
Operational investigation of multi feed amine process performance in comparison with conventional process

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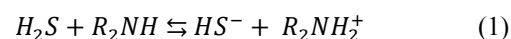
Abstract: The alkanolamines are the most generally accepted and widely used of the many available solvents for removal of acid gases from natural gas streams. Amongst different amine sweetening processes like conventional scheme, split flow, absorbers in series or parallel and multi feed, selecting the proper scheme has great impact on acid gas removal. Using multi feed scheme in Fajr-e-Jam gas refinery has provided the chance for better analysis of conventional and multi feed schemes. In current work, the most important parameters in gas sweetening refineries like CO₂, H₂S and mercaptan removal, caustic solution consumption and temperature distribution throughout the absorption column were investigated for sweetening trains utilizing DEA. For all the parameters mentioned above, multi feed scheme shows good acid gas removal capability and lower caustic solution consumption compared to the conventional process with single feed.

Keywords: Alkanolamines, Acid Gas, Multi Feed, Mercaptan, Caustic Solution

1. Introduction

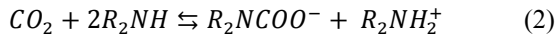
To bring natural gas to the market, either via pipeline to nearby consumers or via liquefaction to distant markets, various impurities in the produced gas must be removed among these are H₂S and CO₂. The removal of H₂S from the gas is termed the sweetening process. The sweet gas specification is ¼ grain H₂S /100 SCF [1]. These acid gas components are removed from the sales gas using traditional absorption processes also known as acid gas removal (AGR) units. Typically, AGR units utilize an amine solvent but depending on the gas composition AGRs can use hot potassium carbonate, a physical solvent, or a blend of amine and physical solvent. 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 (DGA). Secondary amines react directly with H₂S, CO₂ and COS. The most common secondary amine is diethanolamine (DEA). Tertiary amines like methyldiethanolamine (MDEA) react directly with H₂S and indirectly with CO₂ and COS [2]. Beside the conventional

amine sweetening process, several modifications have been proposed [3,4,5]. One traditional alternative is known as a multi feed configuration which is used when acid gas concentration is high in the feed sour gas. In this case if conventional amine sweetening process (single feed) is used, the rate of required amine will be so high that results in increase in the diameter of the absorption column which is not economical. In multi feed scheme, a portion of the lean amine from the regeneration column after being cooled, is introduced to the column from multi mid points. To determine the rate of absorption of CO₂ and H₂S in an aqueous amine solution, the rates of reaction of these gases in the solution must be estimated. H₂S reacts with DEA to form hydrogen sulfide and protonated amine according to the following reaction:

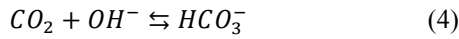
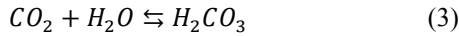


The mechanism of this reaction involves a proton transfer and is considered instantaneous with infinite reaction rate. The rate of absorption of H₂S in an aqueous solution containing a single amine can be determined analytically. This was done by Onda et al. 1970 [6]. They used the two-film theory to derive a general analytical expression of the enhancement factor for systems comprising a single

instantaneous chemical reaction. As the reaction between H₂S and aqueous alkanolamines involves only a proton transfer, this reversible reaction can be considered to be infinitely fast [7]. Hence the absorption rate is entirely mass transfer controlled under practical conditions [8]. The reactions between CO₂ and alkanolamine solutions, however, proceed at a finite rate, different for the various amines [7]. From a purely kinetic point of view the selectivity for H₂S therefore only depends on the CO₂ reaction rate. Until recently the mechanism and kinetics for this reaction were considered to be simple and straightforward for all alkanolamines, although large discrepancies in data have been reported for DEA which reacts with CO₂ to form amine carbamate [9-11]:



But CO₂ can also react with water or hydroxyl ions to form carbonic acid or bicarbonate ions:



These acids will react with amine to form amine bicarbonate (HCO₃⁻, R₂NH₂⁺) and amine carbonate (CO₃²⁻, (R₂NH₂⁺)₂). Reactions (3) and (4) are very slow compared to reaction (2); so ignoring these reactions does not affect the calculation of the rate of absorption of CO₂ in amine systems. The absorption of CO₂ in aqueous solution of DEA has been extensively studied in the literature. Several techniques have been used to collect the kinetics data. These include laminar jet falling film, rapid mixing, falling film, diffusion across a porous media, and stirred reactor. Descriptions of the methodology and experimental set up are given by Van Krevelen and Hofstijzer (1948), Nunge and Gill (1963), Coldrey and Harris (1976), and Ko and Li (2000) [12-15]. Blanc and Demarais (1984) revised the data and the proposed mechanisms for the rate of reaction of CO₂ with DEA and they realized that the researchers' results vary significantly [16]. The dependence of the reaction rate on the concentration of DEA was reported as first or second order.

The reported rate constants were also not comparable. Blauwhoff *et al.* (1984) revised the reported kinetics data for this system and concluded that the reaction rate of CO₂ with DEA is too complicated to be interpreted by a simple kinetic model [17].

In our previous work we compared the performance of different kinds of amines used in Fajr-e-Jam gas refinery including DEA, MDEA, DEA/MDEA and a MDEA (activated MDEA). In current work the effect of multi feed configuration on several important factors in gas sweetening refineries like H₂S, CO₂ and mercaptan removal, caustic solution consumption rate and temperature profile throughout the absorption column are investigated; the results are then compared to conventional amine sweetening process (single feed) based on 32% wt diethanolamine (DEA) solution. DEA is especially favored for sweetening refinery and manufactured gas streams where the contaminants like H₂S, CO₂, COS and CS₂ are prevalent. DEA is non-selective agent and removes both H₂S and CO₂. However it sometimes fails to reduce H₂S concentrations to pipeline specifications. Wendt and Daily (1967) described the SNPA modification of the DEA process and reported its capability for removing H₂S to the level of approximately 0.1 grains per 100 SCF [18]. All the data presented in current work were gathered in a period of one week and each is a mean average of all the daily recorded data in the control room and log sheets.

2. 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 8 parallel sweetening trains which use different kinds of amines. The inlet gas to the refinery which is a mixture of the gases from the two mentioned reservoirs is distributed between 8 sweetening trains. The basic flow scheme for multi feed configuration used in one of the trains of the refinery is shown in Fig. 1.

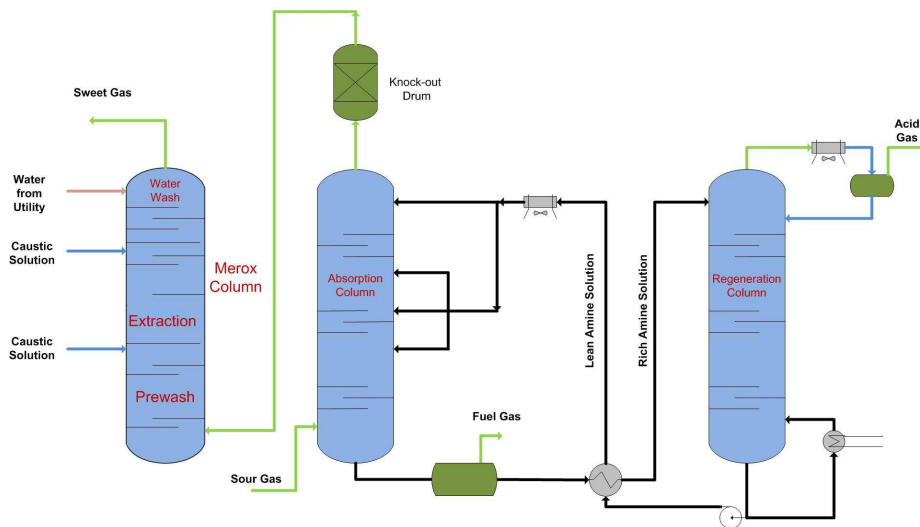


Figure 1. Multi feed scheme process used in Fajr-e-Jam gas refinery

In the sweetening trains, amine enters absorption column via a 10 inch pipeline. As there are three 2 inch connections for sampling of amine solutions from trays 15, 20 and 25, the multi feed configuration can be used in these trains using these connections. To do so, a 3 inch branch which is taken from main 10 inch pipeline, introduces amine to absorption column via the sampling connections. The inlet feed gas and absorption column 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.

Table 1. Inlet sour gas composition to sweetening trains

Component	Mole%
C ₁	86.22
C ₂	4.47
C ₃	1.21
i-C ₄	0.23
n-C ₄	0.33
i-C ₅	0.13
n-C ₅	0.11
C ₆	0.12
C ₇ ⁺	0.17
N ₂	5.09
CO ₂	1.92
H ₂ S (mg/sm ³)	1409
RSH (mg/sm ³)	39

Table 2. Absorption column specifications

Tray type	Valve tray
Tower diameter, m	3.7
Tray spacing, cm	61
Tray weir height, mm	76
Passes per tray	Even Trays= 2 & Odd Trays=3
Tray area percent of tower	85%

3. Results and Discussion

Gas flow rate and amine circulation rate from the bottom of the regeneration column for both scenarios (conventional process and multi feed configuration) are presented in the following table:

Table 3. Gas flow and amine circulation rates for the two cases

day	Gas Flow Rate (MMSCMD)		Amine Circulation Rate (m ³ /hr)	
	Conventional	Multi feed	Conventional	Multi feed
1	14.5	14.95	358	347.9
2	14.1	14.95	360	347.9
3	14.16	14.95	360	347.9
4	14.2	15	360	347.9
5	14.1	15	360	347.9
6	13.6	15	360	347.9
7	14.1	15	358	347.9

3.1. Temperature Distribution in Absorption Column

Fig. 2 shows the temperature profile throughout the absorption column for the two cases.

The temperature profile shows that in multi feed scheme maximum temperature in the absorption column is 99.5°C

while for conventional process this value is 107°C. When introducing three side steams to the absorption column, the amine stream coming from top tray is being mixed with these streams, so the temperature of the amine mixture descending the column is lower than single feed amine stream in conventional process. As the absorption process accomplishes better in higher pressures and lower temperatures, so in the case of multi feed scheme, amine encounters the inlet sour gas with lower temperature compared to single feed scheme, which results in better acid gas removal, which will be discussed later.

In the conventional amine sweetening process, the entire amine stream is introduced from top tray of the absorption column, while in the case of multi feed scheme, the amine stream coming from the regeneration column, is distributed between 4 lines (3 side streams and 1 top tray). As the rate of amine in top tray feed line is lower for multi feed scheme compared to conventional process, for the trays located between top tray feed introduction and the first side stream introduction point, the raise in amine temperature is higher in multi feed scheme.

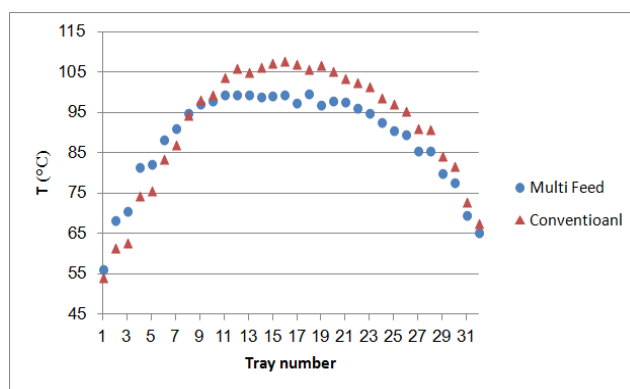


Figure 2. Temperature profile throughout the absorption column for two cases

3.2. H₂S and CO₂ Absorption

Figures 3 to 6 show H₂S and CO₂ concentrations in inlet gas streams to absorption columns of sweetening trains and in outlet sweetened gas for both scenarios.

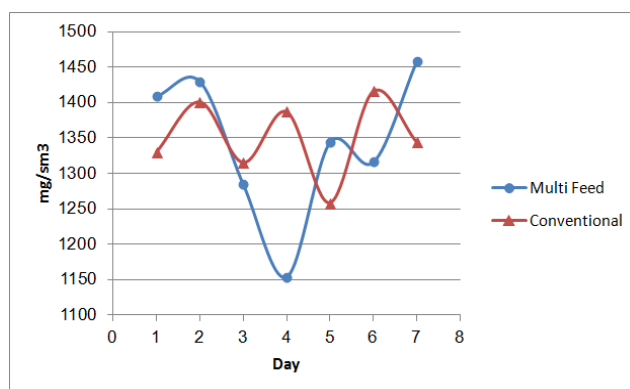


Figure 3. H₂S concentration in inlet sour gas in the two cases

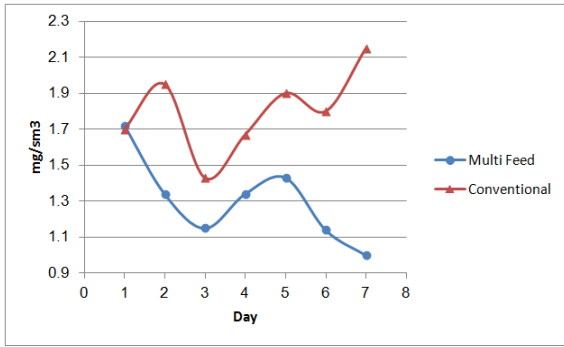


Figure 4. H₂S concentration in sweetened gas in the two cases

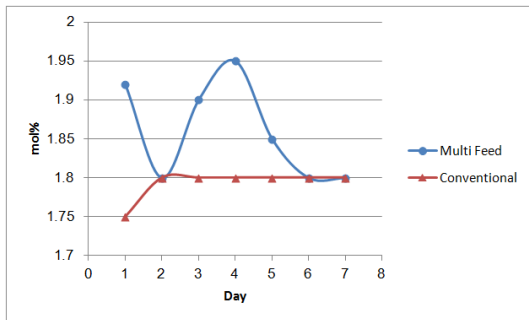


Figure 5. CO₂ concentration in inlet gas to absorption column in the two cases

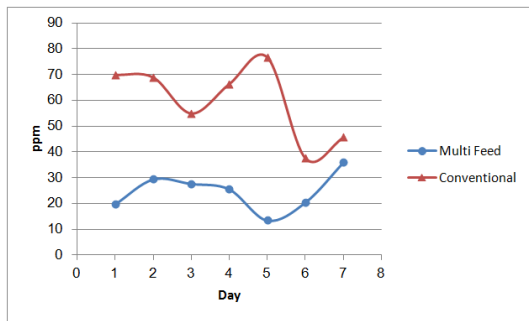


Figure 6. CO₂ concentration in sweetened gas in the two cases

H₂S removal capacity and percentage can be obtained using equations (5), and (6).

$$H_2S_{Rremoved} = [H_2S_{in} - H_2S_{out}(1 - \{(CO_{2in} - CO_{2out}) - RSH_{in} - RSH_{out}/1.43\})] Gas_{in} \quad (5)$$

$$H_2S \text{ Removal}\% = \frac{H_2S_{Rremoved}}{H_2S_{in} Gas_{in}} * 100 \quad (6)$$

The results of calculations are presented in Table 4.

Table 4. H₂S removal data for the two cases

day	H ₂ S removed, Kg/day		H ₂ S removal%	
	Conventional	Multi feed	Conventional	Multi feed
1	19260.78	21064.55	99.874	99.88
2	19727.1	21378.5	99.863	99.907
3	18600.51	19210.75	99.893	99.912
4	19672.11	17310	99.881	99.907
5	17711.49	20160	99.851	99.895
6	19233.56	19740	99.875	99.95
7	18920.63	21870	99.842	99.932

Similarly, we can find amount of CO₂ absorbed from inlet sour gas into DEA solution using equations (7) and (8).

$$m_{CO_{2in}} = \frac{y_{CO_{2in}} Gas_{in} P_s MW_{CO_2}}{RT_s} \quad (7)$$

Where R=0.08206 bar.m³/kmole.k, MW_{CO₂}=44, and subscript s stands for the standard condition which are as T_s=15°C and P_s=1 bar. And,

$$m_{CO_{2out}} = \frac{y_{CO_{2out}}(1 - (y_{CO_{2in}} - y_{CO_{2out}})) Gas_{in} P_s MW_{CO_2}}{RT_s} \quad (8)$$

The results of calculations are presented in Table 5.

Table 5. CO₂ removal data for the two cases

day	CO ₂ removed, Kg/day		CO ₂ removal%	
	Conventional	Multi feed	Conventional	Multi feed
1	470570.2	533867.9	99.60	99.899
2	470741.3	500201.8	99.62	99.839
3	473106.9	528082.6	99.7	99.856
4	474147.4	543870	99.63	99.871
5	470542.7	516274.3	99.58	99.928
6	45829.1	502118.8	99.8	99.888
7	471342	50169.3	99.75	99.803

The two important parameters in absorption of the acid gases from sour gas are temperature and pressure. As the pressure increases and the temperature decreases throughout the column, acid gas removal capacity increases. In the case of multi feed configuration, the multi feed pressure remains the same as conventional process and doesn't affect CO₂ and H₂S pick up. Usually the only parameter available for control of the column temperature is the lean amine temperature. A high temperature of absorption column will increase the reaction rate. However, once the lean amine temperature reaches about a maximum design temperature (121°C), the decrease in solubility of the CO₂ and H₂S in the amine solution will usually become the overriding factor and the net acid gases pickup will begin to decrease. Multi feed configuration introduces the cooled amine stream mixture to the bottom trays of the absorption column where amine encounters the inlet sour gas with lower temperature compared to single feed scheme, which results in a better acid gas removal.

3.3. Mercaptan Absorption and Caustic Solution Consumption

Figs. 7 and 8 show mercaptan concentrations in inlet gas streams to absorption columns of sweetening trains and in sweetened outlet gas for both scenarios.

Mercaptan is an organic sulfur compound composed of an alkyl or aryl group and a thiol group. General formula of mercaptan is R-SH where R is an alkyl or aryl group. To remove mercaptan from the outlet gas from the absorption column, the gas enters Merox contractor from the bottom. This contractor consists of three sections: water wash

section (trays 1 to 3), extraction section (trays 4 to 18) and prewash section (trays 19 to 33). In the bottom section gas consisting mercaptan and traces of H₂S and CO₂ ascends the column and caustic solution introduced from top of tray 19 absorbs H₂S, CO₂ and part of mercaptan. As the reaction rate between H₂S and CO₂ with caustic solution is higher than with mercaptan, in the bottom section of Merox contactor, H₂S and CO₂ are absorbed into the caustic solution which causes the caustic to be consumed irreversibly. H₂S reacts with caustic solution to form sodium sulphate which can precipitate out of the solution, causing plugging problems. Therefore if there are high levels of H₂S in the gas stream to the Merox contactor, which indicates weak H₂S removal in absorption column (Fig. 1), the sweetening unit shall be shut down for troubleshooting.

The portion of the caustic solution consumed by CO₂ and H₂S is known as the spent caustic and is routed to the sewer. For multi feed configuration, as the outlet gas from the absorption column has lower H₂S and CO₂ content compared to the conventional process, the spent caustic rate is lower which led to higher mercaptan absorption into the caustic solution.

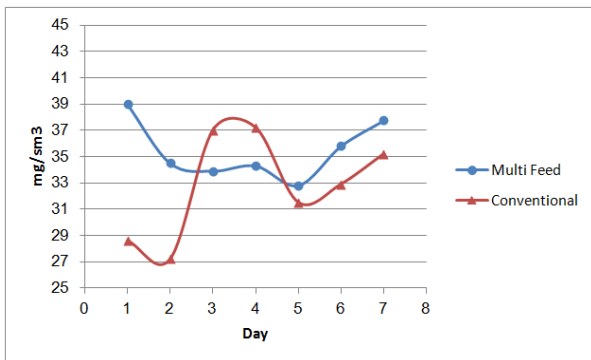


Figure 7. Mercaptan concentration in inlet gas to absorption column in the two cases

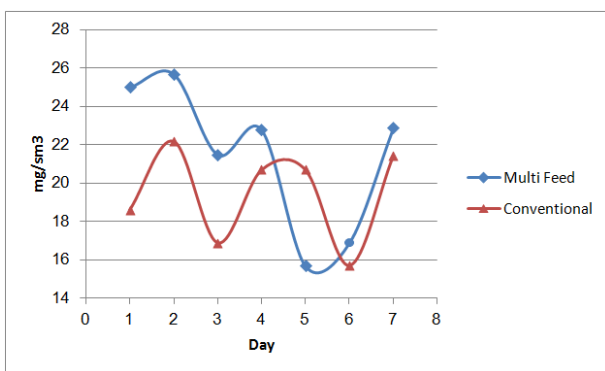


Figure 8. Mercaptan concentration in sweetened gas in the two cases

Using gas flow rate to the absorption column, mercaptan removal capacity and percentage can be obtained from equations (9) and (10).

$$RSH_{Removed} = [RSH_{in} - RSH_{out}(1 - \{(CO_{2in} - CO_{2out}) - H_2S_{in} - H_2S_{out}/1.43\})] Gas_{in} \quad (9)$$

$$R = \frac{RSH_{Removed}}{RSH_{in} Gas_{in}} * 100 \quad (10)$$

The results for the percent of spent caustic and mercaptan removal rates for the two cases are shown in Fig. 9 and Table 6, respectively.

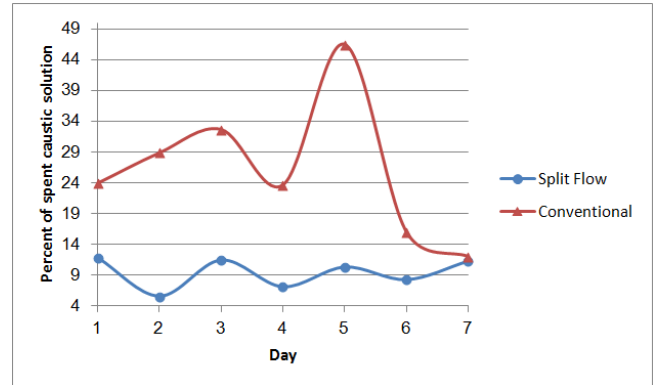


Figure 9. Spent caustic solution rate for the two cases

Table 6. Mercaptan removal data for the two cases

day	RSH removed, Kg/day		RSH removal%	
	Conventional	Multi feed	Conventional	Multi feed
1	149.95	216.83	36.16	37.2
2	76.42	138.85	19.92	26.9
3	289.13	191.76	55.18	37.8
4	239.85	179.43	45.4	34.87
5	157.76	261.07	35.5	53.06
6	237.83	288.29	53.15	53.68
7	199.59	229.56	40.21	40.54

4. Conclusion

The technology of using alkanolamines for removal of hydrogen sulfide and carbon dioxide from natural gases has been used for decades. In the design of the process, the primary concern is that the sweetened gas meets the required purity specifications with respect to H₂S and CO₂. In current work, we investigated the most important parameters in gas sweetening refineries including CO₂, H₂S and mercaptan removal, caustic solution consumption and temperature distribution throughout the absorption column for sweetening trains utilizing DEA and multi feed scheme. Compared to the conventional amine process utilizing single amine feed, in multi feed scheme acidic gases and mercaptan removal efficiency was slightly higher compared to the conventional process. Besides, the rate of caustic solution in the former process was lower than the latter process which makes multi feed amine sweetening process more economic.

Nomenclature

M	Mass (kg)
MW	Molecular weight (kg/mol)
P _s	Pressure in standard condition (1 bar)
R	Universal gas constant (J/mol.K)
T _s	Temperature in standard condition (15°C)
y	Vapor mole fraction

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