## AHP-Based Amine Selection in Sour Gas Treating Process: Simulation and Optimization

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**ABSTRACT:** The acid gases  $(H_2S \text{ and } CO_2)$  are unpleasant groups in the natural gas (sour gas) stream, which must be reduced. The presence of acid gases will have operational problems such as corrosion in the processing facilities and, environmental issues like air pollution and greenhouse effects. Therefore, the reduction of acid gases from sour gas is essential via a reliable process. The most common method for natural gas sweetening is the utilization of the amine solution. In the current work, the analytic hierarchy process (AHP) is employed to consider the advantages and disadvantages of each amine solution. The four process criteria and seven alternatives were intended based on the AHP procedure. Then, the natural gas sweetening process was simulated, and finally, operation conditions were optimized. MDEA as an alternative and cost as process criteria were introduced with 21% and 53% as the highest priority, respectively. The reduction of acid gas contents and reboiler duty were chosen as objective functions. The optimization results indicated that the best feed gas temperature and MDEA concentration are 30 °C and 39 wt.%, respectively. The amount of  $H_2S$  and  $CO_2$  as one of the optimization objectives of gas sweetening achieved 2.4 and 88 ppm in the optimal condition. Accordingly, the MDEA solution consumption was reduced by 5%, and reboiler duty decreased by approximately 0.04% compared to the conventional process.

# **KEYWORDS:** Analytic hierarchy process; Simulation case study; Amine scrubbing; Natural gas, MDEA solution.

#### INTRODUCTION

Natural gas is a non-renewable resource that is considered a primary energy source for industrial and commercial utilization [1, 2]. The raw natural gas (sour gas) contains different compounds, including combustible hydrocarbons, carbon dioxide, mercury vapors, and various sulfur compounds (hydrogen sulfide and light mercaptans) [3, 4]. Due to the benefits of natural gas as non-renewable energy, but it caused environmental issues by the presence of several compounds. The generated pollutants by these substances have a very detrimental effect on the life and health of industrialized countries [5, 6]. Carbon dioxide and hydrogen sulfide as acid gases (among these pollutants) in hydrocarbon streams could be mentioned. Sour gas contains 7,000 ppm hydrogen sulfide and about 20 percent vol. of carbon dioxide gas typically. The acceptable amount of carbon dioxide and hydrogen sulfide in the sweet gas stream is 40 ppmv and 4 ppm, respectively [7]. Carbon dioxide has a significant role in global warming. The heat rate of natural gas

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decreased if the amount of carbon dioxide does not reach the standard level [8]. Besides, a high level of carbon dioxide in the sweet gas causes many operational problems, including pipe collapse and corrosion equipment [9-11]. Hydrogen sulfide and mercaptans are toxic, corrosive, and flammable, which causes many problems in the process [12, 13]. Catalyst poisoning is an issue of hydrogen sulfide gas and also damages the equipment of various units [14]. In the presence of water, Hydrogen sulfide acts as a weak acid so caused corrosion in industrial equipment and natural gas piping [15].

There are various technologies for removing acid gas, such as absorption [16], adsorption, membrane [7, 13], cooling, and microbial processes [3, 12, 17, 18]. It is necessary to explain that some of the above methods are applicable only on the lab scale. Kooper could accomplish the elimination of acid gas with the absorption process, by using carbonate for the first time in 1920 [19]. Using of amines and glycol compounds was proposed in 1939. Amine solutions are the most widely employed in gas sweetening operations. The natural gas sweetening is not limited to the amine solution and, adsorption is also part of the sweetening processes [20]. The reaction of carbon dioxide and hydrogen sulfide in an alkaline medium is one of the other methods, like treating via high-alkali caustic and low-alkali ammonia that could be accomplished for this purpose [19]. Alkanolamines are derivatives of ammonia wherein one, two, or three alkyl groups are substituted for bonded hydrogens. Alkanolamines contain three classes of including primary amines like Monoethanolamine (MEA), secondary amines such as Diethanolamine (DEA), and Tertiary amines such as Triethylamine (TEA), Methyl diethanolamine (MDEA), and 2-(2-tert-butylaminoethoxy) ethanol (BTEE). Different amines are applied for the sweetening of sour gas [21].

The MEA has been used extensively over the past decades, but it has been replaced with other amines. MEA is mainly employed in the sweetening of pressurized natural gas for the reduction of low amounts of hydrogen sulfide and carbon dioxide. This solution should be applied in the absence of carbon disulfide and carbonyl sulfide [22]. DEA solution has mildly alkaline properties and is less corrosive than the MEA solution [5, 23]. Di-isopropanolamine (DIPA) could be known as a selective absorbing of hydrogen sulfide in the presence of carbon dioxide. MDEA solution is another selective absorbing that due to low vapor pressure, leads to low loss. Also, MDEA has slight corrosion in comparison to other amines solutions [21, 24].

MEA amine solutions could be used in sweetening

natural gas. MEA is the primary amine that has high vapor pressure, appropriate thermal stability, high corrosion, and is suitable for use in mild-pressure operations [25]. The high vapor pressure of this amine leading to loss of the solvent (water). Another type of amine employed in the natural gas sweetening process is DEA. DEA is a Secondary amine that has less reactivity and corrosion than MEA. DEA is cheaper than MEA, and it absorbs carbonyl sulfide as well as carbon dioxide and hydrogen sulfide [25]. TEA as a tertiary amine has better kinetics, lower price, and higher absorption enthalpy compared to DEA. Therefore, TEA is an optimal choice over DEA. MDEA is a tertiary amine that uses more than another amine, industrially. A distinguished specification of this amine is the higher selectivity on hydrogen sulfide absorption over carbon dioxide. The characteristic of MDEA indicates lower vapor pressure, lower corrosion, higher thermal stability, and lower energy consumption than other amines for regeneration [25]. Piperazine (PZ) is added into the MDEA solution to enhance absorbing carbon dioxide, which acts as a catalyst in the chemical reaction between MDEA and carbon dioxide [26]. As well as reduces the cost of amine regeneration. This component has been applied industrially and was shown a proper consequence [25]. It is noteworthy; the results obtained from the MDEA-PZ did not much alter in comparison with MDEA [26].

The MDEA solution has been used to eliminate acid gas (hydrogen sulfide and carbon dioxide) in the most natural gas sweetening plants. This solution is applied when the ratio of carbon dioxide to hydrogen sulfide in the gas feed is less than 1, and the amount of acid gas absorbed is less than or equal to 0.2. Due to the selectivity of hydrogen sulfide (in the presence of carbon dioxide) and unit energy consumption, the efficiency of the unit is about 40% [27]. Nevertheless, for situations where the amount of carbon dioxide per hydrogen sulfide in feed is greater than 1, or the demand of the absorption acid gas per amine solution is high, the selectivity of hydrogen sulfide is significantly reduced. In recent years, the amount of carbon dioxide in oil and gas has been steadily increasing. On the other hand, MDEA solutions could not remove more acid gas and could not meet the needs of refineries and petrochemical plants [27]. In some natural gas sweetening plants, 5 to 20 wt. % Tert-Butylamine (TBA) are added to the lean amine stream. Due to the steric hindrance effect of TBA, the selectivity of acid gas improves by 30%. The boiling temperature of this amine mixture is 90 °C; it's leading to TBA vaporizes in the regeneration column completely. Therefore, there is no economic justification since, in each cycle,

TBA must be re-added to the lean amine stream, which increases operating costs greatly [27].

These problems have inevitably led to a change in the lean amine solution to the absorption column. In some countries, including the United States and China, MDEA has been replaced by BTEE. BTEE was first synthesized and discovered by ExxonMobil Research and Engineering Company in 1984 [28]. A reaction yield of 73% was reported for making an amine solution. In 2005, ExxonMobil Company invented two additional synthesis processes for BTEE with the catalyst [29, 30]. Also, the Companies of China invented a process for BTEE synthesis in 2003 [27]. BTEE is applied in exclusive countries because it is lately newly used for this process. BTEE amine solution, in comparison to MDEA, could eliminate acid gas per volume unit and as well as capable of enhancing the selectivity of hydrogen sulfide. Also, with a low concentration of BTEE (about 10% lower), some consequences are better than MDEA in the absorption column [31]. It should be noted that Expert Choice software has been used for calculating the criteria and alternatives weights by AHP.

Nowadays, numerous activators (e.g., piperazine, Tetra-ethylenepentamine, polyethyleneimine branched, and so on) are added in alkanolamine solutions for enhancing the performance of the absorption process [32]. Piperazine improves the performance of amine solutions by increasing the absorption capacity of carbon dioxide. This event is based on a series of multiple reactions between piperazine and carbon dioxide that result in the production of carbamate and bi-carbamate [33]. The removal of acid gas accomplished an absorption column (generally trayshaped). The absorption and stripping column (regeneration) are the most commonly natural gas sweetening technology on an industrial scale. Despite many advantages, the stripping column requires a great deal of energy for the regeneration of the amine solution [16, 24, 26, 33, 34]. The influence of each parameter on the sweetening process should be considered until it could increase the yield of the process [35]. Therefore, making decisions and optimization of this process with high efficiency could be very important. The process of sour gas sweetening is economically expensive. Therefore, chemical process simulation and the economic optimization of processes should have special consideration [36-37]. There are various methods for optimizing and improving the absorption process such

as the neural networks, the genetic algorithm, or the use of ASPEN ONE software [38, 39]. Using ASPEN HYSYS could be simulated the suitable operating condition with minimum energy consumption [38, 40].

Also, the different factors impress the economics of the gas sweetening process, such as the recycle flow rate of amine and its concentration, sour gas temperature and pressure. The predominant part of the operating costs in the gas sweetening process is related to the heat load of the Reboiler stripping column, which Includes up to 70% of the operating costs [41].

The main effective factor (in the Reboiler energy) is the recycle flow rate of amine. Also, the type of amine solution and the design of the process (number of column trays, condenser temperature, etc.) are other effective factors in economic costs. Considering various factors and relationships with the optimal point is essential and vital [26]. The simulations of the gas sweetening in different software have many economic benefits, like changing operating conditions, varying the rate of flow and the concentration of circulating amines, and generally achieving an optimal point. By adjusting the operational parameters at the optimal point, energy consumption will also be reduced. [42-44].

Extensive studies have recently been conducted on the gas desalination process. Karthigaiselvan et al. [45], A dynamic model for acid gas treatment developed using two-film & surface-renewal theory. Elsewhere, Farzaneh et al. [46], Investigated the role of hydrolysis of COS and heat stable amine salts on the transient increase of H<sub>2</sub>S in the effluent of the gas sweetening unit. In addition, Hamad et al. [47], also studied the membrane-solvent hybrid process from a Techno-Economic perspective. They found that the Membrane process diverted significant bulk of acid gas directly to the Sulfur Recovery Unit (SRU) and that the Membrane process cuts on amine process load, equipment size, and costs. In 2020, a simulation-based study by Zahid et al. [48] was done on the sweetening of associated and non-associated sour gas using an amine blend. Then the issue was examined from an economic point of view.

In this study, at the primary step, the AHP method was employed to simplify decision-making for selecting amine solution in the natural gas sweetening. For this purpose, parameters such as boiling point, vapor pressure, adsorption rate, etc., were considered

(	Saaty's Numerical Rating	Linguistic Equivalent for Comparison of Criteria	Linguistic Equivalent for Comparison of Alternatives	
1		Equally important	Equally preferred	
2		Equally to moderately important	Equally to moderately preferred	
3		Moderately important	Moderately preferred	
4 Moderately to strongly importa		Moderately to strongly important	Moderately to strongly preferred	
5 Strongly important		Strongly important	Strongly preferred	
6 Strongly to Very strongly importat		Strongly to Very strongly important	Strongly to Very strongly preferred	
7 Very strongly important		Very strongly important	Very strongly preferred	
8 Very strongly		Very strongly to extremely important	Very strongly to extremely preferred	
	9	Extremely important	Extremely preferred	

Table 1: Saaty's fundamental pair-wise comparison 9-point scale corresponding linguistic equivalent [50, 51].

operating conditions for comparing solvents. In the second step, the simulation and optimization of the natural gas sweetening (based on amine choosing from the AHP step) were developed at the ASPEN HYSYS software. The novelty of this study is the general optimization of gas sweetening processes that have been established before and after many years; without wanting to make much physical change, they want to increase productivity.

#### METHODOLOGY

#### Analytic Hierarchy Process

To select the appropriate amine solution in the natural gas sweetening process used AHP method. One of the significant comprehensive systems designed for judging by numerous criteria is the hierarchical analysis process. This technique provides the equation hierarchically and applies the consideration of different criteria in decision making. It is also capable of analyzing sensitivity to criteria and sub-criteria. The AHP method is based on pair-wise comparisons that facilitate judgment and computation, also show the degree of inconsistency and inconsistency of the decision. The qualitative criteria for making decisions have been employed, which is the greatest advantage of this method. AHP method could consider unstructured and complex decisions [49]. There are various ways to use the AHP method, which are manual and systematic. Expert Choice software could be applied for systematic and human error-free and decision-making [18]. Therefore, it is necessary to study related literature for analyzing criteria and alternatives in sour gas treating

via amine solution. The AHP multistep procedure was performed as follow: In the primary step, the criteria and options are compared using Table 1:

With the numbers attributed to the criteria or options, a matrix such as Equation (1) is formed, which indicates the preference of the criterion or option i over the criterion or option j [52].

$$A = \begin{bmatrix} d_{1,1} & \cdots & d_{1,n} \\ \vdots & \ddots & \vdots \\ d_{n,1} & \cdots & d_{n,n} \end{bmatrix}$$
(1)

In the next step, if there is more than one decisionmaker, the average of their preferences is derived from Equation (2) [52].

$$\widetilde{d_{i,j}} = \frac{\sum_{k=1}^{k} \widetilde{d_{i,j}^{k}}}{K}$$
(2)

Based on the results of the calculations related to Equation (2), Equation (3) is updated as follows [52].

$$\widetilde{\mathbf{A}} = \begin{bmatrix} \widetilde{\mathbf{d}_{1,1}} & \cdots & \widetilde{\mathbf{d}_{1,n}} \\ \vdots & \ddots & \vdots \\ \widetilde{\mathbf{d}_{n,1}} & \cdots & \widetilde{\mathbf{d}_{n,n}} \end{bmatrix}$$
(3)

In the next step, the normalized principal eigenvector of matrix  $\tilde{A}$  should be prepared. In the final step, the Inconsistency Ratio (IR) of matrix  $\tilde{A}$  was calculated. To do that, initially, the inconsistency index (CI) should be provided. The CI was established through Equation 4 [50]. The *n* in this equation is the number of matrix comparison sizes, and  $\lambda_{max}$  is the largest eigenvalue of the matrix.

 Table 2: The random index (RI) value for AHP Method.

Number of Elements (n)	RI Value		
1	0.00		
2	0.00		
3	0.52		
4	0.89		
5	1.11		
6	1.25		
7	1.35		
8	1.40		
9	1.45		
10	1.49		
11	1.51		
12	1.54		
13	1.56		
14	1.57		
15	1.58		

$$CI = \frac{\lambda_{max} - n}{n - 1}$$
(4)

Then IR of the matrix can be calculated by dividing the CI by its random Reliability Indicators (RI) as presented by Equation 5. The IR value is the ratio between the consistency of a given evaluation matrix and the consistency of a random matrix [50].

$$IR = \frac{CI}{RI}$$
(5)

The required RI values were adopted from [52] and illustrated in Table 2.

In cases that IR values of the matrices are less than or equivalent to 0.10, decision-making results are acceptable and reliable. On the other hand, if higher amounts than 0.10 are observed, the judgments and comparison performance are not validated and the process is required to be rechecked to enhance the IR value.

According to previous studies, it could be illustrated the AHP method flowchart for gas sweetening in Fig. 1 in which the criteria and alternatives of the gas sweetening process and the relationship between them are shown.

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#### **Process description**

Natural gas sweetening plants differ slightly depending on the type of amine or licenser Company. For this purpose, one of Iran's gas refinery plants was investigated (as a case study). In general, the sour gas stream containing acid gas (hydrogen sulfide and carbon dioxide) enters the lower tray of the absorption column after passing through a separator. Also, the lean amine stream enters from the top of the absorption column. The heat of reaction between the amine and the acid gas caused the temperature of gas flow to increase in the absorption column. The sweet gas stream and rich amine stream are two main product which comes out of the top and bottom of the column, respectively. Typically, the absorption column operates at ambient temperature. The absorption column has 34 trays in this case study. The rich amine stream enters a stripping column after passing through a vapor-liquid separator and shell and tube exchanger. The stripping column (regeneration column) has tray-shaped with 24 trays typically. The reboiler operates at ambient pressure and 110 to 130 °C. The bottom of the regeneration column (regenerated amine solution) must be recycled to the absorption column. Due to the regenerated amine stream has a high temperature. So, the amine stream temperature is reduced by a cooler before entering the absorption column. Since the amount of water of the amine solution in the regeneration column has evaporated, make-up water is added. The amount of hydrogen sulfide and carbon dioxide in the sweet gas stream and as well as reducing the reboiler heat load (duty) of the regeneration column, are objective functions in this simulation. The PFD of the case study unit is shown in Fig. 2. Also, some specifications of sour gas (natural gas) are given in Table 3. ASPEN HYSYS software was employed to simulate the process. Also, Acid Gas-Chemical solvents as calculation packages was employed.

#### **RESULTS AND DISCUSSION** *The Analytic Hierarchy Process*

According to previous studies and industrial processes, seven alternatives MEA, DEA, MDEA, MDEA+PZ, TEA, MDEA+TBA, and BTEE were selected as the main alternatives for amine-based natural gas sweetening. The four criteria, including

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	Component (ppm Mole basis)	Value		
	$H_2S$	6800		
	$CO_2$	17470		
	$N_2$	35230		
	C1	853950		
	$C_2$	53255		
	C <sub>3</sub>	21050		

Table 3: The amount of some compounds in the feed gas (Sour Gas).



Fig. 1: Flowchart of AHP method for amine-based natural gas sweetening.



Fig. 1: Process flow diagram of natural gas sweetening plant.

	Availability	Cost	Operational Condition	Yield
Availability	1	1/4	1/2	1/4
Cost		1	5	3
Operational Condition			1	1/2
Yield				1
Inconsistency 0.04			0.04	

 Table 4: Pair-wise comparison of criteria scale.

availability, cost, operational condition, yield, and two sub-criteria, including material cost and operating cost, are chosen. In this multi-criteria decision-making, the purpose is to maximize the availability, ease of operation (operational condition), yield, and minimize the solvent and operating cost (cost). The pair-wise comparison among criteria was accomplished based on previous case studies. Paired comparison is performed based on various parameters such as numerical, graphical, and alphanumerical, which numerical paired parameters because of simplicity are chosen. The concept of numerical pair-wise comparison is illustrated in Table 1 [8, 18]. The preference of each criterion and alternatives was evaluated based on the various conditions in the natural gas sweetening process and finally was compared. The pair-wise comparison matrix of the criteria is presented in Table 4. Inconsistency was achieved for the pairwise comparison of criteria.

The inconsistency ratio is one of the most critical evaluations in the analytic hierarchy process. If the achieved inconsistency is below 10%, then responses to this method could be valuable and reliable. The value of inconsistency for the criteria is obtained by 4%. The pair-wise comparison of the criteria and alternatives is illustrated in Fig. 3. As could be seen from Fig. 3, the cost parameter with the highest percentage (53%) than other criteria have the most preference, and then the yield parameter has the second preference by 26% priority. Due to that the cost parameter has the highest priority among the criteria. Therefore, the cost of energy and kind of materials should be considered in particular. Hence, choosing a suitable amine (alternatives factor) will greatly affect the cost of the process. As well as, based on cost criteria should be paid specific attention to energy consumption, especially in the reboilers and condensers.

Each of the seven alternatives has benefits and disadvantages that for paired comparison should be



Fig. 3: The result of the pair-wise comparison (a) Criteria factor (b) Alternative factor.

studied carefully. The properties of each alternative (amine solution) are noted in the materials and methods section [25]. According to the obtained evaluation, it could be mention that the MDEA with 22% than other alternatives was the highest preference. Additionally, due to former studies the BTEE alternative has less precedence than MDEA by 21% priority. Generally, the BTEE amine solution has better efficiency and selectivity than the other amine solutions and could remove more moles of acid gas. According to the criteria of cost, the MDEA solution has a relative superiority over BTEE. BTEE has a high yield for reducing acid gas, but one of the disadvantages of this

	-		
Item	Simulation Value	Actual Value	Percentage Error
H <sub>2</sub> S in Sweet Gas (ppm Mole basis)	1.7	2	15
Reboiler duty (MJ/h)	139995	139978	0.012
Recycle Amine Temp. (°C)	42.6	46.4	8.2
Absorption Overhead Temp. (°C)	49	43	14
Regeneration Bottom Temp. (°C)	138	132	4.5

Table 5: Validation of the simulation results with the actual value.

solution compared to MDEA is its low cost and nonindustrialization. If the price of the BTEE solution decreases in the future, it will be of higher priority than the MDEA solution. Because the BTEE solution performance is better in the natural gas sweetening process than other alternatives, it causes higher precedence. The TEA alternative had the lowest precedence in this comparison.

According to the obtained consequence, the inconsistency ratio for alternative comparison is 7 %. that could be valuable in the AHP method.

#### Consequence of process simulation (Validation)

The validation of data is the first step in each software simulation, which error in the software data has by 15% considering the case study information. Table 5 is shown simulation results and objective function errors.

According to defined objective functions, the acid gases must be decreased as much as possible. The weight percent of the amine solution in the case study unit is 44% (1055 kgmole.h<sup>-1</sup> MDEA component molar flow rate). Reduction in the amount of amine is an effective factor that is decreases operating costs incredibly, while the hydrodynamic conditions of the absorption column did not alter. Also, the sweet gas must meet the sales gas specification (H<sub>2</sub>S and CO<sub>2</sub> below 4 and 40 ppmv, respectively). The simulation and optimization were implemented to achieve an optimal amount of MDEA. Therefore, according to the above constraints and studies, the flow rate of MDEA could be changed from 1080 kmole/h to 850 kmole/h. Less than 850 kmole/h, the hydrodynamic conditions of the absorption column changed completely. Also, the amount of hydrogen sulfide and carbon dioxide rises below 880 kgmole/h sharply. Therefore, it is reasonable that the amount of MDEA in the solvent stream is not less than 880 kgmole/h (39 wt. %).

#### The influence of MDEA flow rate

In this case study, the purpose is to reduce the energy consumption of the reboiler and reduce the amount of acid gases in the final product of the unit. Therefore, the effect of the MDEA flow rate on reboiler energy consumption is surveyed, which is demonstrated in Fig. 4.

The profile of the reboiler heat load (duty) is decreased from 1055 to 880 kgmole.h<sup>-1</sup>. Reboiler heat load will be improved by reducing of MDEA flow rate. It should also be noted that the reboiler duty is reduced by 0.04% at 880 kgmole.h<sup>-1</sup> (39 wt. % MDEA) relative to the operating flow rate.

#### The influence of feed gas temperature

The effect of feed gas temperature on the reboiler duty has been investigated by considering the primary objective function (reducing as much as possible reboiler duty). Fig. 5 exhibits the reboiler heat load (duty) on feed temperature changes at two MDEA concentrations.

According to Fig. 5, it could be stated that the reboiler energy consumption improves via developing feed temperature by 30 °C slightly. As the feed gas temperature increased from 30 to 40 °C, the reboiler duty also grew. Based on the results (in Fig. 5), reboiler energy consumption improves via reducing MDEA concentration. The results of Fig.5 demonstrated that feed gas temperature of 30 °C seemed to be suitable for reboiler duty. At 39 wt. % MDEA in comparison with 44 wt., % the reboiler duty has been reduced by 0.03 % in 30 °C. Since the effect of feed gas temperature on reboiler duty was considered, the effect of feed temperature on the concentration of hydrogen sulfide and carbon dioxide (for two concentrations of MDEA) should be studied [53]. Fig. 6 indicated the influence of feed gas temperature on the amount of acid gas in sweet gas. By increasing the feed temperature from 20 to 30 °C,



Fig. 4: The effect of the MDEA flow rate on reboiler energy consumption.



Fig. 5: Reboiler energy consumption changes on feed gas temperature.



Fig. 6: The weight changes of acid gas versus feed temperature a) The variations of hydrogen sulfide, b) The variations of carbon dioxide.

the amount of hydrogen sulfide and carbon dioxide reduced less and considered almost constant. The higher feed gas temperature leads to an increase in hydrogen sulfide and carbon dioxide that verify the exothermic reaction behavior. As could be seen, even with 5% reduction in the concentration of MDEA, the amount of hydrogen sulfide and carbon dioxide in the sweet gas is acceptable. Due to Fig. 6, the optimum point for feed gas temperature (on average) is at 30 °C. Because carbon dioxide reaches lower concentrations sulfide at this temperature, also hydrogen concentration is rational.

The influence of feed temperature on the acid gas loading per unit of MDEA should also be surveyed to obtain the optimum feed temperature. Fig. 7 illustrates these variations for two concentrations of MDEA. The achieved consequence presents that by growing the feed gas temperature 20 to 30 °C, enhanced the acid gas loading per unit of MDEA. Then, the acid gas loading reduces slightly. It is worth noting that the acid gas loading per unit of MDEA has been improved with 39 wt. % MDEA (11% approximately at 30°C).

Altering the operating conditions (e.g., inlet feed temperature, inlet solvent flow rate) will affect the solvent uptake and selectivity. Therefore, the selectivity of MDEA for absorbing each acid gas has been studied. Selectivity could be calculated through equation 6 and 7 [31].

Selectivity of 
$$H_2S =$$
 (6)  

$$\frac{\text{mol}(H_2S)}{\text{mol}(CO_2)} \text{ in liquid phase} / \frac{\text{mol}(H_2S)}{\text{mol}(CO_2)} \text{ in gas phase}$$



Fig. 7: Influence of feed temperature variation on the acid gas loading per unit of Amine. a) 44 wt. % MDEA, b) 39 wt. % MDEA.



Fig. 8: The selectivity of MDEA for the absorption of hydrogen sulfide and carbon dioxide.

Selectivity of 
$$CO_2 =$$
 (7)  
 $\frac{\text{mol}(CO_2)}{\text{mol}(H_2S)}$  in liquid phase /  $\frac{\text{mol}(CO_2)}{\text{mol}(H_2S)}$  in gas phase

Fig. 8 indicates the selectivity of MDEA on acid gas via developing feed gas temperature. According to the results, by increasing feed gas temperature, the selectivity of MDEA for hydrogen sulfide absorption decreases slightly.

However, on the other hand, the selectivity of MDEA for carbon dioxide absorption enhances.

The results of Fig. 8 have a good agreement with Fig. 6. Fig. 8 shows that the selectivity of MDEA

did not differ too much with decreasing MDEA concentration. As shown in Fig. 8, the selectivity of MDEA for hydrogen sulfide absorption is about 1.

The selectivity value should be around 6 based on previous studies. The ratio of carbon dioxide to hydrogen sulfide in this case study is 2.57 and the acid gas loading per unit of MDEA is 0.27 optimally. Also, according to the obtained ratio and previous researches, two parameters are very high, which dramatically reduces the efficiency and selectivity of the MDEA solution in the absorption of acid gas. In future work, the efficiency of this unit could be improved by changing the operating parameters as well as varying the amines solution or combining several amines.

#### CONCLUSIONS

The simulation and optimization of the natural gas sweetening process via amine solution led to the following outcomes:

The analytic hierarchy process was employed to choose the best amine solution among the MEA, DEA, MDEA, MDEA+PZ, TEA, MDEA+TBA, and BTEE.

The achieved results from AHP were indicated that cost criteria have the highest priority, with 52 % in comparison to other criteria. Also, the MDEA solution was selected as the premium alternative. Notwithstanding, BTEE could be the best amine solution (due to high yield) compared to MDEA if it has a low price and is produced industrially.

The amount of hydrogen sulfide and carbon dioxide in sweet gas, also reduction of reboiler duty were defined as two objective functions. The achieved results were indicated that MDEA concentration could decrease by 39 wt. %, without changing the concentration of acid gases (in range of standard level) in the sweet gas. Due to 5 wt. % reduction in the MDEA, the mass flow rate of amine will decrease to 819000 tons (in one batch). As a result of this decrease in a year, the operating cost of the unit reduces by approximately 98 thousand dollars a year.

The achieved optimal feed gas temperature was insignificant in comparison to the current operating conditions. Although the optimization results showed that the best mole flow rate of MDEA and the feed gas temperature were 880 kgmole/h and 30 °C, respectively.

The reboiler heat load also decreased by up to 0.04% in the regeneration column. Via improving the reboiler duty, the energy cost will reduce by 98 thousand dollars a year, which leads to enhancing the unit profitability.

The obtained consequences were shown that selectivity and acid gas loading of 39 wt. % compared to 44 wt. % is improved.

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