Improve Your Gas Plant's Performance in the Middle East

Part I: The Amine Plant

Abstract

This is Part I of a series of papers detailing a method to optimize a gas plant, while being thoughtful of downstream implications. Amine sweetening units are often at the front end of the gas plant and pose significant design and operation challenges to downstream operations. This paper compares DGA®, DEA, MDEA and MDEA + piperazine when selecting the amine solvent to use. It also shows the steps taken to determine the correct operating conditions for high pressure, high temperature and highly sour environments. While MDEA is routinely lauded for selectively removing H_2S, this paper shows the selectivity is greatly diminished in these conditions and that DGA® may be the more appropriate solvent.

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Introduction

A study was performed to establish a method to optimize amine sweetening units operating at conditions typically found in the Middle East. The study utilized ProMax, a popular process simulator, and was based on operating data from hundreds of amine sweetening units. ProMax has matched operating data very closely in many cases (Polasek & Bullin, 1994) (Ochieng, et al., 2012) (Spears, Hagan, Bullin, & Michalik, 1996) (Bullin, 2003). For this study, a feed composition with inlet conditions similar to those encountered in the Middle East was used, as shown in Table 1. The goal is to sweeten the gas to below 4 ppm H_2S. The CO_2 specification greatly depends on whether the downstream gas processing plant is recovering or rejecting ethane. However, it is good to design the amine unit assuming ethane recovery. A subsequent study is recommended to show how the amine unit can affect the freeze out temperatures in cryogenic processes. Both cases are presented here.

Temperature	45 C
Pressure	73 bar
Standard Vapor Flow	250 MMSCFD
Composition (mole %)	
CO2	6
H2S	7
Methane	74
Ethane	4
Propane	4
Isobutane	1
n-Butane	2
Isopentane	1
n-Pentane	1

Table 1: Gas Inlet Conditions Upstream of Amine Unit

The feed also had small amounts of mercaptans (thiols) and other impurities.

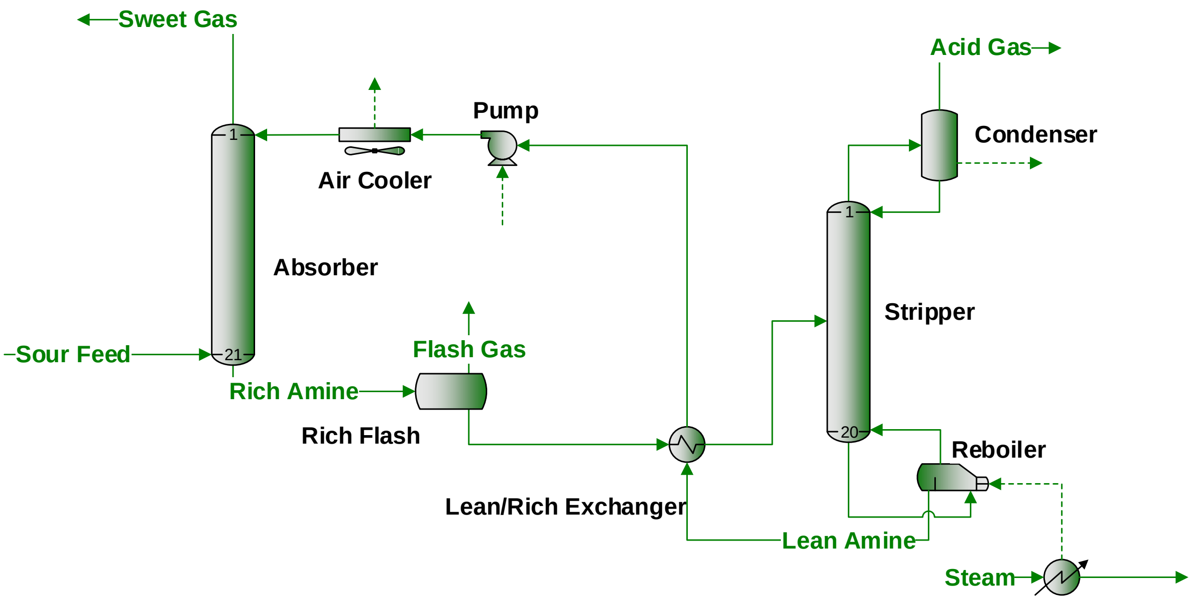

Figure 1: Flow Diagram for Typical Amine Sweetening Unit

While most amines remove little mercaptans (primarily methyl mercaptan), DGA® has been reported to remove significantly more (Kohl & Nielsen, 1997). If more than trace amounts of mercaptans are present, a polishing treater may be necessary, even if DGA is used. The layout of the amine plant may be observed in Figure 1.

A list of the optimization parameters studied are shown in Table 2, along with others that were not used in this study since in general they are not viable in the Middle East.

Included in Study	Not Included in Study
Solvent selection	Inlet gas compression
Solvent concentration	Inlet gas cooling
Solvent circulation rate	Refrigerant cooling of solvent
Rich loading	Regenerator pressure
Reboiler duty	
Column internals	
Lean/Rich exchanger and flash vessel	
Condenser	

Table 2: A list of parameters that may optimize an amine unit

Inlet gas compression and cooling are very expensive and seldom implemented. Low pressures are typically not a concern the Middle East, either. The same concept applies to the lean solvent temperature. The amine temperature is controlled by an air cooler, as seen in Figure 1. Cooling the amine much further than 60 C is difficult with ambient temperature around 50 C.

The regenerator pressure is another parameter which is relatively fixed. While the regenerator pressure regulates the reboiler temperature, it is typically kept at a pressure between 1 and 2 bar.

The remaining parameters are discussed in detail below.

Solvent Selection

The first step in optimizing an amine unit is the selection of the solvent. Keeping with the standard rules of thumb for amine sweetening units, various amines including DGA®, DEA, MDEA and MDEA with piperazine were considered (Addington & Ness, 2010). Some trends were produced showing the advantages and perhaps the justification for the popularity of particular solvents.

The amine sweetening plant consists of the absorber, regenerator, flash vessel, lean/rich exchanger and air cooler, as shown in Figure 1. The lean amine entering the absorber is kept at 60 C, well above the rule of thumb due to high temperatures in the Middle East. Due to the high pressure and high acid gas content in the Middle East, all amines are loaded to the maximum allowed by corrosion and process considerations. The maximum rich loading is varied, based on the amine as recommended in the GPSA handbook and is shown in Table 3 (Gas Processors Suppliers Association, 1998). The solvent flowrates are automatically adjusted by the simulator to achieve the desired rich loadings. The rich loading for each amine is held constant throughout this section. While there are many solvents to choose from, the ideal one will achieve the sweet gas specification at the lowest operating cost. There may be many other considerations, such as capital costs, equipment sizes if limited space is available and solvent availability. However, this paper evaluates the operating costs.

The most significant contribution to the operating cost of an amine sweetening unit is the reboiler. Therefore, the first step in selecting an amine is to compare the solvents' reboiler duties while operating at the recommended rich loading, shown in Table 3.

Rich Loading Used (mol/mol)	
DGA®	0.4
DEA	0.35
MDEA	0.45
MDEA + 5% piperazine	0.45

Table 3: Rich Loadings Used to Calculate Flow Rates in Study

While the rich loading is kept constant, the effects of varying the reboiler duty on the sweet gas H_2S purity are presented in Figure 2.

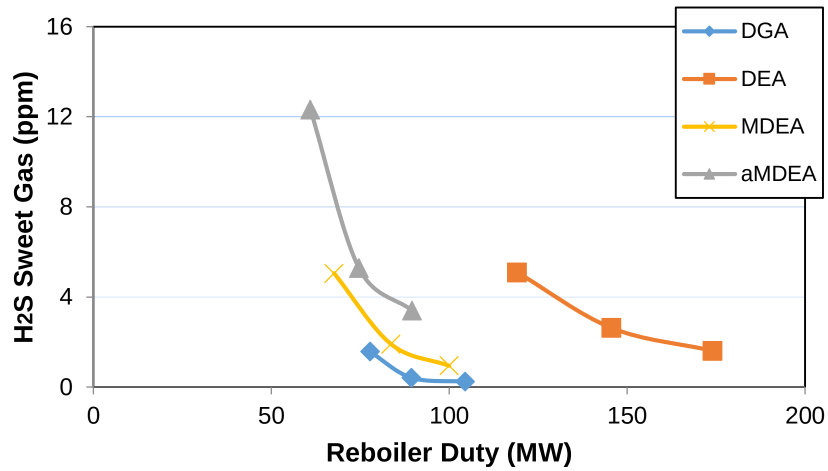

Figure 2: H_2S Content in Sweet Gas with Varying Reboiler Duty Using Different Amines at Maximum Absorber Loading

It is observed that the H_2S purity for each solvent begins to level off, giving diminishing returns, as the reboiler duty increases. DGA®, at first sight, gives the best results, consistently staying below the MDEA trend. However, it depends on the goal – Figure 2 only shows the effect the reboiler duty has on the H_2S. The same study for CO_2 is shown in Figure 3.

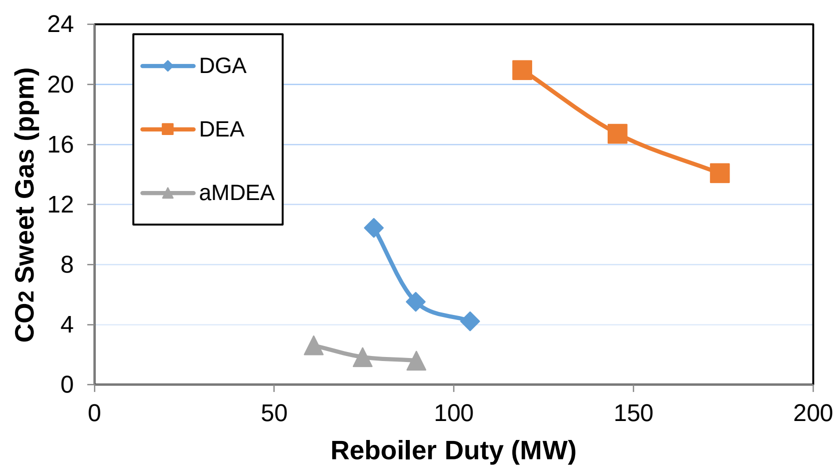

Figure 3: CO_2 Content in Sweet Gas with Varying Reboiler Duty Using Different Amines at Maximum Absorber Loading

Once CO_2 is included in the discussion, there are additional considerations. If the goal is to remove both H_2S and CO_2, aMDEA appears to be the best amine to use. The trend for MDEA is not pictured in Figure 3 because the CO_2 content of the sweet gas is literally off the chart. At these temperatures and pressures, CO_2 content in the sweet gas is in the order of magnitude of the 100s for MDEA. Therefore, if the goal is to leave some CO_2 in the sweet gas, MDEA may be the correct choice. For this study, it is preferred to leave some CO_2 in the sweet gas, as additional CO_2 in the acid gas only increases the size of the downstream SRU.

With that in mind, additional cases are presented comparing DGA® and MDEA – DGA® because the trend indicates it removes H_2S efficiently – MDEA because it is best at leaving the CO_2 in the sweet gas.

MDEA is expected to be the best performing amine, as it is a selective, tertiary amine; it has a lower heat of reaction with both H_2S and CO_2 than the other amines (Gas Processors Suppliers Association, 1998).

Solvent Concentration

The amine concentration is a significant aspect of optimizing an amine sweetening unit. DGA® is ordinarily used at concentrations between 50 and 70 weight percent, while MDEA is commonly used between 40 and 50 weight percent (Bullin, 2003) (Gas Processors Suppliers Association, 1998). Since DGA® is more concentrated, it can be used at lower flow rates as shown in Figure 4. However, the heat of reaction for DGA®/H_2S and DGA®/CO_2 are significantly higher than MDEA/H_2S and MDEA/CO_2.

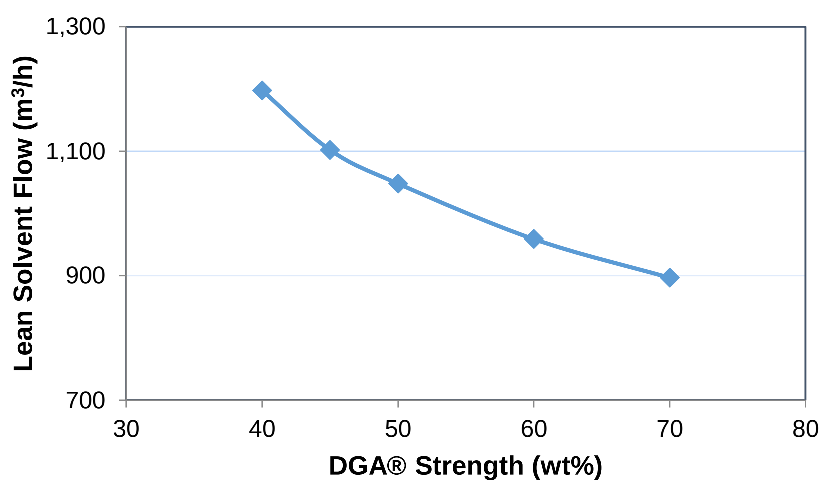

Figure 4: The Effect DGA® Concentration on Amine Circulation

While the amine concentration is varied, it is important to see the effects on the sweet gas composition and the reboiler duty. It is important to remember, as the amine concentration increases, the circulation rate decreases, due to the rich loading specifications used for MDEA and DGA®. Neither solvent significantly removed any more H_2S when the amine concentration increased. That is due to the high H_2S

approach at the top of the column. However, Figures 5 and 6 show increased CO_2 slip at higher amine concentrations.

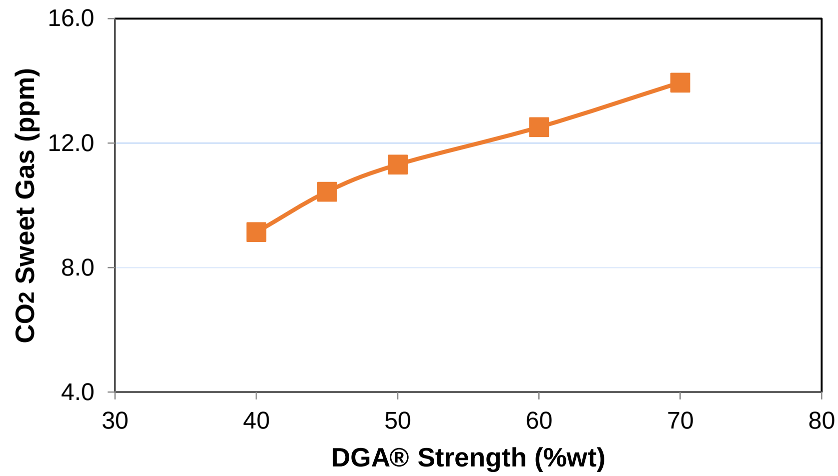

Figure 5: DGA® Concentration Effect on CO_2 Absorption

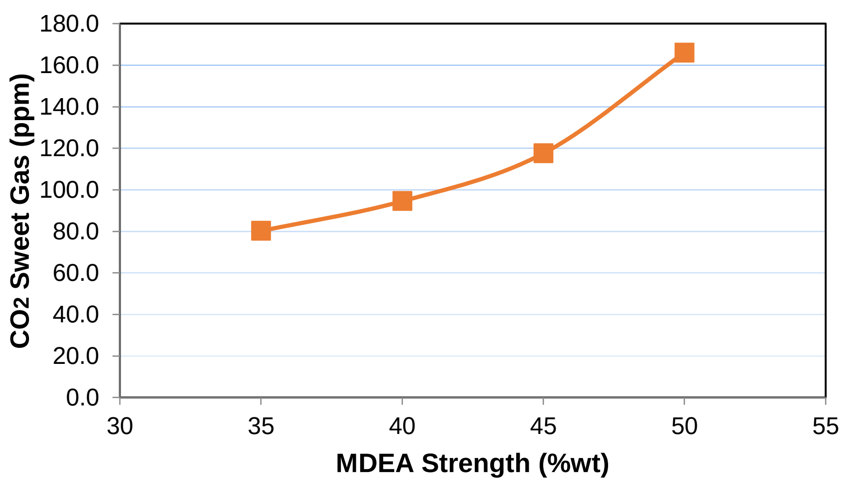

Figure 6: MDEA Concentration Effect on CO_2 Absorption

When the rich loading is maintained at a constant value, the flow rate decreases as the amine concentration increases since the partial pressure of the carbonate ions increases. More CO_2 escapes due to the increasing concentration of CO_2 in a decreasing volume of solvent.

The reboiler duty in this study remains at a constant steam rate ratio of 1 lb of steam per gallon of amine in circulation (0.12 kg/L), consistent with the rules of thumb (Addington & Ness, 2010). The steam rate will be varied later in this work.

When comparing MDEA and DGA®, it is observed that DGA® cleans the gas completely, down to 0.1 ppm H_2S and 14 ppm CO_2, while MDEA brings the gas to 5 ppm H_2S and 118 ppm CO_2 at approximately the same reboiler duties. Therefore, further comparisons of MDEA and DGA® must take place

Solvent Circulation Rate

From the concentration portion of the study, it is apparent that the circulation rate and concentration of the amine are related to one another when calculating the rich loading. Rather than specifying the rich loading, the loading is calculated based on the circulation rate at a constant amine strength. For this part of the study, 45 weight percent MDEA and 60 weight percent DGA® are used.

The steam flow rate increases with the solvent flow according to the steam ratio specified, which remains constant at 1lb/gal (0.12 kg/L). Therefore, the higher circulation rate corresponds to a higher reboiler duty. The effect of the DGA® circulation rate on H_2S and CO_2 content in the sweet gas are presented in Figure 8.

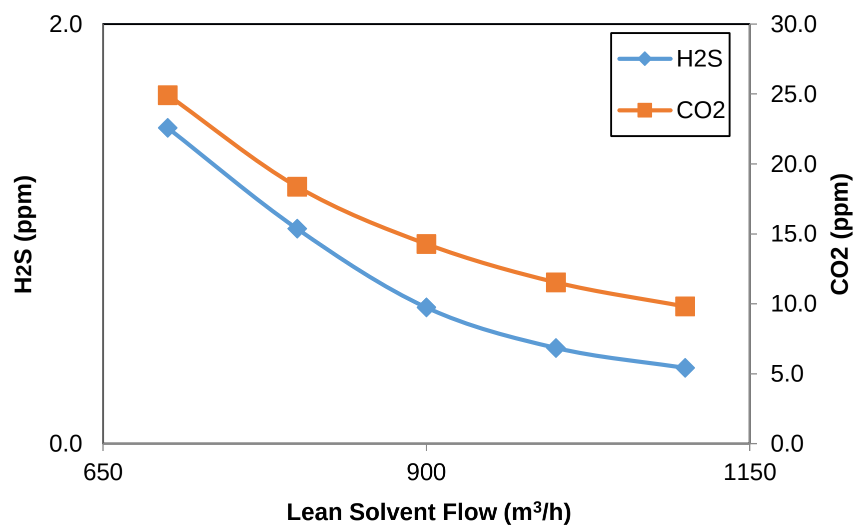

Figure 8: DGA® Circulation Rate Effect on H_2S and CO_2 in the Sweet Gas

The same relationship is shown in Figure 9 for MDEA.

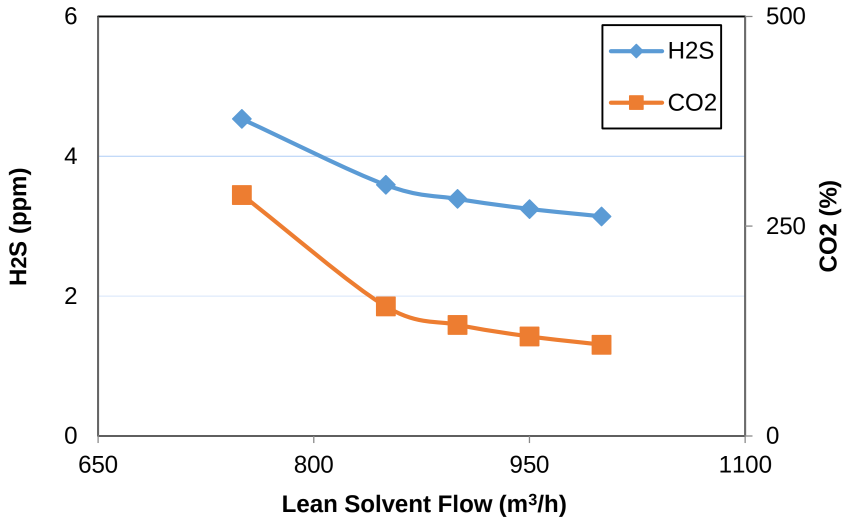

Figure 9: MDEA Circulation Rate Effect on H_2S and CO_2 in the Sweet Gas with 1.1 lb/gal Steam Ratio

Both Figure 8 and 9 show there are diminishing returns once the circulation is increased past approximately 900 m^3/hr. It is also seen that DGA® is able to remove more H_2S, at lower circulation rates, than MDEA. That also translates to a lower reboiler duty in this study. However, it is important to consider the rich loading. If the rich loadings are constrained by industry guidelines, a MDEA flow rate of 850 m^3/hr and reboiler duty of 60 MW may be used (Gas Processors Suppliers Association, 1998) (Polasek & Bullin, 1994). Using the same guidelines, a DGA® flow rate of 1000 m^3/hr and reboiler duty of 70 MW may be used.

As predicted, DGA® has the higher reboiler duty. It comes back to the heats of reaction. It takes about 150 more BTU/lb for H_2S and 250 more BTU/lb for CO_2 to use DGA® (Gas Processors Suppliers Association, 1998).

Reboiler Duty

Up to this point, the steam to amine ratio has been kept at a constant ratio of 1 lb of steam for every gallon of amine being circulated. Now, the steam ratio is varied, while keeping the circulation rate constant. It is important to note that the 1 lb of steam per gallon of circulating solvent rule of thumb was generated for plants operating their lean amine cooler at 40° C. While rules of thumb are generally just starting points, it is especially so for this case, with a 60° C lean amine.

DGA® removes the H_2S and CO_2 very well for steam ratios as low as 0.8, maintaining the sweet gas content below 3 ppm and 50 ppm, respectively.

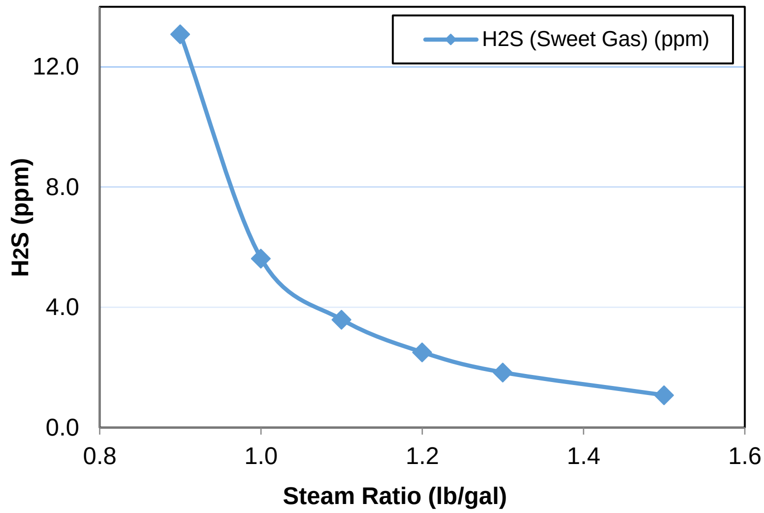

Figure 10: Effects of Steam Ratio (lb of steam for reboiler: gallons of amine circulated) on H_2S Content in Sweet Gas

MDEA has a little more fluctuation, as seen in Figures 10 and 11. As displayed in Figure 10, the H_2S removal capability of MDEA is highly dependent on the steam ratio when trying to achieve ultra-low H_2S specifications in the sweet gas. When compared to Figure 12, it is understood that once steam ratios above 1.0 are considered, less benefits are shown for increases in the steam ratio. An increase of 5 MW results in a decrease of 6 ppm H_2S when below a 1.0 steam ratio, while the same increase in duty results in less than 2 ppm reduction above a 1.1 steam ratio. As the steam ratio increases, the lean amine acid gas loading decreases. At a certain until the lean loading gets so low it has little effect on absorption.

Of course, if the reboiler duty is decreased such that acid gas is stripped in the reboiler, there may be major corrosion issues to deal with. It is important to maintain the acid gas content, especially CO_2, of the reboiler vapors below 5%.

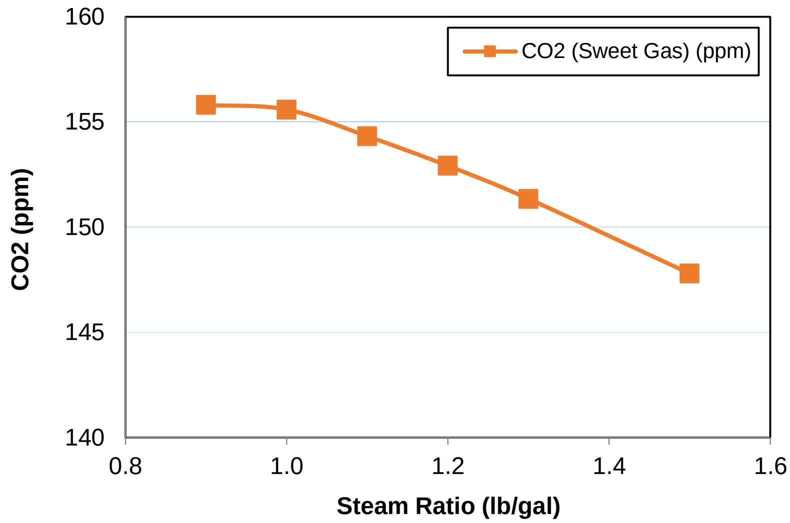

Figure 11: Effects of Steam Ratio (lb of steam for reboiler: gallons of amine circulated) on CO_2 Content in Sweet Gas

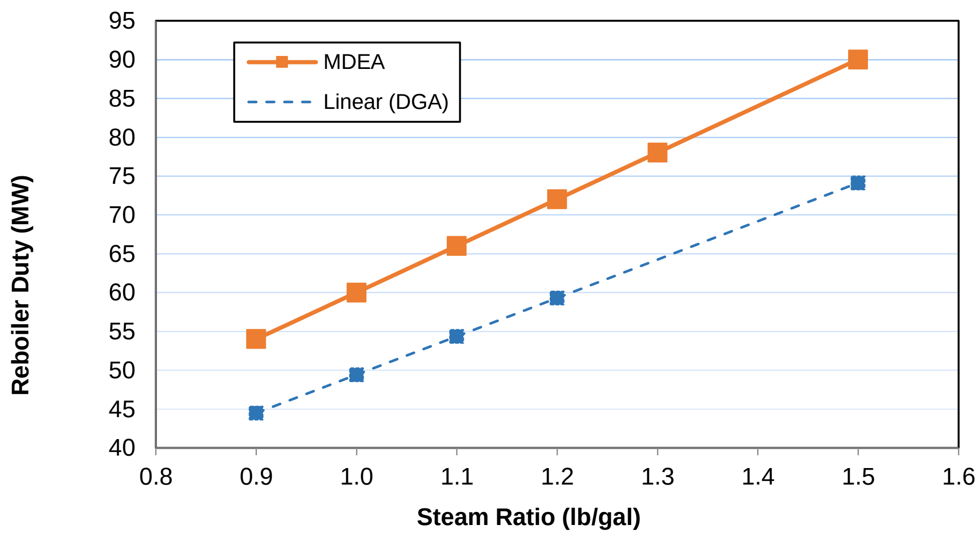

Figure 12: The Relationship between Steam Ratio and Reboiler Duty for MDEA (850 m^3/hr) and DGA® (700 m^3/hr)

When looking at the reboiler duties of the two solvents in Figure 12, it is clear that two data points for DGA® fall below MDEA's lowest reboiler duty. A 0.9 steam ratio for DGA® leads to a reboiler duty of 45 MW, but leaves too much residual acid gas in the circulating amine, resulting in over 1,000 ppm H_2S in the sweet gas. The lean loading is 0.2, while a lean loading of 0.1 is more typical for DGA® (Gas Processors Suppliers Association, 1998). The lean approach for H_2S is also nearly 100%, meaning it is lean end pinched. The lean end pinched column explains why the H_2S content spikes as the reboiler duty decreases. The next point under the MDEA line corresponds to a steam ratio of 1.0, or a reboiler duty of 50 MW. At this steam ratio, the lean loading is 0.16, which leads to 1.51 ppm H_2S and 25 ppm CO_2 in the sweet gas. That can be compared to MDEA with a reboiler duty of 66 MW achieving 3.6 ppm H_2S and 154 ppm CO_2 in the sweet gas.

Lean/Rich Exchanger

The lean/rich exchanger is a vital component of the amine plant, with significant influence on the regenerator, as demonstrated in Figures 13-16. The parametric study performed simultaneously varied the rich amine temperature exiting the lean/rich exchanger and the flash tank pressure for both DGA® and MDEA. The reboiler duty for the DGA® unit is reported in Figure 13.

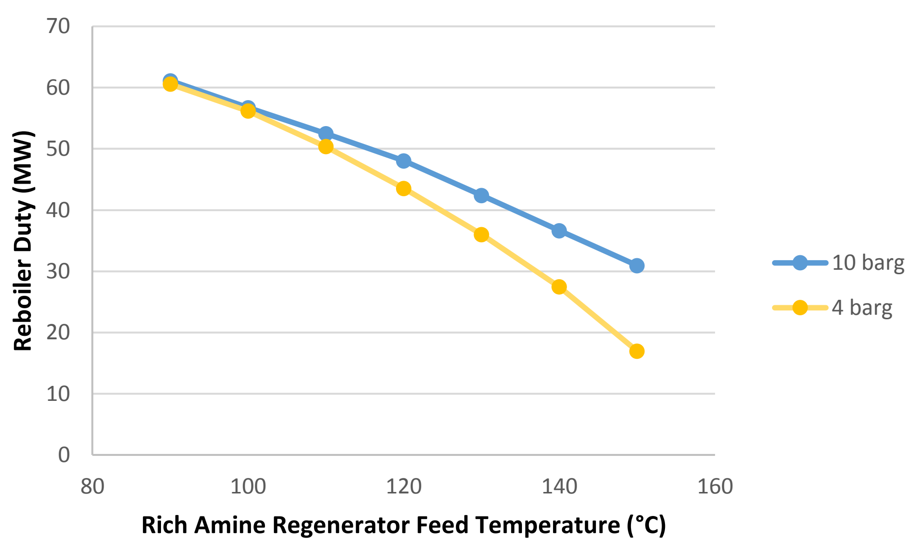

Figure 13: The Effect of the Rich Amine Temperature and the Flash Temperature on the Reboiler Duty for DGA®

It is important to also view the relationship between the rich amine temperature and the condenser duty, as displayed in Figure 14.

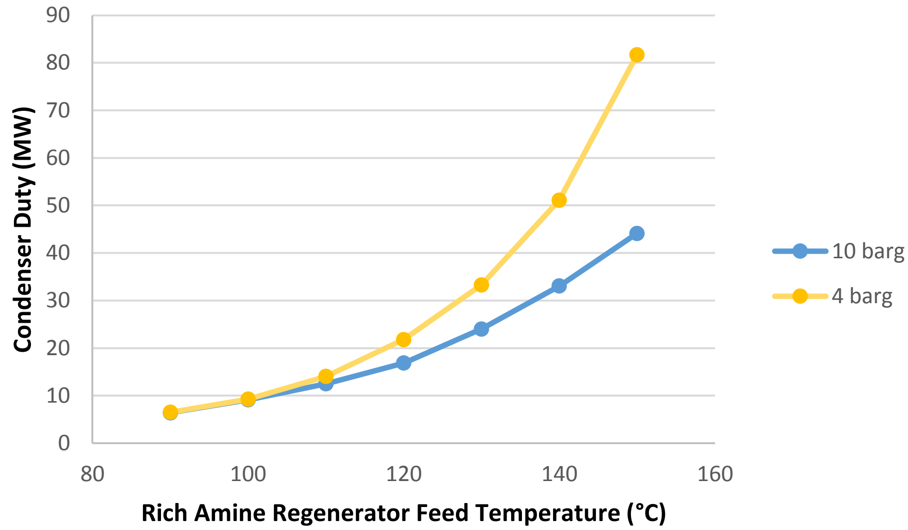

Figure 14: The Effect of the Rich Amine Temperature and the Flash Temperature on the Condenser Duty for DGA®

While the reboiler duty decreases as the rich amine increases, the condenser duty shows a clear benefit to avoiding rich amine temperatures above 100 C for DGA®.

The effect of the rich amine temperature on the reboiler duty is quite different for MDEA, as shown in Figure 15.

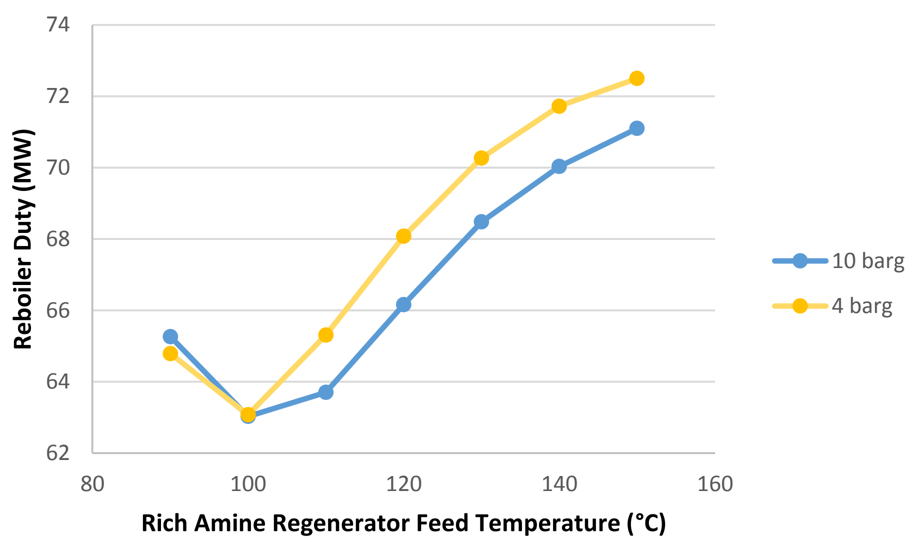

Figure 15: The Effect of the Rich Amine Temperature and the Flash Temperature on the Reboiler Duty for MDEA

For MDEA, the reboiler duty greatly increases for temperatures greater than 100 C. In fact, 100 C is the optimum value. Increasing the rich amine temperature does not benefit condenser duty, as shown in Figure 16.

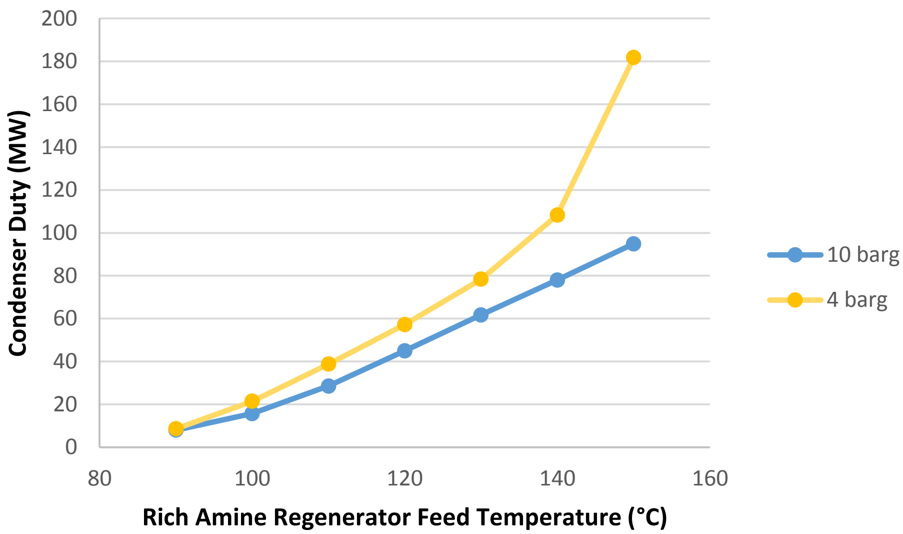

Figure 16: The Effect of the Rich Amine Temperature and the Flash Temperature on the Condenser Duty for MDEA

A low flash pressure proves to be slightly superior, as shown in Figures 13-16.

Therefore, it is best to keep a low pressure, 100 C rich amine entering the regenerator for both the MDEA and the DGA® options. 100 C is also recommended in order to prevent acid gas breakout in the exchanger (Gas Processors Suppliers Association, 1998). While the above graphs show rich amine temperature as high as 150 C, it is important to note a temperature cross is likely in the lean/rich exchanger at the high temperatures. The temperature cross can be avoided by adding an additional heat exchanger, though none of the temperature cross cases proved to be advantageous.

Column Internals

There would not be a complete picture without including a discussion on the column internals. The amine process is a chemical process, which relies heavily on reaction kinetics for absorption of CO_2. Amine kinetics are greatly documented (Gas Processors Suppliers Association, 1998) (Ochieng, et al., 2012) (Polasek & Bullin, 1994). The ProMax model incorporates the kinetic rates of reaction into the calculations. As such, it is important to understand how long the amine and acid gases are in contact with one another. The residence time is essential to predicting how far the reaction proceeds towards equilibrium. For DGA®, the residence time does not have as much significance since it is a primary amine with free protons available, as shown in Figure 17.

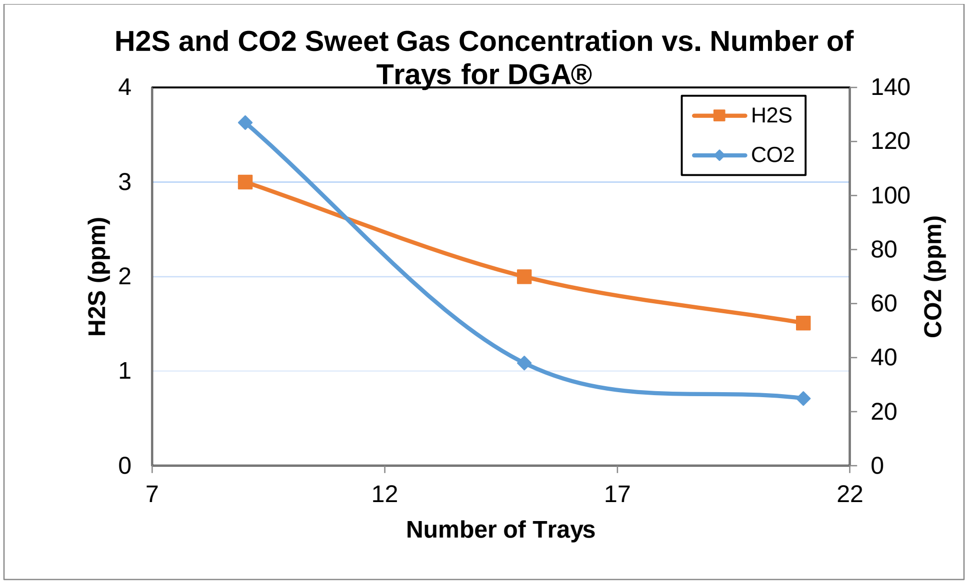

Figure 17: The Effect of the Number of Trays on the Acid Gas Absorption in the Absorber for DGA®

The number of trays effectively changes the total residence time of the column as well as well as the equilibrium. Another option for increasing residence time is to change the diameter, tray spacing and weir heights. When interpreting Figures 17 and 18, it is best to view the number of trays as directly affecting the residence time. Therefore, the more trays present, the higher the residence time. In contrast to DGA®, MDEA is a tertiary amine with no free protons, which has an intermediary reaction for CO_2 absorption, resulting in relatively slow CO_2 absorption (Ochieng, et al., 2012). The results for MDEA are shown in Figure 18.

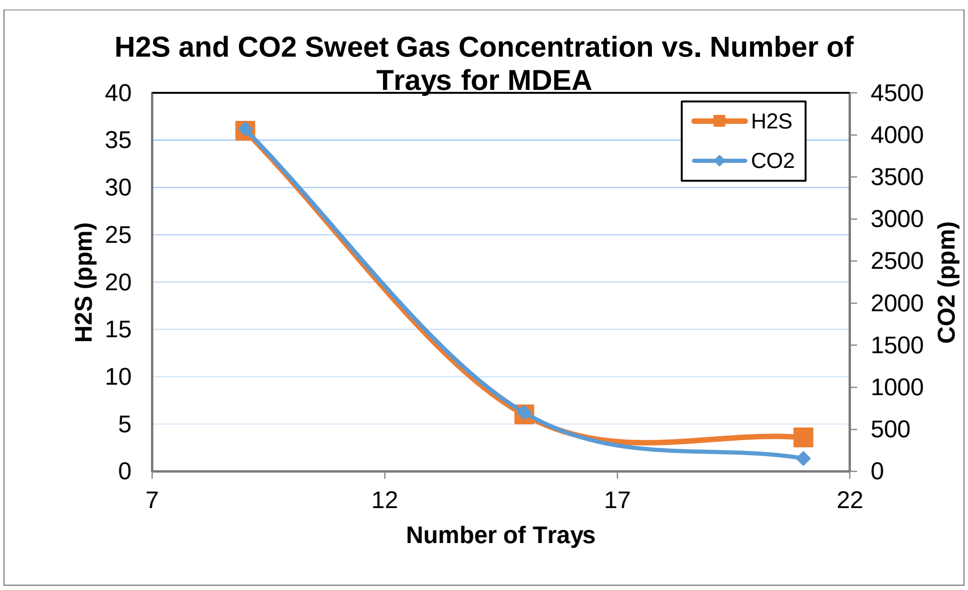

Figure 18: The Effect of the Number of Trays on the Acid Gas Absorption in the Absorber for MDEA

There is a large swing for both H_2S and CO_2 when the residence time changes. It is also much less linear than the DGA® curve.

Of course, the column internals are determined in the design phase. A poorly designed amine unit will often not take into account reaction kinetics. The kinetics are the most influential factors resulting in the absorption of CO_2 and indirectly H_2S, far outweighing mass transfer coefficients and surface tensions (Skowlund, Hlavinka, Lopez, & Fitz, 2012).

Conclusion

Amine plant studies often lead to good savings in plant design and operation (Bullin, 2003). This study shows that any amine can achieve the H_2S specification, but at very different costs.

DGA® and MDEA were closely compared, as shown in Table 4.

	MDEA	DGA®
Flowrate (m^3/hr)	850	700
Concentration	45	60
Sweet Gas H_2S (ppm)	3.6	1.5
Sweet Gas CO_2 (ppm)	154	25
Rich Loading (mol/mol)	0.5	0.56
Reboiler Duty (MW)	66	50

Table 4: Comparison of MDEA and DGA® Results

Choosing DGA®, in this case, may be able to save 24% in operating the reboiler. Depending on the cost of steam, this could save an operating company up to $8 million USD a year (Dubai, 2013).

Part II Preview

The next part of this series of papers will show the impact of the amine unit optimization on the sulfur recovery unit. The paper will compare the acid gas from the DGA® unit to the MDEA unit and how they impact the SRU. Part II will also show optimization steps for the SRU.

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