

Selecting Optimal Acid Gas Enrichment Configuration for Khangiran Natural Gas Refinery

A. Garmroodi Asil and A. Shahsavand*

Chemical Engineering Department, Faculty of Engineering,
Ferdowsi University of Mashhad, Mashhad, Iran

Abstract: Performance and capacity of sulfur recovery unit (SRU) are greatly affected by the $\text{H}_2\text{S}:\text{CO}_2$ ratio of the acid gas stream. The acid gases in Iran contain around 35 mol% H_2S and 60 mol% CO_2 . This low concentration of H_2S calls for more complex sulfur plant, larger equipments, and higher costs. Acid gas enrichment processes (AGE) is run to upgrade low quality acid gas collected from gas treating units in to higher quality Claus plant feed stream. Using specially formulated solvents or modifications of the existing gas treating units are the most popular approaches for efficient acid gas enrichment.

Three different enrichment schemes are considered and simulated for Khangiran refinery acid gas stream. The results are then compared with each others to select the optimal AGE scheme, which can maximize the H_2S content of SRU feed stream while minimizes H_2S emission to atmosphere. In the first scheme, part of the acid gas leaving the GTU regenerator overhead is recycled back to the main contactor. In the other two, a separate enrichment tower is utilized between the amine flash drum and regenerator. In the second scheme, the enrichment tower pressure is set between regenerator pressure and ambient pressure, while in the third scheme, the enrichment tower pressure is fixed between amine flash drum pressure and regenerator pressure. The simulation results revealed that the SRU feed stream can be significantly enriched from its original value of 33.5 mol% H_2S to about 70 mol%, by applying to the third scheme.

Keywords: Acid Gas, Enrichment, SRU, AGE, Simulation, Khangiran Refinery

1. Introduction

Many sour natural gas reservoirs contain significant amounts of carbon dioxide. Upon treating, the resulting acid gas stream is likely to contain relatively low H_2S concentrations making it inappropriate for Sulfur Recovery Unit (SRU), which uses the conventional Claus process (Weiland, 2008).

Carbon dioxide acts as an inert component in SRU feed. Although it does not participate in most of SRU chemical reactions, but it can thermodynamically affect many sulfur production reactions. The existence of CO_2

dilutes the SRU feed, retards most reactions and reduces the overall conversion to elemental sulfur.

Furthermore, extreme dilution of SRU feed stream by very high amounts of CO_2 may cause severe flame instability in the combustion chamber. In the worst case, excessive amounts of CO_2 can completely quench the combustion chamber flame. Reducing furnace temperature is another side effect of too much CO_2 existence in SRU feed stream which in some situations can even lead to incomplete H_2S combustion (Al Khateeb & Al Utaibi, 2009; Palmer, 2003).

* Corresponding Author.

Authors' Email Address:

Ali Garmroodi Asil (ali_garmroodi@yahoo.com), Akbar Shahsavand (Shahsavand@um.ac.ir)

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It is evident that for higher Claus process reaction furnace temperatures ($T \geq 926^\circ\text{C}, 1700^\circ\text{F}$), great conversions of H_2S to elemental sulfur will be achieved (B ZareNezhad & Hosseinpour, 2008). Moreover, many aromatic components such as Benzene, Toluene, Ethyl Benzene and Xylene (BTEX), not destructed at low flame temperatures, can severely damage SRU catalysts in catalytic converters and drastically reduce their lifetime (Bahman ZareNezhad, 2009). Many acid gas enrichment schemes, designed to reduce CO_2 contents of SRU feed streams, can severely decrease the BTEX content of the enriched gas.

The combustion chamber adiabatic flame temperature versus acid gas H_2S content of SRU feed shows in Figure 1. As observed, the aromatics (BTEX) are not destroyed when acid gas contains less than 60 mol% H_2S and the same is true for heavy paraffinic hydrocarbons if acid-gas H_2S concentration is less than 50 mol% (Bahman Zarenezhad, 2011).

Various versions of Claus process used for different concentrations of H_2S in acid gas stream and sulfur production capacity are illustrated in Figure 2. The most common scheme is the split flow design where a portion of the dilute acid gas bypasses the main reaction furnace. All of the combustion air and a fraction of the acid gas are fed to the main burner. If the acid gas H_2S concentration is below 20%, the split flow design cannot achieve the required temperature in the main reaction furnace. In these cases, the oxygen enrichment combustion is suggested. For acid gas feeds with an H_2S concentration greater than 50%, a reaction furnace temperature in excess of 926°C ($1,700^\circ\text{F}$) can be achieved through the simple straight-through Claus process (Parks, Perry, & Fedich, 2010). Acid gas enrichment can be applied before SRU to produce a richer acid gas stream and air enrichment may be used in combination with any of the other versions of the Claus unit ("Sulfur Process Technology,").

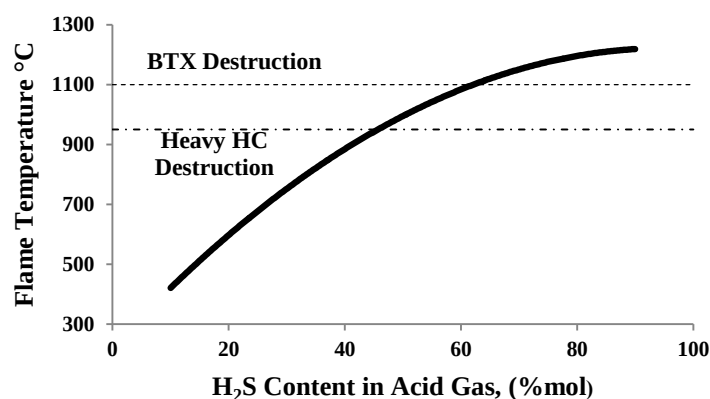


Figure 1. Furnace adiabatic flame temperature versus acid gas H_2S content (Zarenezhad, 2011)

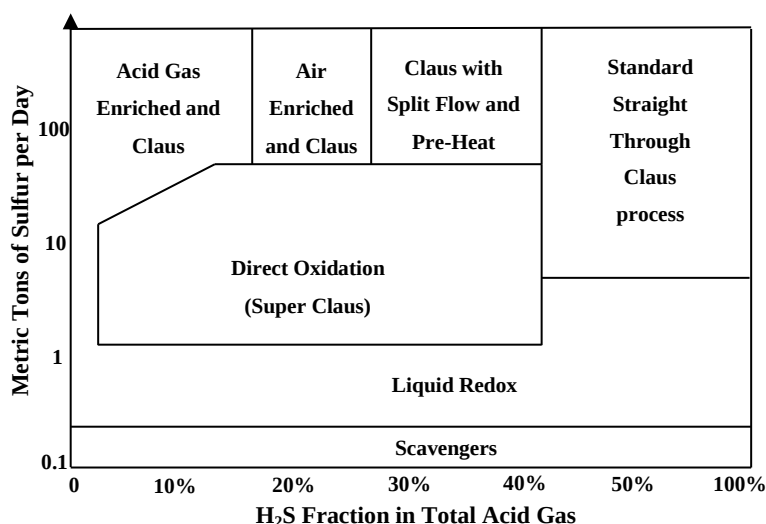


Figure 2. Various schemes of sulfur recovery units (Sulfur Process Technology)

As specified above, the quality of the acid gas feed stream of sulfur recovery units is crucial for proper operation and achieving maximum sulfur recovery efficiency. Improving combustion process and maintaining higher and stable flame temperature in the combustion chamber strongly depends on the $\text{CO}_2\text{:H}_2\text{S}$ ratio in the SRU feed stream. In this regard, acid gas streams with low H_2S concentration should be enriched with H_2S . In the last two decades, a new option for processing dilute acid gas streams which is called Acid Gas Enrichment (AGE) has grown in economical option (Chludzinski & Iyengar, 1993).

AGE processes can be applied to upgrade the low-quality off gas stream obtained from sour Gas Treating Unit (GTU) to high-quality Claus plant feed. The objective of AGE process is to minimize the hydrogen sulfide (H_2S) leaks into the system's vent gas; therefore, producing a gas enriched in H_2S to the greatest extent will be possible. There are various approaches for acid gas enrichment:

a) Solvent oriented approach: This methodology is based on using specifically formulated solvents which selectively absorb H_2S from lean acid gases (with less than 10% H_2S in the presence of CO_2) to produce a high-quality acid gas with an H_2S concentration of up to 75 mol%. Since, the solvent used for enrichment process is different from the GTU solvent, therefore, unlike conventional GTU, this approach usually requires extra absorption-regeneration facility prior to SRU. In this approach, CO_2 is rejected and slips into the off gas which is flared or incinerated (Weiland, 2008).

Sterically hindered amines, either primary or secondary with large bulky alkyl or alkanol groups attached to the nitrogen (Seagraves & Weiland, 2007), exhibit suitable results for selectively absorbing H_2S in presence of CO_2 (by reducing carbamate stability). These amines with their specific molecular configuration selectively absorb H_2S while rejecting CO_2 .

In 1981, ExxonMobil scientists recognized the effect of molecular structure and synthesized the FLEXSORB SE amine for high H_2S selective absorption (Parks et al., 2010; Perry, Fedich, & Parks, 2010; Royan, Warchola, & Clarkson, 1992). Around 6 billion cubic feet per day (BCFD) of sour gas is treated by FLEXSORB SE with another 4 BCFD in the engineering evaluation and design phase (Parks et al., 2010).

In a similar research, in 1983, Satori *et al* designed a process for the selective removal of H_2S from gaseous mixture with severely

sterically hindered secondary aminoether alcohols (Satori, Savage, & Stogryn, 1983). They compared the selectivity of H_2S against moles of H_2S and CO_2 loading per moles of amine for tertiary butyl amino ethoxy ethanol (TBEE), tertiary butyl amino ethanol (TBE) and MDEA. The results indicate that the TBEE has a significant higher selectivity in comparison to other two solvents.

Lu *et al.* used a specific mixture of TBEE and MDEA (1 kmol/m³ TBEE +1.5 kmol/m³ MDEA) in a packed column at atmospheric pressure and a constant liquid flow rate to absorb H_2S and CO_2 from different acid gases (Lu, Zheng, & He, 2006). The effects of H_2S lean solution loading and temperature, the $\text{CO}_2\text{/H}_2\text{S}$ mole ratio in gas mixtures, and the gas flow rate on absorption performance are investigated. Based on the mass balance, the overall volumetric mass-transfer coefficient of H_2S is determined. The performance of simultaneous absorption of CO_2 and H_2S into the MDEA and TBEE aqueous blend is compared with that of the single MDEA aqueous solution. The MDEA and TBEE aqueous blend is found to be an efficient mixed solvent for selective H_2S removal. The experimental results testify the advantages of severe sterically hindered amines (e.g., TBEE) over traditional amines in selective H_2S absorption.

b) Structural oriented approach: here, the existing configuration of GTU is usually modified without changing solvent. Generally, the aim of AGE operation is to enhance the H_2S selectivity by contacting the rich amine leaving the main contactor with a second gas with much higher $\text{H}_2\text{S}/\text{CO}_2$ ratio. Various schemes are used to achieve this task (Al Khateeb & Al Utaibi, 2009; Mak, 2012; Palmer, 2003, 2004, 2006).

All three AGE schemes which are originally introduced to the literature by Palmer (Palmer, 2006), are optimized in this article for efficient enrichment of acid gases leaving Khangiran refinery gas treating unit.

2. Description of Various Enrichment Schemes

Three different acid gas enrichment (AGE) schemes are considered and simulated through Aspen HYSYS V8.3. The obtained results are then compared with one another in order to select the optimal AGE scheme based on enriching the H_2S concentration and overall sulfur recovery efficiency. All three schemes for AGE unit are actually a modification of gas

treating unit (GTU) by adding a few facilities into standard GTU process.

2.1 First Scheme

The schematic diagram of the first scheme for acid gas enrichment is presented in Figure 3 where the dotted lines show the added facilities into standard GTU process. Here, the acid gas leaving the GTU regenerator overhead is split, and a certain fraction of the SRU acid gas feed stream is recycled and returned back to the main GTU contactor. Since the regenerator overhead pressure is around 27 psia and the contactor pressure is usually as high as 1050 psia (to attain maximum desorption and absorption efficiencies, respectively), therefore, three separate acid gas proof compressors (with compression ratio of about 3.5) equipped with intercoolers are required.

This scheme is mostly effective when MDEA solution is used as the absorbent. Since MDEA has much higher selectivity compared to other alkanol amine solvents (e.g. Di ethanol amine (DEA) and Mono ethanol amine (MEA) solutions) and usually has extra capacity for H_2S absorption, it can easily absorb all the hydrogen sulfide returned to contactor by recycling stream. Evidently, this scheme may not be practicable when DEA or MEA are used as solvents. Obviously, the mole fraction of carbon dioxide will be increased in sweet gas stream compared to standard GTU process.

The main drawbacks of this scheme are the limitations of operational capacity due to premature flooding of the contactor and expensive acid gas proof compressors requirement. The main advantage of this scheme is its capacity to enrich hydrogen sulfide in SRU feed stream with several positive implications leading to higher sulfur recovery efficiency.

Assuming fixed amine flow rate enter the main contactor, the extent of enrichment depends on both lean amine stream flow rate entering the packed column and acid gas split ratio (Figure 3). Hence, these two parameters are used as the adjustable variables which should be manipulated to obtain maximum H_2S composition in the SRU feed which would lead to maximum sulfur recovery efficiency.

2.2 Second Scheme

According to Figure 4 and in the second scheme, the selectivity of H_2S toward CO_2 is improved in SRU feed stream by adding a new tower known as "enrichment tower" to the main GTU flow-sheet. As before, a certain fraction of the SRU acid gas feed stream is split and recycled back to "enrichment tower" with no compression required. In this scheme, the "enrichment tower" pressure should be in the range of 17-25 psia, to ensure proper acid gas stream flow from regenerator pressure of around 27 psia and adequate discharge of the off-gas to flare.

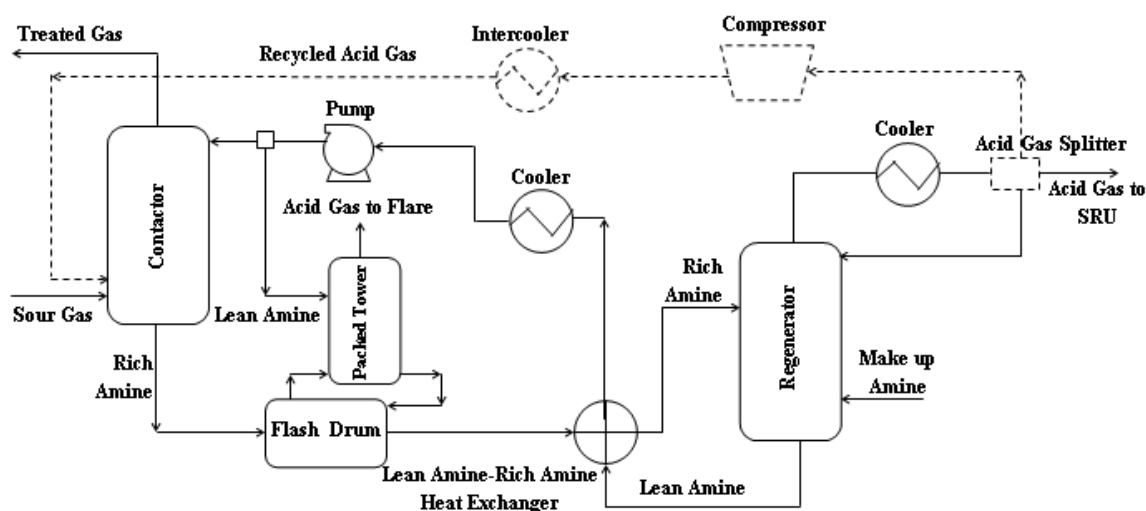


Figure 3. Simplified schematic diagram first scheme

The acid gas is fed into the base of the enrichment tower, where it comes in contact with counter-current flow of rich amine from high pressure contactor entering around the mid-section of "enrichment tower". While the amine solution picks up additional H_2S from recycled acid gas, the CO_2 loading of rich solvent does not change dramatically leading to an increase in the H_2S concentration of the amine solution leaving the base of enrichment tower.

In order to achieve a useful separation in the enrichment tower, it is necessary to eliminate almost all the H_2S from the rectification section vapors. This can be accomplished by introducing a lean stream of tertiary amine which preferentially absorbs the H_2S directly come from amine regenerator and enters the top tray of enrichment tower. Hence, a specific part of lean amine leaving the GTU regenerator bottom is recycled back to the top of enrichment tower. The lean amine stream will nearly absorb the entire H_2S content of rising vapors in the rectification section leading to an overhead stream which essentially contains CO_2 , water vapor plus remaining non-condensable hydrocarbons which are dissolved in the rich amine solution in the high pressure contactor.

Carbon dioxide which is an undesirable contaminant in the SRU feed stream, is pulled out by two means. Firstly, the CO₂ is only partially absorbed in the high pressure contactor, allowing a portion of CO₂ to slip and

remains in the sweet gas. Secondly, CO₂ is slipped in overhead stream of the enrichment tower.

Hydrogen sulfide absorption in rectification section and carbon dioxide desorption in the stripping section occurs simultaneously in the "enrichment tower". Furthermore, since the pressure of the "enrichment tower" is less than the regenerator's overhead pressure; the booster pumps require to pump the rich amine from the bottom of "enrichment tower" to generate the desired regenerator pressure. Three key operational parameters (the portion of acid gas returning to "enrichment tower", the recycled lean amine ratio and the enrichment tower pressure) are the main variables which can be adjusted to achieve optimal SRU feed in terms of H_2S composition which can ultimately provide maximum sulfur recovery efficiency.

The internal recycle of the lean amine can be equipped with a make-up stream to compensate for some of lean amine which may be carried over to the "enrichment tower" overhead. If the recycled acid gas flow to the enrichment tower is limited, then weeping phenomenon will occur inside the "enrichment tower". On the other hand, when extremely high acid gas flow rates are recycled back to the enrichment tower, then flooding will occur. These occurrences can be avoided through more accurate design. The main disadvantage of this scheme is the susceptibility of the regenerator tower to premature flooding specially at high recycle ratios of both acid gas and lean amine.

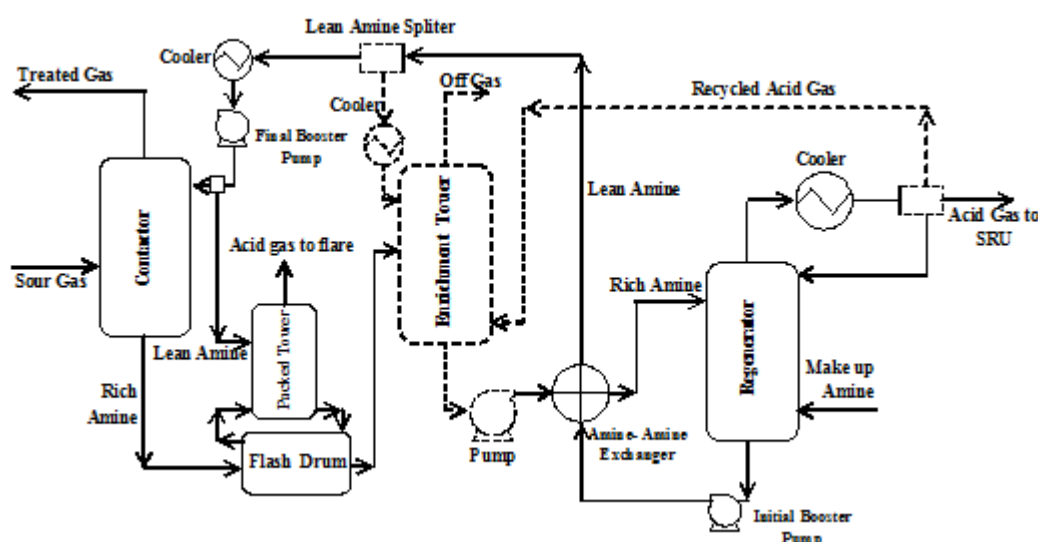


Figure 4. Simplified schematic diagram of second scheme

2.3 Third scheme

A simplified diagram of the third scheme is drawn in the Figure 5. In this scenario, the "enrichment towers" pressure lies between the flash drum and regenerator pressures (90 and 27 psia, respectively). Evidently, at least one corrosion proof compressor is required to compress the acid gas recycle stream to the "enrichment towers" pressure. All the other facilities and operating conditions are similar to the previous scheme.

Obviously, this scheme should provide better H_2S absorption in "enrichment tower", since it operates at much higher pressure, but it requires some expensive equipment (such as corrosion proof compressor), which can be considered as a major drawback.

3. Gas Treatment of Khangiran Refinery

To compare the three enriching schemes with one another, a real case study is required. Khangiran natural gas refinery located at the North Eastern of Iran was founded in late 1970s and commissioned in early 80s. It is expanded in several steps in 2000 and 2004

(Shahsavand & Garmroodi, 2010). It consists of five sour gas treating units (GTUs) with maximum total capacity of around 50 MMSCMD, four sulfur recovery units with a maximum total sulfur production capacity of 2600 tons per day and two topping plants each receiving 183.6 CMD (1155 bbl/day) sweet condensate (Moaseri et al., 2013).

The refining capacity of the plant will rise to 60 MMSCMD by next year (2015) after setting up new sweetening unit. All sweetening units are designed using 34wt% DEA in water as the solvent. To decrease amine circulation rate and save energy in regenerator reboilers and provide extra sweetening capacity of sour gas, 47wt% MDEA solution in water is substituted for DEA solution in 2006. The wet sour gas analysis for the contactor feed of the Khangiran GTUs is presented in Table 1. Many studies are conducted for different parts on Khangiran GTU process in the past decade (Adib, Sharifi, Mehranbod, Kazerooni, & Koolivand, 2013; Farzaneh-Gord & Deymi-Dashtebayaz, 2009; Mahmoodzadeh Vaziri & Shahsavand, 2013; Saghatoleslami, Salooki, & Mohamadi, 2011; Torabi Angaji, Ghanbarabadi, & Karimi Zad Gohari, 2013).

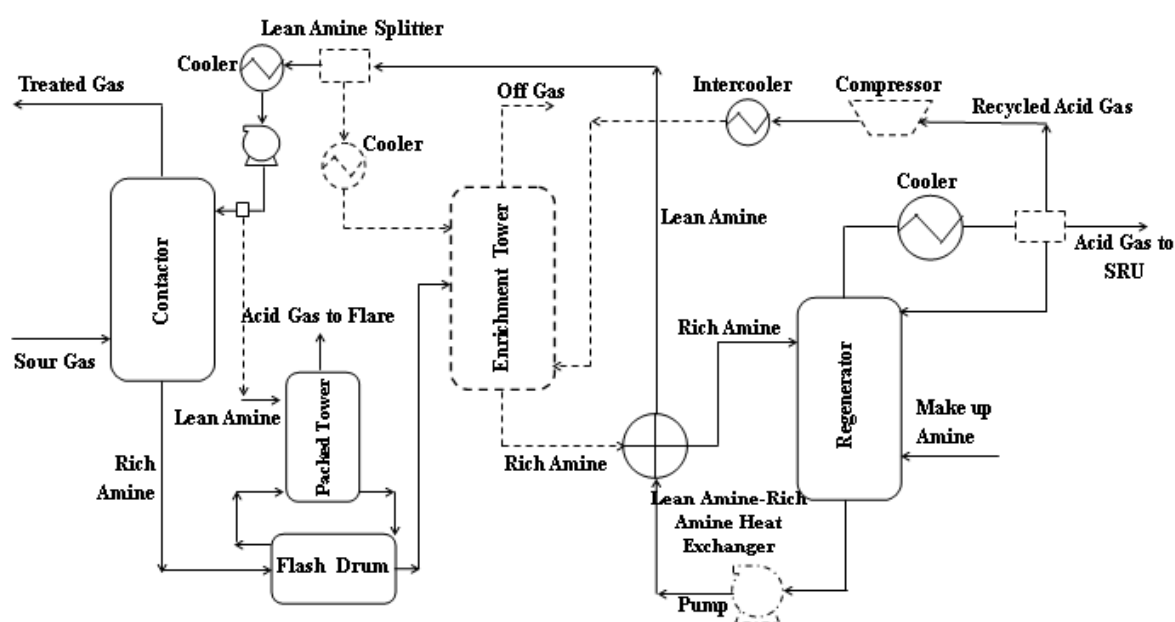


Figure 5. Simplified schematic diagram third Scheme

Table 1. Wet sour gas analysis (mol%) of Khangiran refinery GTUs feed

Components mol %	C ₁ 88.57	C ₂ 0.53	C ₃ 0.06	iC ₄ 0.01	nC ₄ 0.03	iC ₅ 0.01	nC ₅ 0.014	H ₂ O (g) 0.38
Component mol %	C ₆ ⁺ (MW=156) 0.03	H ₂ S 3.57	N ₂ 0.37	CO ₂ 6.43	C ₆ H ₆ 0.015	C ₇ H ₈ 0.005	C ₈ H ₁₀ 0.002	- -

As shown in our previous work, each GTU consists of two parallel trains with two distinct absorbers and two strippers (Shahsavand & Garmroodi, 2010). Therefore, the entire refinery has 10 contactors (with ID=2.895m, H=21m, NT=20) and 10 regenerators (with ID=3.8m, H=24m, NT=24). Although both the trains of each GTU share the same amine and gas flash drums, it is always assumed that each train performs independently and there is no interaction between the two adjacent parallel contactors or strippers. Depressurization of the rich amine stream from 1050 psia to around 90 psia leads to considerable release of volatile gases (such as CO₂, H₂S and methane). The packed column is used to ensure minimum emission of H₂S to the atmosphere. The rich amine stream enters regenerator at the fourth tray (Shahsavand, Derakhshan Fard, & Sotoudeh, 2011; Shahsavand & Garmroodi, 2010).

The acid gas leaving Khangiran refinery's GTU contains about 35 mol% hydrogen sulfide. According to Figure 2, shows that such low quality SRU feed stream requires a split flow with pre-heat scheme for 500 tons per day production of elemental sulfur by each sulfur recovery unit. In the absence of sufficient pre-heat process, serious operational problems rise like combustion chamber low flame temperature, unburned BTEX components, low quality and impure produced elemental sulfur with dark yellowish color. Low acid gas quality combined with the premature catalyst deactivation will eventually decrease the overall efficiency of the entire Claus process from the standard value of 97% to less than 90%.

The entire Khangiran GTU process is initially simulated using Aspen HYSYS (V8.3) simulator by applying the actual operating conditions which has been described in full detail in our previous article (Shahsavand & Garmroodi, 2010). "The simulation results are validated because they indicate close agreement with the real plant data collected

from Khangiran refinery and reported in our previous article" (Garmroodi Asil & Shahsavand, 2014; Shahsavand & Garmroodi, 2010). The most important operating conditions are tabulated once more in Table 2.

The following sections provide the detailed simulation results of various AGE schemes described earlier using Aspen HYSYS simulator. The optimal scheme should maximize the H₂S concentration in SRU feed and minimize the H₂S slippage to atmosphere through the flare. Since in a standard Claus process, less than 3% of the total H₂S entering SRU should be slipped to atmosphere, therefore, this criterion is used for all schemes to ensure minimum H₂S slippage.

4. Simulation Result

All three schemes are simulated and the corresponding simulation results are compared with one another in the coming sections.

4.1 First Scheme

The adjustable parameters of the scenario are molar flow rate of lean amine entering the packed tower (ID=0.762 m, H=6.4 m, positioned above amine flash drum) and split ratio of recycled acid gas stream. These input parameters can be manipulated to obtain the maximum H₂S composition in SRU feed. Due to flooding limitations in the regenerator (or packed tower) and contactor, the molar flow of lean amine to the packed tower and acid gas split ratio should not exceed 170 kmol/hr and 0.7, respectively. Excessive use of lean amine for packed tower can flood the regenerator or packed tower, which extremely high split ratios can lead to flooding of contactor tower.

It should be emphasized that since H₂S concentration of the treated gas remained below the permissible value of 4 ppm for all runs, therefore, the flow rate of lean amine entering the contactor is not required to be varied as an operational parameter.

Table 2. Some operational conditions of Khangiran GTUs.

Stream	Parameter	Temp. (°C)	Pres. (psia)	Flow (kmol/hr)	H ₂ S (mol%)	CO ₂ (mol%)
Sour gas (To contactor)		52	1050	7319	3.57	6.43
Treated Gas		36	1050	6574	0	0.66
Lean Amine (To Contactor)		57	1050	18650	0.03	0.01
Rich Amine (From Contactor)		72	1050	19380	1.35	2.21
Lean Amine (To Flash Drum)		57	90	70	0.03	0.01
Rich Amine (To Regenerator)		99	90	19445	1.35	2.19
Lean Amine (From Regenerator)		121	27	18670	0.03	0.01
Acid Gas (From Flash Drum)		69	90	28.5	0.04	6.81
Acid Gas (From Regenerator)		55	27	755	33.48	56.05

The H_2S mole percent of SRU feed at various amine flow rates entering the packed tower are shown in Figure 6. As it is obvious, the amine flow rate to the packed tower has no practical effect on SRU feed composition. The reason is the low flow rate of amine entering the packed tower (70-170 kmol/hr), compared to the high lean amine flow rate entering main contactor (18650 kmol/hr).

It is observed that the H_2S concentration of the SRU feed stream is relatively constant

(which is not desirable) when acid gas split ratio varies from 0.1 to 0.4. The H_2S mole fraction in SRU feed stream increases for larger split ratios drastically. This phenomenon occurs due to larger slippage of carbon dioxide in sweet gas stream (Figure 7) which decreases the carbon dioxide content of SRU feed stream and hence increases its H_2S mole fraction. Consequently, based on Figures (6 and 7), the optimal split ratio of acid gas stream should be as big as possible (which is around 0.7).

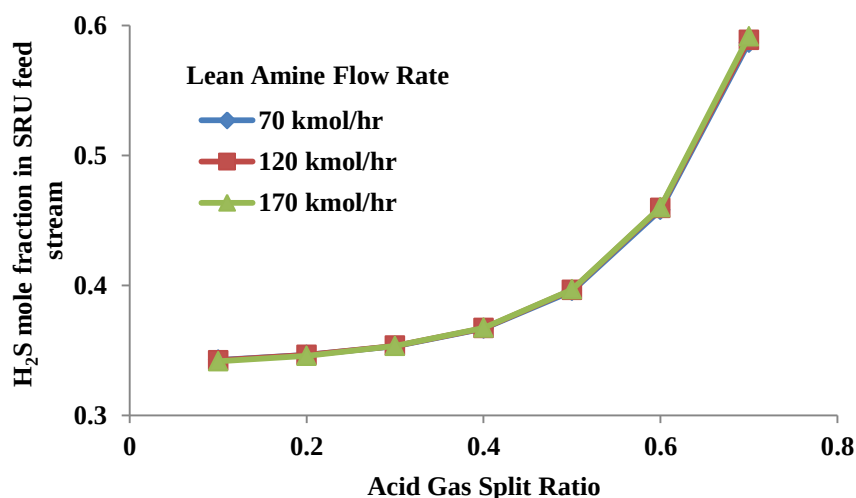


Figure 6. Hydrogen sulfide mole fraction of SRU feed stream versus acid gas split ratio at different amine flow rates entering packed tower

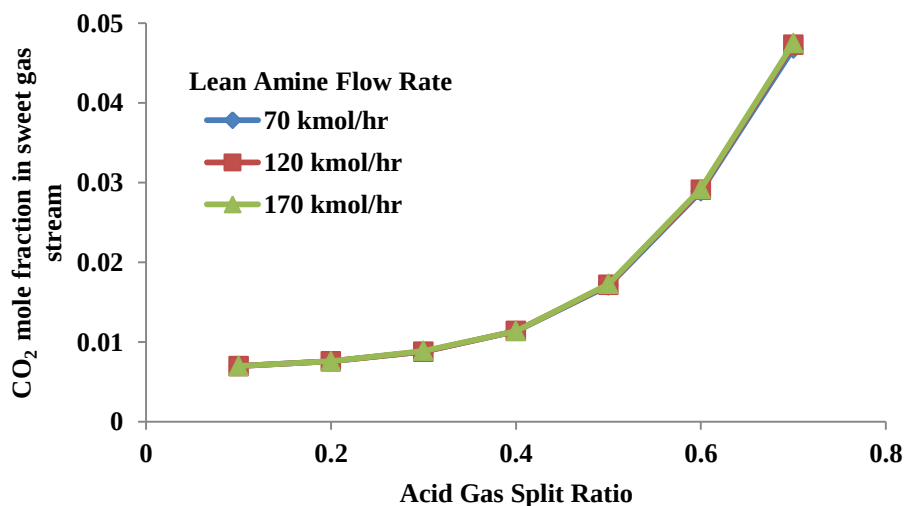


Figure 7. Carbon dioxide mole fraction in sweet gas stream versus acid gas split ratio at various amine flow rates entering packed tower

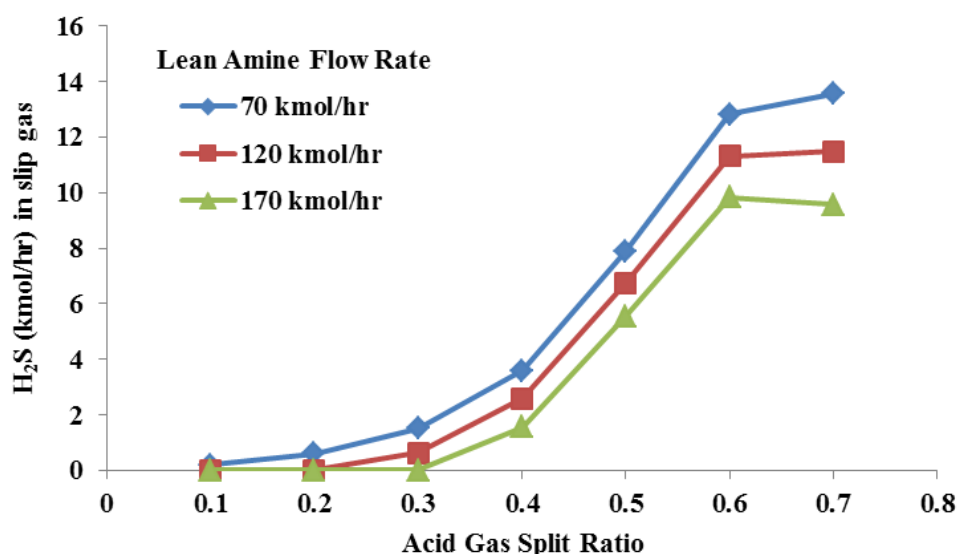


Figure 8. Molar flow of H₂S slipped to atmosphere from acid gas to flare stream (packed tower overhead) versus acid gas split ratio at various amine flow rates entering packed tower

The environmental standards dictate that the H₂S slippage to atmosphere should be as low as possible. As mentioned earlier, this limit is around 3% of the total sulfur entering refinery (around 7.9 kmol/hr out of 262 kmol/hr) for the standard Claus process. According to Figure 8, for acid gas split ratios of less than 0.3, no H₂S is allowed to slip into atmosphere when maximum amine flow rate is used for packed tower. However, using such low split ratio provides minimum enrichment of SRU feed stream. For sufficient enrichment, the optimal split ratio and lean amine flow rate should be around 0.5 and 170 kmol/hr which enriches the SRU feed stream from 33.5 mol% to around 40 mol%.

4.2. Second Scheme

The three adjustable parameters of the second scheme can be manipulated to achieve maximum H₂S concentration in SRU feed stream.

In order to visualize the effects of these three input parameters on various response variables (e.g. H₂S concentration of SRU feed stream, H₂S and CO₂ slippages to atmosphere), one of the input variables is kept constant while the other two variables are varied in their entire ranges. After close examination of the collected simulation results, the optimal values for the two varied parameters are selected and these values are used in consequent simulations to draw future graphs.

As the first attempt, the enrichment tower pressure is kept constant at the midrange value of (21psia). Since, in this scheme, the enrichment tower pressure should be less than regenerator pressure, no acid gas compression is required which is a great advantage of this scheme. Furthermore, the enrichment tower pressure must be kept slightly above the atmospheric pressure to ensure that the overhead off gas has enough energy for ventilation or incineration. Therefore, the enrichment tower pressure can vary in the range of 17-25psia range. Similar to the previous scenario, the flow rate of lean amine entering the main contactor is kept constant for all runs.

The H₂S mole percent of SRU feed versus acid gas split ratio at various lean amine split ratios (fraction of total amine leaving regenerator) at midpoint pressure of 21 psia are shown in Figure 9. The weeping phenomenon is responsible for unstable operation of enrichment tower below the acid gas split ratio of 0.2. Also the amount of the recycled lean amine entering to the enrichment tower should not exceed over 17% of the total lean amine leaving the regenerator tower, since the flooding phenomenon occurs in regenerator. Hence, various split ratios between these extremes are used for lean amine flow.

According to Figure 9, illustrates that the mole fraction of H₂S in SRU feed stream increases drastically when acid gas split ratio

increases to 0.7. No significant change in H_2S concentration is observed when acid gas split ratio exceeds 0.7. Based on results obtained in Figure 9, the optimal values of acid gas and lean amine split ratios are 0.7 and 0.17, respectively.

A detailed examination of figure 10 clearly indicates that using the above optimal values leads to H_2S slippage of around 25 kmol/hr something much higher than the permissible

value of 3%. Note that a standard Claus unit has also its own H_2S slippage to atmosphere, therefore the H_2S escaping to atmosphere should be kept as low as possible. The acid gas and lean amine split ratios of 0.6 and 0.14 can provide sufficiently low H_2S slippages in off gas, respectively. Note that these optimal values are applicable, when the enrichment tower pressure is kept at midpoint value of 21 psia.

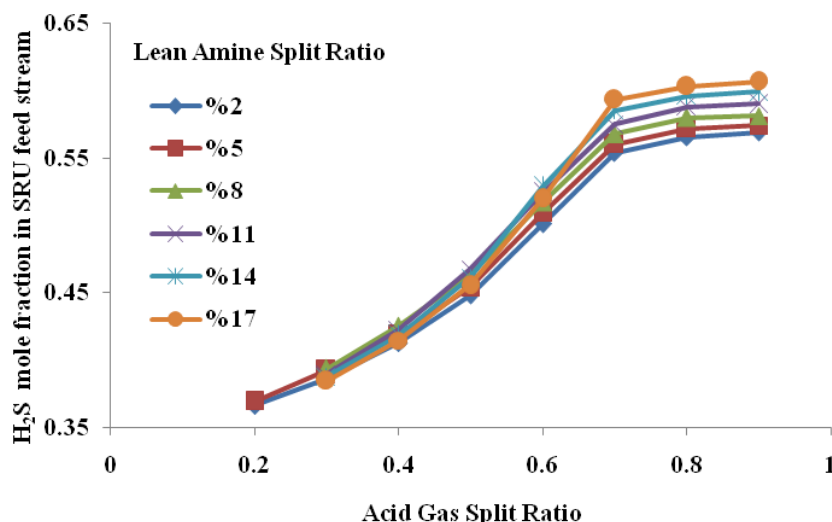


Figure 9. Hydrogen sulfide content of SRU feed stream versus acid gas split ratio at various lean amine split ratios for "enrichment tower" midpoint pressure of 21 psia

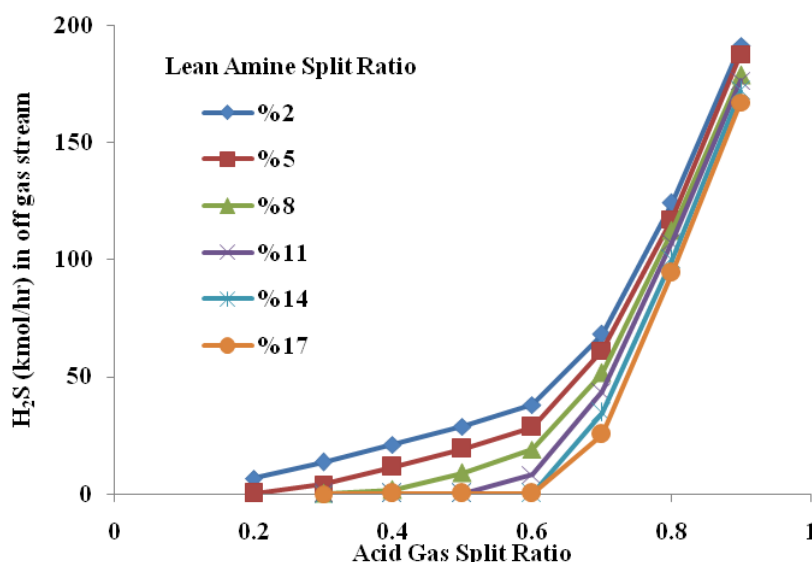


Figure 10. Hydrogen sulfide molar flow in off gas stream versus acid gas split ratio at various lean amine split ratios and midpoint "enrichment tower" pressure (21 psia)

This issue strongly supports in Figure 11 where the distinct maxima at acid gas split ratio of 0.6 and lean amine split ratios of 0.14 are illustrated. Carbon dioxide mole fraction in off gas stream reaches a maximum level of 0.86 at above optimal values. Up to acid gas split ratio of 0.6, the CO_2 slippage increases due to efficient rejection of CO_2 by selective absorption of H_2S in enrichment tower. On the other hand, a sharp increase in H_2S slippage values for acid gas split ratios of higher than 0.6 is the main reason for the decrease in overall CO_2 mole fraction in off-gas stream.

With respect to the fact that the optimal values found so far are valid when the enrichment tower pressure is kept constant at

midpoint value of 21 psia. In Figure 12, it is observed that the H_2S mole percent in SRU feed stream decreases with an increase in the enrichment tower pressure (in the previously specified range of 17-25 psia) up to certain acid gas split ratio of 0.63. After that, the reverse functionality can be observed.

Figure 13 depicts that at acid gas split ratios of less than 0.6 (actually 0.63), the H_2S slippage remains negligible for lean amine split ratios of greater than 0.14. For large H_2S slippage values, the higher pressures of enrichment tower improves its absorption efficiency and provides more H_2S to the regenerator tower which finally enriches its overhead stream with more hydrogen sulfide.

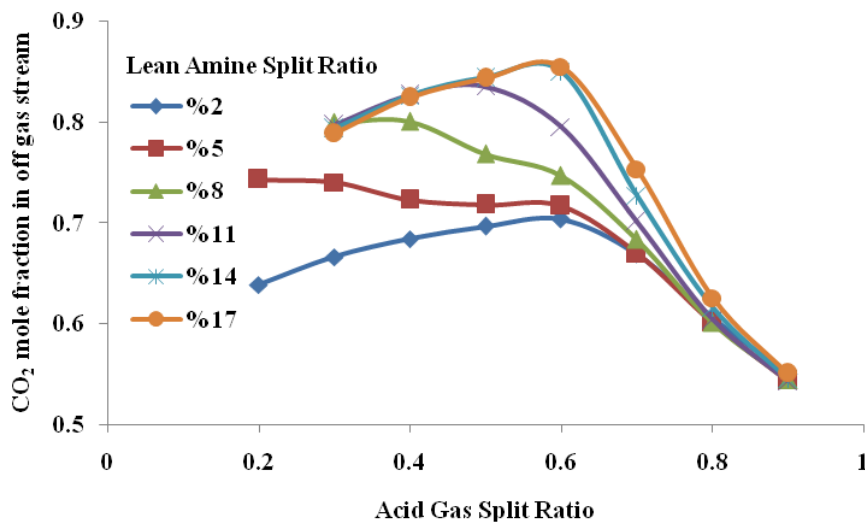


Figure 11. Carbon dioxide content of off Gas stream versus acid gas split ratio at various lean amine split ratios and midpoint "enrichment tower" pressure (21 psia)

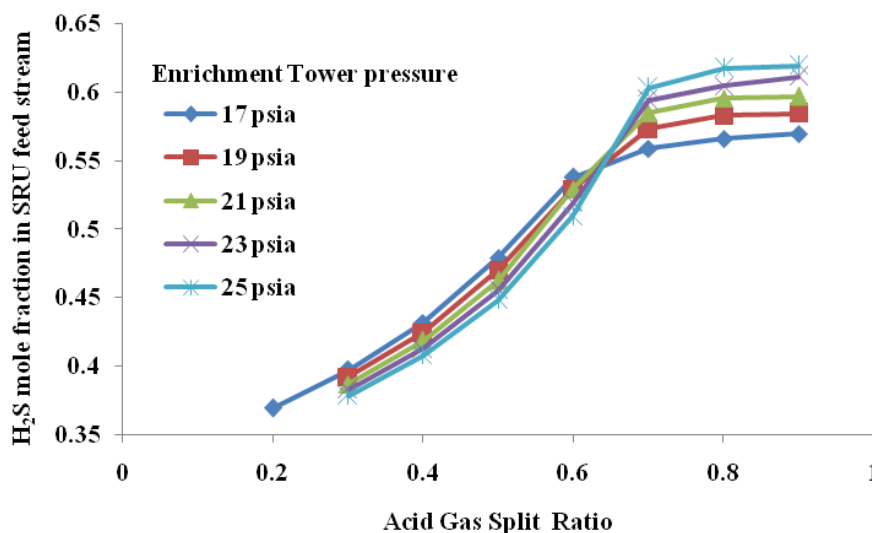


Figure 12. Hydrogen sulfide concentration of SRU feed stream versus acid gas split ratio at various "enrichment tower" pressures and 14% split ratio of recycled lean amine

The distinct maxima around acid gas split ratio of 0.6 is shown in Figure 14. As before, the CO_2 slippage increases due to efficient rejection of CO_2 by selective absorption of H_2S in enrichment tower, up to acid gas split ratio of 0.6. This is followed by a sharp increase in H_2S slippage values mainly causing a decrease in CO_2 concentration in off-gas stream. Thorough examination of Figures 13-15 reveals that the optimal values for acid gas split ratio and enrichment tower pressure are

0.63 and 19, respectively, when the recycled amine split ratio is kept constant at 0.14.

Once again, the acid gas split ratio is fixed at 0.63 and various simulations are performed at different values of recycled lean amine ratios and enrichment tower pressures to find their optimal values.

Figure 15 shows that two distinct sets of (0.17 & 17psia) and (0.14 & 19psia) can be nominated as the optimal values of recycled lean amine split ratio and enrichment tower pressure, respectively.

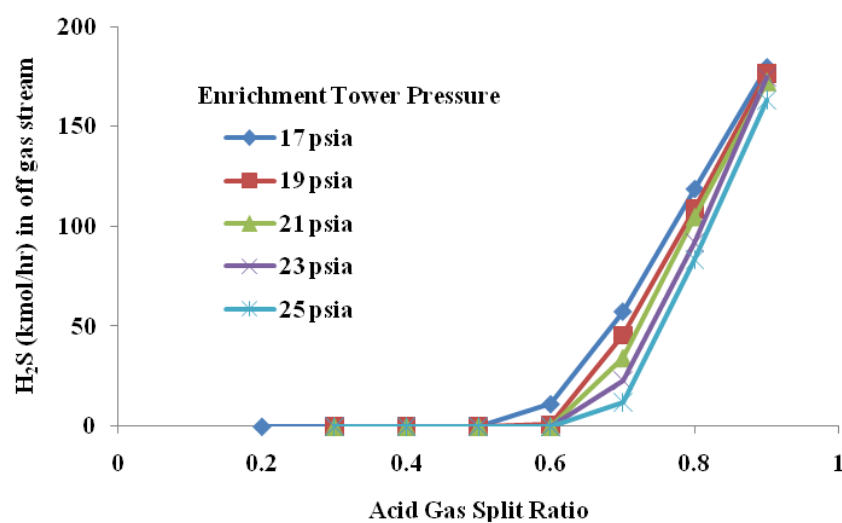


Figure 13. Hydrogen sulfide molar flow rate via off gas stream versus acid gas split ratio at various "enrichment tower" pressures and 14% split ratio of recycled lean amine

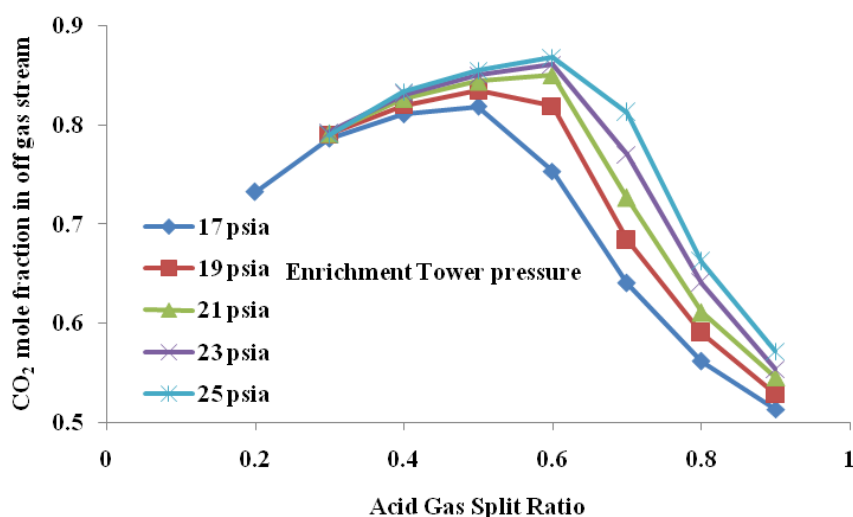


Figure 14. Carbon dioxide concentration of off gas stream versus acid gas split ratio at various "enrichment tower" pressures and 14% split ratio of recycled lean amine

It is revealed in Figure 16 that the first choice provides relatively less H_2S slippage, therefore it should be selected as the optimal values. However, close examination of Figure 17 demonstrates that both sets actually provide very similar CO_2 slippages. The second set (i.e. 0.14 & 19psia) is assumed to be a more realistic

choice since it provides higher ventilation or incineration pressures. Hence, the final optimal values for acid gas split ratio, recycled amine split ratio and enrichment tower pressure are 0.63, 0.14 and 19, respectively which enriches the SRU feed stream from 33.5 mol% hydrogen sulfide to around 54 mol%.

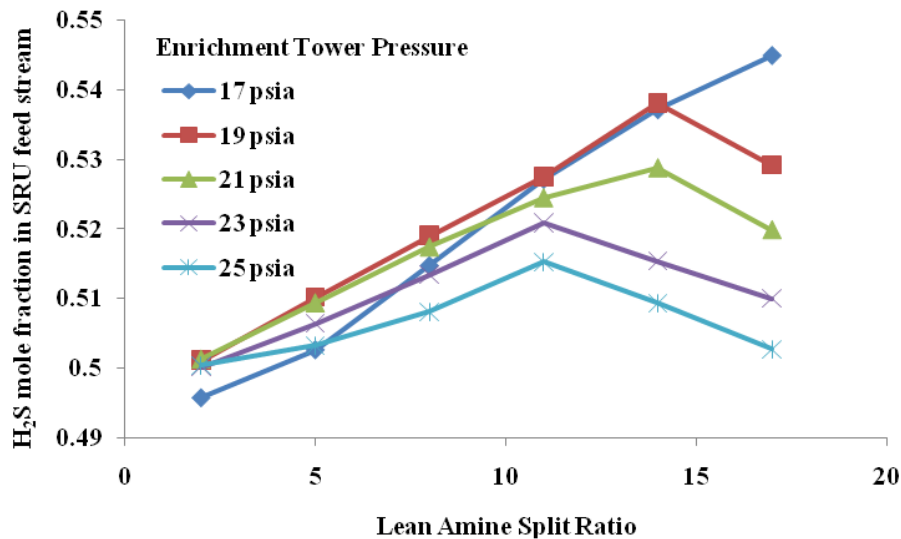


Figure 15. Hydrogen sulfide concentration of SRU feed stream versus recycled lean amine split ratios at various "enrichment tower" pressures and acid gas split ratio of 0.63%

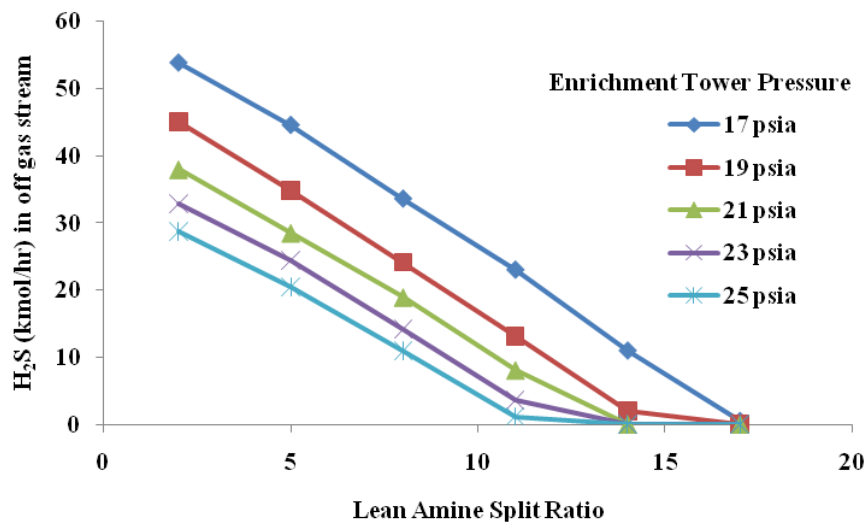


Figure 16. Hydrogen sulfide molar flow rate via off gas stream versus acid gas split ratio at various "enrichment tower" pressures and acid gas split ratio of 0.63%

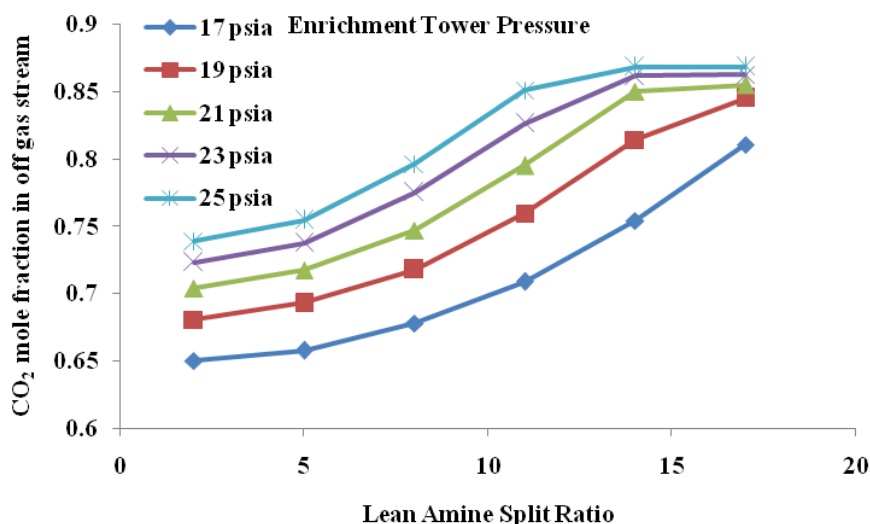


Figure 17. Carbon dioxide concentration of off gas stream versus recycled lean amine split ratios at various "enrichment tower" pressures and acid gas split ratio of 0.63%

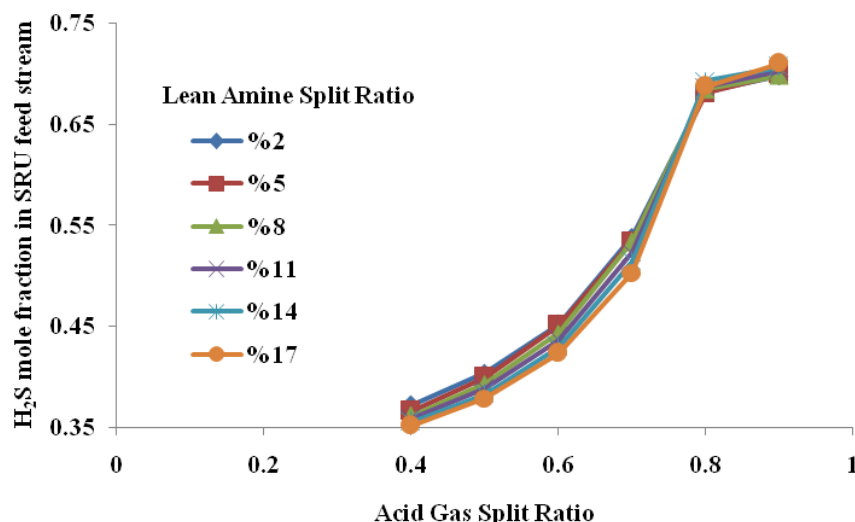


Figure 18. Hydrogen sulfide mole percent of SRU feed versus acid gas split ratio at various lean amine split ratios and midpoint "enrichment tower" pressure (60 psia)

4.3 Third Scheme

In a similar manner to previous scheme, again one of the input variables is kept constant while the other two parameters are varied in order to investigate their effects on H₂S concentration of SRU feed stream and H₂S plus CO₂ slippages to atmosphere via off gas stream. Here, the enrichment tower pressure lies between flash drum pressure (90 psia) and regenerator pressure (27 psia), hence, an acid gas proof compressor is required to compress the recycled gas to the enrichment tower pressure (in the range of 30-90 psia).

As a first trial, the enrichment tower pressure was kept constant around its

midrange value (60 psia) and as before, the lean amine flow rate entering the main contactor was kept constant for all runs. The H₂S mole percent of SRU feed versus acid gas split ratio at various lean amine split ratios at midpoint pressure of 60psia is shown in Figure 18. Once again, weeping occurs below the acid gas split ratio of 0.4 and flooding happens when the lean amine ratio exceeds 17%. These extremes are used to select various split ratios for both the acid gas and lean amine flow rates entering the enrichment tower. Figure 18 clearly shows that the mole percent of H₂S in SRU feed stream tremendously increases when acid gas split ratio goes beyond 0.8. After this value, no significant change in H₂S

concentration is observable. According to the results obtained in Figure 18, the optimal value for acid gas split ratio is 0.8, while the lean amine split ratio has no significant effect and all values between 0.02 and 0.17 provide similar results at optimal acid gas ratio (of 0.8).

Figures 19 and 20 shows that the acid gas and lean amine split ratios of 0.8 and 0.14 provide optimal conditions which can maximize the CO_2 slippage in the off gas stream while minimizing the H_2S slippage. Note that these optimal values are only valid when the

enrichment tower pressure is kept at midpoint value of 60psia.

Carbon dioxide mole fractions in the off gas stream is as high as 90% when those optimal split ratios are used (Figure 20). Up to acid gas split ratios of 0.8, effectual rejection of CO_2 (as a result of selective absorption of H_2S in enrichment tower by tertiary amines) increases the CO_2 slippage rate. On the other hand, sharp increase in H_2S slippage values for acid gas split ratios of higher than 0.8 is the main reason for decreasing the overall CO_2 mole fraction in off-gas stream.

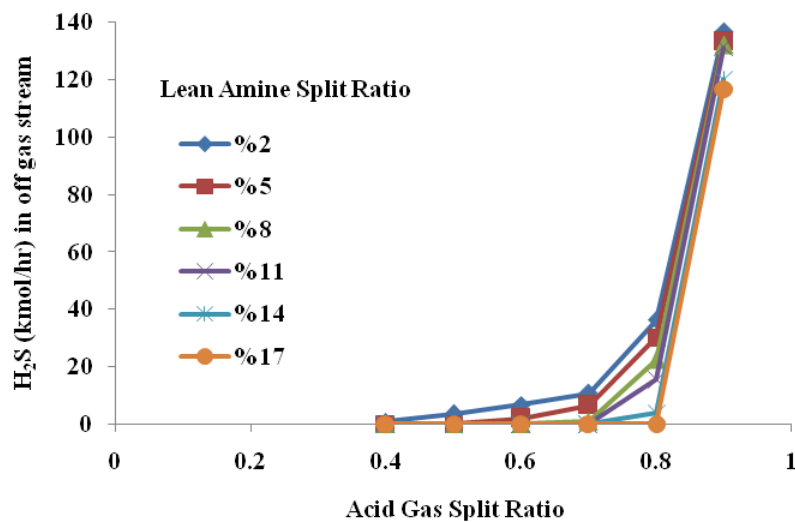


Figure 19. Hydrogen sulfide molar flow in off gas stream versus acid gas split ratio at various lean amine split ratios and midpoint "enrichment tower" pressure (60 psia)

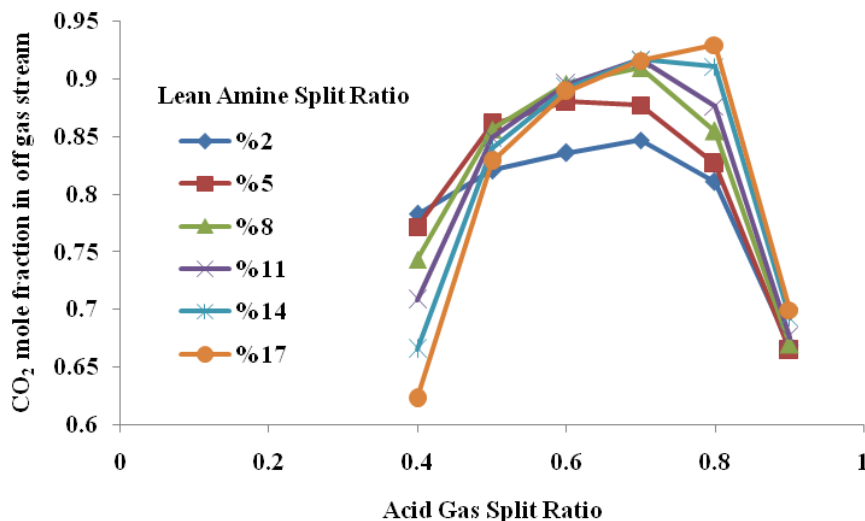


Figure 20. Carbon dioxide content of off gas stream versus acid gas split ratio at various lean amine split ratios and midpoint "enrichment tower" pressure (60 psia)

The effect of the enrichment tower pressure on the H_2S mole percent of the SRU feed stream is shown in Figure 21. The feed enriches with hydrogen sulfide as the enrichment tower pressure decreases from 90 psia to 30 psia, up to a certain acid gas split ratio of about 0.8, followed by opposite trend. At acid gas split ratios of less than 0.8, the H_2S slippage remains negligible for lean amine split ratios of greater than 0.14 and enrichment

tower pressures of over 60 psia (Figure 22). Evidently, the absorption efficiencies improve at higher pressures and supply more H_2S to the regenerator feed which finally suppress the hydrogen sulfide slippage in off gas stream. The mole percent of carbon dioxide in the off gas stream at different acid gas split ratios and various "enrichment tower" pressures for 14% split ratio of recycled lean amine is shown in Figure 23.

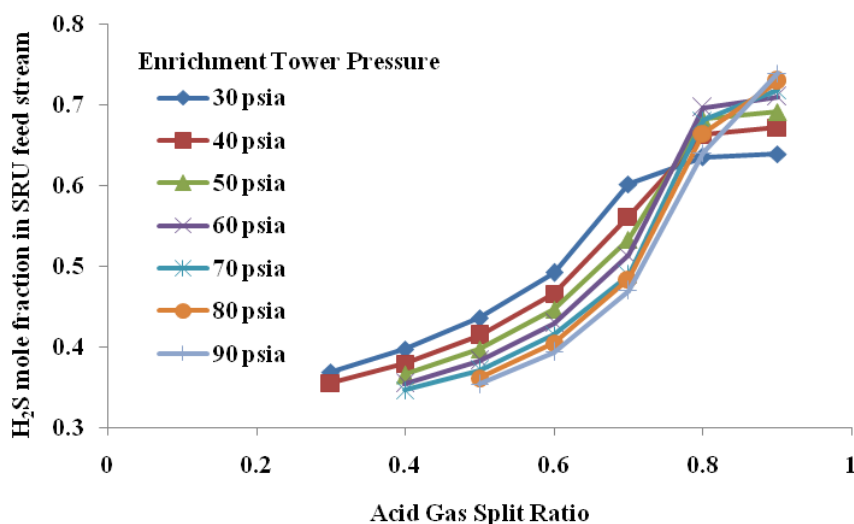


Figure 21. Hydrogen sulfide concentration of SRU feed stream versus acid gas split ratio at various "enrichment tower" pressures and 14% split ratio of recycled lean amine

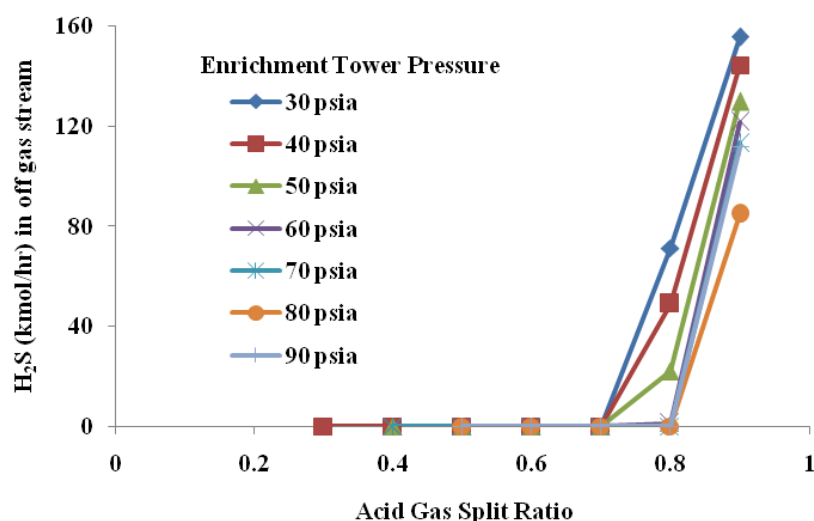


Figure 22. Hydrogen sulfide molar flow rate via off gas stream versus acid gas split ratio at various "enrichment tower" pressures and 14% split ratio of recycled lean amine

Distinct maxima around the acid gas split ratio of 0.8 are clearly observable. Once again, sudden increase in H_2S slippage of the off gas stream is responsible for reducing CO_2 mole percent for extremely high acid gas split ratios. At the optimal conditions of (0.8 & 0.14), the mole percent of carbon dioxide reaches as high as 0.93 and no noticeable difference can be observed when the enrichment tower pressure varies between 60-90 psia. Accordingly, lower enrichment tower pressures are desirable since they require less compression of acid gas stream. Therefore, the optimal values for acid gas split ratio and enrichment tower pressure are 0.8 and 60 psia, respectively, when the

recycled amine split ratio is kept constant at 0.14.

In order to find the global optimal operating conditions, the acid gas split ratio is fixed at 0.8 and several runs are implemented at different lean amine split ratios and enrichment tower pressures.

Up to the enrichment tower pressure of 60 psia, the mole percent of hydrogen sulfide in the SRU feed stream increases as the lean amine split ratio is raised (Figure 24). The reverse phenomenon can be observed for greater pressures. A clear interpretation may not be available due to the high complexity of the overall process.

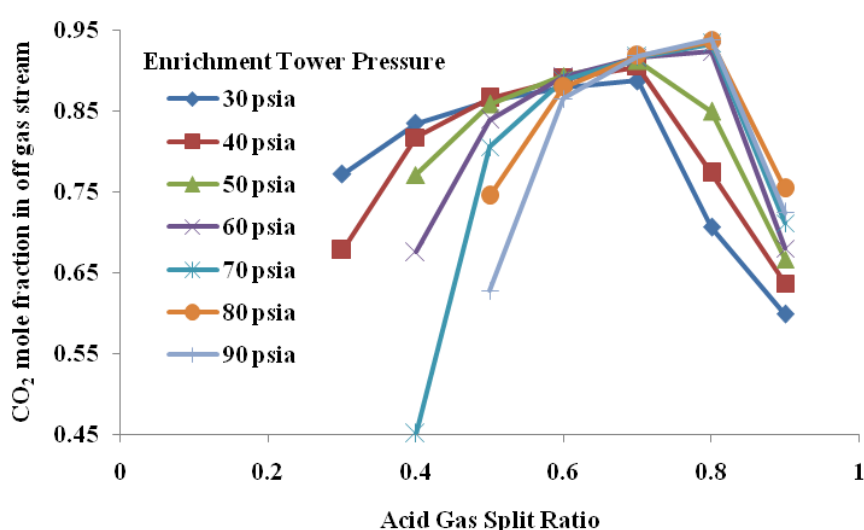


Figure 23. Carbon dioxide concentration of off gas stream versus acid gas split ratio at various "enrichment tower" pressures and 14% split ratio of recycled lean amine

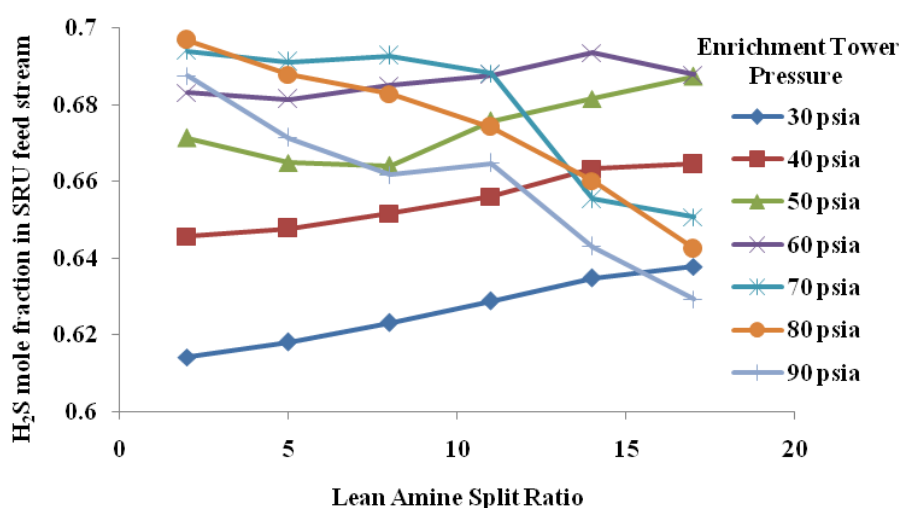


Figure 24. Hydrogen sulfide concentration of SRU feed stream versus recycled lean amine split ratios at various "enrichment tower" pressures and acid gas split ratio of 0.8%

It is observed in Figure 24 that both sets of lean amine split ratio and enrichment tower pressure of (0.2 & 80 psia) and (0.14 & 60 psia) can be considered as the optimal choices, since both provide maximum mole percent of hydrogen sulfide in the SRU feed stream (around 0.7). It is revealed in Figure 25 that at these optimal points, the H_2S slippages in the off gas stream are about 15 and 4 kmol/hr, respectively. Evidently, the first set (i.e. 0.2 & 80 psia) leads to excessive H_2S slippage which is not desirable, while the second set provides acceptable H_2S slippage which is below the permissible limit. Close examination of Figure 26 verifies the previously found optimal values which can raise the carbon dioxide mole percent in the off gas stream as high as 91 mol%.

The overall result of the entire simulation indicate that the final optimal values of acid

gas split ratio, recycled amine split ratio and enrichment tower pressure for the third scheme are 0.8, 0.14 and 60, respectively which can enrich the SRU feed stream from 33.5 mol% hydrogen sulfide to around 70 mol% . Such great enrichment of the acid gas stream has profound effect on the operation of sulfur recovery efficiency at the Khangiran sulfur recovery unit.

Various specifications of different streams for schemes 1 to 3 at the corresponding optimal performances are tabulated in Tables 3 to 5. The acid gas stream leaving the overhead of the packed bed mounted on amine flash drum is exactly the same for all schemes and is not reported in tables 4 and 5. The overall effectiveness of the three different schemes for selective enrichment of H_2S in Khangiran acid gas stream is compared in Table 6.

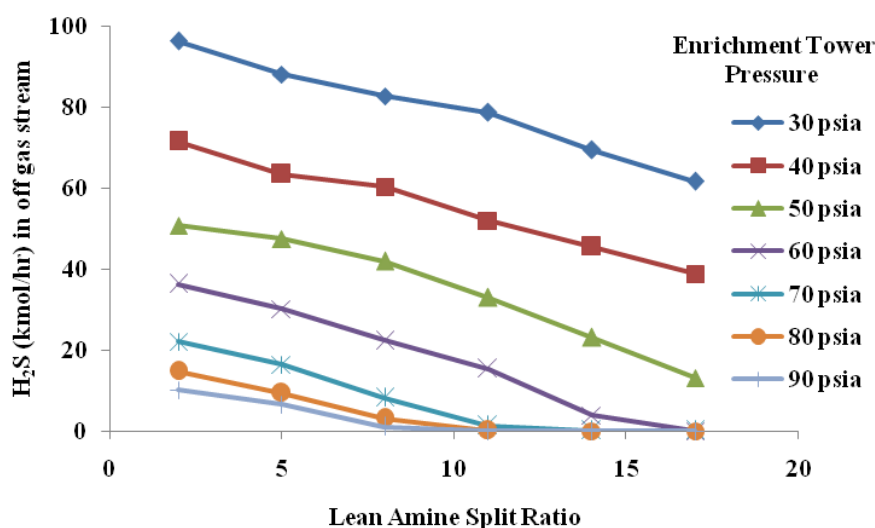


Figure 25. Hydrogen sulfide molar flow rate via off gas stream versus acid gas split ratio at various "enrichment tower" pressures and acid gas split ratio of 0.8%

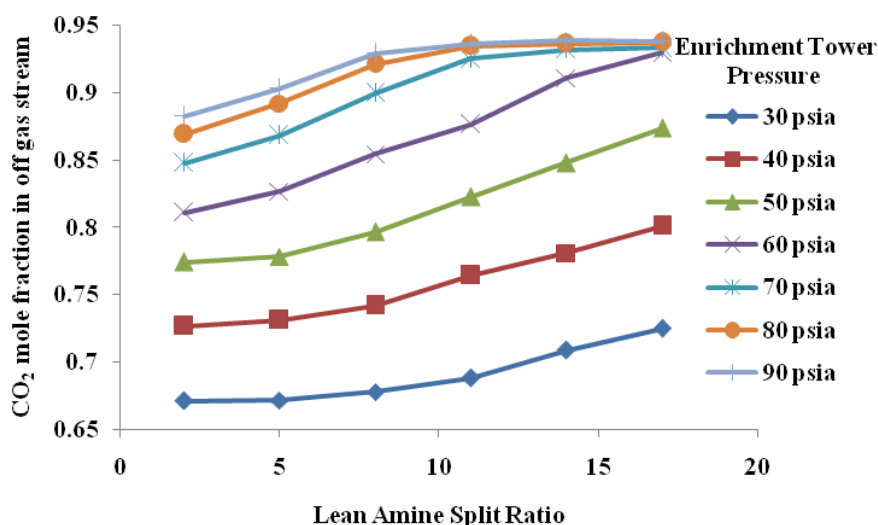


Figure 26. Carbon dioxide concentration of off gas stream versus recycled lean amine split ratios at various "enrichment tower" pressures and acid gas split ratio of 0.8%

Table 3. Specifications of various streams for first scheme at optimal condition

Stream	P (psia)	T (°C)	Flow (kmol/hr)	CO ₂ mol%	H ₂ S mol%
Treated Gas	1050	36	6645	1.70	0.00
Rich Amine (From Contactor)	1050	82	19300	3.44	2.63
Lean Amine (To Flash Drum)	90	57	170	0.02	0.03
Rich Amine (To Regenerator)	90	99	19490	3.27	2.58
Lean Amine (From Regenerator)	27.2	121	18871	0.02	0.03
Acid Gas (From amine Flash Drum)	90	80.57	68	39.81	8.5
Acid Gas (To SRU)	27	55	639	51.11	39.95

Table 4. Specifications of various streams for second scheme at optimal condition

Stream	Pres. (psia)	Temp. (°C)	Flow (kmol/hr)	CO ₂ (mol%)	H ₂ S (mol%)
Treated Gas	1050	36	6687	5.00	0
Rich Amine (From Contactor)	1050	71.58	19380	2.21	1.35
Rich Amine (To Regenerator)	27.2	107	22081	1.85	2.78
Lean Amine (From Regenerator)	27.2	121	21285	0.02	0.05
Off Gas (From Enrichment Tower)	19	60.34	302	82.32	0.6
Acid Gas (To SRU)	27	58.29	452	36.68	54.10

Table 5. Specifications of various streams for third scheme at optimal condition

Stream	Pres. (psia)	Temp. (°C)	Flow (kmol/hr)	CO ₂ (mol%)	H ₂ S (mol%)
Treated Gas	1050	36	6698	5.20	0
Rich Amine (From Contactor)	1050	72.23	19380	2.21	1.35
Rich Amine (To Regenerator)	60	99	21415	1.56	5.24
Lean Amine (From Regenerator)	27.2	121	21296	0.01	0.06
Off Gas (From Enrichment Tower)	60	63	376	91.11	1.20
Acid Gas (To SRU)	27	60.43	305	20.86	69.55

Table 6. Comparison of various schemes for enrichment of Khangiran acid gas stream

	Scheme 1	Scheme 2	Scheme 3
Initial H ₂ S mole percent	0.335	0.335	0.335
Final H ₂ S mole percent	0.400	0.540	0.700

5. Conclusion

Three different acid gas enrichment (AGE) schemes are simulated using Aspen HYSYS V8.3 and compared together for their sulfur recovery efficiency. The simulation results are used in selecting the optimal AGE scheme based on the enrichment H₂S level for the acid gas stream at Khangiran natural gas refinery.

In the first scheme, the optimal enrichment conditions are obtained when the corresponding acid gas split ratios is 0.5 and the lean amine flow rate entering the packed tower (situated over the amine flash drum) is increased to 170 kmol/hr. The enrichment level increased in this scheme from initial 33.5 mol% of hydrogen sulfide in original acid gas stream to around 40 mol%. Since only 19.4% improvement is attained, therefore, both the split flow and pre-heat scenarios should be applied in Claus process. Furthermore, severe limitations of operational capacity due to

premature flooding of the main GTU contactor and requirement of at least three expensive acid gas proof compressors are the most disadvantages of this scheme.

It is found that in the second scheme, the final optimal values for acid gas split ratio, recycled amine split ratio and enrichment tower pressure are 0.63, 0.14 and 19, respectively. The second scheme could enrich the SRU feed stream from its initial value of 33.5 mol% of hydrogen sulfide up to around 54 mol%. Over 60% improvement in the H₂S content of the acid gas stream changes the Claus unit from its present split flow with pre-heat version to the standard straight through Claus process. Merely, a relatively inexpensive booster pump is required to supply rich amine from enrichment tower (19 psia) to the regenerator column (27.2psia).

In the third scheme, the optimal values for the acid gas split ratio, the recycled amine split

ratio and the enrichment tower pressure are 0.8, 0.14 and 60, respectively. This scheme could enrich the Khangiran refinery's SRU feed stream from 33.5 mol% of hydrogen sulfide to around 70 mol%. Once more, such large improvement doubles the hydrogen sulfide content of the acid gas stream which is an appropriate feed for standard straight through Claus process. Using only one compressor to compress the regenerator column overhead stream from 27.2 psia to 60 psia is the only cost born for such drastic improvement.

In the light of above simulations, the second scenario can be considered the best, if minimum capital investment is anticipated. Otherwise, the third scheme can provide efficient enrichment with minimal expenditure.

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References

- Adib, H., Sharifi, F., Mehranbod, N., Kazerooni, N. M., & Koolivand, M. (2013). Support Vector Machine based modeling of an industrial natural gas sweetening plant. *Journal of Natural Gas Science and Engineering*, 14, 121-131.
- Al Khateeb, W. R., & Al Utaibi, A. (2009). Enhancement of acid gas enrichment process: Google Patents.
- Chludzinski, G., & Iyengar, J. (1993). Lean Acid Gas Enrichment with Selective Hindered Amines. *World Intellectual Property Organization, Patent Number WO, 93, 10883*.
- Farzaneh-Gord, M., & Deymi-Dashtebayaz, M. (2009). A new approach for enhancing performance of a gas turbine (case study: Khangiran refinery). *Applied Energy*, 86(12), 2750-2759.
- Garmroodi Asil, A., & Shahsavand, A. (2014). Reliable estimation of optimal sulfinol concentration in gas treatment unit via novel stabilized MLP and regularization network. *Journal of Natural Gas Science and Engineering*, 21, 791-804.
- Lu, J.-G., Zheng, Y.-F., & He, D.-L. (2006). Selective absorption of H₂S from gas mixtures into aqueous solutions of blended amines of methyldiethanolamine and 2-tertiarybutylamino-2-ethoxyethanol in a packed column. *Separation and purification technology*, 52(2), 209-217.
- Mahmoodzadeh Vaziri, B., & Shahsavand, A. (2013). Analysis of supersonic separators geometry using generalized radial basis function (GRBF) artificial neural networks. *Journal of Natural Gas Science and Engineering*, 13, 30-41.
- Mak, J. (2012). Methods and configurations for h₂s concentration in acid gas removal: Google Patents.
- Moaseri, E., Mostaghisi, O., Shahsavand, A., Bazubandi, B., Karimi, M., & Ahmadi, J. (2013). Experimental study and techno-economical evaluation of Khangiran sour natural gas condensate desulfurization process. *Journal of Natural Gas Science and Engineering*, 12, 34-42.
- Palmer, G. (2003). Acid gas enrichment process: Google Patents.
- Palmer, G. (2004). Acid gas enrichment process: Google Patents.
- Palmer, G. (2006). Acid gas enrichment process: Google Patents.
- Parks, L., Perry, D., & Fedich, R. (2010). *FLEXSORB® SE A Proven Reliable Acid Gas Enrichment Solvent*. Paper presented at the Proceedings of the 2nd Annual Gas Processing Symposium: Qatar, January 10-14, 2010.
- Perry, D., Fedich, R., & Parks, L. (2010). Better acid gas enrichment. *Sulphur*, 326, 38-42.
- Royan, T., Warchola, R., & Clarkson, M. (1992). *Acid Gas Enrichment Using FLEXSORB®*. Paper presented at the Proceedings of the 1992 Laurance Reid Gas Conditioning Conference, Norman, Oklahoma, USA.
- Saghatoleslami, N., Salooki, M., & Mohamadi, N. (2011). Auto-Design of Neural Network-Based GAs for Manipulating the Khangiran Gas Refinery Sweetening Absorption Column Outputs. *Petroleum Science and Technology*, 29(14), 1437-1448.
- Sartori, G., Savage, D. W., & Stogryn, E. L. (1983). Process for the selective removal of hydrogen sulfide from gaseous mixtures with severely sterically hindered secondary aminoether alcohols: Google Patents.
- Seagraves, J., & Weiland, R. (2007). *Troubleshooting amine plants using*

mass transfer rate-based simulation tools. Paper presented at the PROCEEDINGS OF THE LAURANCE REID GAS CONDITIONING CONFERENCE.

- Shahsavand, A., Derakhshan Fard, F., & Sotoudeh, F. (2011). Application of artificial neural networks for simulation of experimental CO₂ absorption data in a packed column. *Journal of Natural Gas Science and Engineering*, 3(3), 518-529.
- Shahsavand, A., & Garmroodi, A. (2010). Simulation of Khangiran gas treating units for various cooling scenarios. *Journal of Natural Gas Science and Engineering*, 2(6), 277-283.
- Sulfur Process Technology.
- Torabi Angaji, M., Ghanbarabadi, H., & Karimi Zad Gohari, F. (2013). Optimizations of Sulfolane concentration in propose Sulfinol-M solvent instead of MDEA solvent in the refineries of Sarakhs. *Journal of Natural Gas Science and Engineering*, 15, 22-26.
- Weiland, R. H. (2008). *Acid Gas Enrichment-Maximizing Selectivity.* Paper presented at the PROCEEDINGS OF THE LAURANCE REID GAS CONDITIONING CONFERENCE.
- ZareNezhad, B. (2009). An investigation on the most important influencing parameters regarding the selection of the proper catalysts for Claus SRU converters. *Journal of Industrial and Engineering Chemistry*, 15(2), 143-147.
- Zarenezhad, B. (2011). Consider different alternatives for enriching lean acid gases. *HYDROCARBON PROCESSING*.
- ZareNezhad, B., & Hosseinpour, N. (2008). Evaluation of different alternatives for increasing the reaction furnace temperature of Claus SRU by chemical equilibrium calculations. *Applied Thermal Engineering*, 28(7), 738-744.