

Application of MDEA in Natural Gas Sweetening on Laboratory Scale – Case Study: Bidboland Gas Refinery

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ABSTRACT

Sour gas is put through separation systems in the first stages of processing after being extracted from wells. Separators are specifically designed to separate out liquids and solids from gases. Quality for standard refined gases usually requires the separation of sulfur and carbon dioxide compounds down to the desired values. The purpose of this study was to examine the applicability of MDEA amine in natural gas sweetening on a laboratory scale in the Bidboland gas refinery. Units 300 and 500 of Bidboland Gas Refinery were employed for measuring the amounts of H₂S, CO₂, and weight percentage for lean and rich amines. The findings of this study indicated that the amount of loading in MDEA, and the amount of H₂S and CO₂, and its sum increases as the density increases. This increase in rich amine indicates a high adsorption percentage.

Keywords

MDEA, Sweetening, Bidboland Gas Refinery

Introduction

In general, gas sweetening, also known as acid gas removal, refers to a set of processes employed to remove acidic gases H₂S and CO₂ from natural gas, which occurs as the result of the direct contact of sour gases with a solution of MEA (monoethanolamide) or DEA (diethanolamine) in the absorber tower [1].

Adsorption is one of the gas sweetening methods in which acid gases and impurities associated with the gas are transferred to the solid surface due to the concentration gradient of the gas flow. At room temperatures, the adsorption occurs owing to the formation of intermolecular forces between the adsorbate and adsorbent molecules, and under these conditions, no new chemical bond is formed. This type of adsorption is called physical adsorption. Adsorbents are natural or synthetic materials that have a microcrystalline structure and produce high contact surfaces per unit of weight. One of the most common commercial adsorbents used in this method is molecular sieves that usually create a contact area of 650 to 800 square meters per gram of adsorbent [2].

The most important feature of molecular sieves is their selectivity for unsaturated and polar compounds. Polar compounds such as water, carbon dioxide, hydrogen sulfide, sulfur dioxide, ammonia, carbonyl sulfide, and mercaptans are readily absorbed by molecular sieves in the presence of non-polar compounds such as natural gas components and hydrogen.

If the adsorption occurs at higher temperatures (i.e., above 200 °C), there would be sufficient activation energy to form or break the chemical bonds, and if this mechanism overcomes the intermolecular gravitational forces, chemical adsorption takes place. In this method, the adsorbent acts as a catalyst for the reaction, and usually, the compounds resulting from this reaction are not as harmful as the initial impurities, and therefore can remain in the gas stream or are simply removed from the gas stream.

The main instruments employed for the gas sweetening process are absorption and disposal towers which are used together with converters and separation devices and pipelines. Sour gas usually contains H₂S and CO₂, which enters the gas sweetening unit through a scrubber. In this part, liquids and solid particles are separated along with the gas. Sour gas enters the adsorption tower from below and gets in contact with the amine solution while moving upwards, which flows in the opposite direction of the gas movement (downwards). The acid-free gas exits the tower as sweet gas and is then sent to the dehumidification unit.

The active amine (i.e., the lean amine) passes through the lower part of the separator tower through the amine-amine heat exchanger, and its temperature decreases. The pressure of the amine solution is increased by a pump so that the

inlet amine pressure is higher than the pressure of the adsorption tower. This pressure drop at the inlet of the adsorption tower causes the amine flow to be biphasic at the inlet. The active amine here passes through a water or air heat exchanger (i.e., cooler), and its temperature decreases, and then enters the upper part of the adsorption tower. In the adsorption tower, the low temperature of the amine improves the adsorption effect. The temperature of the amine here is 120 ° F. The saturated amine from the sour gas (i.e., the rich amine) gas exits the bottom of the adsorption tower and is sent to a flash tank. In the flash tank, the adsorbed hydrocarbons are released as steam. The saturated amine passes through the amine-amine heat exchanger, its temperature reaching about 220 ° F in the process. Consequently, it is inputted to the regenerator tower from the top, where acidic gases are absorbed, hydrocarbons are dissolved and water is reclaimed. The regenerator tower must operate at the highest possible pressure. This is because in this case the boiling temperature increases, resulting in better desorption. Some of the adsorbed acid gases separate from the amine as soon as the saturated amine enters the separator tower and move to the top of the tower. The remaining saturated amines move down the tower in the opposite direction to the vapor produced as the result of boiling. The vapor emitted from the boiling water, which is mainly water vapor, is rising due to the buoyancy and good solubility of the amine in the water, absorbing the amino acid gases and carrying them to the top of the tower. Acid gases and water vapor are separated from the top of the separator tower, consequently entering the heat exchanger. In this heat exchanger, water vapor is liquefied and separated from acid gases in a separating tank and sent back to the top of the tower from under the tank. Acid gases are sent from the top of the regenerator tower to the burner system or its consuming unit. The amine-amine heat exchanger is installed in the system to absorb heat from the active amine and prevent energy loss. In the exchanger, not all of the amine heat can be transferred to the saturated amine. Because in this case, with increasing temperature of saturated amine, a two-phase interface tube may be formed and problems may arise. Accordingly, a water or air heat exchanger is placed thereafter, so that the temperature of the active amine would reach about 100 ° F. If the temperature of the active amine gets more than the range of 100-120 °F, there is the possibility of losing some amine from the top of the adsorption tower and also absorbing less acidic gases by the amine owing to the high temperature.

One of the characteristics of MDEA solvent is its low vapor pressure. This solvent is also heat-resistant and has low reaction heat and fewer corrosion-related problems. Methyl diethanolamine is a 40 to 50% weight solution. The use of the maximum concentration in selective H₂S separation systems in the presence of CO₂ significantly reduces the investment volume and operating costs by reducing the circulating amine. Given the low heat required for the regeneration of the MDEA solvent, the energy consumption for the regeneration of the circulating solution operation is very low as well.

Henry et al. (2016) examined the limiting factors in biofilms. It has been already reported that bio-nitrogen can be removed through pre-denitrification and may be used as a practical way to treat effluents containing carbon dioxide-based amines. To determine the limiting factors for successful up-seeding, the author compared the nitrifying activities of biofilm (MBBR) layered reactors with and without loading organic matter, the results of which indicated that the long-term presence of heterotrophic bacteria is an important factor in inhibiting the effects of nitrification, after which the inhibitory potential of common amines including monoethanolamine (MEA), 2-amine-2-methyl-1-propanol (AMP), diethanolamine (DEA), methyl diethanolamine (MDEA) and piperazine (PIP) were tested on the nitrification and denitrification of separate MBBRs. The results further revealed that at a concentration of EC₅₀ from 9 to 120 mm, nitrification was prevented up to 50%, however, denitrification was stimulated by all the aforementioned materials to a concentration of 100 mm [3].

Alhesinat et al. (2015) examined the behavior of the foam resulting from aqueous methyldiethanolamine (MDEA) in the presence of N,N,N-tris-(hydroxyethyl) (THEED), hydroxyethyl ethylamine (HEED), bis(hydroxyethyl)piperazine. The physical properties of the solutions were also tested to understand the behavior of the foam. The propensity of MDEA aqueous solution foam was reported per unit volume of foam. Foam stability was reported based on the time required for the last bubble to form. The effect of THEED, HEED, BHEP, BICINE, acetic acid, and octanoic acid on the physical properties of the solution such as density, surface stress, and viscosity was also examined. The results of this study showed that adding 5 ppm of THEED increased the foam volume by approximately 17% and the foam stability by 180%. The findings also revealed that adding 5 ppm of HEED increased the foam volume by 20% and the foam stability by 222%. BHEP and BICINE had very little effect on foam volume, yet they had a pronounced effect on foam stability. Octanoic acid had a much greater effect on foam volume and burst time compared to acetic acid. Adding THEED, HEED, BHEP, BICINE, acetic acid, and octanoic acid increased the viscosity of the solution. Moreover, THEED, HEED, BHEP, and BICINE increased the surface tension of the solution but did not affect the density of the solution. Adding 8%-weight octanoic acid reduced the

surface tension by 7.3% and slightly increased the density of the solution. In this study, the effect of different degreasing products on the behavior of foam and physical properties of 50% weight MDEA solution was tested. It was observed that THEED and HEED increased the foam volume while BHEP and BICINE had no significant effect on the foam volume. Consequently, THEED and HEED increased the foam volume to 65 ml and 75 ml respectively, while BHEP and BICINE had a significant effect on foam stability. BHEP and BICINE also increased the burst time by 467% and 344%, respectively. Adding THEED, BHEP increased the foam volume to 63ml and the foam burst time to 80s. It can be concluded that the volume of foam obtained from the mixture of THEED and BHEP was slightly less than that obtained by adding pure THEED while adding the THEED-BHEP mixture increases foam stability compared to pure THEED. Moreover, the THEED-HEED mixture increased the foam volume and resulted in less foam burst time compared to those of both pure THEED and pure HEED. The addition of degreasing products increased the surface tension and viscosity of the solution. The effect of acidic amine degradation products was examined by adding light and heavy organic acids such as acetic acid and octanoic acid to 50%-weight MDEA solutions [4]. Based on the aforementioned discussion, MDEA was examined in the sweetening of natural gas on a laboratory scale in the Bidboland gas refinery.

Methodology

Determining the weight percentage of DEA and MDEA solutions

The purpose of this process is to determine the weight percentage of lean and rich amines. About 50 ml of distilled water is poured into 250 ml flask and 1 ml of DEA or MDEA is added to the flask and then a few drops of mix indicator are added thereto. While stirring, the solution is titrated with a hydrochloric acid solution (0.5N) until the color of the solution changes from blue to pale red. The density of a DEA or MDEA solution is finally measured with a hydrometer.

Calculating the weight percentage of MDEA

$$\text{weight percentage of MDEA (Wt\%)} = \frac{\text{volume of hydrochloric acid solution (0.5N)} \times 5.958}{\text{Density of amine solution}}$$

Measuring H₂S in the lean and rich amine solution

Here, the ultimate goal was to determine the amount of H₂S in lean and rich amine solution in gas treatment.

For lean amine solution, the first 5 ml of 0.02 N iodine solution was added to a flask. Then, about 10 ml of distilled water and then 10 ml of 35% nitric acid was added to the solution. While stirring, 10 ml of lean amine solution and a few drops of starch is mixed with the solution. The solution was then titrated with 0.02 N sodium thiosulfate until the blue color disappeared.

Hence, for the lean amine solution:

$$\text{Consumption difference of thiosulfate with iodine} \times 0.2034 = \text{amount of } H_2S(VOL/VOL) \quad (2)$$

Conversely, for the rich amine solution, the first 10 ml of 0.01 N iodine solution was added to a flask. Then, about 10 ml of distilled water and then 5 ml of 35% nitric acid was added to the solution. While stirring, 5 ml of rich amine solution and a few drops of starch is mixed with the solution. The solution was then titrated with 0.01 N sodium thiosulfate until the blue color disappeared.

Hence, for the rich amine solution:

$$\text{Consumption difference of thiosulfate with iodine} \times 0.2034 = \text{amount of } H_2S(VOL/VOL) \quad (3)$$

Measuring the amount of CO₂ in the lean and rich amine solution

Here, the ultimate goal was to determine the amount of CO₂ in lean and rich amine solution in gas treatment.

First, the measuring device is checked for leaking valves, then the valve of the device is set in the vent position, then 1 ml of the amine solution is poured into the two-way flask of the device, and a burette containing 10% sulfuric acid is installed firmly on it. The device valve is then removed from the vent position and placed in the direction of the burette. Then 3 ml of 10% sulfuric acid is transferred to the flask through the burette. The volume of gases produced is measured after shaking the flask and leveling the gas solution in the funnel and the calibrated part. This volume includes the volume of added acid (3 ml) and the volume CO_2 and H_2S released from the amine solution, and by reducing the volume of acid and H_2S , which were already measured by their relevant test, the volume CO_2 released is determined under laboratory conditions. The volume of CO_2 is then calculated in standard conditions using Equation 4.

$$\begin{aligned} &\text{the volume of } \text{CO}_2 \text{ in 1 ml amine is standard conditions (V)} \\ &= \frac{(730 - w) \times 0.359v}{273 + t^\circ\text{C}} \text{ mmHg} \end{aligned} \quad (4)$$

w: water vapor pressure in mmHg
v: volume of CO_2 in laboratory conditions
V: volume of CO_2 in standard conditions
t: the temperature of the laboratory

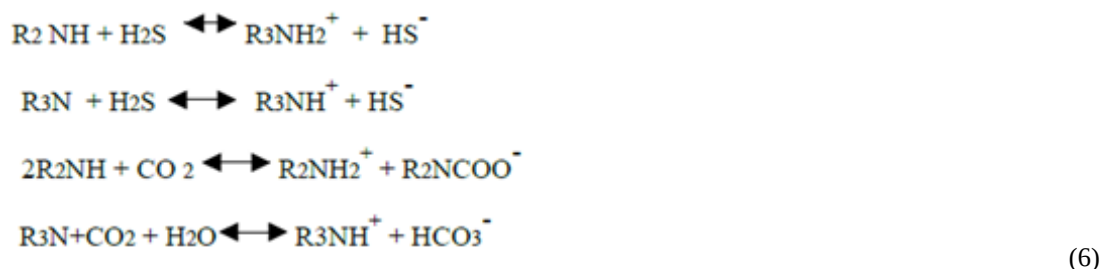
Equation 5 is then used to calculate the loading of acid gases in lean and rich MDEA amine samples:

$$\text{Loading} = \frac{\text{CO}_2 + \text{H}_2\text{S} (\text{vol/vol}) \times 0.487}{\% \text{wt} \times \text{SPG}} \quad (5)$$

Ultimately, the natural gas analysis was performed using gas chromatograph (GC) to determine the molar percentage of combinations of natural gases inputted to the refinery and sweetened gas of refining units.

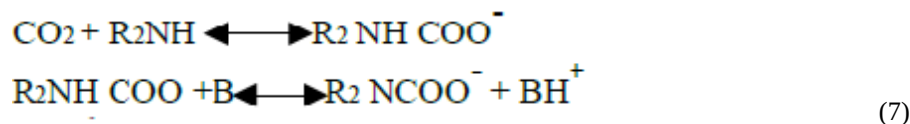
Selective adsorption of amines

The reaction between amines and H_2S equilibrates rapidly, while the reaction with CO_2 has its complexity depending on the type of amine, and is, in fact, the sum of various reactions with different mechanisms.



An amine molecule has at least one hydroxyl group and one amine group. The hydroxyl group reduces vapor pressure and helps increase solubility in water, while the amine group produces alkaline properties required for excluding acidic gases in aqueous solutions. In the reaction of CO_2 with the first type of amine, the CO_2 adsorption capacity is limited to approximately 0.5 mol of CO_2 per mol of amine, as the carbamate resulting from the reaction with the first type of amine is very stable and its hydrolysis rate is low. Nevertheless, employing the second type of amine does not lead to the formation of carbamate.

The overall efficacy of amines in the adsorption of both acidic gases depends on their alkalinity and the amount of alkalinity of the amines. CO_2 can combine directly with the first and second-type amines to stabilize carbamate production. The second type of amine does not produce stable carbamate when combined with CO_2 . When an amine reacts with CO_2 , a molecule with an equal number of positively- and negatively-charged functional groups called Zwitterion is formed, which can react with any alkaline substance and lose a proton.



The formation or consumption of Zwitterion is delayed or accelerated depending on the number of reaction constants that differ from one amine to another, consequently inhibiting or enhancing the adsorption of CO₂. The CO₂ reaction with the components in the amine, which sometimes include catalysts to control the direction of the reaction, is interpreted under the following two mechanisms:

- Homogeneous catalytic mechanism
- SHUTTEL mechanism

Results

Amines Selection Criteria

MDEA is a tertiary amine with weak alkalinity properties and CO₂ adsorption capacity but reacts well with H₂S, thus having the advantage of selective H₂S adsorption.

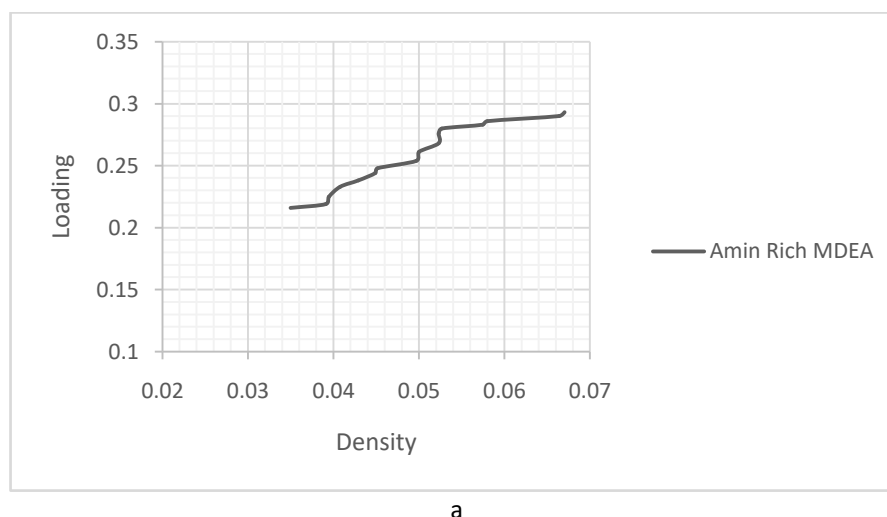
Table 1 reveals the selected indicators and criteria for MDEA from the operational point of view and the type of inlet gas of the gas sweetening unit.

Table 1: Amine selection indicators

Selection criteria	Indicator for reaction with CO ₂ and H ₂ S	Type of Amine	Amine Solvent
Alkalinity much less than MEA, adsorption capacity less than MEA, the weight percentage of 30-50%, low vapor pressure, low corrosion, selective adsorption of H ₂ S, low reaction heat	-	Type II	MDEA

Results of application and examination of amine behavior

To make a correct comparison, the values pertaining to H₂S and CO₂ are considered dimensionless. Therefore, the amount of H₂S and CO₂, as well as their sum (H₂S + CO₂), increases as the density increases, which is a desirable feature. This is a positive factor in the process as shown in figure 1(a), which is related to the adsorption process, but in diagram 1(b), which is related to the regeneration process, the increase in H₂S and CO₂ and the total (H₂S + CO₂) indicates a negative factor in the process, indicating the non-optimality of the regeneration process.



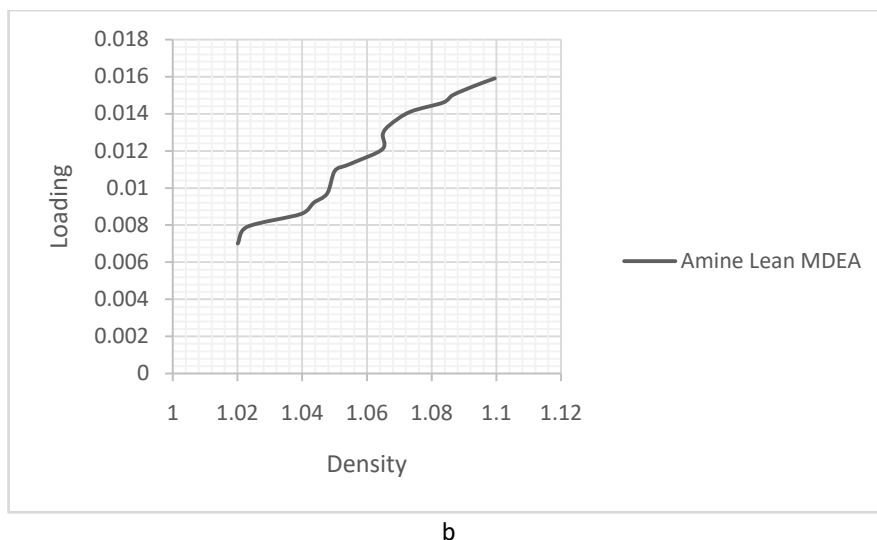


Figure 1: Changes in loading based on changes of density of (a) rich MDEA and (b) lean MDEA

The relationship between density and loading is established as follow:

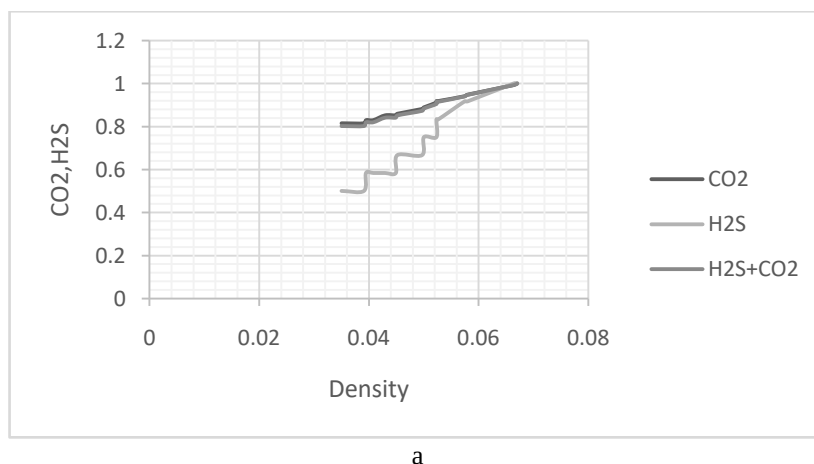
$$Loading = \frac{(CO_2 + H_2S) \times 0.487}{\%wt \times SPG}$$

Figure 1(a) shows the increase in loading as a result of the increase in density of the rich MDEA in the 500 unit of Bidboland gas refinery, clearly indicating that an increase in the density leads to the increase in loading also increases based on the increase in lodging density. The fluctuations of the diagram are the result of laboratory errors during different days

Increased loading as a result of increased density indicates the desirable feature of high adsorption.

In Figure 2(b), which illustrates the results for the lean MDEA, it can be seen that with increasing density, loading increases as well. This is an undesirable feature in the regeneration process, indicating that the process is not performed optimally. Since the regeneration process requires high temperature and low pressure, the temperature of the regeneration tower should be increased. Besides, by increasing the amount of steam to the reboiler and also improving the circulation, the amount of amine in the adsorption tower should be increased to lower the loading rate.

It is noteworthy that MDEA, due to the selective absorption of H_2S in the presence of CO_2 , absorbs a higher amount of H_2S in the 500 unit than the 300unit. This can be seen in the results of the CG device, which is presented in chapter 6.



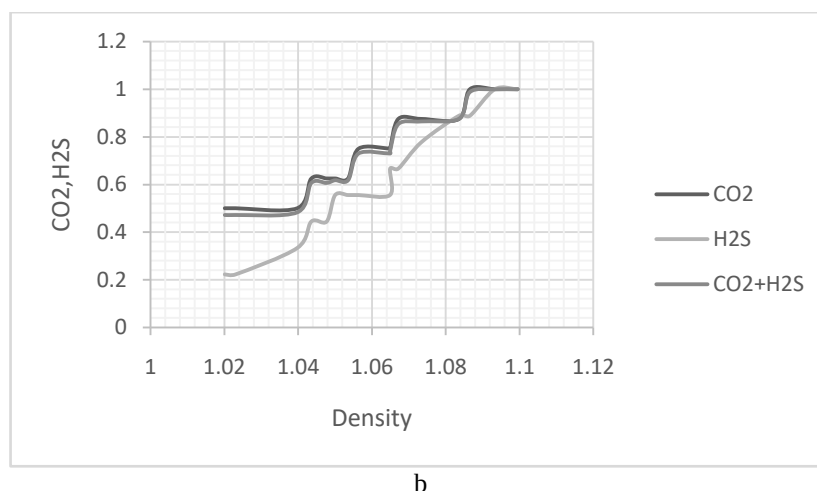


Figure 2: Changes in H₂S, CO₂ and their sum based on changes of density of (a) rich MDEA and (b) lean MDEA

In Figure 2(a), changes in levels of CO₂, H₂S, and their total (that is, H₂S + CO₂) are investigated in terms of density of the rich MDEA, clearly indicating that the absorption is performed optimally.

Figure 2(b) depicts the findings for lean MDEA, according to which the level of H₂S and CO₂ and (H₂S + CO₂) increases as the density increases, which is a negative factor in the regeneration process and indicates, hence indicating that the regeneration process has not been performed desirably. As such, improvements must be implemented to the process by raising the temperature in the regeneration tower and increasing the amine circulation in the adsorption tower.

Table 2: MDEA Laboratory Data of Bidboland Refinery

Lean-Loading	density	H ₂ S	CO ₂	Rich-Loading	density	H ₂ S	CO ₂
0.007	1.02	0.02	0.4	0.216	0.034	0.3	11
0.0079	1.02	0.02	0.4	0.219	0.039	0.3	11
0.0086	1.03	0.03	0.4	0.225	0.039	0.35	11.2
0.0092	1.04	0.04	0.5	0.233	0.040	0.35	11.2
0.0097	1.04	0.04	0.5	0.238	0.042	0.35	11.5
0.0109	1.05	0.05	0.5	0.244	0.044	0.35	11.5
0.0112	1.05	0.05	0.5	0.248	0.045	0.4	11.6
0.0114	1.05	0.05	0.6	0.254	0.049	0.4	11.9
0.0121	1.06	0.05	0.6	0.261	0.050	0.45	12
0.0129	1.06	0.06	0.6	0.268	0.052	0.45	12.3
0.0134	1.06	0.06	0.7	0.276	0.052	0.5	12.4
0.0141	1.07	0.07	0.7	0.28	0.052	0.5	12.4
0.0146	1.08	0.08	0.7	0.283	0.057	0.55	12.7
0.015	1.08	0.08	0.8	0.286	0.058	0.55	12.8
0.0155	1.09	0.09	0.8	0.29	0.066	0.6	13.4
0.0159	1.09	0.09	0.8	0.293	0.067	0.6	13.5

Conclusion

The application of alkanolamines, which have high alkalinity, and in particular DEA, in the gas sweetening units of the country's refineries, with the ultimate aim of removing acidic pollutants (that is, H_2S and CO_2) from the gas, reduce these pollutants from the gas to the desired PPM level. The acceptable and desirable amount of these pollutants after leaving the gas sweetening unit is 5-20PPM for H_2S and 1 to 3% by volume for CO_2 , that is, that the exclusion of CO_2 in the sweetening process is performed regardless of the desired PPM levels, and consequently the maximum adsorption of CO_2 by amine solvents is highly desirable, hence leading to an increase in the consumption of amine solvents in this process.

Therefore, given the recent breakthroughs in the oil and gas industry, which have been proposed to minimize the consumption of materials and energy, reduce costs, increasing production capacity, and improving operations while maintaining the basics of the process, in case it would possible to replace amine solvents with amine mixtures that have the advantage of selective adsorption of acidic pollutants in the sweetening process, these gas pollutants (that is, H_2S , CO_2) can be reduced to necessary and even desirable levels. . This is possible by mixing an amine solvent (having one or two alcohol bases and high alkalinity) with an amine solvent (having three alcohol bases and selective H_2S adsorption properties). The selective adsorption property of this type of solvent amine, which has three alcoholic bases, is owing to the molecular structure, nature, and mechanism of the reactions performed and the type of unstable carbamate formed. There are various operational advantages in using these types of amine mixtures, namely, less corrosion, lower dissolution heat, lower vapor pressure, lower levels of exhaust hydrocarbons with the mixture after adsorption and less operating load on sulfurization unit, lower energy consumption in amine regeneration tower, lower overall costs and ultimately increased operating capacity of the gas sweetening unit. In this study, various types of amine solvents were examined in terms of alkalinity and selective adsorption properties, solvent selection measures and pollutant removal mechanisms, amine mixture behaviors, and a suitable mixture of amine solvents for removing pollutants (i.e., H_2S , CO_2) from gas. The results obtained from replacing this mixture in the gas sweetening unit of Bidboland refinery indicate the increased operational capacity of the unit.

One of the factors that were examined in this study was the type of amine used in different units. In this study, the amines used in 300 and 500 units of Bidboland Gas Refinery were examined.

In this laboratory process, DEA and MDEA were the amines used in units 300 and 500, respectively. The percentage of the weight of the amine, the amount of H_2S and CO amine, and the density of the amine for lean and rich amines were calculated on different days.

For the MDEA solvent, loading was calculated using the following equation:

$$\text{Loading} = \frac{(CO_2 + H_2S) \times 0.487}{wt\% \times SPG}$$

By considering fixed values for weight percentage in different experiments for each amine, a loading diagram was drawn in terms of density and the amount of H_2S and CO_2 and their sum ($H_2S + CO_2$) in terms of density for rich and lean amines of 300 and 500 units.

Based on which the following results were obtained:

Regarding the MDEA amine, which is a more concentrated amine than DEA, the diagrams from chapter 5 illustrate that as the density increases, the amount of loading also increases, as a result of which the amount of H_2S and CO_2 and its total also increases, which, for rich amines, is translated to more efficient adsorption.

In the lean MDEA, increasing density results in higher loading, as well as higher amounts of H_2S and CO_2 , hence leading to an adverse effect on the regeneration operation.

Since MDEA amine has a selective absorption of H_2S in the presence of CO_2 , it absorbs more H_2S ; therefore, it is safe to say that the 300 unit absorbs more CO_2 than 500 unit while the 500 unit absorbs more H_2S , which is also implied in the results obtained from the application of GC device on Bidboland gas refinery.

Gas analysis of 300 and 500 units with GC device shows that H_2S adsorption in the 500 unit is performed using MDEA.

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