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Title: Highly Sour Amine Sweetening Process Study for Conditions Common in the Middle East

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Abstract: Highly sour gas is an increasingly viable gas to treat and process in the Middle East. This paper details the optimization methodology necessary when operating or designing a highly sour gas plant at high pressures and temperatures, more commonly seen in the Middle East. The study explores 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. A similar unit's operating data is used to create a base case for comparing various process enhancements. The study shows this particular unit may be able to save roughly 50% - 75% of its steam consumption by switching from 35% DEA to 50% MDEA or 70% DGA.

Introduction

Amine sweetening is the process of removing sour components (typically H_2S and CO_2) from a sour gas using an amine. The liquid contacts with the gas for the purpose of causing a kinetic reaction. The rate of reaction and extent of reaction depends on the conditions at which the reaction takes place. There is a long history of these units operating at conditions between 20-35 C, up to 30 bar and with sour gas content up to 5%.

Increasingly, these conditions are becoming less typical. The Middle East has seen a boom in development of gases at greater temperatures, pressures and sour gas content. This highly sour gas is observed at concentrations of up to 20-30% combined H_2S and CO_2 and with the presence of COS and mercaptans. When preparing to design, optimize or troubleshoot a highly sour gas plant, it is important to understand how solvents perform in these conditions.

Although few mercaptans react in the amine absorber, DGA has been reported to be significantly more reactive with mercaptans than other amines (Kohl & Nielsen, 1997). If more than trace amounts of mercaptans are present, a polishing caustic treater may be necessary, even if DGA is used. The typical layout of an amine plant may be observed in Figure 1.

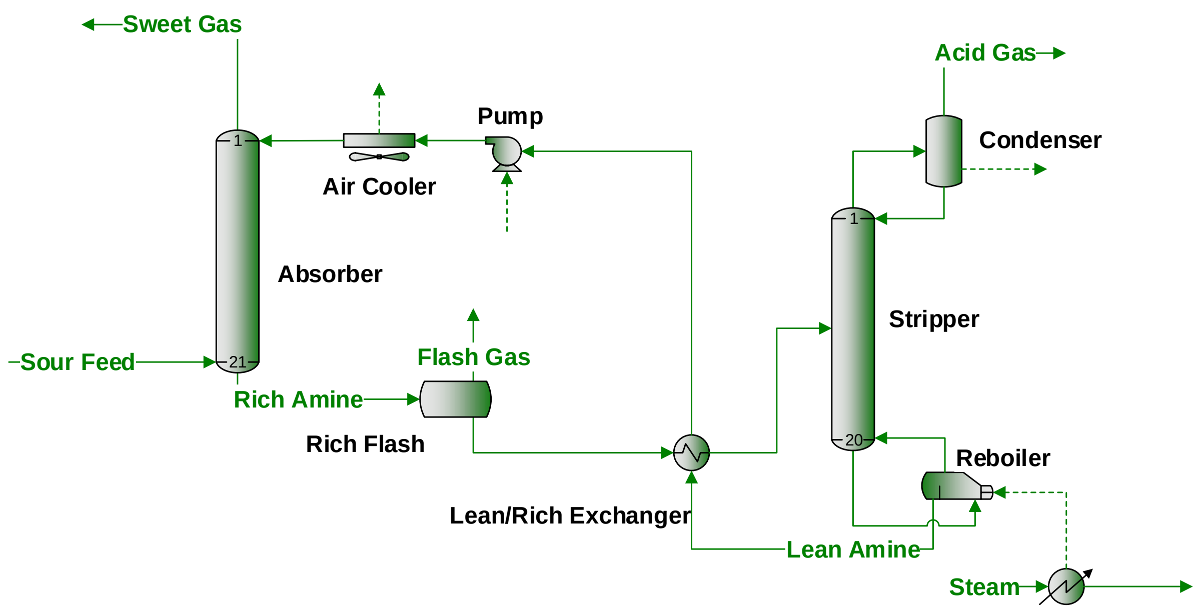

Figure 1: A Typical Amine Sweetening Unit

There are two major components of a sweetening plant which dictate the majority of the capital and operating costs of the plant: the gas and amine flow rates. The gas flow rate accounts for the majority of the absorption column size, while the amine flow rate controls the size of the rest of the plant. Assuming the gas flow rate is established, optimization efforts need to initially focus on reducing the amine flow rate.

Case Study

A process simulator suitable for modeling highly sour gases and based on operating data from hundreds of amine sweetening units is utilized (Bryan Research & Engineering, Inc., 2013). The simulator has been demonstrated to match plant operating data very closely (Polasek & Bullin, 1994) (Ochieng, et al., 2012) (Spears, Hagan, Bullin, & Michalik, 1996) (Bullin, 2003).

For this study, a feed composition of an operating plant consistent with some of the most sour fields currently exploited in the world is used, as shown in Table 1. The goal is to sweeten the gas to below 10 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 in order to prevent solids formation.

The operating conditions of the plant are detailed in Table 1. This gas contains 20% sour gas, with a 3:1 H_2S:CO_2 ratio.

Temperature	37 C
Pressure	68 bar
Standard Vapor Flow	425 MMSCFD
Composition (mole %)	
CO_2	5
H_2S	15
Methane	64
Ethane	10
C3 +	4
Mercaptans	2

Table 1: Gas Inlet Conditions Upstream of Amine Unit

The plant data is compared to simulated data in Table 2.

	Operating Data	Simulator
H_2S Sweet Gas (ppm)	4.5	3.8
Steam Rate (kg/h)	301524	301524
Column Diameter (m)	4.5	4.5
Absorber Trays	21	21
Amine	35 wt% DEA	35 wt% DEA
Amine Circulation Rate (m^3/hr)	1,750	1,750
Sweet Gas T (C)	49	50
Rich Amine T (C)	72	69

Table 2: Model Validation - Comparing Operation Data to Model

For accuracy, a kinetic model is used (Skowlund, Hlavinka, Lopez, & Fitz, 2012). The data shows the model is valid for such sour environments. Therefore, a study may be performed to gain more information about ways to optimize this unit and provide lessons for future projects using this simulator.

Improving Performance

When evaluating areas for improvement, it is important to model many cases in order to form trends or operating envelops. This evaluation should be done on every amine sweetening unit operating in the world in addition to any design studies.

Various trends are shown here detailing how the above operating unit would perform under different conditions.

The first series of graphs show how the rich loading and solvent choice effect the reboiler duty. The results are shown in Figures 2,3 and 4. The rich loading is determined by calculating the molar flow rate of the amine and the acid gases (H_2S and CO_2) in the rich amine stream. Therefore, the rich loading depends on the amine flow rate and the amount of acid gases picked up by the amine. As a result, the rich loading is primarily influenced by the amine circulation rate. As the circulation rate is decreased, the rich loading will increase.

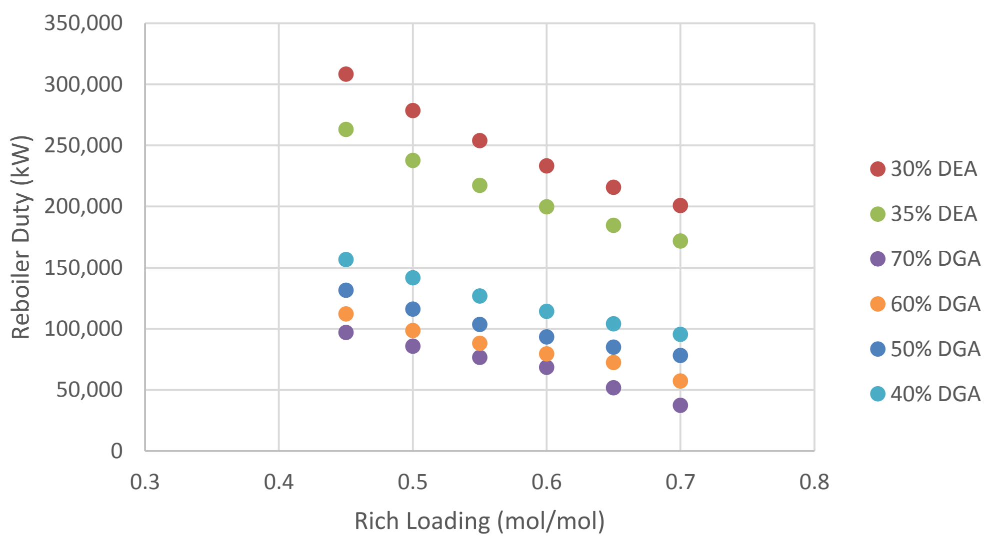

Figure 2: Effect of Rich Loading on the Reboiler Duty for DEA and DGA

While the lean loading is held constant, Figure 2 shows the current unit may realize significant improvements in steam consumption by increasing the solvent concentration, increasing the rich loading (by decreasing solvent flow rate) or changing solvents. In fact, the best option would be to switch to DGA, saving roughly 50% reboiler duty. Both DEA and DGA show a decreasing reboiler duty as the solvent concentration is increased. The trend is primarily due to the decreased amount of water entering the reboiler. As the water flowrate decreases, so does the duty attributed to the heat of vaporization of the water.

The same trend is seen for MDEA and MDEA + piperazine in Figure 3.

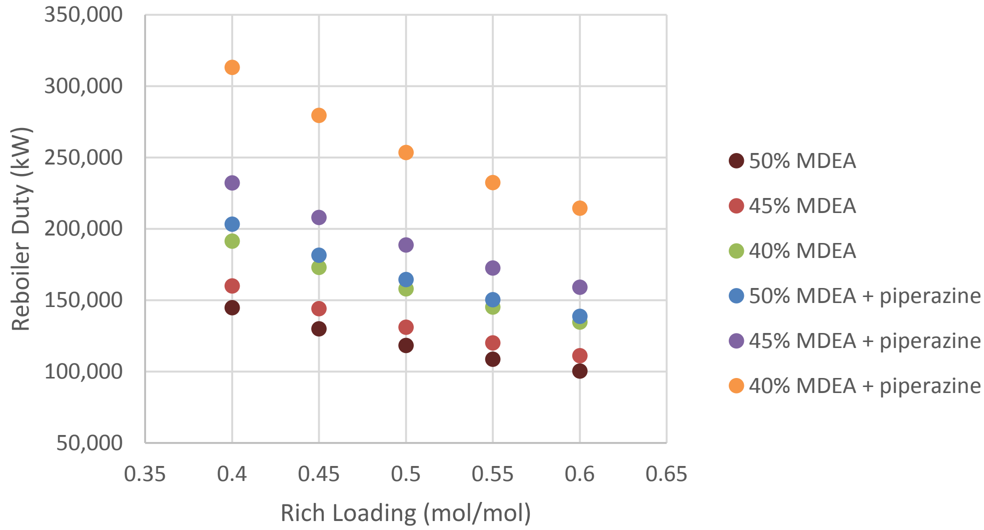

Figure 3: Effect of Rich Loading on the Reboiler Duty for MDEA and MDEA + 5% Piperazine

The results of the lowest reboiler duties are displayed in Figure 4, as a single graph for easy comparison.

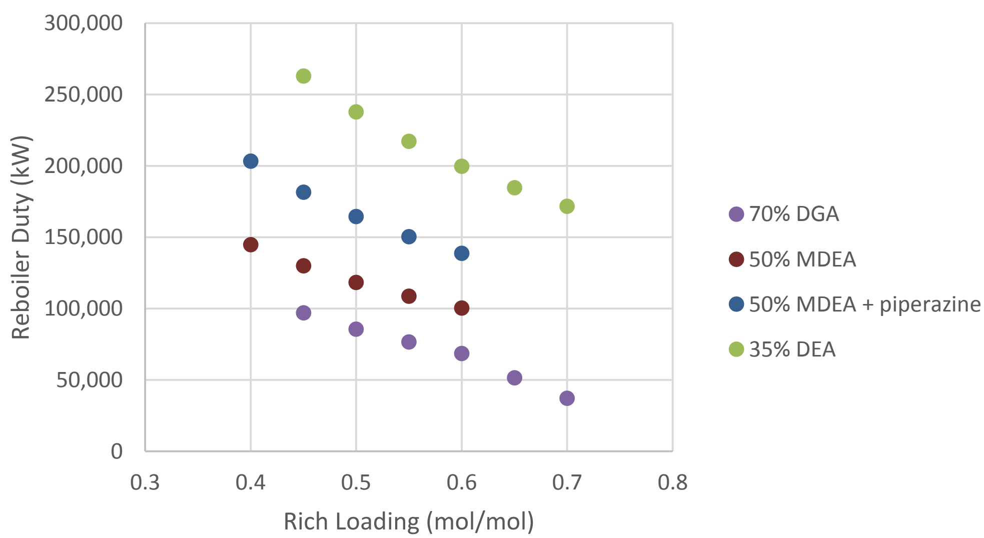

Figure 4: Effect of Rich Loading on the Reboiler Duty for Various Solvents

The lean/rich exchanger in the treating plant is designed to provide the greatest amount of heat recovery. The most efficient designs will achieve the lowest reboiler duty. The rule of thumb advises the rich amine exiting the lean/rich exchanger to be set at 99 C (Addington & Ness, 2010). In order to verify this, a wide range of temperatures were applied to the above case study. The simulated results show that the lowest reboiler duty is achieved when the rich amine is heated to 99 C.

A typical curve is shown in Figure 5.

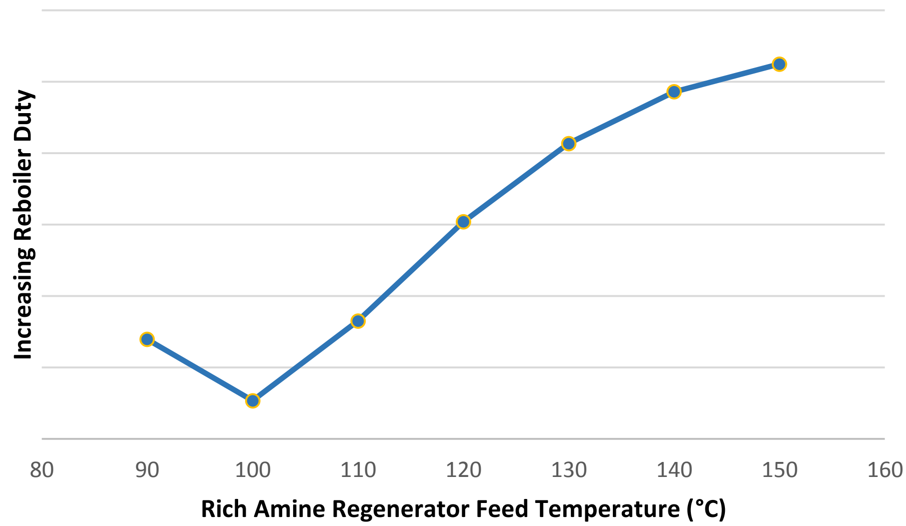

Figure 5: Effect of lean/rich Exchanger Temperature on the Reboiler Duty

There are three main concerns with the lean/rich exchanger. First, it needs to modelled to ensure the reboiler duty is minimized. Second, the design needs to be possible. More times than not, temperatures of 120 C or higher would produce a temperature cross in the lean/rich exchanger. Third, the design needs to appropriately mitigate acid gas break-out (Gas Processors Suppliers Association, 1998).

However, when the regenerator pressure is increased to 2.5 barg, the lean amine becomes warmer without any additional reboiler duty. Therefore, the lean/rich exchanger may be set at a higher temperature. A simulation was run, while keeping the lean loading and rich loading constant. The regenerator is shown in Figure 6 at 2.0 barg (current operating pressure) and 2.5 barg.

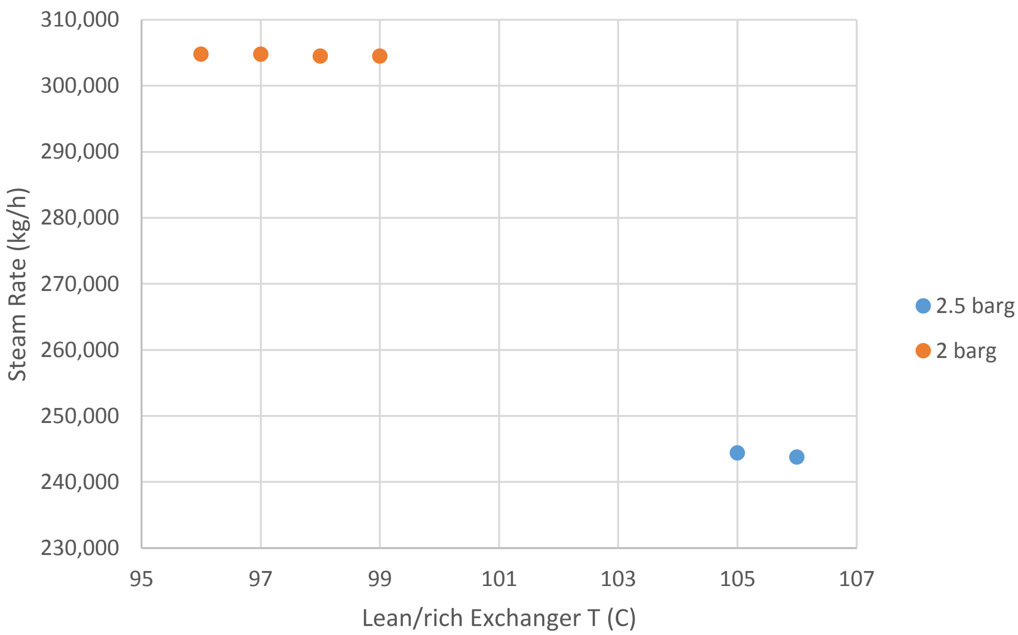

Figure 6: Effect of Regenerator Pressure and Rich Amine Temperature on the Reboiler Duty

Figure 6 displays only possible exchanger design temperatures, which is why the trend appears linear. Using this information, the plant may save roughly 60,000 kg/h of steam consumption, or 20%. The observed increase in efficiency is in line with a similar study from experimental data (Komi, et al., 2012).

Coupling the two improvements yields even greater results. Modeling the 50% MDEA case with a rich loading of 0.5 mol/mol and regenerator pressure of 2.5 barg predicts a steam rate of 200,000 kg/hr or a total reduction in steam consumption of roughly one third. Similar results are observed with DGA.

CAPEX, OPEX and Operational Flexibility

The initial investment is the capital cost, or the CAPEX. The plant studied here is obviously already operating. However, there are some lessons to be learned from the plant, for those concerned about designing a highly sour gas plant. Going back to the introduction, and observing Figure 1, there are two major aspects when evaluating the CAPEX. The gas flow rate largely determines the size of the absorber, while the solvent flow rate determines the size of the rest of the plant. Using this general rule, the absorber size will be relatively the same (at least at this point of the design). Therefore, the solvent flow rate will be the major difference in all the cases. As the rich loading increases, the solvent flow rate decreases, yielding a lower reboiler duty. The result is a smaller lean/rich exchanger and reboiler.

The operating plant chose to increase the rich loading by installing stainless steel equipment for the rich side of the plant. Therefore, the operator was able to reduce the energy consumption by about 30%. Stainless steel is a very expensive material of construct, no doubt increasing the CAPEX significantly.

It may have been a wiser decision to use a different solvent, as other solvents have higher allowable rich loading thresholds than DEA. MDEA can be safely loaded to 0.55 mol/mol without the need for stainless steel (Gas Processors Suppliers Association, 1998).

Now that the plant has already been built, it is primarily concerned about OPEX, or the operating costs. The primary operating cost in an amine plant is the reboiler (Kohl & Nielsen, 1997). If the reboiler duty can be decreased, the OPEX will decrease. Therefore, the best option would be 70% DGA, as seen in Figure 4.

The operational flexibility is also a good aspect of the plant to evaluate. While DGA may be the lowest OPEX option by a large margin for highly sour cases, it also may be the least flexible option. It will likely require reclaiming, as the solvent is relatively less stable and is destroyed by various contaminants. Also, while DGA production is on the rise, it is in short supply. Only a handful of suppliers are available.

MDEA on the other hand is the most flexible. It is the most stable, allowing the design to encompass a wide range of loadings, safely. It does not need to be reclaimed. Most interestingly, it may also be used to selectively remove H_2S while letting CO_2 to slip through the absorber. Along the same lines, it may also be "activated" or "promoted", as licensors like to market, with components such as piperazine, phosphoric acid and DEA. More recently, MDEA is even being mixed with DGA and TEA. For all these reasons, MDEA has a wide advantage with operational flexibility.

Flexibility wise, DEA will fair somewhere between DGA and MDEA. It will not require a reclaimer, but otherwise will operate very similarly to DGA.

Additional Concerns

The rich loading specification is primarily monitored to avoid corrosion in the rich amine portion of the plant. Corrosion occurs when there are excess H+ and Fe++ ions in solution. The ions move to reduce the negative charge of the steel in the equipment or piping. Seeing as this is an electrolytic model, the simulator can accurately model the H+ ions in solution. However, it is difficult to know the Fe++ ion concentration. It is also difficult to know the negative charge of the steel, or at what rate the negative charge is reduced. It is, therefore, not included in the model. Since it is difficult to model, there are maximum rich loading guidelines set forth by GPSA (Gas Processors Suppliers Association, 1998).

However, it is not a worry if stainless steel is used. The main concern is then erosion due to high velocity acid gas break-out in the lean/rich exchanger. It is specifically worrisome in this case, as the plant transitions from DEA to MDEA. Greater rates of acid gas break-out are observed with MDEA than DEA, even when operating at similar loadings (Gas Processors Suppliers Association, 1998).

The capital cost of stainless steel is about four times that of carbon steel (World Steel Prices, 2013). Hence, there is a large incentive to accomplish the design using carbon steel. On the other hand, a higher rich loading can significantly reduce the size of equipment, including the columns and reboiler. This cost analysis must be done.

The plant studied here chose stainless steel. As such, the plant is currently run at a rich loading greater than 0.6 mol/mol with no noticeable negative effects.

Another concern is the temperature at which the process operates. Obviously, the Middle East is much warmer than most other places in the world. While all the other conditions are similar in this case study to conditions in the Middle East (high pressure, high flow rate, highly sour), it is noted that the temperature is lower than the typical Middle Eastern plant. The model shows very little differences when the temperature is increased. That may be attributed to the constant rich and lean loadings, however, the amine circulation rate and the reboiler steam rates stay virtually the same.

There are very small changes in the H_2S and CO_2 content in the sweet gas, but it is so small, it is hardly worth mentioning. Perhaps at lower pressures, greater differences may be observed.

Conclusion

Using trends and case studies are helpful when designing, optimizing or troubleshooting an amine sweetening unit, especially at high pressures and ultra-sour concentrations. Observing the guidelines from GPSA, the trends set forth in this paper and proper simulation greatly aids engineers.

DGA exhibits advantages for sweetening highly sour gases in the Middle East, as shown in this paper. DGA's main advantage is reducing the diameter of the absorber and reducing the reboiler duty, a result of DGA's ability to circulate at higher concentrations than even MDEA. In addition, DGA works very well in high temperatures. That allows DGA to take advantage of faster hydrolysis reaction rates for deeper removal of COS (Schulte, Mangas, Almuhairi, Sahoo, & Ross, 2011). However, DGA is relatively unstable. It often requires a reclaimer in order to mitigate degradation of the amine. Figure 4 shows that DGA achieves basically the same specifications as MDEA, but at a lower cost. DGA is being utilized in ultra-sour gas fields, such as the Shah Field in the UAE.

MDEA is also a good option, especially if COS is not present and deep CO_2 removal is not necessary. MDEA will likely have lower operating costs if the plant is not comfortable going above 0.5 rich loading and carbon steel materials are used. It also has the added benefit of not requiring a reclaimer.

DEA is the least efficient option. It is recommended that ultra-sour gas treating plants move from DEA to MDEA or DGA.

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