Energy Optimization For Amine Gas Sweetening Process By Mixed Amines Using Simulations

ISSN (e) 2520-7393
ISSN (p) 2521-5027
Received on 14th Sept, 2019
Revised on 28th Sept, 2019
www.estirj.com

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Abstract: Pakistan produces 26% of its energy through natural gas and this seems to be increasing every year. However, as natural gas is produced from deep underground reservoirs it contains significant amount of acid gas components as H_2S and CO_2. Natura gas sweetening through chemical absorption is a most commonly known process in gas processing industry which is known for its efficiency and capacity to remove acid gases however, the process requires heavy operating cost, which tend to be reduced by using various theoretical approaches to improve and optimize the process. It has been proved by different scholars about the positive effect of using blended or mixed amines on the efficiency of amine gas sweetening process in terms of acid gas removal and reduction in operation costs. This work reviews the current operation of Hala Gas Field, Tando Adam, Sindh. The facility processes gas from two wells Adam X-1 and Adam West X-1, both having different feed composition. The plant uses standardized MDEA 45% solution to treat natural gas. A model amine gas processing unit was developed using a simulator Aspen HYSYS to study the effects of using different amine blends to enhance the CO_2 capture capacity of the plant incorporating the high reactivity of primary and secondary amines towards acid gases. The results conclude that by the use of these blends it is possible to increase CO_2 capture capacity by 2.62%.

Keywords: *Natural gas; Sweetening; Amine Blends*

1. Introduction

Natural gas is one of the mostly used Hydrocarbon in the world. The gas is drilled from deep reservoirs where it also contains some unwanted components that are needed to be removed from gas before reaching to the consumers end. CO_2 and H_2S the components that are needed to be removed due to their acidic properties. Amine gas sweetening process is one of the frequently used technology for the removal of acid gases from untreated gas for few decades. The research in this process has always been in the since 1960's and several different amines have been developed regarding the best amine suited for the service. It is observed that, for the processes that may be operating inefficiently can be optimized by simply making some changes in the amine solution. Figure 1. Shows the basic PFD for an Amine gas sweetening unit. H_2S and CO_2 carry acidic properties and provided proper conditions, these gases cause corrosion to the pipeline and equipment. Along with that H_2S being highly toxic gas, if in enough concentration can kill a person right away and CO_2 decreases the heating value of gas which reduces overall BTU'S of the gas. The primary focus for a natural gas sweetening process is to meet the sale gas or pipeline gas specification with respect to CO_2 and H_2S. The other objective will then be the selection of the process that should be best suited for the process condition, mostly depending upon the composition of Natural gas.

Few of the points that can be well thought off in the selection of suitable amine. Which will help in design and evaluation of an existing Plant.

- Manipulation of main process parameters like Amine circulation rate be reduced by using a different concentrated amine or by using different amine blends.
- Studying the effects of using an Alkanolamine solution which requires lesser energy for its regeneration or has lower heat of reaction with acid gases on the performance of an equipment.
- Can the removal of one particular acid gas be increased by incorporating an amine solution that is selective towards either H_2S or CO_2.
- Could a mixture of amine be used in a system that is more reluctant to degradation and prevents corrosion in process.

A lot of work has been published followed by the objective of studying the amine gas sweetening process. We used Aspen HYSYS V.10 in this work and studied the sensibility of the process with respect to its current process and main parameters. In this study the parameters considered were the Amine circulation rate, Amine reboiler duty and acid gas removal by using different amine blends. Different alkanolamine solutions are being used for gas treatment in the industry depending on process conditions. These amines have different properties and different reactivity with acid gases. Hence, they also have some advantages and disadvantages over each other.
Amine circulation rate and energy required for regeneration are the key parameters on which the plant is based. 50% to

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70% of plant's total cost depends on the magnitude of amine circulation throughout the system as very high pressure and high flow pumps are required to serve this purpose and other 10% to 20% of total cost is dependent upon the energy required for amine regeneration. Hence, the selection of best suited amine solution is very important in this manner.[1]

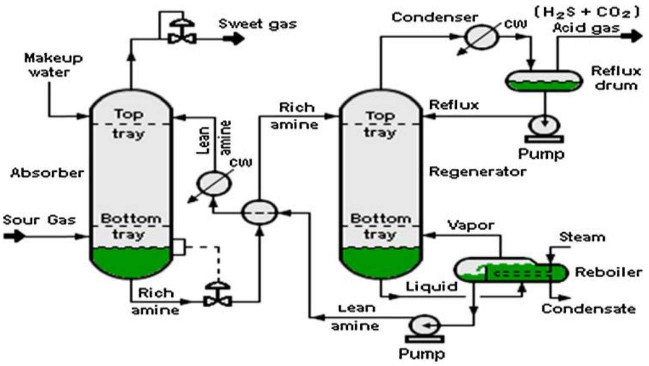

Fig.1 PFD of Amine gas sweetening unit

1.1. General criteria for Selecting Amines:

The criteria for choosing an amine solution for gas processing has changed over a period of time. The study has always been there to develop processes that are more efficient and require lesser energy. Until the early 1970's Monoethanolamine (MEA), a primary amine was preferred amine for any gas sweetening process, and it has been for long. But due to highly corrosive nature of MEA very high standard piping was supposed to be used and which was added to the cost of process. Diethanolamine was then introduced in late 1970's and there was a switch from MEA to DEA. For long time DEA was the most effective amine. For the last decade MDEA, DGA and blended amines have quickly gained popularity.

Each of the Alkanolamine solution has different properties and applications in process industry. They are used depending on the application required by the process.

1. Monoethanolamine (MEA)

MEA is a primary amine, which has had a broad utilize as a gas sweetening solvent. The response of primary amines towards CO_2 is generally higher. MEA could be a steady compound on temperatures underneath its boiling point and does not endure any degradation if functioned beneath the parameters [3]. The most impediments of MEA are: Its increase in corrosivity due to increase in temperature, high heat of reaction with CO_2 and H_2S which comes about in high energy necessities for its recovery and subsequently the entire fetched of the method increments, moderately high vapor pressure which brings approximately unwanted amine losses through vaporization [4]. Although the CO_2 capture capacity of MEA is generally higher, it is additionally the foremost destructive amine. Warm heat stable salts are produced in gas by the presence of CS_2 (Carbonyl sulphide) and COS (Carbon disulfide), which are impossible to recover at normal stripping temperatures and on increased temperatures above 245°F MEA becomes more corrosive and a side reaction of MEA is created with CO_2 which produces a heat stable salt Oxazolidone-2 that consumes MEA and slowly degrades it.

2. Diethanolamine (DEA)

DEA has been one of the foremost used amines for years till early 1990's. DEA initially got its popularity in industry due to its less corrosive nature compared to MEA. The solution of DEA is normally maintained up to 25% to 35% by weight with water. For gas plants carbon steel piping is normally preferred for construction material which is why the acid gas loading for DEA should be between 0.30 to 0.35 mole/mole. DEA is also degraded if comes in contact with oxygen, but its degradation products are less corrosive then MEA. On getting in contact with oxygen, DEA starts degrading and more corrosive acids like CS_2 and COS are produced. DEA being a secondary amine has reduced reactivity towards CO_2 and H_2S compared to MEA and for low pressure gas streams it may not be able to process the gas to pipeline quality gas [5].

3. Methyl-diethanolamine (MDEA)

Methyl diethanolamine (MDEA) these days is considered to be one of the mostly used amine in the gas processing industry. Due to its lesser corrosivity and lower heat of reaction compared to other primary and secondary amines it has wider industrial applications. If compared to the other primary and secondary amines which been in the industry for a while, for MDEA completely optimized operating conditions have not yet been established. The chemical structure of MDEA has three alkyl groups (C_NH_{2N+1}) connected to its Nitrogen atom. Solution of MDEA is normally kept from 40% to 45% in concentration with water. Water serves the purpose of a medium here in which CO_2 is initially dissolved before the reaction as MDEA does not react directly to CO_2. CO_2 initially dissolves in water and make carbonic acid (H_2CO_3) and that reacts with MDEA [6].

The reaction of amine with CO_2 is written as:

$$CO_2 + H_20 + R_2NCH_3 \leftrightarrow R_2NCH_4^+ + HCO^-_3 \qquad (1)$$

The reaction of MDEA with H_2S is same proton transfer reaction as other primary and secondary amines:

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

The other main advantage of MDEA is its selectivity towards H_2S. Which can be increased by increasing liquid holdup time in absorber by means of temperature between 1.5 to 3.0 seconds on each tray. MDEA has very low vapor pressure which dramatically decrease its chances of degradation as it will require lesser regeneration energy. In addition, very little miscibility of MDEA with hydrocarbons cuts the loss of hydrocarbons to almost negligible [7] [8].

4. Mixed Amines

The alkanolamine solution currently being used in the process industry have different chemical and physical properties. Primary and secondary amines are well known for their reactivity towards acid gases and are normally used for the processes where almost no percentage of CO_2 can be allowed at the consumers end. For example, MEA is used for acid gas removal from natural gas for liquified natural gas. But as MDEA being a tertiary amine is a bit more stable solvent in terms of reactivity and thermodynamically. As already discussed, that the reaction of MDEA with CO_2 is not direct and is a slow reaction and MDEA provides selectivity towards H_2S if treated accordingly [9]. The blended amines serve the purpose of incorporating different properties of these amines in a single solvent. The commonly used amine blends in gas processing industry are MDEA+DEA or MDEA+DGA. [10,11]. It is possible to bring in extraordinary savings in energy requirement for regeneration and reduced amine circulation rate. Working issues that are normally related with amine blends are finding an ideal and optimum concentration for the solutions. [12]

2. Case study

This study is conducted on Hala gas processing plant which has one 270 GPM amine gas sweetening plant for CO_2 and H_2S removal. The facility processes gas from two wells (Adam X-1 and Adam West X-1) having different acid gas proportions. The facility uses MDEA as an absorbent which is a tertiary amine. It is established that primary and secondary amines are more reactive towards acid gases comparative to tertiary amines. So, by creating amine blends plant's overall CO_2 and H_2S capture can be increased. Which can have many applications like increasing plant's overall gas processing capacity or reducing regeneration energy requirement and amine circulation rate.

Table 2.1 Feed Gas Composition

Component	Mole Fraction	
	Adam X-1	Adam West X-1
Methane	0.6620	0.85602
Ethane	0.0634	0.04524
Propane	0.0207	0.00623
i-Butane	0.0033	0.00255
n-Butane	0.0048	0.00239
n-Pentane	0.0014	0.00042
i-Pentane	0.0018	0.00071
n-Hexane	0.0019	0
n-Heptane	0.0000	0
n-Octane	0.0026	0
n-Nonane	0.0013	0
n-C11	0.0004	0
n-C14	0.0002	0
n-C15	0.0002	0
CO2	0.1552	0.08047
H2S	0.0000	0
Nitrogen	0.0809	0.00597

Amine gas sweetening process is one of the most widely used processes and is considered as an efficient method for treating Natural gas. Wang, (2015) reported that 50% of the current acid gas removal technologies use aqueous solutions of Alkanol Amines for treating Raw Natural gas (5). This study aims to study and evaluate the current plant operations of Hala gas processing plant by using Aspen HYSYS. The purpose of this work is to study the effect of mixed amines to reduce overall regeneration energy requirement, decreasing amine circulation rate and enhance the CO_2 capture capacity, technical and economic valuation of the plant along with the optimization of key operating parameters.

Table 2.1 Amine Plant main operating parameters

Parameter	Typical value
Amine circulation rate [GPM]	180
Absorber column Top/bottom pressure [Psig]	1038/1030
Absorber column Top/bottom temperature [°F]	198/160
Stripper Column Top/Bottom Pressure [Psi]	12/14
Stripper Column Top/Bottom temperature [°F]	165/255
Number of trays in Amine contactor	20
Number of trays in still column	20
Amine reboiler temperature [°F]	255
Amine reboiler duty [MMBtu/hr]	18.99

For this study different models were developed by using different amine blends and fixing the amine flow rate for different models and compared their results to the base model. The base model is the existing plant model using MDEA as solvent for acid gas removal and as for the other models, I have used different amine blends i.e. MEA+MDEA, DEA+MDEA and DGA+MDEA as solvents. The study focuses on any possible increase in CO_2 capture capacity of the plant from gas stream at given amine concentration and look for any probable decrease in overall plant duty.

Loading in amine system is understood as the allowable presence of acid gas in Amine solution.

$$\text{Rich amine loading: } \left(\frac{mole\ of\ CO2+mole\ of\ H2S}{moles\ of\ MDEA}\right) \tag{2.1}$$

$$H_2S\ (V/V) = \frac{H2S\ Vol\ Flow}{Amine\ volFlow} \tag{2.2}$$

$$CO_2\ (V/V) = \frac{CO2\ Vol\ Flow}{Amine\ Vol\ Flow} \tag{2.3}$$

$$\text{Lean Amine Loading: } \left(\frac{mole\ of\ CO2+mole\ of\ H2S}{mole\ of\ MDEA}\right) \tag{2.4}$$

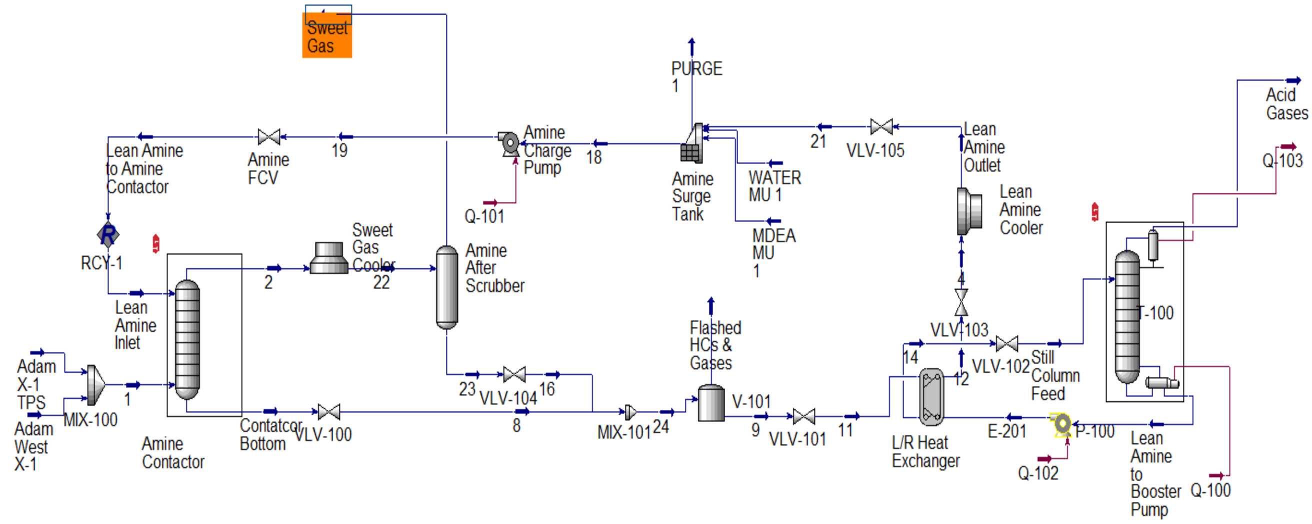

Fig. 2 PFD of Amine gas Sweetening unit HGPP

3. Methodology:

Process simulation is a powerful tool in process industry where one can study and evaluate running plants or designing a new plant. The model created in theses simulators are amenable to manipulation which would be impossible, impractical or too expensive to perform on a running plant or a system that it portrays.

A model of Hala gas processing was developed to conduct this study. The main purpose of this project is to develop a model of the Amie gas sweetening unit of HGPP and study the effect of using mixed amine solvents against the currently used MDEA.

Table 3. Amine Concentration used in the study

Amine	MDEA	MDEA+MEA	MDEA+DEA	MDEA+DGA
Solution Strength	45%	40%+5%	40%+5%	40%+5%
ΔH_T for CO_2 [Kj/Kg]	1394	1917	1518	1975
ΔH_T for H_2S [Kj/Kg]	1213	1278	1188	1566

The software used in this study is Aspen HYSYS V-10, the work was divided in two parts. First part is the collection of data from Hala gas processing facility and the other part is the modeling of its amine gas sweetening unit. The developed model was then used as a base model in this study. Several different amine blends were then used in the research and studied their effects on key plant parameters like Amine circulation rate, Amine reboiler duty and Rich/Lean amine loading.

Four cases were used in this work with fixed amine circulation rate for each case and studied the effect of the change in the key parameters.

- Case-1 (180 GPM)
- Case-2 (146 GPM)
- Case-3 (175 GPM)
- Case-4 (155 GPM)

4. Results and Discussions:

1. Case-1 (180 GPM)

The plant currently operates at 180 GPM and uses MDEA as solvent for acid gas removal. Case-1 is the study that depicts the current operating condition of HGPP and then it is the study of effects of using different amine blends at same amine circulation rate. Three different models were run at this flow rate using the amine blends and when studied the effects of using primary and secondary amines mixed with tertiary amines as a solvent it essentially increased the overall CO_2 pick up rate of the solvent with variations in Amine reboiler duty respectively. As MEA reaction with CO_2 is direct and it requires more energy for regeneration, amine reboiler duty has increased to 22.46 MMBtu/hr. but that also allows to reduce amine circulation rate throughout the system.

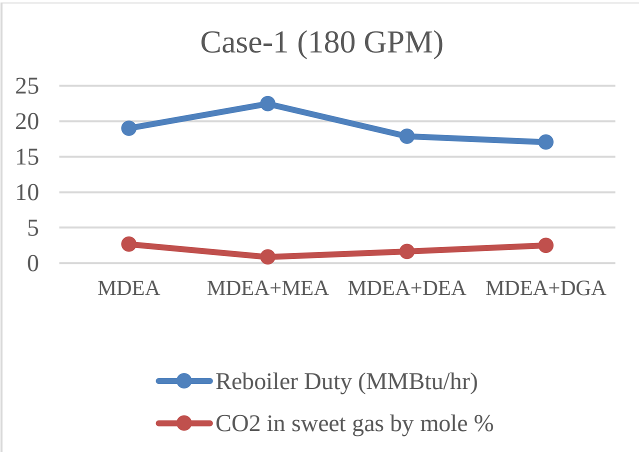

Fig. 4.1 CO_2 and Amine Reboiler duty variation plot for case 1.

2. Case-2 (146 GPM)

This case is optimized for the amine gas sweetening unit using (MDEA+MEA) as a solvent for acid gas removal. It can be seen in the graph that adding MEA in MDEA dramatically increases the CO_2 pick up rate of the solvent. Which allowed to reduce the amine circulation rate from 180 GPM to 146 GPM keeping the gas flow rate untouched. The effect of other solvents can also be seen in the graph for this flow rate.

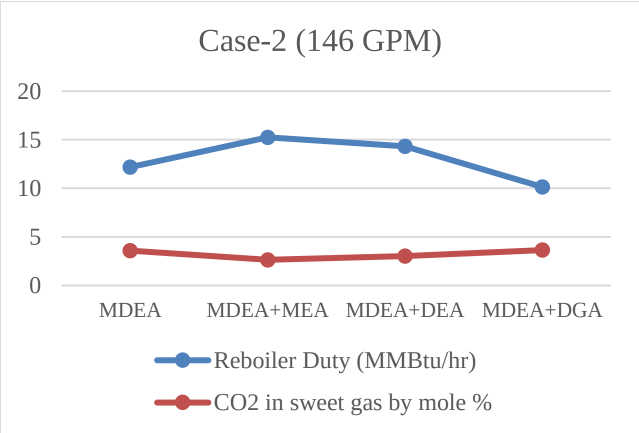

Fig. 4.2 CO_2 and Amine Reboiler duty variation plot for Case 2

3. Case-3 (175 GPM)

This case is optimized for using (MDEA+DGA) as a solvent for amine gas sweetening unit. It was understood by the study that DGA is more stable solvent compared to other primary amines and requires much lesser regeneration energy compared to other solvents.

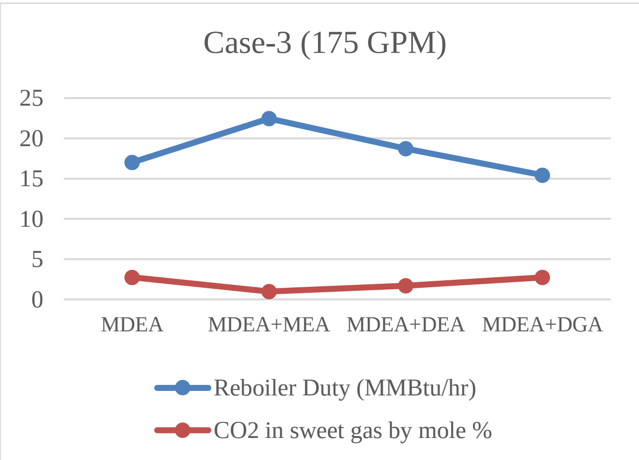

Fig. 4.3 CO2 and Amine Reboiler duty variation plot for Case 3

4. Case-4 (155 GPM)

This case is optimized for using MDEA and DEA as blends. DEA is considered less corrosive and less reactive compared to primary amines but due to its better stability and less corrosivity it has always been recommended in replacement of MEA. The 5% addition of DEA with MDEA helps reducing the amine circulation rate to 155GPM from 180 GPM. Which can also allow the increase of total gas through put into the plant.

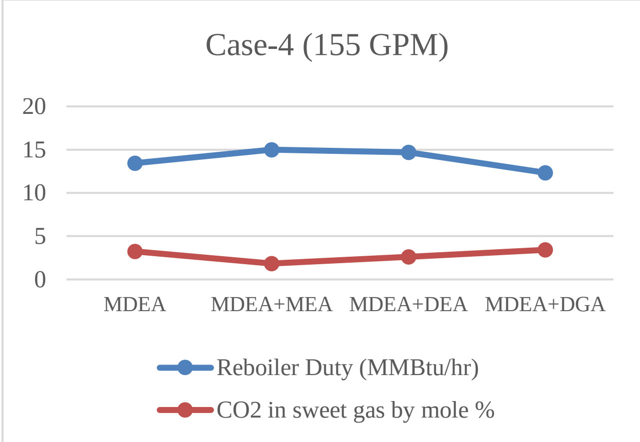

Fig. 4.4 CO_2 and Amine Reboiler duty variation plot for Case 4

Loading of lean and rich amine is a very important concern because it shows the amount of acid gases absorbed in the solvent. On the basis of acid gas loading in amine whether it is rich or lean process conditions can be understood easily. It is very important that lean and rich amine loading are under specified limits as increased lean amine acid gas loading can cause serious process parameter disturbances like foaming and channeling in the absorber. Increased rich amine loading will increase amine reboiler duty and other process disturbances. Below are the graphs for lean and rich amine loading for each solvent in the process.

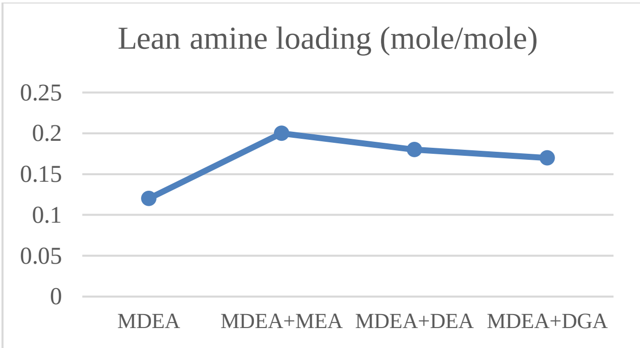

Fig. 4.5 Lean Amine loading plot for different Solvents at 180 GPM

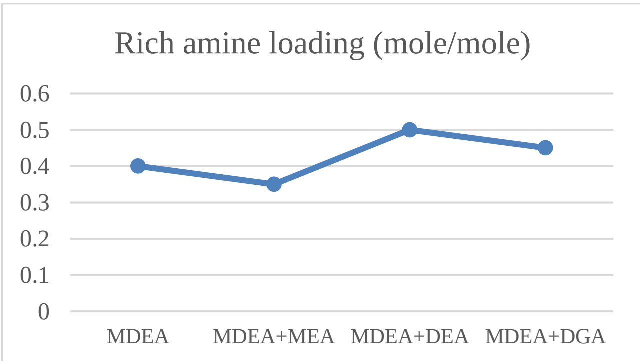

Fig. 4.5 Lean Amine loading plot for different solvents at 180 GPM

Conclusion:

Due to its higher corrosion rate use of MEA in carbon steel pipelines and vessels is non recommended as it certainly results in leaks and reduces the life of equipment. The results obtained from this research show that by adding 5%

of DGA in current MDEA solution can be very helpful in reducing plant operational cost as mixing DGA with current MDEA solution reduces amine reboiler duty from 18.99 MMBtu/hr. to 15.43 MMBtu/hr. The mixture is recommended for its low corrosion and proper viscosity. On the other end MDEA+DEA can also be used with a slight increase in regeneration energy requirement but increases overall acid gas pick up with reduced amine circulation rate from 180 GPM to 155 GPM.

References:

[1] Polasek, J.C., Bullin, J.A., Donnelly, S.T., *"How to Reduce Costs in Amine-Sweetening Units*," Chemical Engineering Progress, March 1983, PP. 63-69.

[2] Beck, J.E., *"Diethanolamine an Energy Conserver*," Laurence Reid Gas Conditioning Conference, Norman Oklahoma, 1975.

[3] Anufrikov YA, Kuranov GL, Smirnova NA (2007) Solubility of CO2 and H2S in alkanolamine containing aqueous solutions. Russian Journal of Applied Chemistry 80:515-527.

[4] Sadegh, N., Stenby, E.H. and Thomsen, K., 2013. Acid Gas Removal from Natural Gas with Alkanolamines: A Modeling and Experimental Study.

[5] Khakdaman, H.R., ZOUGHI, A., Abedinzadegan, M. and Ghadirian, H.A., 2008. Revamping of gas refineries using amine blends.

[6] Khakdaman, H.R., ZOUGHI, A., Abedinzadegan, M. and Ghadirian, H.A., 2008. Revamping of gas refineries using amine blends.

[7] Posey M, L. (1997) Thermodynamic Model for Acid Gas Loaded Aqueous Alkanolamine Solutions. PhD Disseration.

[8] Jou FY, Otto FD, Mather AE (1994) Vapor-Liquid-Equilibrium of Carbon-Dioxide in Aqueous Mixtures of Monoethanolamine and Methyldiethanolamine. Ind Eng Chem Res 33:2002-2005.

[9] Polasek, J.C., Iglesias-Silva, G.A., Bullin, J.A., *"Using Mixed Amine Solutions for Gas Sweetening*," Proceedings of the 71st GPA Annual Convention, 1992, PP. 58-69.

[10] Mandal, B.P., Guha, M., Biswas, A.K., Bandyopadhyay, S.S., *"Removal of Carbon Dioxide by Absorption in Mixed Amines: Modelling of absorption in Aqueous MDEA / MEA and AMP/MEA Solutions,*" Chemical Engineering Science, Vol. 56, 2001, PP. 6217-6224.

[11] Schubert, S., Grunewald, M., Agar, D.W., *"Enhancement of Carbon Dioxide Absorption into Aqueous Methyl diethanolamine Using Immobilized Activators*," Chemical Engineering Science, Vol. 56, 2001, PP. 6211–6216.

[12] Weilanda, R.H., Sivasubramanianb, M.S., Dingmanc, J.C., "Effective Amine Technology: Controlling Selectivity, Increasing Slip, and 53rd Reducing Sulfur," the Annual Laurance Reid Gas Conditioning Conference, Norman, OK, February 2003

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