

Research article

Comparison of amine solutions performance for gas sweetening

Vahid Abkhiz* and Isa Heydari

Gas Engineering Department, Petroleum University of Technology, Ahwaz, Iran

Received 2 August 2013; Revised 17 January 2014; Accepted 21 January 2014

ABSTRACT: Using different kinds of amines, in Fajr-e-Jam gas refinery, including mixed or activated amines, have provided the chance for better analysis of different kinds of amines performance. In the current work, the most important parameters in gas sweetening refineries such as amine circulation rate, steam consumption, CO₂ and mercaptan removal were investigated for sweetening trains utilizing diethanolamine (DEA), methyldiethanolamine (MDEA), DEA/MDEA and activated methyldiethanolamine (aMDEA). In the case of steam consumption and circulation rates, MDEA and aMDEA, show the less required rates to meet lean amine loadings. For CO₂ removal aMDEA has the best efficiency. In the case of mercaptan removal, DEA shows the best absorption rate compared with other three amines. © 2014 Curtin University of Technology and John Wiley & Sons, Ltd.

KEYWORDS: activated amines; circulation rate; mercaptan removal; mixed amines; steam consumption

INTRODUCTION

Chemical absorption processes with aqueous alkanolamine solutions are used for treating gas streams containing hydrogen sulfide and carbon dioxide. Depending on the composition and operating conditions of the feed gas, different amines can be selected to meet the product gas specification. Amines are categorized as being primary, secondary and tertiary depending on the degree of substitution of the central nitrogen by organic groups. Primary amines react directly with H₂S, CO₂ and carbonyl sulfide (COS). Examples of primary amines include monoethanolamine (MEA) and the proprietary diglycolamine agent. Secondary amines react directly with H₂S, CO₂ and COS. The most common secondary amine is diethanolamine (DEA). Tertiary amines such as methyldiethanolamine (MDEA) react directly with H₂S and indirectly with CO₂ and COS^[1]. In the past few years, MDEA-based amines including formulated amines (such as activated methyldiethanolamine (aMDEA) and mixed amine solvents such as (DEA/MDEA) for the removal of acid gases have received increased attention. The main reason behind using MDEA-based amines is to benefit the sweetening process from the high reactivity of the primary and secondary amines and the low energy requirement of tertiary amines. It can also decrease the effects of the relatively higher vapor pressure and

consecutively amine loss, and corrosion rates of the primary and secondary amines as well as the relatively higher selectivity of tertiary amines toward H₂S.^[2] aMDEA, a kind of activated amine, is a mixture of MDEA and piperazine. In this tertiary amine, piperazine activates MDEA, so rate of CO₂ absorption increases considerably, which will be discussed later.

In design of the amine sweetening process, the primary concern is that the sweetened gas meets the required purity specifications with respect to H₂S and CO₂. The secondary objective is to select the amine, which optimizes equipment size and minimizes plant operating costs. Between 50 and 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 sweetening unit. Moreover, the flow scheme for amine sweetening plants has an important effect on operating costs.^[3]

In Fajr-e-Jam gas refinery, using different kinds of amines including DEA, MDEA, DEA/MDEA and aMDEA in sweetening trains has provided the

*Correspondence to: Vahid Abkhiz, Gas Engineering Department, Petroleum University of Technology, Ahwaz, Iran. E-mail: aaabkhizz@gmail.com

opportunity for better analysis of amines performance in gas sweetening units. In this paper, the most important factors in gas conditioning units, as amine circulation rate, CO₂ and mercaptan removal and steam consumption are discussed. All the data presented in current work were gathered in a period of 1 month, and each is a mean average of all the daily recorded data in the control room and log sheets.

PROCESS CHEMISTRY

Fajr-e-Jam gas refinery, located in the south of Iran, has been in operation since 1989 and purifies the gas from Nar and Kangan gas reservoirs. In this refinery, there are eight parallel sweetening trains, which due to the availability of amine solutions, use different kinds of amines. The inlet gas to the refinery, which is a mixture of the gas from two mentioned reservoirs is distributed between eight sweetening trains. The basic flow scheme for an amine sweetening unit is shown in Fig. 1. The inlet feed gas and amine solutions specifications are presented in Tables 1 and 2, respectively. The pressure of absorption column in all sweetening trains is kept constant at 78.5 barg. In the case of aMDEA solution, 5 wt% of Piperazine and 40 wt% of MDEA, and in the case of DEA/MDEA solution 20 wt% of DEA and 25 wt% of MDEA are used. The type of trays in both absorption and stripping columns are valve tray type. Other specifications of these columns are as follows:

Absorption column: diameter: 3.24 m, length: 21.6 m, tray spacing: 61 cm

Stripping column: diameter: 3.24 m, length: 21.6 m, tray spacing: 61 cm

RESULTS AND DISCUSSION

Rich and lean amine loading

The average rich and lean amine loadings in sweetening trains are presented in Table 3. These loadings are design specifications that control main parameters such as amine circulation rates, steam consumption and reboiler duty and are taken as independent parameters in the refinery.

Table 1. The inlet feed gas to absorption columns composition.

Component	Mole%
C ₁	86.13
C ₂	3.88
C ₃	1.25
i-C ₄	0.27
n-C ₄	0.4
i-C ₅	0.2
n-C ₅	0.14
C ₆	0.19
C ₇ ⁺	0.27
N ₂	5.42
CO ₂	1.78
H ₂ S (mg/sm ³)	505
RSH (mg/sm ³)	42

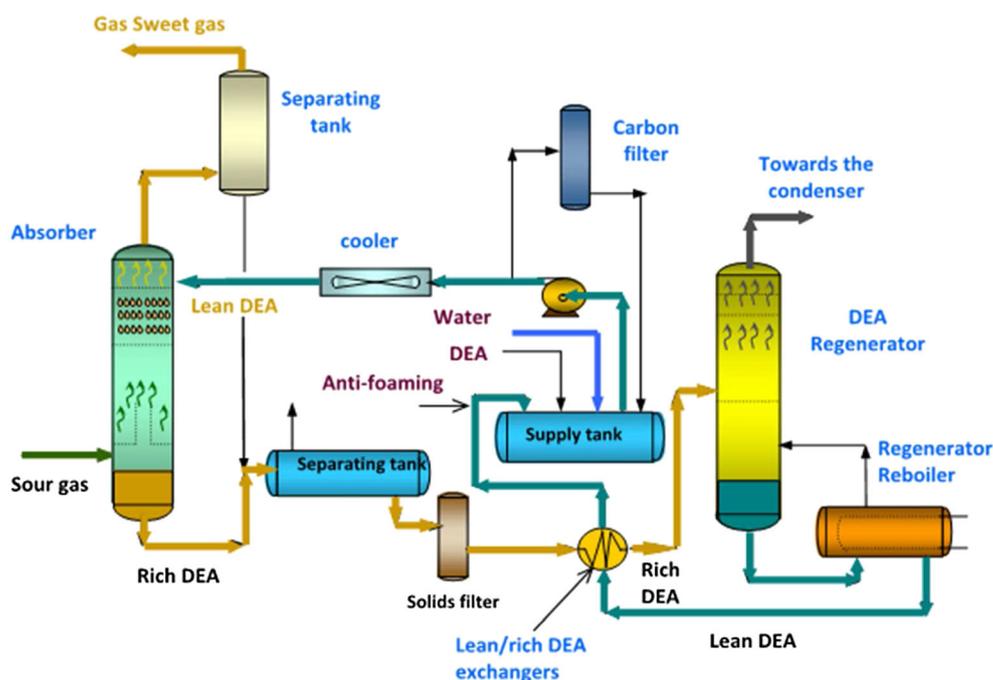


Figure 1. Basic flow scheme for an amine sweetening unit. DEA, diethanolamine. This figure is available in colour online at www.apjChemEng.com.

Table 2. The inlet feed gas and amine solutions specifications.

Parameter	DEA	MDEA	aMDEA	DEA/MDEA
Inlet gas temperature to absorption column (°C)	47	47	47	47
Inlet gas flow rate to train (MMSCMD)	13.45	12.37	12.78	12.73
Inlet amine solution temperature to absorption column (°C)	55	55	55	55
Amine solution concentration (Wt%)	30	45	5/40	20/25

DEA, diethanolamine; MDEA, methyldiethanolamine; aMDEA, activated methyldiethanolamine.

Table 3. The average rich and lean amine loadings in Fajr-e-Jam gas refinery.

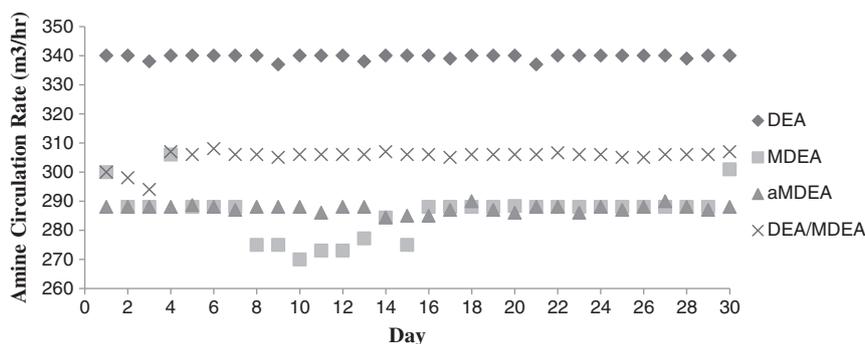
Loadings	DEA	MDEA	aMDEA	DEA/MDEA
Lean amine loading	0.03	0.022	0.03	0.024
Rich amine loading	0.32	0.27	0.25	0.27

DEA, diethanolamine; MDEA, methyldiethanolamine; aMDEA, activated methyldiethanolamine.

Amine circulation rate

Amine circulation rate is one of the most important parameters in the gas sweetening units, which depends mostly on gas flow rate, amine solution concentration and rich amine loading. Amine circulation rate data for sweetening trains are presented in Fig. 2. Considering feed gas flow rate to absorption column and rich amine loadings presented in Table 3, the amine circulation rate for 1 MMSCMD of gas will be as Table 4.

Diethanolamine has higher acid gas removal capacity than MDEA; but as MDEA is less corrosive, it can be used in higher concentration than that of DEA.^[4] This allows for lower circulation rates of MDEA compared with DEA. Another reason for MDEA's less circulation rate and make-up is attributed to the formation of carbamate ion. It has been proven that primary and secondary amines react with CO₂ to form carbamate ion, which in appropriate thermodynamic condition reacts with amine repeatedly.^[5] The carbamate ion is the main cause of formation of basic degradation products. The presence of amine carbamates enhances the corrosivity of primary and secondary amines.^[5] The formation of abovementioned amine polymers reduces the active amine concentration and consequently, increases amine circulation rates and so makeups. As tertiary amines do not form carbamate ion in reaction with CO₂, avoid this chain reactions. So it results in less MDEA degradation and circulation rates and makeups. However, in the case of aMDEA, as Table 4 shows, it has even less circulation rate compared with MDEA, which can be attributed to its increased activation due to piperizen; so aMDEA has the least makeup.

**Figure 2.** Amine circulation rates in four sweetening trains. DEA, diethanolamine; MDEA, methyldiethanolamine; aMDEA, activated methyldiethanolamine.**Table 4. Amine circulation rate for 1 MMSCMD of gas.**

Parameter	DEA	MDEA	aMDEA	DEA/MDEA
Amine circulation rate (m ³ /h)	25.2	23.1	22.5	23.5

DEA, diethanolamine; MDEA, methyldiethanolamine; aMDEA, activated methyldiethanolamine.

Steam consumption

In Fajr-e-Jam gas refinery, each stripping column has two identical reboilers. Figure 3 shows steam consumption rates for different amines. The rate of steam consumption is in direct relation with amine circulation rate. Using Figs 2 and 3 and lean amine loadings (Table 3), the rate of steam consumption and consecutively, reboiler duty for stripping column for 1 m³ amine are presented in Table 5.

The heat of reaction of amines with acid gases has a great effect on heat loading of reboiler. As the heat of reaction decreases, heat loading and steam consumption rates decrease. Heat of reaction of amines with acid gases is presented in Table 6.

Heat of reaction of acid gases with tertiary amines is lower than with primary and secondary amines. The main problem in designing the stripper is estimating the heat duty of the reboiler. This heat load includes the following:

1. The sensible heat required to raise the temperature of the feed amine solution to that of the regeneration solution leaving the reboiler. As declared before, the use of amines with higher concentrations reduces amine circulation rates, which in turn decreases this

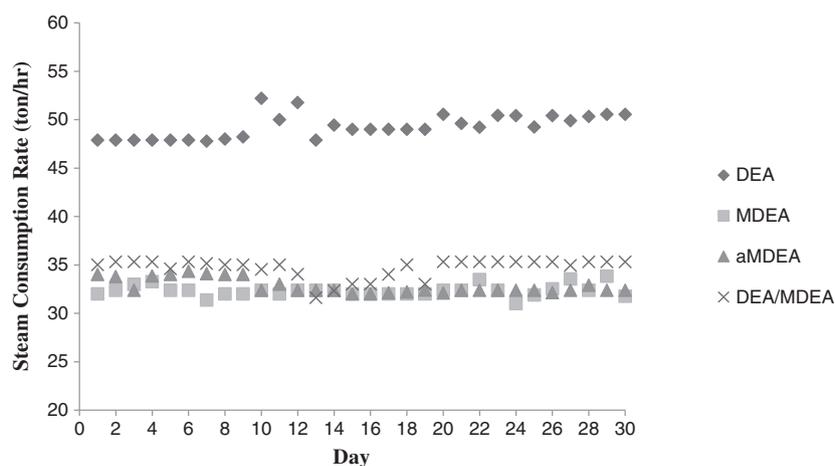


Figure 3. Steam consumption rates for amine solutions. DEA, diethanolamine; MDEA, methyldiethanolamine; aMDEA, activated methyldiethanolamine.

Table 5. Rate of steam consumption and reboiler duty for 1 m³/h amine solution.

Parameter	DEA	MDEA	aMDEA	DEA/MDEA
Rate of steam consumption (ton/h)	0.145	0.113	0.1139	0.1135
Reboiler duty (KJ/h)	309700	242200	242200	242200

DEA, diethanolamine; MDEA, methyldiethanolamine; aMDEA, activated methyldiethanolamine.

Table 6. Heat of reaction of amines with acid gases.

Heat of reaction (BTU/h)	DEA	MDEA
H ₂ S	550	525
CO ₂	650	575

DEA, diethanolamine; MDEA, methyldiethanolamine.

heat load. Besides, the heat capacity of tertiary amines is lower than primary and secondary amines, so the sensible heat for tertiary amines is lower for these amines.

2. The heat of reaction required for dissolution of the acid gases from the amine. So, tertiary amines, which have lower heat of reaction with acid gases, need less heat for this dissolution compared with primary and secondary amines.
3. The stripper column condenser duty, which is essentially the heat of vaporization of the water leaving the stripper section of the column that is condensed and returned to the stripper as reflux.

So stripper total heat load in trains, which utilize tertiary amine is lower than primary and secondary amines, which the results obtained in the current work justifies.

CO₂ absorption

Figures 4 and 5 show CO₂ concentration in sweetened outlet gas for different kinds of amines. As is shown, CO₂ concentration for DEA, aMDEA and DEA/MDEA is 10 to 20 ppm, whereas for MDEA is 1200 to 1800 ppm.

The results presented in these figures can again be attributed to the formation of carbamate ions. Pure aqueous MDEA (a tertiary amine) does not react with CO₂ directly because it lacks the N–H bond required to form the carbamate ion with CO₂. In these amines, at first, CO₂ reacts with water to form carbonate or bicarbonate, which is very slow and controls the CO₂ absorption in amine solutions. CO₂ absorption can be increased significantly just by the addition of DEA or

appropriate additive such as piperazine, to form activated amines known as aMDEA. In this case, the free CO₂ diffuses away from the interface toward the bulk liquid. Along the way, it meets large amounts of MDEA and smaller amounts of the additive. Being unable to react with the MDEA, and finding only relatively small amounts of hydroxyl ion (with which it can react), most of the CO₂ reacts with the additive. The reaction product (the carbamate of the reactive amine) then continues to diffuse into the bulk liquid and eventually, it dissociates, converting its CO₂ into carbonate. The liberated H⁺ ion reacts with the more plentiful MDEA, and the released additive is free to return to the interfacial region to react with more, freshly arriving CO₂.^[6–9] As it is clear from Table 7 which represents rate of reaction constant between amines/

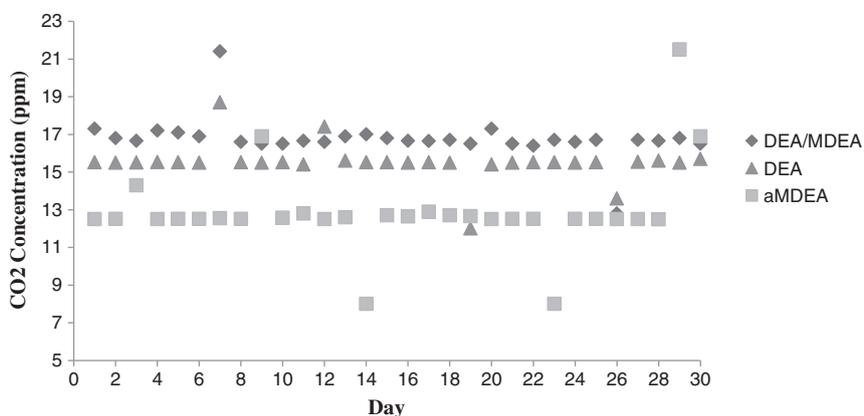


Figure 4. CO₂ concentration in sweetened outlet gas for diethanolamine (DEA), activated methyldiethanolamine (aMDEA) and DEA/methyldiethanolamine (MDEA) solutions.

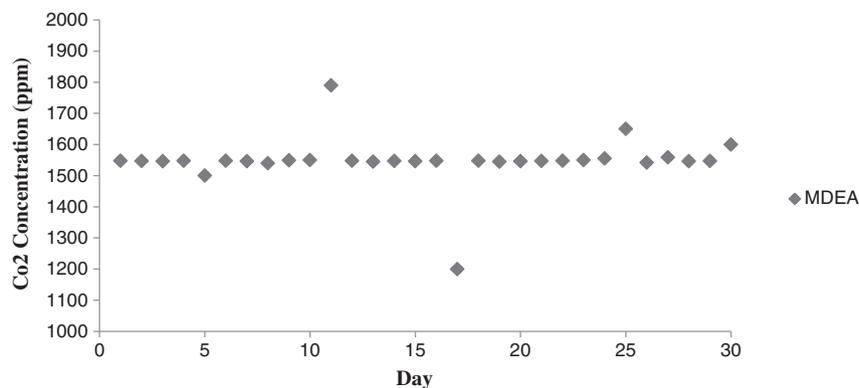


Figure 5. CO₂ concentrations in sweetened outlet gas for methyldiethanolamine (MDEA) solution.

Table 7. Rate of reaction constant between amines/piperazine with CO₂.

Amine/piperazine	Rate of reaction constant between amines/piperazine with CO ₂ (lit/mol.s)
Diethanolamine	1300
Methyldiethanolamine	4
Piperazine	59 000

Piperazine and CO₂,^[10] aMDEA has the most absorption capacity for CO₂ due to Piperazine great reactivity with CO₂ which is in agreement with industrial data.

Mercaptane absorption

Mercaptan is an organic sulfur compound composed of an alkyl or aryl group and a thiol group. General formula of mercaptans is R-SH where R is an alkyl or aryl group. Table 8 shows mercaptan concentrations in inlet gas streams to absorption columns of sweetening trains.

Table 8. Mercaptan concentration in inlet gas streams to absorption columns.

Component	mg/sm ³	%
Methanethiol	20.5	48.8
Ethanethiol	10.7	25.5
2-propanethiol	2.2	5.2
1-propanethiol	6.3	15
1-me-1prop thiol	1.2	2.8
1-butyl thiol	1.1	2.7

According to this table, about 50% of this content is methyl mercaptan, which in comparison with other mercaptans has smaller molecular weight and more solubility in amine solutions. Figures 6 and 7 show mercaptan concentration in inlet and outlet gas streams to four sweetening trains, respectively. Using these figures, the average mercaptan removal efficiency by four amine solutions used in Fajr-e-Jam gas refinery can be calculated. Table 9 shows the result.

From this table, it is obvious that DEA has the greatest efficiency for mercaptan removal. Mercaptans do not react with amines but are removed primarily by physical absorption in the solvent. Because all amine solutions are comprised mostly of water on a mole % basis and mercaptan solubility in water is very low, amine solutions are generally not an efficient solvent for mercaptan removal. Mercaptans are much weaker acids than H₂S and CO₂, and short chain mercaptans such as methyl and ethyl mercaptans form weakly bonded mercaptide salts in solution. Therefore, more basic amines tend to give better absorption characteristics for methyl and ethyl mercaptan than less basic amines such as MDEA and aMDEA. This verifies DEA greater mercaptan efficiency compared with other amine solutions used in this refinery. On the other hand, long chain mercaptans are expected to behave much more like hydrocarbons and may be better removed by amines or solvents that exhibit higher hydrocarbon solubility. It should be noted that presence of H₂S and CO₂ interferes with the absorption of mercaptan in amines. Acid gases reduce the alkalinity of the amine solution, which reduces mercaptan absorption. The data of Jou, *et al.* show that the solubility of methyl and ethyl mercaptan in MDEA and DEA is reduced by twofold to threefold when H₂S and/or CO₂ are present.^[11–13]

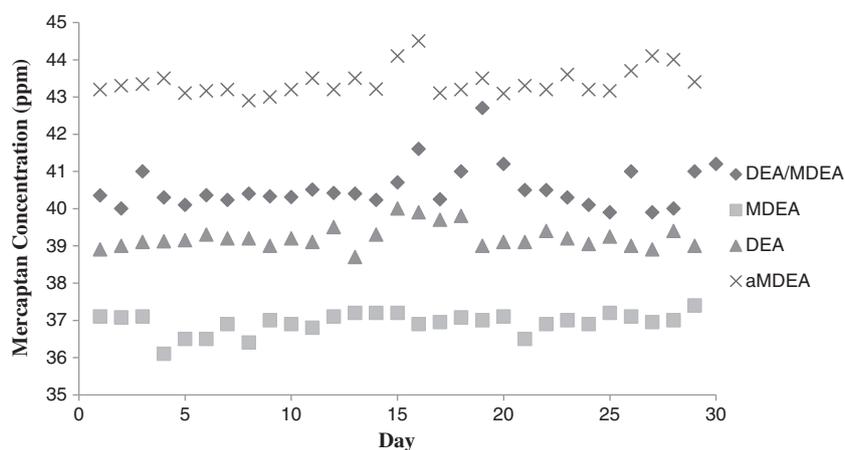


Figure 6. Mercaptan concentration in inlet gas streams to four sweetening trains. DEA, diethanolamine; MDEA, methyldiethanolamine; aMDEA, activated methyldiethanolamine.

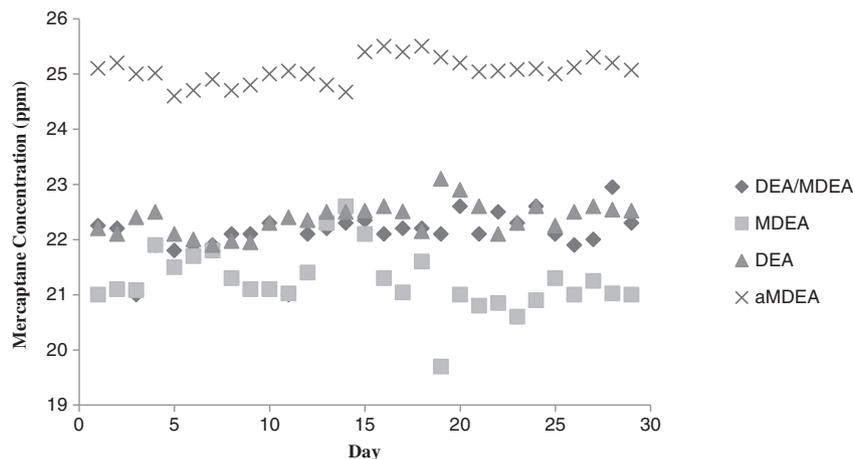


Figure 7. Mercaptan concentration in outlet gas streams from four sweetening trains. DEA, diethanolamine; MDEA, methyldiethanolamine; aMDEA, activated methyldiethanolamine.

Table 9. Average mercaptan removal efficiency.

Parameter	DEA	MDEA	aMDEA	DEA/MDEA
Average mercaptan removal efficiency (%)	48.045	42.87	42.71	42.41

DEA, diethanolamine; MDEA, methyldiethanolamine; aMDEA, activated methyldiethanolamine.

CONCLUSIONS

In the current work, we investigated the most important parameters in gas sweetening refineries including amine circulation rate, CO₂ and mercaptan removal, and steam consumption using operational data from sweetening trains in Fajr-e-Jam gas refinery, which utilizes DEA, MDEA, DEA/MDEA and aMDEA. In the case of steam consumption and circulation rates, MDEA and aMDEA show the less required rates to meet lean amine loadings. For CO₂ removal, aMDEA shows the best result. For mercaptan removal, DEA shows the best efficiency compared with other three amines.

REFERENCES

- [1] S. Mokhatab, W.A. Poe, J.G. Speight. Handbook of Natural Gas Transmission and Processing, Gulf Professional Pub., c2006, Elsevier Inc, Burlington, MA, 2006.
- [2] A. Fouad, S. Abdallah. *J. Nat. Gas Sci. Eng.*, **2013**; *11*, 12–17.
- [3] J.C. Polasek, J.A. Bullin, S.T. Donnelly. *Eng. Prog.*, **March 1983**; 63–69.
- [4] M.S. Dupart, T.R. Bacon, D.J. Edwards. Understanding corrosion in alkanolamine gas treating plants; hydrocarbon processing, **April and May 1993**.
- [5] P.J.G. Huttenhuis, N.J. Agraval, E. Solbraa, G.F. Versteeg. *Fluid Phase Equilibria*, **2008**; *264*, 99–112.
- [6] P.M. Blauwhoff, G.F. Versteeg, W.M. van Swaaij. *Chem. Eng. Sci.*, **1984**; *39*(2), 207–225.
- [7] G.F. Versteeg, W.P.M. Van Swaaij. *Chem. Eng. Sci.*, **1988**; *43*(3), 587–591.
- [8] R.J. Littel, G.F. Versteeg, W.P.M. Van Swaaij. *Chem. Eng. Sci.*, **1992**; *47*(8), 2027–2035.
- [9] C.-H. Liao, M.-H. Li. *Chem. Eng. Sci.*, **2002**; *57*(21), 4569–4582.
- [10] Piperazine – why it's used and how it works, The Contactor, Vol. 2, No. 4, **2008**.
- [11] F.Y. Jou, H.J. Ng, A.E. Mather. *Fluid Phase Equilibria*, **1999**; *158/160*, 933–938.
- [12] F.Y. Jou, A.E. Mather. *J. Chem. Eng. Data*, **1999**; *44*, 833–835.
- [13] F.Y. Jou, A.E. Mather. *J. Chem. Eng. Data*, **2000**; *45*, 1096–1099.