

HYDROCARBONS AND BTEX PICKUP AND CONTROL FROM AMINE SYSTEMS

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ABSTRACT

HC and BTEX absorption into amine solutions has received increased attention over the last decade due to emissions to the atmosphere or to problems in downstream equipment. The collection of VLE and VLLE data by GPA and others have facilitated the development of a model for the absorption and removal processes. The amount of HC and BTEX emitted or passed to downstream equipment may be controlled by reducing the absorption or by removal from the rich amine.

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INTRODUCTION

Over the last decade, the problems created by the absorption of hydrocarbons (HC) and aromatic compounds consisting of benzene, toluene, ethylbenzene and xylenes (BTEX) in various areas of gas processing have become widely recognized. The problems include HC and BTEX emissions to the atmosphere as well as to further downstream processes. The two primary areas for BTEX absorption occur in amine sweetening and glycol dehydration. In many cases, the amine sweetening unit is followed by a glycol dehydration unit.

In a typical amine sweetening unit as shown in Figure 1, acid gases (consisting mainly of H₂S and CO₂) along with some HC and BTEX (if present in feed gas) are absorbed by the amine solution in the contactor. Depending upon the pressure in the contactor, a flash tank immediately downstream of the contactor allows some of the acid gases, HC and BTEX to be flashed from the amine solution. Nearly all of the remaining acid gases, HC and BTEX are removed from the amine solution in the regenerator.

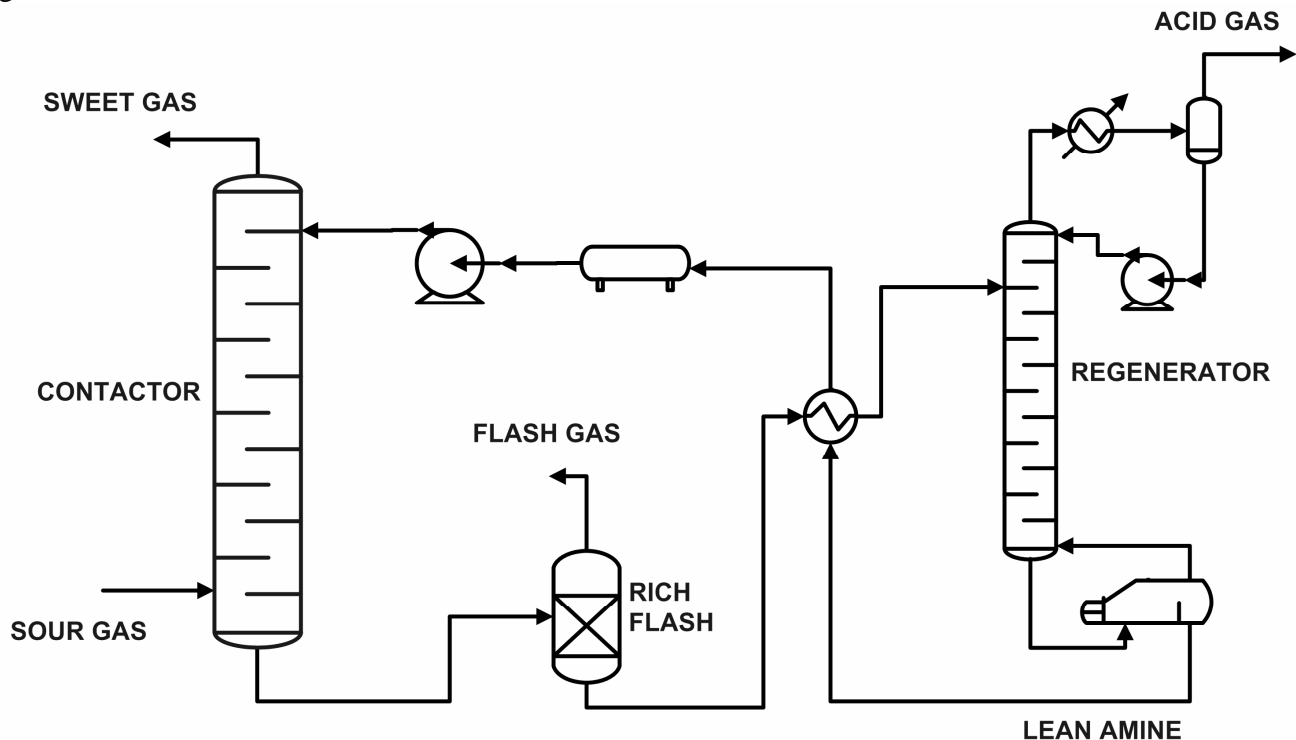


Figure 1 – Simple Amine Sweetening Facility

If the flash tank and regenerator are vented, the acid gases, HC and BTEX would be directly emitted to the atmosphere. The Clean Air Act limits the amounts of heavy hydrocarbons (Volatile Organic Compounds) which may be emitted from a facility to 250 tons per year. Aromatic compounds such as BTEX are limited to a cumulative amount of 25 tons per year and 10 tons per year of any individual aromatic.

If the acid gases are fed to a sulfur recovery unit, the heavy HC and, particularly, BTEX are known to cause problems. BTEX are difficult to burn and can cause coking in the catalyst beds. In split flow plants where part of the acid gas stream is passed around the burner, some of the BTEX can pass through the catalyst beds and into the tail gas.

Thus, to adequately investigate HC and BTEX pickup and control, it has become increasingly important to develop accurate and reliable methods to predict the absorption, desorption and control of HC and BTEX in amine sweetening units. For the development of the methods, vapor-liquid equilibria (VLE), vapor-liquid-liquid equilibria (VLLE) and thermodynamic data must be available along with plant operating data for verification. As reviewed below, this data has, historically, been very limited.

VLE AND OPERATING DATA

McIntyre et al. [1] presented an excellent review and summary of the VLE, VLLE and operating data for HC and BTEX in amine systems. Their review is summarized below and extended to cover other sources of data as well as the recently available Project 971 [GPA Research Report 971 (RR-971)] by Valtz et al. [2] and to include the impact of acid gas loading on the solubility of HC and BTEX in amine solutions. Since increased acid gas loading can reduce the HC and BTEX solubility by as much as 30 to 40% (RR-971), it is an essential feature in any analysis.

VLE Data

The published VLE data are summarized in Table 1. As can be seen from this table, prior to the data by Critchfield et al. [13] in 2001, the HC data were limited to methane and ethane except for the propane and n-butane in MDEA data by Carroll, et al. [5] and Jou et al. [6]. Furthermore, the propane and n-butane in MDEA data did not include the impact of acid gas loading.

As can also be seen from Table 1, prior to the data by Hegarty and Hawthorne [11] in 1999, and the RR-971 [2] data in 2002, there was almost a total void of data for BTEX. From the BTEX data, the only data including acid gas loading was for toluene with CO₂ (RR-971).

Operating Plant Data

As discussed by McIntyre et al. [1], there are only about 10 cases reported in the literature where some absorption data for HC and BTEX are measured from operating plants. From these, only about 4 or 5 give nearly complete data. The sources of the available plant operating data are presented in Table 2. Further details on the operating data can be obtained from McIntyre et al. [1] or from the original work cited in Table 2.

MODEL DEVELOPMENT

Along with the data for solubility of the various HC and BTEX in water, the above referenced data were used to develop a model for the solubility of HC and BTEX in amine solutions. This model has been incorporated in TSWEET® and is currently being incorporated into ProMax® with TSWEET and PROSIM.

The current TSWEET model calculates the HC and BTEX solubility as a function of temperature, pressure, amine type and amine concentration. The TSWEET model does not include the effect of acid gas loading on solubility and is based on a limited portion of the RR-971 data. The ProMax model will include the effect of acid gas loading and will incorporate all of the available data. The TSWEET model was used in this work to perform parametric studies and illustrate trends except as noted in the discussion.

Table 1 – Sources of Solubility Data for HC and BTEX in Amine Solutions

<u>Year</u>	<u>Authors</u>	<u>Solvent</u>	<u>Concentration</u>	<u>Component</u>	<u>Temperature</u>	<u>Acid Gas Loading</u>
1976	Lawson and Garst [3] ^a	MEA, DEA	5, 15, 25, 40 wt%	Methane, Ethane	100 - 250°F	-
1986	Dingman [4]	DGA [®]	50 wt%	Methane	150 - 190°F	-
1992	Carroll <i>et al.</i> [5]	MDEA	3 M	Propane	25 - 150°C	-
1996	Jou <i>et al.</i> [6]	MDEA	3 M	<i>n</i> -Butane	25 - 125°C	-
1996	Jou <i>et al.</i> [7]	TEA	2, 3, 5 M	Ethane	25 - 150°C	-
1998	Jou <i>et al.</i> [8]	DGA	3, 6 M	Methane	25 - 125°C	-
1998	Jou <i>et al.</i> [9]	MDEA	3 M	Methane, Ethane	25 - 130°C	-
1998	Carroll <i>et al.</i> [10]	MEA, DEA, TEA	3 M	Methane	25 - 125°C	-
1999	Hegarty and Hawthorne [11]	MDEA	25, 50 wt%	Benzene, Toluene	25 - 120°C	-
		DGA	35 wt%	Benzene, Toluene	60°C	-
2001	Addicks, <i>et al.</i> [12]	MDEA		Methane	40, 80°C	Limited
2001 2002	Critchfield <i>et al.</i> [13] Jou <i>et al.</i> [14]	MEA, DEA, DGA, MDEA, DIPA	3, 4.5 M	Methane, Ethane, Propane, <i>n</i> -Butane, <i>n</i> -Pentane, Benzene	40°C	-
2002	Valtz <i>et al.</i> [2]	MDEA, DGA, DEA, MEA	Varying	Benzene, Toluene, Ethylbenzene, Xylene	Varying	Limited
2002	Addicks and Owren [15]	MDEA	30 – 50 wt%	Methane	40 - 80°C	Yes

^aAddendum in 1996 by Mather and Marsh [23].

Table 2 – Sources of Plant Operating Data for HC and BTEX in Amine Sweetening Units

<u>Year</u>	<u>Authors</u>	<u>Amine</u>	<u>Number of Plants with Data</u>
1972	Harbison and Dingman [16]	DGA	1
1981	Huval and Van de Venne [17]	DGA	1
1984	Law and Seidlitz [18]		1
1996	Morrow [19]	-	1
1997	Skinner et al. [20]	DEA MEA	5 1
1999	Hegarty and Hawthorne [11]	MDEA	1

METHODS TO CONTROL HC AND BTEX ABSORPTION AND EMISSIONS

The methods to control HC and BTEX absorption and emissions may be divided into two types. The first is the selection of amine process conditions to reduce absorption. The second is the use of additional equipment to capture the absorbed HC and BTEX and prevent their emission into the acid gases.

Reducing HC and BTEX Absorption

Although in most cases many of the amine process conditions will not be flexible, full advantage should be taken of those that can be adjusted. In some cases, the process conditions to reduce the HC and BTEX absorption will conflict with the primary objective of acid gas removal and thus are not feasible. Since essentially all of the HC and BTEX absorbed in the contactor will be removed from the solution in the flash drum and regenerator, the emissions will be essentially equal to the amount absorbed. Again, the primary process conditions affecting absorption of HC and BTEX are temperature, pressure, amine solution circulation rate and amine type, concentration and acid gas loading. The impact of these process conditions were explored by parametric studies using the gas analysis shown in Table 3 except as noted below. In general, the other process parameters were changed to demonstrate the impact of the parameter under discussion. For example, the inlet gas temperature was manipulated to yield a range of rich amine temperatures.

Temperature

The effect of temperature on the absorption of methane, propane and benzene are shown in Figures 2 and 3. Since methane is above its critical temperature, its absorption is not impacted as much by temperature as the other HC and BTEX. The large amount of methane absorption compared to the other HC and BTEX is due to its very high partial pressure relative to the others. As can be seen from these figures, the absorption of the propane and benzene decreases by 30 to 40% with increased temperature from 90 to 140°F. Unfortunately, this same trend applies with acid gases except for some cases where CO₂ absorption is kinetically limited. However, in certain situations, it may be possible

to increase the absorber temperature and still meet the sweet gas specifications. For treating of LPG liquids, the absorption would behave in the opposite manner to gases and would increase with rich amine temperature because the solubility of liquids increases with temperature.

Table 3 - Gas Stream Used for Parametric Studies

<u>Composition</u>	<u>Mole %</u>
C ₁	83
C ₂	6
C ₃	4
C ₄	2
C ₅	0.5
C ₆	0.38
CO ₂	4
Benzene	0.06
Toluene	0.04
Ethylbenzene	0.01
Xylene	0.01

T = 85°F

P = 1000 psia

Flow = 300 MMSCFD

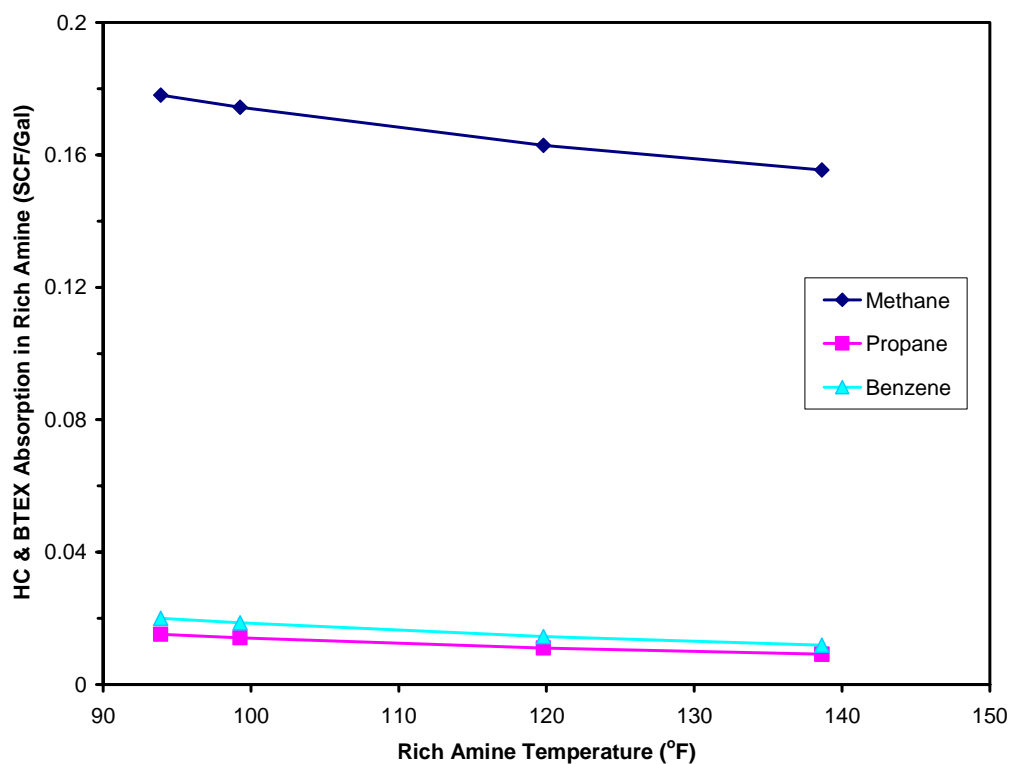


Figure 2 - The Influence of Rich Amine Temperature on HC & BTEX Absorption in 50 wt% MDEA

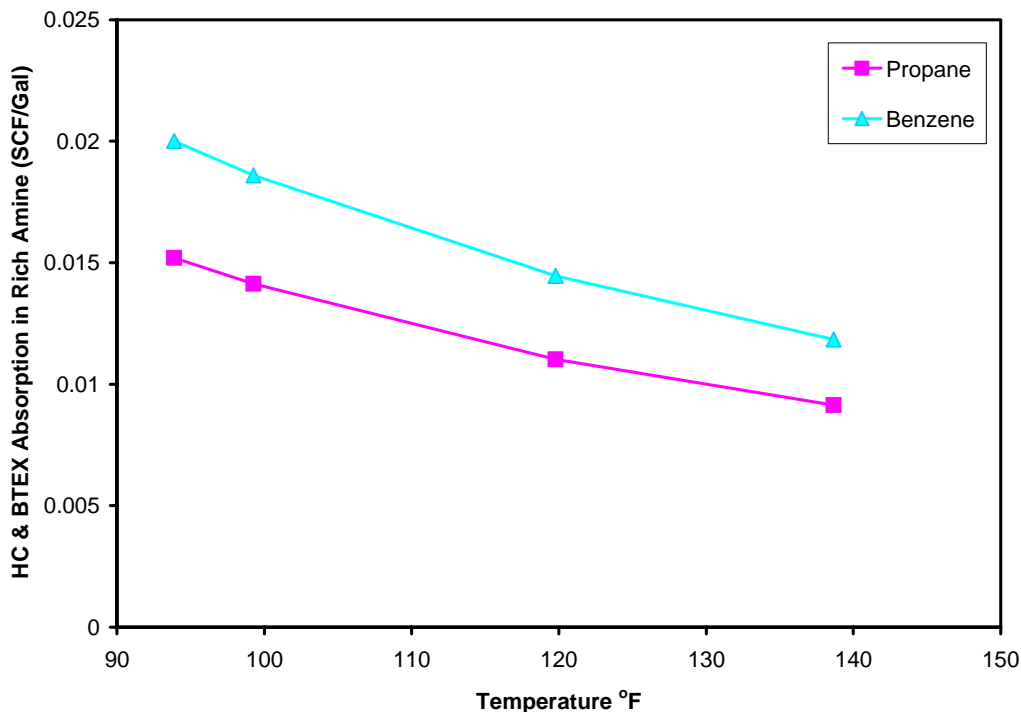


Figure 3 - The Influence of Rich Amine Temperature on HC & BTEX Absorption in 50 wt% MDEA

Pressure

The absorber pressure directly affects the partial pressure of the HC and BTEX and thus the amount absorbed. In almost all cases, the pressure is dictated by other constraints with very little flexibility. For treating of LPG liquids, pressure has little effect on absorption.

Amine Solution Circulation Rate

Since a relatively small portion of the HC and BTEX are absorbed by the amine solution, the amount of HC and BTEX picked up increases directly with circulation rate for any given amine type and concentration as shown in Figures 4 and 5. Thus, the circulation rate should be maintained as low as possible but not exceed the maximum acid gas loading that would lead to excessive corrosion.

Amine Type and Concentration

The RR-971 data for VLLE systems can be used to illustrate the relative solubility of HC and BTEX in various amine solutions as shown in Figure 6 for toluene. In regard to the large solubility differences between the two DGA® and two MDEA concentrations, Valtz et al. [2] have suggested that the solubility is a near logarithmic function of the amine concentration.

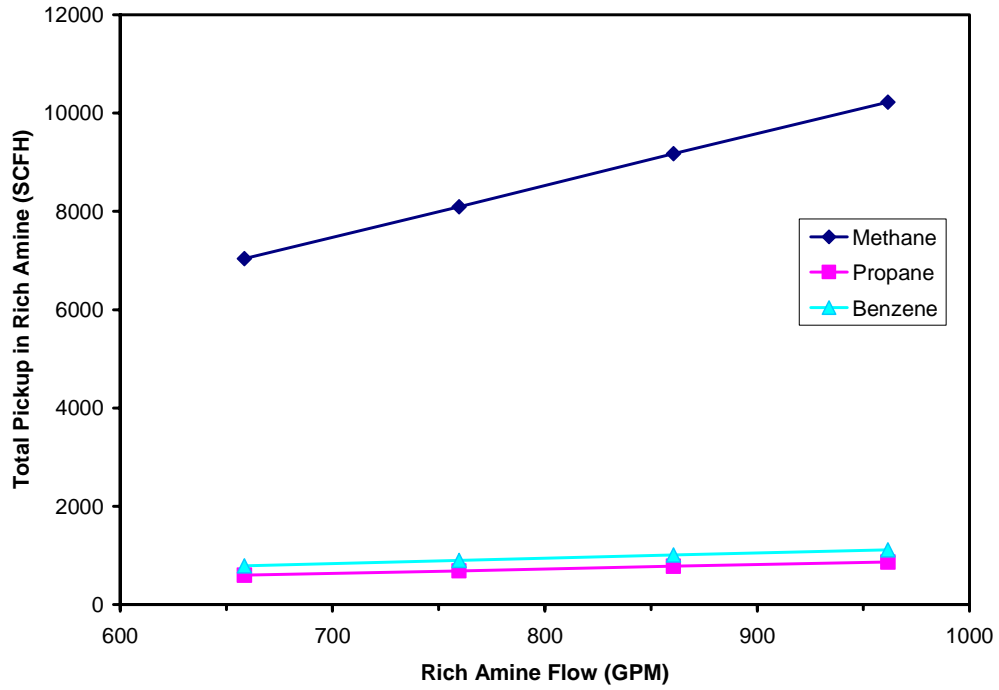


Figure 4 - The Influence of Circulation Rate on Total HC & BTEX Pickup for 50 wt% MDEA

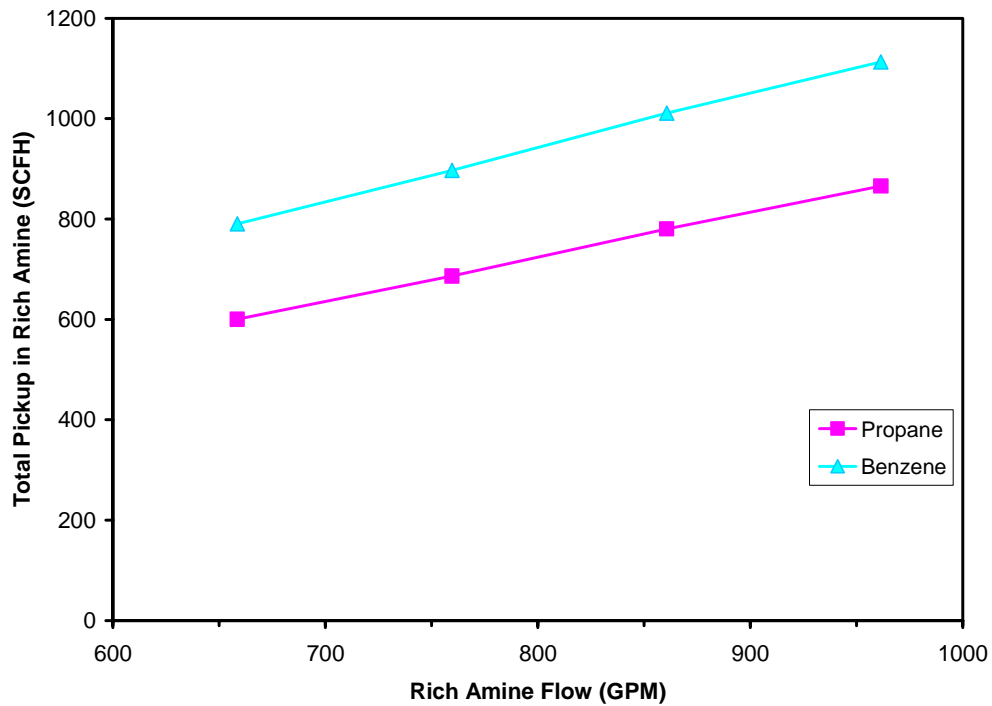


Figure 5 - The Influence of Circulation Rate on Total HC & BTEX Pickup for 50 wt% MDEA

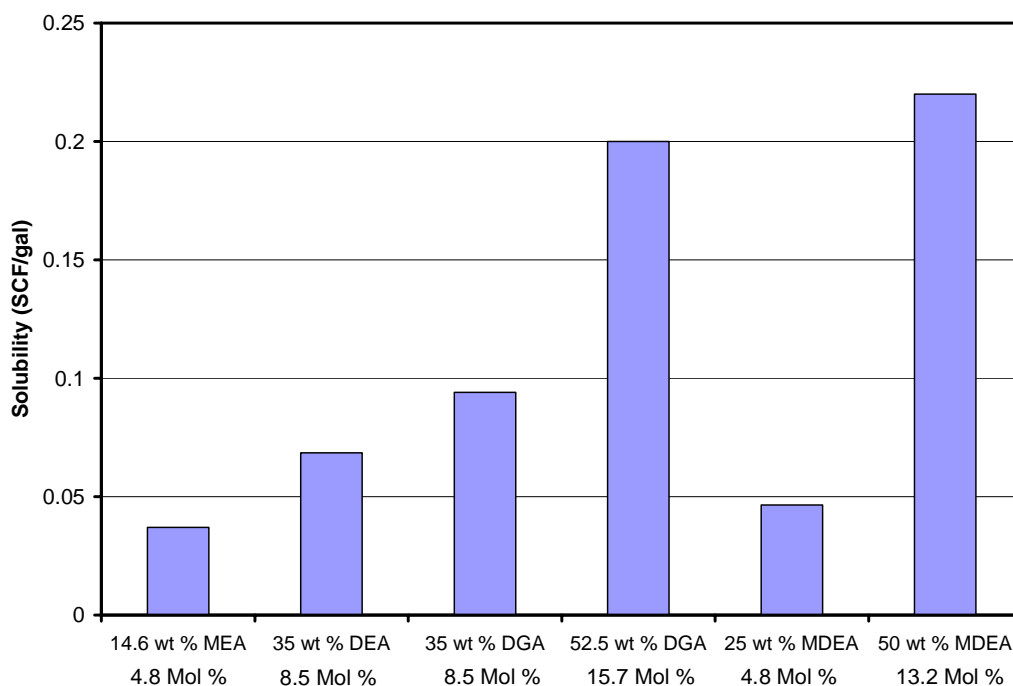


Figure 6 - Relative VLLE Solubility of Toluene in Amine Solutions at 100°F (Data from RR-971 [2])

Using the gas stream described in Table 3, the methane, propane and benzene absorption in the rich amine is compared in Figures 7-9 for water, 25 and 50 wt% MDEA at various rich amine temperatures. Figure 7 shows that the amine has very little impact on the absorption of methane. For propane, Figure 8 shows about a 10% increase in absorption from water to 25 wt% MDEA and about a 20+% increase from 25 to 50 wt% MDEA. For benzene, Figure 9 shows about a 100% increase in absorption from water to 25 wt% MDEA and nearly a 100% increase again from 25 to 50 wt% MDEA. Unfortunately, these are, again, the same trends that favor acid gas pickup. However, it may be possible to select both the amine and the concentration and still meet the sweetening requirements.

Amine Loading

As illustrated in Figure 10 for benzene, the solubility of the HC and BTEX may be reduced by as much as 30 to 40% at higher acid gas loadings. This observation has been verified with the data Critchfield et al. [11] and RR-971 [2] for VLLE systems. Obviously, the acid gas loading must be maintained sufficiently low to prevent excessive corrosion. Higher acid gas loadings have the added benefit of reducing the circulation rate which, in turn, reduces the HC and BTEX absorption. Thus, reducing the circulation rate to yield the higher acid gas loadings has a double benefit on reducing HC and BTEX absorption.

Overall Observations

As previously stated, the above analyses were performed to isolate and illustrate the impact of a single process parameter upon the absorption of HC and BTEX in the rich amine. In any plant application, many parameters will change at once and simulations should be performed to determine the solvent and process conditions that will minimize the total HC and BTEX absorption. In general, the total absorption from a gas into the rich amine can be reduced by higher rich amine temperatures, lower column pressures, lower amine circulation rates, higher acid gas loadings, lower amine concentrations and a lower molecular weight amine.

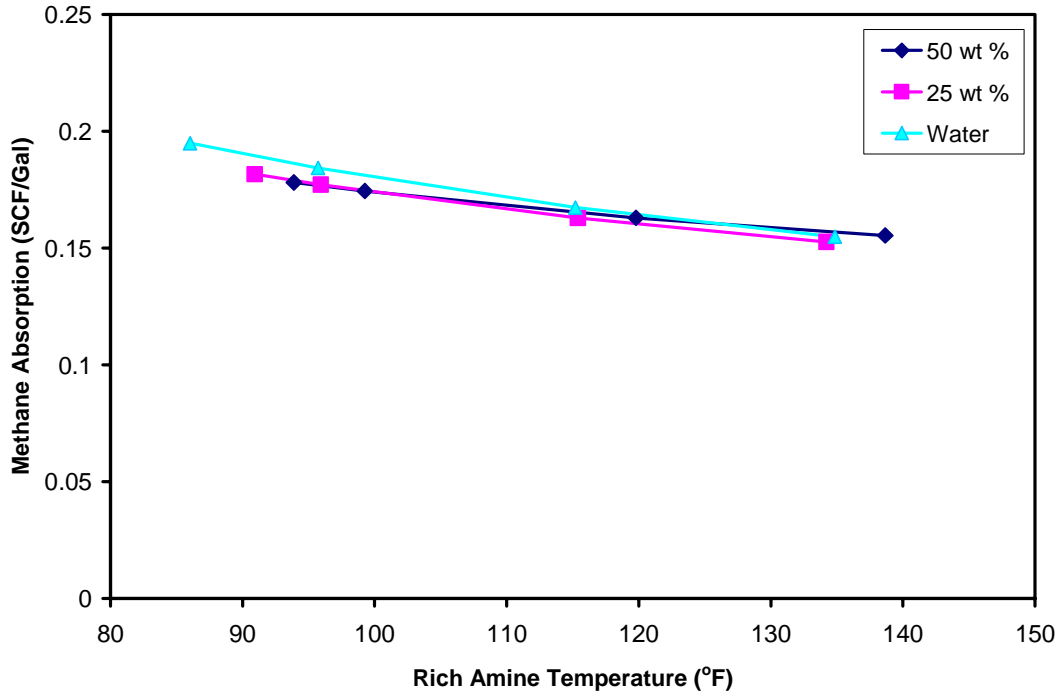


Figure 7 - Methane Absorption in MDEA Solutions

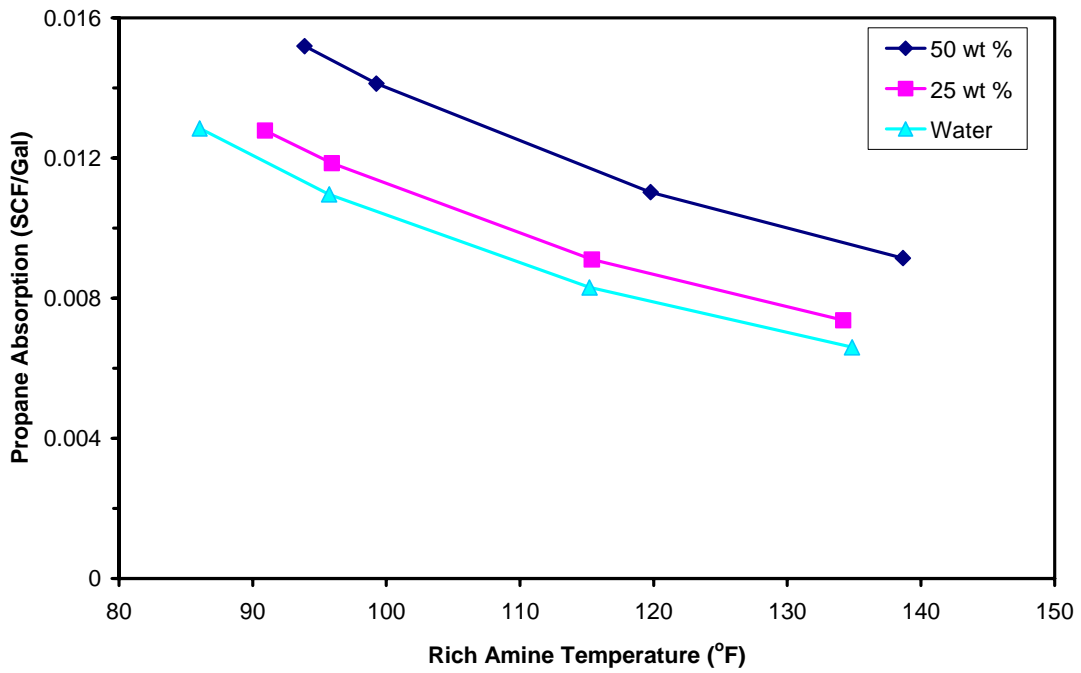


Figure 8 – Propane Absorption in MDEA Solutions

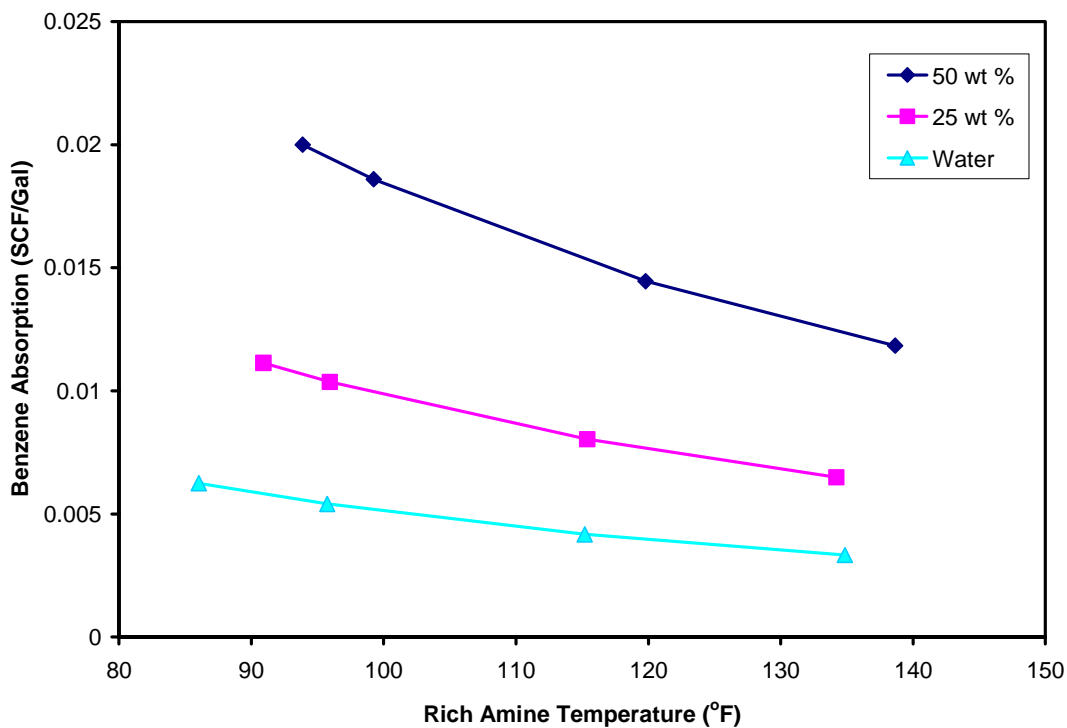


Figure 9 – Benzene Absorption in MDEA Solutions

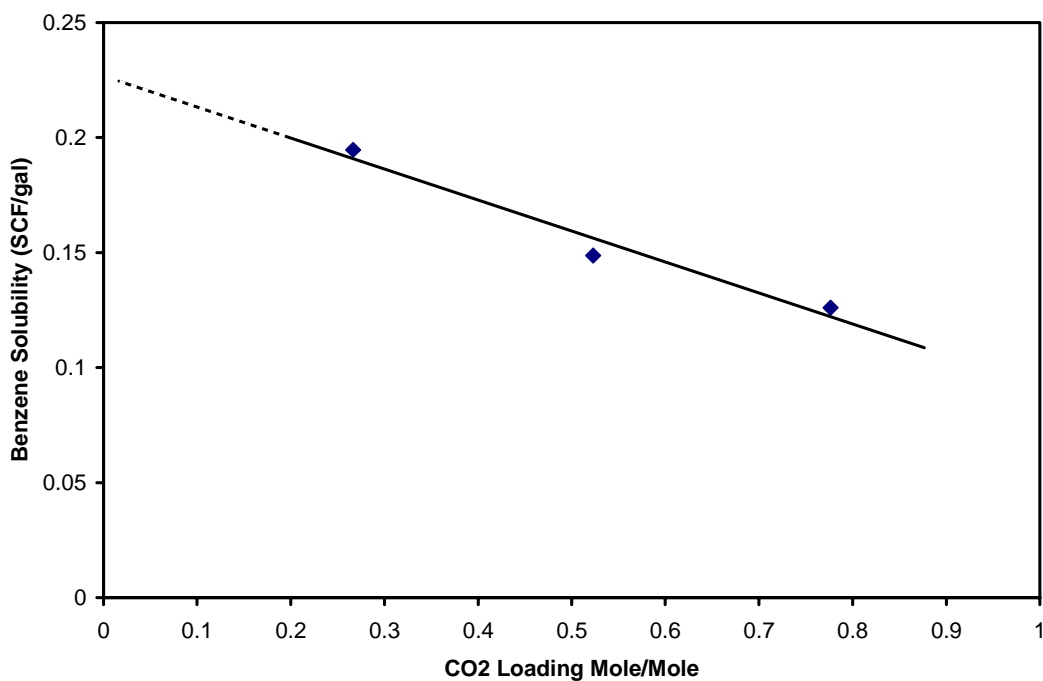


Figure 10 – Solubility of Benzene in 50 wt% MDEA-Water-CO₂ Mixture at 77°F (Data from RR-971 [2])

Removing HC and BTEX from Rich Amine

If the HC and BTEX absorption into the amine solution cannot be reduced sufficiently to meet the emission limits then other control methods must be used. These methods include a hot flash and a stripping column to remove HC and BTEX from the rich amine.

Hot Flash

As can be seen from the schematic of the hot flash method shown in Figure 11, a flash tank can be added in the rich amine stream between the lean/rich exchanger and the regenerator. If the H₂S content of the flash gas is above the site limits, a small amine absorber may be added onto the flash tank. The flash gas may be used as fuel thus destroying the HC and BTEX.

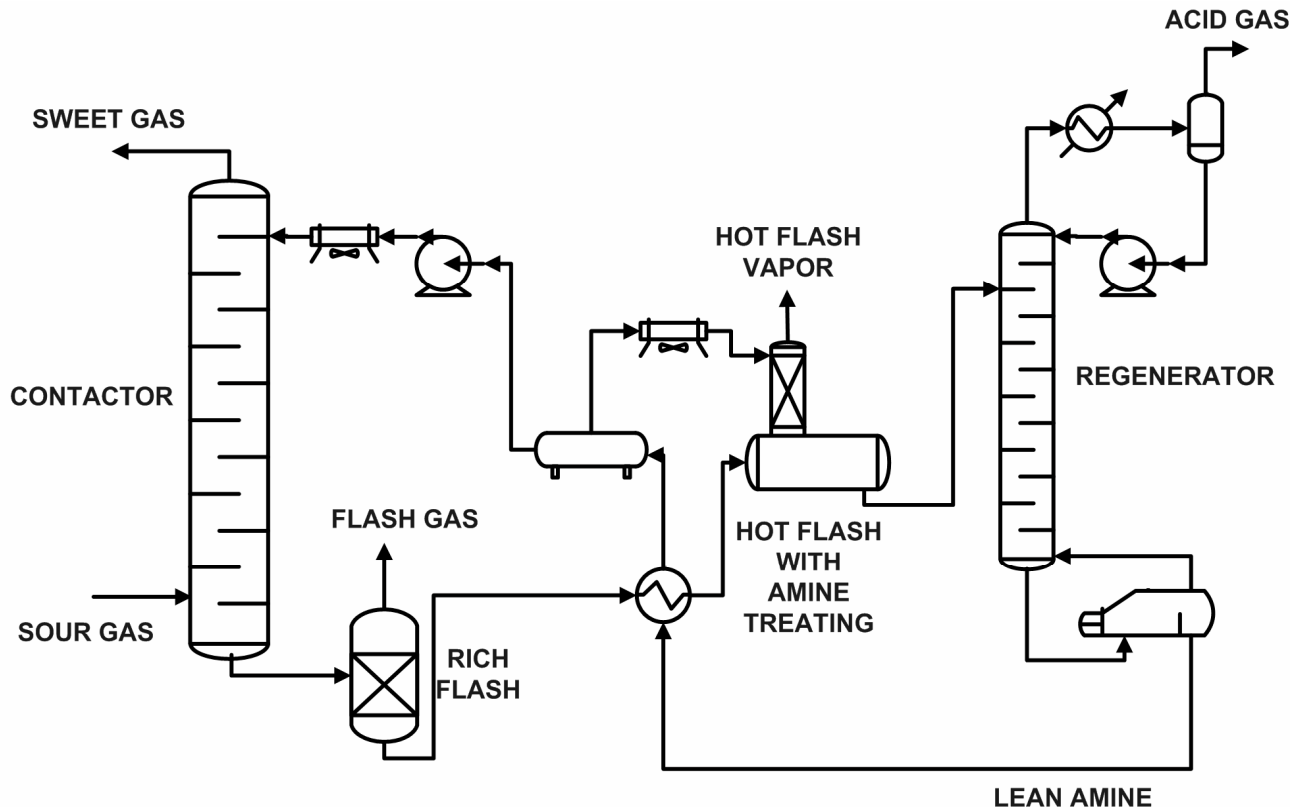


Figure 11 – Amine Sweetening with Hot Flash

To illustrate the performance of a hot flash, an amine system using 50wt% MDEA with the feed gas shown in Table 3 was simulated. As shown in Figure 12, about 80% of the methane and propane would be flashed at 150°F. However, for benzene, significant flashing starts at 150°F. This is most likely associated with and largely resulting from the flashing of the CO₂. It should be noted that, due to the relatively large amounts of CO₂ in the rich amine, the flashing of even 1% of the CO₂ produces very large volumes compared to the benzene. For this example, a hot flash would not be effective due to the large volumes of CO₂ that would also be liberated.

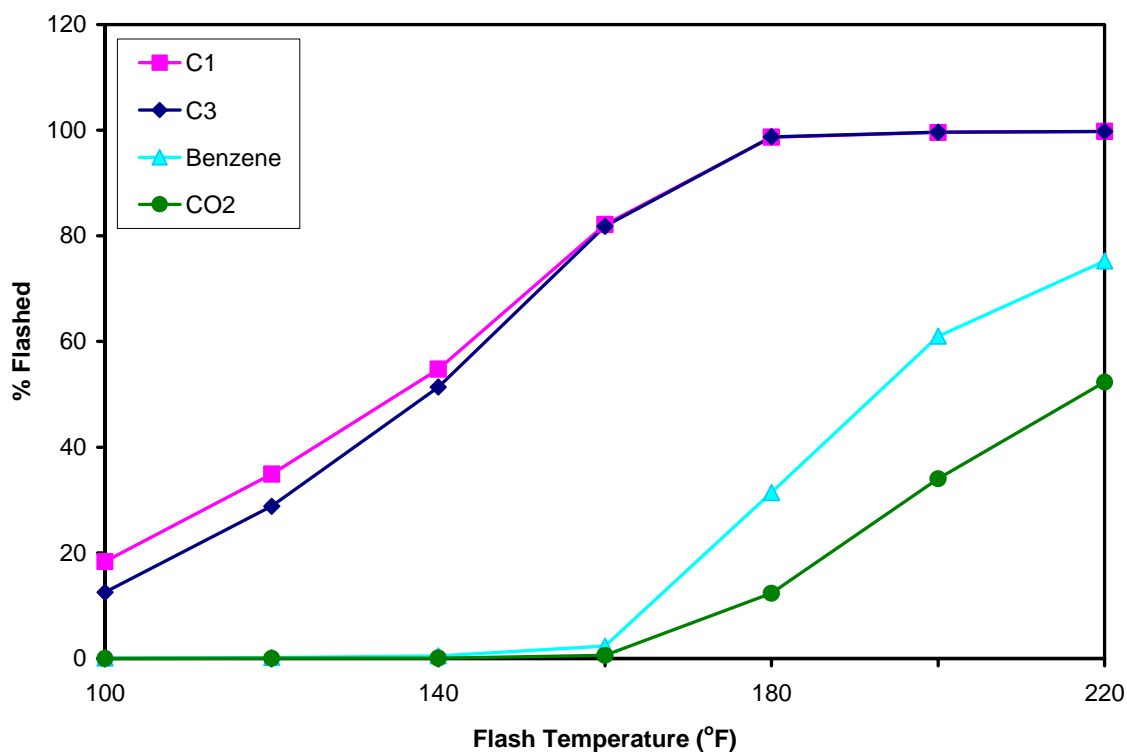


Figure 12 – The Influence of Temperature on HC & BTEX Vaporization from a Heated Flash of the Rich Amine

HC and BTEX Stripping Column

In this control method, a stripping column is added in the rich amine as shown in Figure 13. A portion of the sweet gas is used to strip the HC and BTEX from the amine solution. As in the hot flash, if the H₂S content in the overhead stripping gas is above the site requirements, then an acid gas absorption section must be added to the column. This method has been patented and is described in the literature (McIntyre et al. [1], Morrow [19], Wallender and Morrow [21] and Morrow and Lunsford [22]). HC and BTEX removal greater than 75% are possible with the method (Wallender and Morrow [21]).

The performance of an example HC and BTEX stripping column is shown in Figure 14 for 50 wt% MDEA treating the gas stream shown in Table 3. As can be seen from Figure 14, about 70% of the benzene can be removed from the rich amine at 120°F using about 5 SCF of stripping gas per gallon of solution. At these conditions about 10% of the CO₂ would also be removed. The propane removed increases rapidly up to about 60% with the first introduction of the stripping gas. The drop in methane and propane removal is due to cooling in the stripping column and reabsorption from the stripping gas.

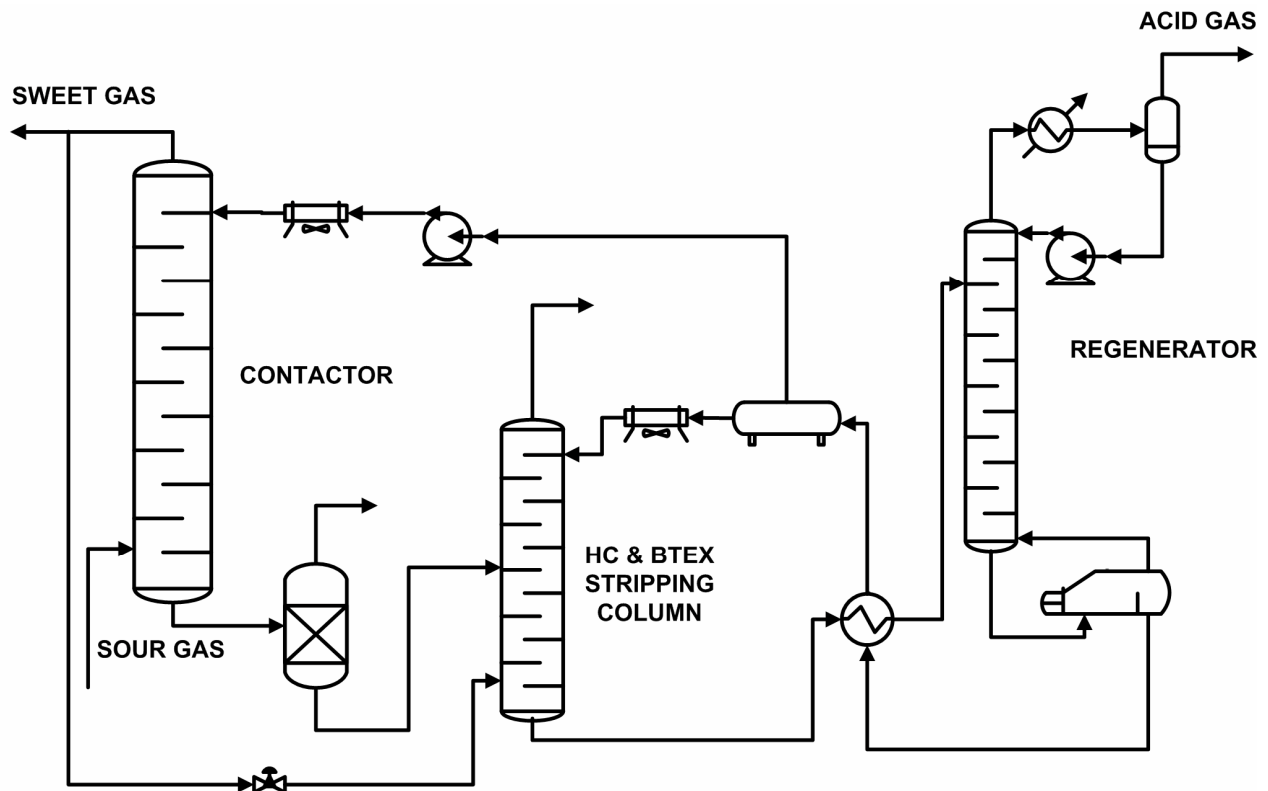


Figure 13- Amine Sweetening with HC & BTEX Stripping Column

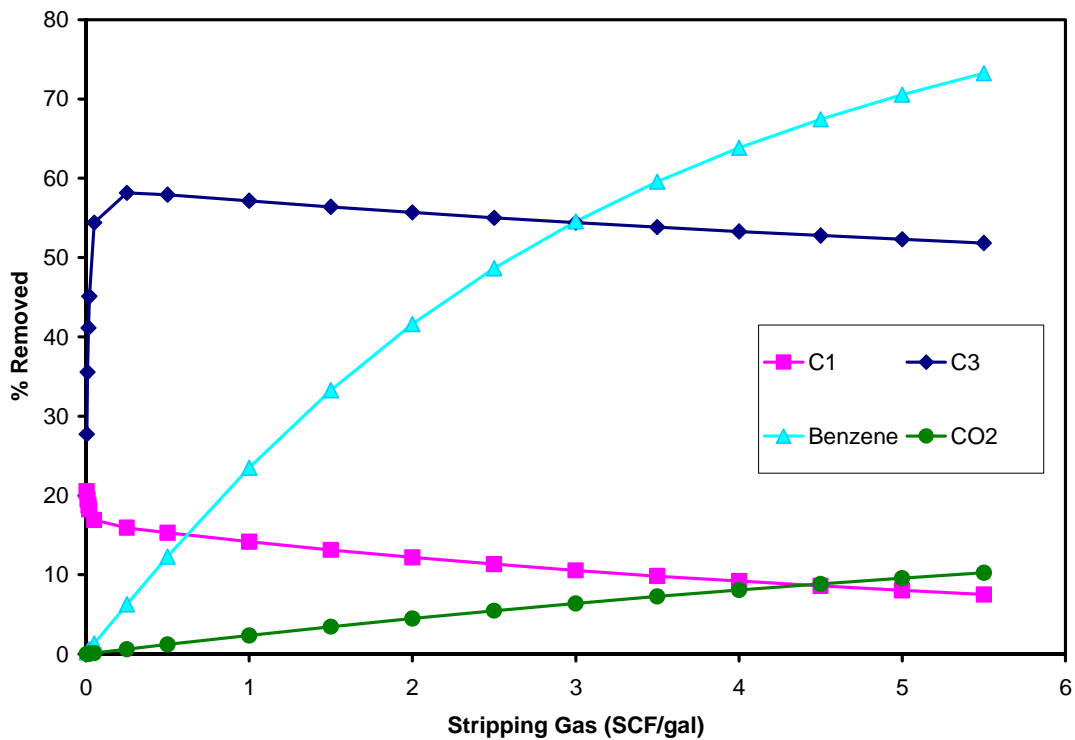


Figure 14 – Performance of a HC & BTEX Stripping Column on a Rich Amine with 50 wt% MDEA at 120°

SUMMARY AND CONCLUSION

HC and BTEX absorption into amine solutions has received increased attention over the last decade due to emissions to the atmosphere or to problems in downstream equipment. The collection of VLE and VLLE data by GPA and others have facilitated the development of a model for the absorption and removal processes. The amount of HC and BTEX emitted or passed to downstream equipment may be controlled by reducing the absorption or by removal from the rich amine.

In general, the absorption of HC and BTEX from a gas into the rich amine solution can be reduced by higher rich amine temperatures, lower column pressures, lower amine circulation rates, higher acid gas loadings, lower amine concentrations and a lower molecular weight amine. For liquid-liquid systems such as treating of LPG's, the above guidelines apply except that higher rich amine temperatures increase the absorption, and the pressure has little effect.

The methods for removing the HC and BTEX from the rich amine include a hot flash and a stripping column. In general, the hot flash is not very effective while the stripping column can remove up to 70% or higher.

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