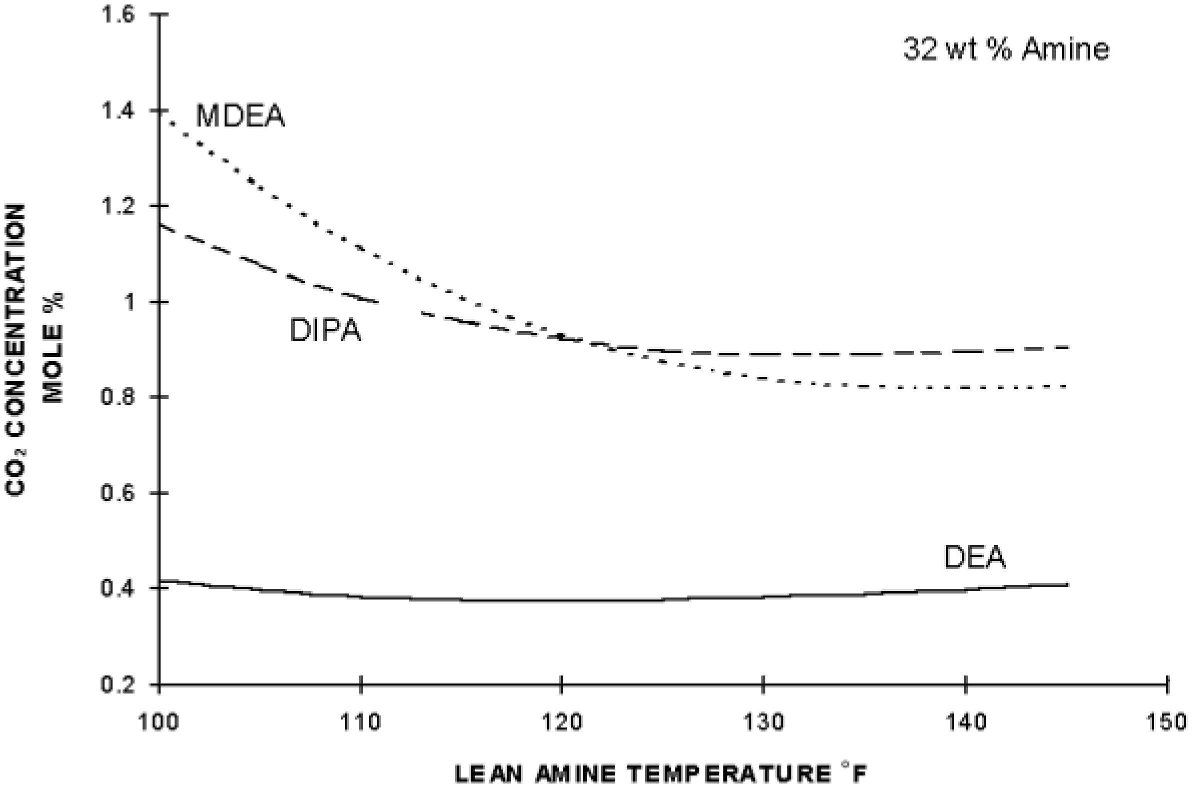

Fig. 8. Comparisons between calculated CO_2 concentrations in the sweet gas as a function of lean amine temperature for DEA, DIPA, and MDEA at 32 wt %.

With increasing lean amine temperatures, water and amine losses should increase. For DEA, DIPA, and MDEA, amine losses approximately doubled from 311 to 333K (100 to 140°F). However, water losses increased by a factor of 6 as shown in Figure 9. The simulator results indicate that most of the water loss occurs in the absorber as the sweet gas exits saturated with water at higher temperatures. Losses in the flash tank and stripper were minimal.

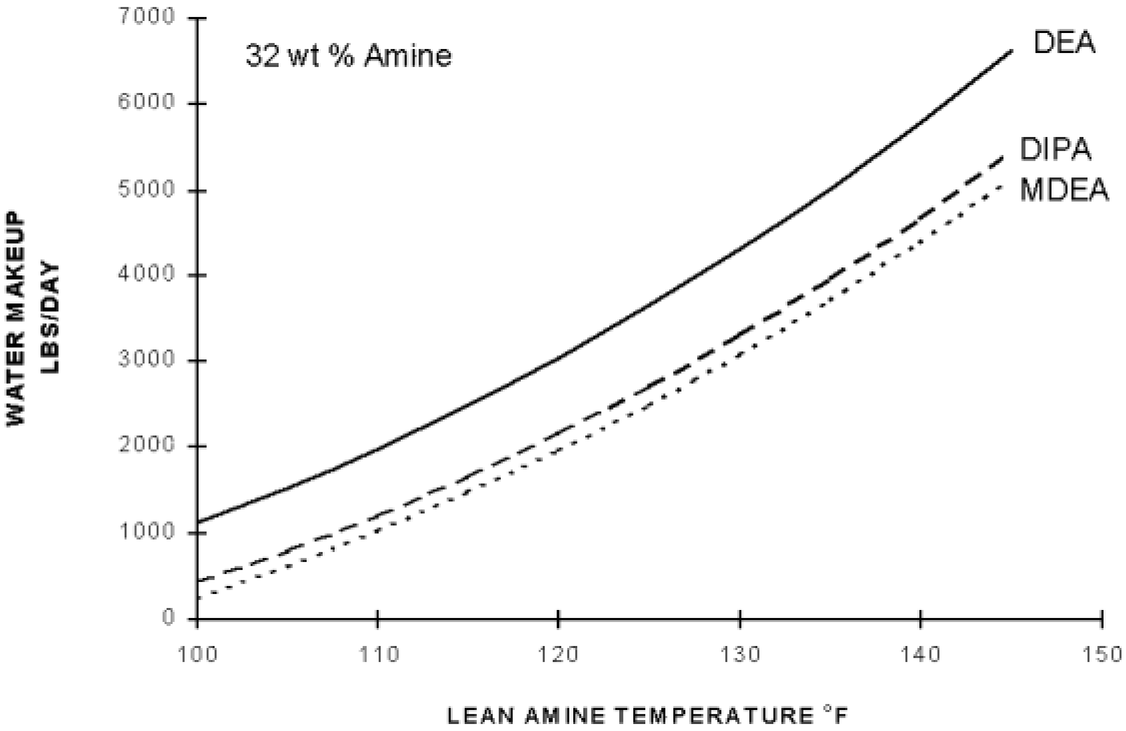

Fig. 9. Comparisons between calculated water makeup as a function of lean amine temperature for 32 wt % DEA, DIPA, and MDEA.

Next, mixtures of amines and lean amine temperature were studied simultaneously. The base concentration was 30 wt % DEA. With the same circulation rate, the MDEA concentration was increased to 30 wt %. The lean amine temperature varied from 311 to 336K (100 to 145°F). Since the single amine concentrations achieved the H_2S specification, the CO_2 concentration in the sweet gas was the only concern. In all cases, increasing the concentration of the MDEA in the solution decreases the concentration of CO_2 in the sweet gas. Addition of further MDEA after 25 wt % appears to have little effect on further CO_2 pickup.

More interesting is the effect of wt % MDEA on the minimum CO_2 concentration in the sweet gas as a function of lean amine temperature. With DEA alone, the minimum concentration is at a temperature of 322K (120°F). With the addition of 5 wt % MDEA the minimum occurs at 319K (115°F). From there, the minimum temperature increases with increasing MDEA concentration.

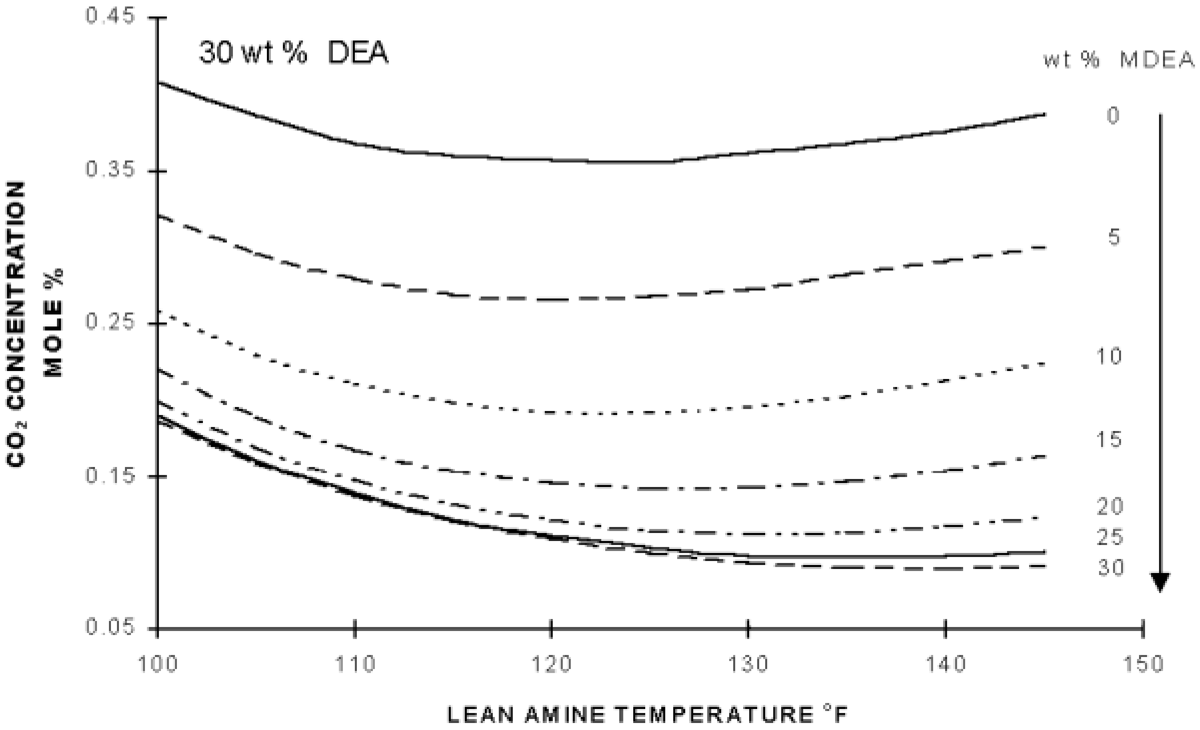

Fig. 10. Comparisons between calculated CO_2 concentrations in the sweet gas for 30 wt % DEA as a function of lean amine temperature and wt % MDEA.

Although this study examined the effect of lean amine temperature on CO_2 pickup for selective amines, the opposite objective can also be explored. By decreasing the lean amine temperature or precooling the inlet gas the operator should be able to realize increased CO_2 slip.

GENERAL GUIDELINES

Using information from the specific case presented here, a few generalities or guidelines can be inferred for other facilities. If the objective is to slip as much CO_2 as possible while meeting the H_2S specification, use the most selective amine (MDEA) at a low concentration and flow rate. Use as few theoretical equilibrium stages as possible and operate the absorber at the lowest temperature possible. Since CO_2 absorption is kinetically controlled, decreasing the contact time and temperature tends to increase the amount of CO_2 slip. The limits of solution concentration, flow rate and equilibrium stages depend on the H_2S specification. The cold absorber temperature also enhances H_2S solubility. Facilities with this objective tend to be fairly stable as the inlet gas composition increases in CO_2 concentration. Furthermore, facilities that were designed using non-selective amines tend to be oversized when switching to selective amines because the lower heat of absorption and lower circulation rates required.

If the objective is to achieve a certain CO_2 specification, then the problem is more complicated and several variables must be considered. The first variable to consider is the base or stock solution. If the amine is a secondary amine, such as DEA, attempts should be made to increase the amine concentration. Higher amine concentration increases CO_2 pickup. However, care should be taken not exceed corrosion limits. If the unit uses a single amine, increasing the amine concentration via an amine mixture is an alternative. Adding MDEA increases the amine concentration with higher corrosion limitations. Furthermore, with MDEA having a lower heat of absorption, problems with an undersized reboilers are unlikely. If the base or stock solution is MDEA, then the only amine mixture to consider is with a primary (MEA) or secondary (DEA) amine. These amines increase the CO_2 pickup but have higher heats of absorption than MDEA and tend to be more corrosive. Problems with undersized reboilers may result. Finally, increasing the lean amine temperature increases CO_2 pickup; however, there is a limit to the maximum temperature. This temperature depends on amine concentration, inlet gas composition, and the amount of CO_2 pickup. Increasing the lean amine temperature decreases H_2S pickup and increases amine and water losses. These variables also need to be checked.

CONCLUSIONS

The ultimate goal of amine sweetening is to produce specification quality product as economically as possible. Amine technology has produced selective absorbents which remove H_2S in the presence of CO_2. The use of selective amines results in lower circulation rates, reboiler sizes and duties while meeting the H_2S specification. Unfortunately, many operators now are exceeding the CO_2 specification in their sweet gas streams due to changes in inlet composition or increased throughput. Achieving specifications within the constraints of the process equipment is most cost effective and desirable.

The process simulator TSWEET was used to analyze an amine sweetening unit with regard to amine concentration, use of amine mixtures, and lean amine temperature. Increasing the amine concentration is advantageous if the concentration does not exceed the corrosion limits. Using mixtures of amines appears to be the best alternative for increasing CO_2 pickup for DEA and MDEA based solutions. Finally, with selective amines such as DEA, DIPA, and MDEA, the lean amine temperature can be varied to further decrease the concentration of the CO_2 in the sweet gas. This improvement is a function of amine concentration but can approach 20%. Unfortunately, increased trim cooler temperature also results in lower H_2S pickup and increases in water losses from the absorber.

In general, if the objective is to slip as much CO_2 as possible, the engineer should consider using the most selective amine at the lowest concentration and circulation rate with the fewest number of equilibrium stages in the absorber to achieve the H_2S specification. Cold absorber temperatures tend to increase the CO_2 slip and enhance H_2S pickup. If the objective is to achieve a certain CO_2 concentration, then the problem is more complicated. Variables to consider include increasing the amine concentration and

using mixtures of amines. However, equipment size may have to be reevaluated. Increasing the lean amine temperature increases CO_2 pickup for the selective amines to a point. The maximum temperature depends on amine concentration, inlet gas composition, and loading. Higher lean amine temperature also increases water and amine losses and decreases H_2S pickup.

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