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REVAMPING OF GAS REFINERIES USING AMINE BLENDS

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Abstract: *The use of mixed amine system in gas treating processes is increasing today. For natural gas sweetening purposes, mixed amines are typically mixtures of MDEA and DEA or MEA that enhance CO_2 removal while retaining desirable characteristics of MDEA such as reduced corrosion problems and low heats of reaction. In this work, a process simulator was used to predict the performance of an Iranian gas sweetening plant with a sour gas feed containing 6.41% CO_2 and 3.85% H_2S on molar basis. Various mixtures of diethanolamine (DEA) and Methyl diethanolamine (MDEA) were used to investigate the potential for an increase in plant capacity. It was noticed that the process simulator is quite capable in predicting the existing plant performance and can potentially guide in selecting the optimum blend composition. It was also noticed that a substantial increase in plant capacity is quite possible by just adding MDEA to the existing solvent and keeping the solvent flow rate and stripper reboiler heat duty. In another word, it is possible to increase the plant capacity from 293 to 357 MMSCFD using a mixed amine system.*

Keywords: *Gas Sweetening, Amine, Mixed Amine, Simulation, HYSYS*

1. Introduction

The technology of using alkanolamines - or amines - for the removal of hydrogen sulfide and carbon dioxide from natural gases has been used for decades. Since the 1960's and 70's several amines have come into general use, however, limited information has been reported in the literature concerning the amine best suited to a particular service. Many amine gas sweetening units, which are operating inefficiently, may be optimized by simply changing their amines solution.

The basic flow scheme for an amine sweetening unit is shown in Fig. 1. In the design of the process, the primary concern is that the sweetened gas should meet the required purity specifications with respect to H_2S and CO_2. The secondary objective is to select the amine, which optimizes equipment size and minimizes plant operating costs. The following points should be addressed in the selection of the proper amine for design, or evaluation of an existing plant:

1. Can the amine circulation rate be reduced by selecting an amine which may be used at a higher concentration and/or at a higher acid gas loading?
2. Could the equipment be designed more efficiently using an amine which requires a lower circulation rate, and/or has lower heats of reaction with H_2S and CO_2?
3. Could H_2S be selectively absorbed from the sour gas while CO_2 is rejected? Can the selective absorption of H_2S and CO_2 from the sour gas be optimized by the use of a suitable amine blend?
4. Could corrosion and solvent loss problems be improved with an amine or mixture of amines more resistant to degradation?

Between 50 to 70% of the initial investment for an amine sweetening unit is directly associated with the magnitude of the solvent circulation rate and another 10 to 20% of the initial investment depends on the regeneration energy requirement. Approximately 70% of operating costs of a gas sweetening plant, excluding labor expenses, is due to the energy required for the regeneration of the solvent. The appropriate selection of the amine can significantly reduce the regeneration energy requirement and solution circulation rate. Therefore the choice of or combination of amines best suited to the process conditions can have a dramatic impact on the overall costs associated with a

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sweetening unit. Moreover, the flow scheme for amine sweetening plants has an important effect on operating costs [1].

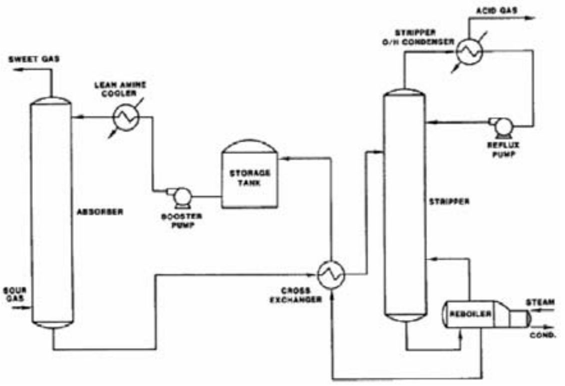

Fig 1. Process flow diagram for a common sweetening plant

2. General Considerations for Selecting Amines

The general criteria for amine selection in sweetening plants have changed over the years. Until the 1970’s monoethanolamine (MEA) was the amine first considered for any sweetening application. In the 1970’s, a main switch from MEA to diethanolamine (DEA) occurred [2]. In the past ten years, MDEA, DGA, and mixed amines have steadily gained popularity.

In order to become accepted on an industry-wide basis, different operating conditions should be tested and proven with a particular amine. Each alkanolamine solution has a "accepted" range of process conditions and parameters associated with it. These "accepted" conditions and parameters are discussed below. Typical operating conditions for common alkanolamines are summarized in Table 1.

2.1. Diethanolamine (DEA)

DEA is the most commonly used amine and is used within the 25 to 35 weight % range. The total acid gas loading for DEA is limited to 0.30 to 0.35 mole/mole for carbon steel as the construction material for equipment. DEA can be safely loaded up to equilibrium level (~1 mole/mole) when stainless steel is used.

The degradation products of DEA are relatively less corrosive than those of MEA. Exposure to oxygen forms corrosive acids and COS and CS_2 may, to some extent, react irreversibly with DEA. DEA is not reclaimable under the regenerator conditions, as at atmospheric pressure it decomposes below its boiling point.

Vacuum reclaimers, however, have been successfully used to reclaim DEA solutions [3,4]. Since DEA is a secondary alkanolamine, it has a reduced affinity for reaction with H_2S and CO_2 and therefore may not be able to produce pipeline quality gas for some low-pressure gas streams. In general, as the gas pressure is lowered, the stripping steam must be increased or a split flow design must be used. In some cases, even these measures will not suffice and another solvent must be used.

Under some conditions, such as low pressures and a liquid residence time on the tray of about 2 seconds, DEA is selective toward H_2S and will permit a significant fraction of the CO_2 to remain in the sales gas.

2.2. Methyldiethanolamine (MDEA)

An accepted set of operating conditions has not been firmly established for MDEA compared to other amines. This has been due to the flexibility and versatility of MDEA and the resulting wide range of applications. MDEA is a tertiary amine and commonly used in the 20 to 50 wt % range. Solutions with lower amine concentration are typically used in low pressure, high selectivity applications such as the selective removal of H_2S in the Shell Claus Offgas Treating (SCOT) units.

Due to the considerably reduced corrosion problems, acid gas loadings as high as 0.7 to 0.8 mole/mole are considered “practical” in carbon steel made equipment. Higher loadings may also be possible with a few problems. Exposure of MDEA to oxygen forms corrosive acids, which, if not removed from the system, can result in the buildup of iron sulfide in the system. MDEA has several distinct advantages over primary and secondary amines, which include lower vapor pressure, lower heats of reaction (Table 2), higher resistance to degradation, fewer corrosion problems and selectivity toward H_2S in the presence of CO_2 [5].

Depending on the application, some of the above advantages have special significance. For example, due to its lower heat of reaction, MDEA can be employed in pressure swing plants for bulk CO_2 removal. In a pressure swing plant, the rich amine is merely flashed at or near atmospheric pressure and little or no heat is added for stripping.

The overwhelming advantage that MDEA currently possesses over the other amines is that it is readily selective toward H_2S in the presence of CO_2. At high CO_2/H_2S ratios, a major portion of the CO_2 can be slipped through the absorber and into the sales gas while removing most of the H_2S.

The enhanced selectivity of MDEA for H_2S is attributed to the inability of tertiary amines to form carbamates with CO_2. MDEA does not have a hydrogen attached to the nitrogen and cannot react directly with CO_2 to form carbamate. The CO_2 reaction can only occur after the CO_2 dissolves in water to form a bicarbonate ion, which then undergoes an acid-base reaction with the amine:

$$CO_2 + H_2O + R_2NCH_3 \leftrightarrow R_2NCH_4^+ + HCO_3^- \qquad (1)$$

At least six different mechanisms for the CO_2-MDEA reaction have been proposed [6,7,8].

Tab. 1. Typical operating conditions and data for amines [14]

Alkanolamine type	**MEA**	**DEA**	**DGA**	**MDEA**
Solution strength, wt.%	15-20	25-35	50-70	20-50
Acid gas loading, mole/mole	0.30-0.35	0.30-0.35	0.30-0.35	Unlimited
Ability for selective absorption of H_2S	No	Under Limited Conditions	No	Under Most Conditions

MDEA can, however, react with H_2S by the same proton transfer mechanism of primary and secondary amines [9]:

$$H_2S + Amine \leftrightarrow [Amine]H^+ + HS^- \qquad (2)$$

Selective absorption of H_2S can be enhanced by optimizing absorber design to obtain a liquid tray residence time between 1.5-3.0 seconds and by increasing the temperature in the absorber. Both of these conditions favor H_2S absorption with CO_2 rejection.

3. Mixed Amines

Mixed amines are generally mixtures of MDEA and DEA or MEA and are used to enhance CO_2 removal by MDEA [10].

Such mixtures are referred to as MDEA-based amines with DEA or MEA as the secondary amines. Mixed amine system which combine the higher equilibrium capacity of the tertiary amine with higher reaction rate of the primary or secondary amine, can bring about considerable improvement in gas adsorption and great saving in regeneration energy requirement [11,12].

The secondary amines generally comprise less than 20% of the total amine content on a molar basis. At lower concentrations of MEA and DEA, the overall amine concentration can be as high as 55wt % without the implementation of exotic metal equipment.

MDEA-based mixtures are normally used to increase the CO_2 pickup in cases where the MDEA is allowing too much CO_2 to slip overhead in the absorber. Spiking the MDEA with MEA or DEA to achieve the desired CO_2 pickup is often advantageous over a complete amine switch out to a DEA or MEA system because the MDEA regenerator reboiler may be undersized for a purely formulated DEA or MEA system. Operating problems associated with mixed amines influence amine mixture concentration and its maintenance.

However, finding an optimum concentration for mixed amines (DEA+MDEA) strongly depends on the H_2S and CO_2 content of the sour gas, operating pressures and sale gas specifications. For natural gas sweetening purposes mixed amines are typically mixtures of MDEA and DEA or MEA which enhance CO_2 removal while retaining desirable characteristics of MDEA such as reduced corrosion problems and low heats of reaction.

With the blend formulation as an additional variable, it is possible, at least in principle, to produce a treated gas having predetermined residual amounts of both H_2S and CO_2. Thus, we no longer have to accept the residual amount of CO_2 that treating to 4 ppmv H_2S leaves in the gas. Using the right amount of additive lets us control the CO_2 level, too. But controlling selectivity is not the only application for blended amines technology [13].

4. Case Study

A typical Iranian gas plant is selected for this study. The gas sweetening facility has five identical amine trains for H_2S and CO_2 removal. The plant management decided to consider one of the units for substituting DEA with a mixture of DEA and MDEA. Each train was composed of two absorbers and two stripper columns, which operated parallel in the unit. The HYSYS Plant simulator was used to simulate the process. The flow diagram of the gas plant is shown in Fig. 2. The absorber feed gas composition is shown in Table 3. Operating conditions are summarized in Table 4.

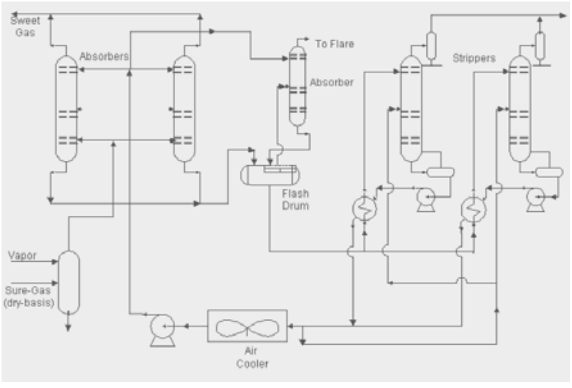

Fig 2. Process flow diagram of the amine unit

Current plant operating conditions were initially simulated to obtain the confidence that the simulation was performed effectively. The simulation produced a very good agreement between the HYSYS-generated results and the actual operating data. The results are listed in Table 5.

The process was subsequently simulated using various mixtures of DEA and MDEA with the following constraints:

Tab. 2. Heat of reaction for different types of amines

Amine	MEA	DEA	DGA	MDEA
Solution Strength	15-20	25-35	40-60	30-50
Acid Gas Loading mole/mole	0.3-0.4	0.3-0.4	0.3-0.4	Unlimited
ΔH_r for H_2S [kJ/kg]	1278	1188	1566	1213
ΔH_r for CO_2 [kJ/kg]	1917	1518	1975	1394

Tab. 3. Absorbers feed gas composition (Design Basis)

Component	Flow Rate (kmole/hr)	Mole %
H_2O	4.28	0.03
N_2	75.94	0.52
CO_2	936.3	6.41
H_2S	562.36	3.85
COS	0.26	17 ppm
C_1	12909.22	88.35
C_2	81.8	0.58
C_3	13.16	0.09
i-C_4	2.92	0.02
n-C_4	4.38	0.03
i-C_5	2.92	0.02
n-C_5	2.92	0.1
C_6^+	14.62	-
DEA	-	0
Total	14611.16	**100**
Pressure (kPa)	7327	
Temperature (^oC)	21	

Tab. 4. Gas sweetening operating conditions

Parameter	Typical value
Amine Circulation Rate [m^3/hr]	935
Absorber Col. Top/ Bottom Pressure [kPa]	7295 / 7326
Absorber Col. Top/ Bottom Temperature [^oC]	55.0 / 77.0
Stripper Col. Top/ Bottom Pressure [kPa]	152 / 192
Stripper Col. Top/ Bottom Temperature [^oC]	52.0 / 120.4
Number of Actual Tray (Absorber)	20
Number of Actual Tray (Stripper)	24

Tab. 5. Comparison between simulation and actual operating data

Parameter	Operating Data	Simulation Results
Rich Amine Loading	0.45 - 0.50	0.49
Lean Amine Loading	0.027 - 0.031	0.028
H_2S (ppm) in Sweet Gas	1.5 - 2.5	2.0
CO_2 (mol%) in Sweet Gas	0.01	0.01
Absorber Col. Top/ Bottom Temperature [^oC]	55.0 / 77.0	61.5/86.2
Stripper Col. Top/ Bottom Temperature [^oC]	52.0 / 120.4	Set 52.0/120.4

- Solution circulation rate was considered constant at 935 m^3/hr
- H_2S content in sweet gas should be kept less than 2 ppm
- CO_2 content in sweet gas should be kept less than 1%
- Duty of each reboiler was considered constant at 1.32e+8 kJ/hr (125MMBTU/hr)
- Condenser temperature equals to 52 ^oC

DEA and MDEA concentrations in the solution were changed from 10 to 30 and from 5 to 39 weight%, respectively. The amine mixtures which met a targeted value for the following parameters were selected as the alternative solvent for optimum mixture concentration:

- Amine System
  - ○ Rich amine loading: ($\frac{\text{mole of } CO_2 + \text{mole of } H_2S}{\text{mole of MDEA} + \text{mole of DEA}}$)

$$H_2S\ (v/v)= \frac{H_2S\ \text{Vol.Flow}}{\text{Amine Vol.Flow}}$$

$$CO_2\ (v/v)= \frac{CO_2\ \text{Vol.Flow}}{\text{Amine Vol.Flow}}$$

- ○ Lean amine loading: ($\frac{\text{mole of } CO_2 + \text{mole of } H_2S}{\text{mole of MDEA} + \text{mole of DEA}}$)

H_2S (v/v) and CO_2 (v/v) as above.

- Acid gas composition in the sweetened gas (absorber overhead).

Fig. 3 shows how the plant capacity could be increased for various amine blends. The through put can be increased from the base value of approximately 14,600 kmole/hr to the indicated gas flow rate shown in Fig. 7 for various amine blend composition. It should be noted that the reboiler duty and other parameters indicated above were fixed and only the gas throughputs were changed. Since the maximum MDEA concentration that is used in industrial application is limited to below 50%, the total composition was kept to below 50%.

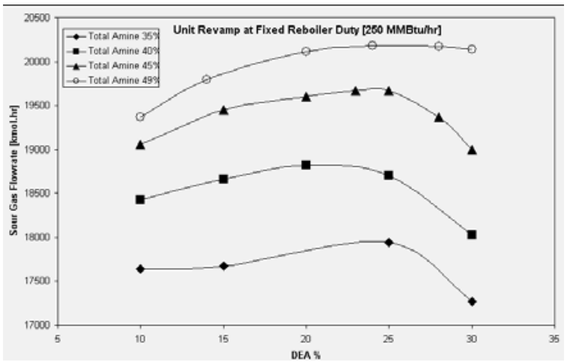

Fig 3. Unit Revamp at fixed reboiler duty

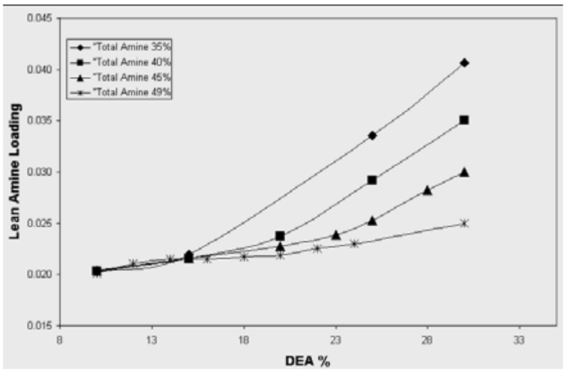

Fig 4. Lean amine loading for different amine mixture

It can be concluded that a 49% amine blend with between 20 to 30% DEA content will be an optimized composition. A lower end (closer to 20%) concentration for DEA will be recommended due to the need for control of corrosion and viscosity of the solution. As can be seen, by blending DEA and MDEA mixture, for the indicated composition, the plant capacity can be increased to between 17,000 to 20,000 kmole - an increase of approximately between 16 to 37%.

In order to check if the plant can handle higher gas flow rate other pieces of equipment including heat exchangers, pumps, pipe sizes, and towers should also be checked for the higher capacity. The diameter of the absorption tower was checked to see if the increased gas flow rate could be handled with the existing absorption columns. It was noticed that the diameter of columns could handle an increase in gas through put of around 22%. Using a 22% increase in gas flow rate the performance of the plant was evaluated using various amine blends. Fig. 4 and 5 show the variation of lean and rich loading for the tested amine blends when the gas flow rate is increased by a factor of 1.22 (22% increase in plant throughput).

The lean loading increases with DEA content as there a higher heat will be required to release the acid gas from the amine. The rich amine loadings remain relatively constant for a particular amine blend, but since a solvent blend with higher concentration of total amine can naturally absorb more acid gas, a reduction of acid gas loading will be expected when the total amine content increases.

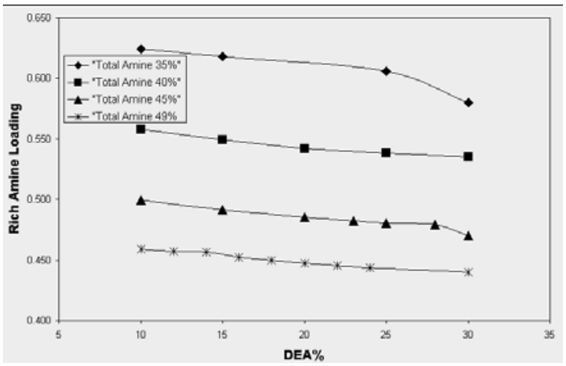

Fig 5. Rich amine loading for different amine mixtures

Fig. 6 and 7 show variation of acid gas (H_2S and CO_2) content of the sweetened gas for the enhanced capacity scenario–an increase of 22% of gas flow rate when the amine flow rate and reboiler duties are kept constant. It is evident that unless the total amine concentration is increased beyond the 35 weight % mark the acid gas specifications could not be met. Beyond this total amine composition, the acid gas content of the sweetened gas remains nearly constant for varying DEA content.

5. Summary and Conclusion

Due to its lower corrosion tendency and heat of reactions with acid gases compared with other amines, MDEA has many favorable capabilities

Some considerations for selecting proper amines mixture using the capabilities of typical process simulators were outlined in this paper. Using the HYSYS Plant simulation, different mixture of DEA and MDEA were investigated.

Since mixed amines have higher capacity for acid gas removal at constant amine circulation rate compare to DEA alone solvents, the capacity of gas processing of gas sweetening unit could be increased. Our results show that the gas flow rate capacity for a typical unit could be easily increased up to 20%. The diameter of the existing towers is suitable for this revamping and therefore there is no need to an investment cost. An optimum amine mixture contains about 20 wt% DEA and 29 wt% MDEA. This mixture is recommended due to its low corrosion and proper viscosity.

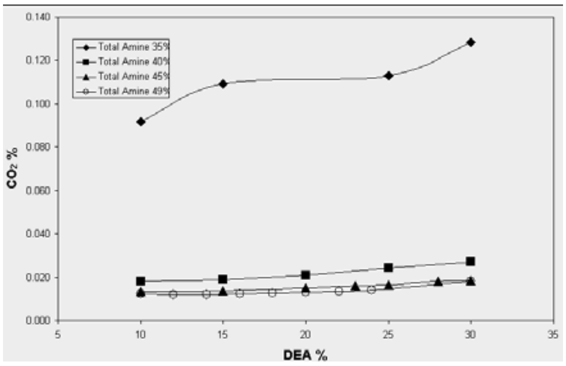

Fig 6. CO_2 concentration in sweet gas for different amine

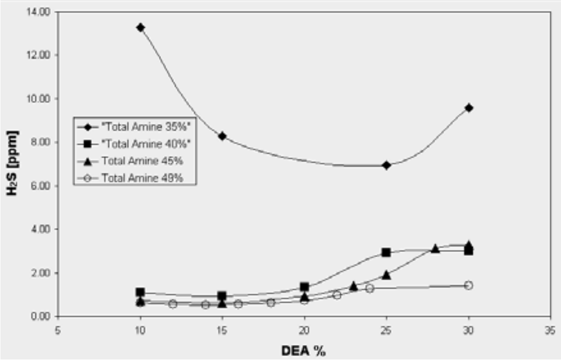

Fig 7. H_2S concentration in sweet gas for different amine

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