

Mixed Amines Application in Gas Sweetening Plants

Reza Mohamadirad^{*}, Omid Hamlehdar, Hamidreza Boor, Abdolali Fattahi Monnavar, Shahram Rostami

Monenco Iran Consulting Engineers Company (Member of MAPNA Group)
NO.20, 23rd St., Gandhi Ave., Tehran. IRAN, P.O.: 1517875714,
Mohamadirad.reza@monenco.com

Natural gas generally contains a large quantity of methane along with considerable amount of acid gases, which shall be removed from natural gas. One of the processes which are used in the industry to remove the acid gases from natural gas is alkanolamines process application. In present paper, a simulation study for an industrial gas sweetening plant has been investigated based on data from gas reservoir located in the south part of Iran. The aim of study is to investigate the effect of using mixed amines as solvent on the gas treatment process. At first simulation tuned with existing gas sweetening plant which uses MDEA solvent and then application of mixed amines has been investigated in constant amine concentration for a variety of cases. Simulation results show that application of MDEA/MEA (39.5/8 wt. %) or MDEA/DEA (23.75/23.75 wt. %) in lieu of MDEA (47.5 wt. %) will reduce H₂S content below 3.5 ppm like MDEA, however CO₂ concentration could be substantially decreased to less than 100 versus 10,000 ppm which is desired for downstream applications, further more this approach will create opportunities for pollution control through carbon capture and storage without any major change in existing plant.

1. Introduction

Gas treating in gas industries is getting more complex due to emissions requirements established by environmental regulatory agencies. This is encouraging gas specialists to look forward to the new technologies, new solvents, and new ways to find solutions. In response to the above trends, simulation software plays a key role in process development to study process alternatives, assess feasibility and improve pollution control. The technology of using alkanolamines or amines for removal of hydrogen sulfide and carbon dioxide from natural gases has been used for decades; 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, may be optimized by simply changing their amines solution (Khakdaman et. al., 2008). The differences in the performance of absorption technology and amine solvents depend on amine reactivity. Primary and secondary amines such as monoethanolamine (MEA) and diethanolamine (DEA), respectively, are very reactive and thus able to effect high volume acid gas removal at a fast rate, whereas tertiary amines like methyldiethanolamine (MDEA) are less reactive. However, the less reactive MDEA is characterized by lower stripping energy requirements compared to MEA or DEA. The

rate of amine degradation is first order and, in magnitude, followed the sequence MDEA < MEA < DEA (Blanc et al., 1982). Blanc et al. (1982) have reported that no degradation compounds were found in industrial MDEA in use for many years but Dawodu and Meisen (1996) study shows that degradation occurs, but at very low rates.

2. Process Description

An amine unit operates by contacting an amine solution with the sour gas or liquid feed counter-currently in an absorber column. H₂S and CO₂ in the feed are absorbed by the amine in the solution, and the sweetened gas exits the top of the column. Rich amine exits the bottom of the column and is sent through the regeneration system to remove the acid gases and dissolved hydrocarbons. The lean solution is then circulated to the top of the absorber to continue the cycle. (Dawodu and Meisen, 1996)

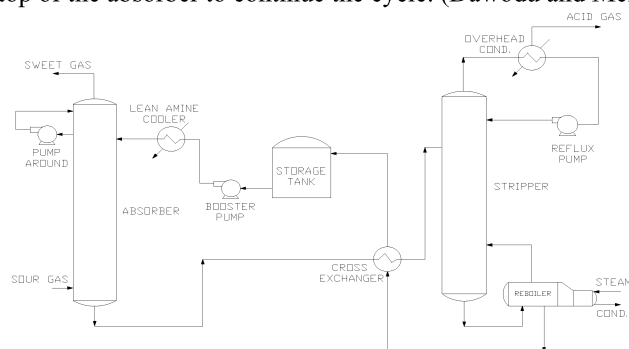


Figure 1: Flow diagram of gas treating plant

For simulation purpose, a typical Iranian gas plant (South pars gas field, Phase 9&10) is selected for this study. The flow diagram of the gas plant is shown in Fig. 1. The concept of using mixed amines is based on utilizing the advantages of each amine characteristics. In general, the H₂S is thought to react almost instantaneously with MDEA by proton transfer as is the case with primary and secondary amines. Since MDEA is a tertiary amine and does not have hydrogen atom attached to the nitrogen, the CO₂ reaction can only occur after the CO₂ dissolves in the water to form a bicarbonate ion. The bicarbonate then undergoes an acid-base reaction with the amine to yield the overall CO₂ reaction. Since the CO₂ reaction with water to form bicarbonate is slow and the H₂S reaction is fast, it is generally assumed that the H₂S reaction with MDEA is gas phase limited while the CO₂ reaction is liquid phase limited (Bullin et al., 1990). MDEA solvent and mixed amines performance is very sensitive to one or more of the operating parameters, such as liquid residence time on the trays, circulation rate, and lean amine temperature. MDEA has a number of properties, which make it desirable for applications, such as: High solution concentration up to 50 to 55 wt %, High-acid gas loading, Low corrosion, slow degradation, Lower heats of reaction.

3. Simulation of Gas treating plant

In this work, a process simulator was used to predict the performance of an Iranian gas sweetening plant with a sour gas feed containing 1.83 % CO₂ and 0.69 % H₂S on molar basis. Various mixtures of DEA and MEA with MDEA were used to investigate the potential for decrease in CO₂ content with minimum change in operating parameter and equipment sizes for the range acceptable for downstream plants. 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 decrease in CO₂ content is quite possible by just replacing DEA or MEA to some extent instead of the existing MDEA solvent and keeping the solvent flow rate and stripper reboiler heat duty. In another word, it is possible to decrease the CO₂ content from 1% mole to below 100 ppm mole using a mixed amine system and keeping maximum 3.5 ppm wt H₂S in sweet gas stream.

However, finding an optimum concentration for mixed amines (DEA+MDEA or MEA+MDEA) strongly depends on the H₂S and CO₂ 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 CO₂ removal while retaining desirable characteristics of MDEA such as reduced corrosion problems and low heats of reaction (Spears et al., 1996). For this case of bulk CO₂ removal together with H₂S using MDEA and mixed amines, the most sensitive operating parameters are; (Bullin et al., 1990): 1) Liquid Residence Time on Tray, 2) Lean Amine Temperature and 3) Circulation Rate

Table 1: Absorber feed composition (Design Basis)

Component	Flow Rate (kgmole/hr)	Mole %
CO ₂	488.3	1.83
H ₂ S	184.3	0.69
H ₂ O	16.6	0.06
N ₂	927.4	3.47
C ₁	22706.6	85.05
C ₂	1451.2	5.44
C ₃	535.3	2.01
i-C ₄	98.8	0.37
n-C ₄	151.4	0.57
i-C ₅	46.1	0.17
n-C ₅	40.9	0.15
C ₅₊	51.1	0.19
Total	26698.0	100.0

The absorber feed gas composition is shown in Table 1. First of all, present plant operating conditions were simulated to acquire the confidence that the simulation was performed effectively. The simulation made a very good agreement between the ASPEN HYSYS results and the actual operating data. The result is listed in Table 2. Also in table 2, two cases for simulation study were introduced for comparison of mixed amine performance. Process simulation was performed for various mixtures of MDEA/DEA and MDEA/MEA. Total concentration of mixed amine was kept in 47.5

Table 2: Comparison of Phase 9&10 of South pars gas field with Simulation

	Plant	Simulation	Simulation	Simulation
	Operating	Operating	Operating	Operating
	Data	Data	Data	Data
Amine Type	MDEA	MDEA	MDEA/DEA	MDEA/MEA
Lean / Rich Amine Conc. (wt.%)	47.5 / 43.1	47.5 / 44.6	47.5 / 43.4	47.5 / 41.9
Circulation Rate (m ³ /hr)	305.1	same	same	same
Gas Flow, (Sm ³ /hr)	629382	same	same	same
H ₂ S/CO ₂ inlet, % mole	0.69/1.83	same	same	same
H ₂ S/CO ₂ out, ppm vol./ppm mole	1 / 8350	1 / 8190	2 / 62	1 / 21
Total Rich Loading, mole/mole	0.378	0.369	0.508	0.485
Reboiler Design Duty, MW	22.85	22.23	23.56	24.52
Absorber Top/Bottom Pres. (bara)	65.9/66.3	same	same	same
Absorber Top/Bottom Temp. (°C)	43.8/36.4	51.3/35.9	56.9/40.5	55.6/42.3
Stripper Top/Bottom Pres. (bara)	2.35/2.6	same	same	same
Stripper Top/Bottom Temp. (°C)	109.7/131.5	109.1/131.6	104.4/131.8	104.5/131.8
NO. of Actual Tray, Absor./Strip.	34 / 25			

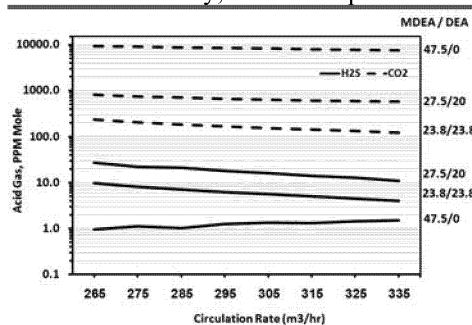


Figure 2: Effect of circulation rate on acid gas overhead in mixing MDEA/DEA case

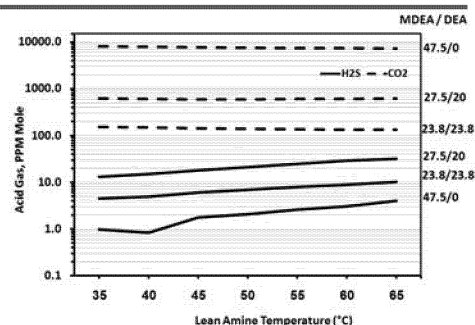


Figure 3: Effect of lean amine temp. on acid gas overhead in mixing MDEA/DEA

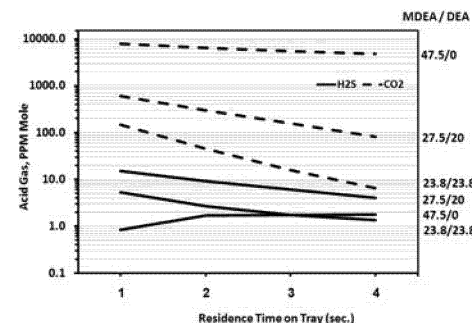


Figure 4: Effect of residence time on acid gas overhead in mixing MDEA/DEA case

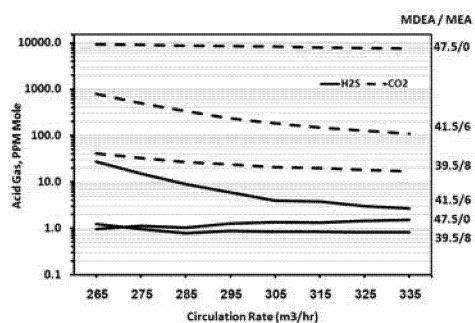


Figure 5: Effect of circulation rate on acid gas overhead in mixing MDEA/MEA case

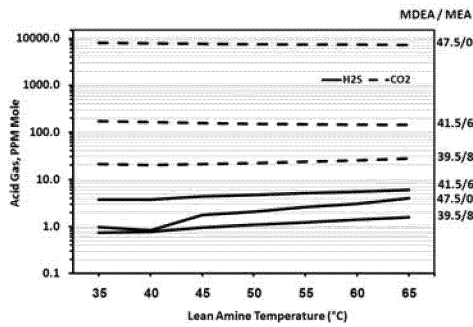


Figure 6: Effect of lean amine temp. on acid gas overhead in mixing MDEA/MEA

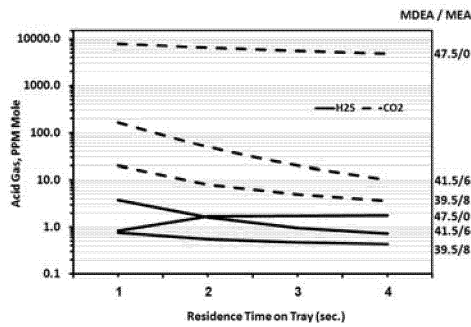


Figure 7: Effect of residence time on acid gas overhead in mixing MDEA/MEA case

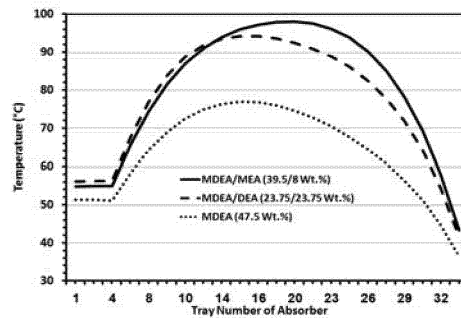


Figure 8: Effect of mixing amines on temperature profiles of absorber column

wt. % based on actual plant total concentration of MDEA, so DEA concentration was altered up to 50 % of total amine concentration and MEA up to 20 %. Other constraints are condenser temperature of stripper fixed on 55 °C and condenser duty on 8.4 MW. Fig. 2 shows although quantity of CO₂ and H₂S decreasing with increasing circulation rate and DEA concentration, but it is not sufficient. This means more leaner amine is needed that cause steam consumption increase, because DEA have higher heat of reaction. It should be noted that the other parameters were fixed and only the circulation rate were changed. Substitution of MEA instead of DEA, as shown in Fig. 5 effectively reduce H₂S and CO₂ below specified level, if MEA concentration increase more than 7 wt. %. In case of MEA addition plant can operate in reduced circulation rate and consequently steam consumption. Lean amine temperature increasing as shown in Fig. 3 and Fig. 6 cause CO₂ absorption improving to some extent, however, H₂S content increases in sweet gas. Rising lean amine temperature up to 50 °C is favorable for CO₂ absorption because the CO₂ reaction with mixed amine is kinetically controlled, a hotter column increases the reaction rate, but above 50 °C solubility of CO₂ in liquid phase and subsequently its absorption will decrease. Whereas reaction of MDEA with CO₂ is slow, increasing residence time will give sufficient time to reaction occur. For this purpose usually weir height or internal diameter would be increased. Fig. 4 and Fig. 7 show variation of CO₂ and H₂S in sweet gas versus residence time. As shown in Fig. 8

maximum temperature of absorber column rise from 77 °C in case of pure MDEA to 94 °C for mixing DEA with MDEA and 98 °C for mixing MEA. This is because of higher heat of reaction of DEA and MEA. It is evident that using mixing amines have enhanced absorption remarkably.

4. Summery and Conclusion

Advantages of selecting proper mixed amines were outlined in this paper. Using ASPEN HYSYS Plant simulation, different mixture of DEA and MEA with MDEA were investigated. Aforementioned gas processing plant uses two amine treatment units, one uses MDEA for removal of H₂S and subsequently after fractionation of methane another unit uses DEA to remove CO₂ below specification in ethane stream providing feed for petrochemical plants. Since mixed amines have higher capacity for acid gas removal at constant amine circulation rate compare to MDEA individually, so second amine unit is not necessary, which cause reduction in operation cost besides improving pollution control with removing bulk of CO₂. The recovered CO₂ can be purified in Tail Gas Clean Up unit and sequestrate in underground reservoir.

Our results show with utilizing this method, CO₂ content could be decreased below 100 ppm beside H₂S content below 3.5 ppm. Size of existing column is adequate for mixed amine and there is no need for new investment. An optimum amine mixture contain about 39.5 wt. % MDEA and 8 wt. % MEA in MDEA/MEA mixture and 23.75 wt. % MDEA and 23.75 wt. % DEA in case of MDEA/DEA mixture. Also by using amine blends in circulation rate and regeneration energy requirement could be reduced by 20%. It has also been shown that the rate of DEA make-up for the MDEA + DEA blends would be higher than the rate of MEA make-up for the MDEA + MEA blends in order to maintain the desired solution capacity. The aforementioned benefits can only translate to operational savings if the loss of amine due to degradation in the amine blend is less than or comparable with the loss in the corresponding single amine system. Plants using MDEA blends should therefore be equipped to monitor and control the concentrations of these compounds so that operational problems such as reduction in mass transfer rate and absorption capacity, foaming and fouling are minimized.

References

- Blanc C., Grall M., Demarais G., 1982, The Part Played by Degradation Compounds in the Corrosion of Gas Sweetening Plants Using DEA/MDEA, *Oil Gas J.*, 15, 128-130
- Bullin J.A., Polasek J.C., Donnelly S.T., 1990, The Use of MDEA and Mixtures of Amines for Bulk CO₂ Removal, *Proceedings of the 69th GPA Annual Convention*, Tulsa, Gas Processors Association, 135-139
- Dawodu O. F., Meisen A., 1996, Degradation of Alkanolamine Blends by Carbon Dioxide, *The Canadian Journal of Chemical Engineering*, Vol. 74, 960-966
- Khakdaman H.R., Zoghi A.T., Abedinzadegan M., Ghadirian H.A., 2008, Revamping of Gas Refineries Using Amine Blends, *IUST Int. J. of Eng. Sci.*, Vol. 19, 27-32
- Spears M.L., Hagan K.M., Bullin J.A., Michalik C.J., 1996, Converting to DEA/MDEA Mix Ups Sweetening Capacity, *Oil & Gas Journal*, Vol. 12, 63-67