Investigation on Zero Flaring during a Gas Refinery Start up: Case study in the South Pars Gas Complex

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Abstract

Flaring is one of the inevitable steps during the gas refineries startup results in production loss and environmental pollution. During the plant start up, off spec gas is sent to flare until it meets the standard specifications and sets in acceptable range. Commonly in refineries the amount of flaring is considerable during start up cause of two main reasons: the first reason is that a good preparation is not being done in gas process units and the second one is trying to meet strict specifications in each process unit.

Some investigations were done on start up procedure, amount of flared gas and flaring duration of refinery start up in Phase 1 South Pars Gas Complex, Located in Assaluyeh the southern area of Iran. It was found averagely 856000 Nm3/train gas is sent to flare which takes 4 hours along during start up with turn down capacity. The main process units including sweetening, dehydration and dew pointing units were simulated by Aspen Plus® simulator. In this paper the effect of all key operational parameters on outlet gas specifications were studied. In sweetening unit the effect of amine feed tray, amine flow rate, inlet gas flow rate, regeneration operational condition, H_2S and CO_2 loading of lean amine on sweet gas H_2S content were investigated. In dehydration unit the main parameters including inlet wet gas flow rate and temperature, moisture content of dry gas, lean TEG, stripping gas flow rate and temperature of TEG reboiler were studied. Moreover in dew pointing unit the thermodynamic condition of inlet gas into the chiller (hydrocarbon dew pointing and hydrate formation) and chiller differential pressure as the most important factors were studied.

The simulated results were compared with operational data and experimental knowledge. The optimum condition was extracted to set the key parameters in order to obtain the minimum flaring and on spec exported product simultaneously during the start up.

Some operational procedures and guidelines were issued. The main parameters such as amine feed tray on 4th branch, amine flow rate of 127-130 m3/hr, amine reboiler temperature of 110 °C, lean amine H_2S loading of 100-150 ppm wt, TEG reboiler temperature of 200-205 °C, stripping gas flow rate of 120-150 Nm3/hr, lean TEG concentration of 99.4% wt, temperature of outlet gas from propane chiller in range of -10 °C were set. Besides that, NACE standard states corrosion is not a concern in case of less than 40 ppmv H_2S content in total pressure of 68 bara based on carbon steel material. From the other side, there is a mercaptane removal unit with molecular sieve adsorption beds as downstream unit which is capable of removing the extra H_2S content of exported gas. So by considering some flexibility, the gas with 25 ppm wt (40 % corrosion safe margin) was introduced from sweetening to downstream units. As the result flaring was decreased with no risk of corrosion and subsequently production loss, energy loss, environmental pollution and finally zero flaring were touched as the main goal.

1. Introduction

The purpose of this report is to set operating parameters during start up of gas trains (sweetening and Dehydration units) to reduce the amount and time of flaring at start up of gas refineries. The results of this paper also can be used for external or internal changes that result in unwanted increase or decrease of the process parameters. In the global petroleum and natural gas industry, flaring of unwanted flammable gases via combustion in open atmosphere flames is regarded as a major environmental concern in addition to wasting the valuable source of energy. Recent estimates from satellite data indicate that more than 139 billion m^3 of gas are flared annually [1],

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an amount equivalent to 4.6% of the world natural gas consumption which totaled 3011 billion m^3 in 2008 (BP, 2010). This amount of flaring produces approximately 281 million tons of CO_2 emissions annually [2]. Emissions from flaring also contribute to the heating of the earth and enhance the natural greenhouse effect of the atmosphere and even climate changes [3] over the coming century. Gas flaring harms the health of the people through emissions that have been linked to cancers, asthma, chronic bronchitis, blood disorders, and other diseases [4-5]. Flaring can also be a source of pollutants such as particulate soot, oxides of nitrogen (NOx), sulfur oxides (SOx), volatile organic compounds (VOCs), unburned fuel, and other undesirable by-products of combustion [6].

A great emphasis has been placed on the source control in modern hydrocarbon processing operations. The technologies contributing to a reduction in the downstream level of source pollutants are costly, and they usually result in the destruction or consumption of valuable hydrocarbon compounds. One exception, where the hydrocarbons are not destroyed, is vapor recovery. In vapor recovery, recovered materials can be recycled to the processing operation, or used as fuel. [7-9] investigated a general methodology on flare minimization for chemical plant start-up operations via plant wide dynamic simulation.

Figure 1 indicates the schematic process diagram of Phase 1. In gas processing plant 1or Phase 1, the 28.3 million cubic meters gas-mixed liquidities are first separated from the pure gas entered into the gas processing plant and then saturated gas is sweetened, moisture-removed, dew point set and mercaptan-removed. Every day, 25 million cubic meters of the produced and refined gas enters into the unified system. Being passed from the two stabilizing gas liquidity units, the separated gas liquidities are sent into the reserving tanks for export, and 40,000 barrels are produced daily. Also, the separated H_2S in the sweetening unit is sent to sulfur recovery units and 200 tons of granular sulfur is produced daily.

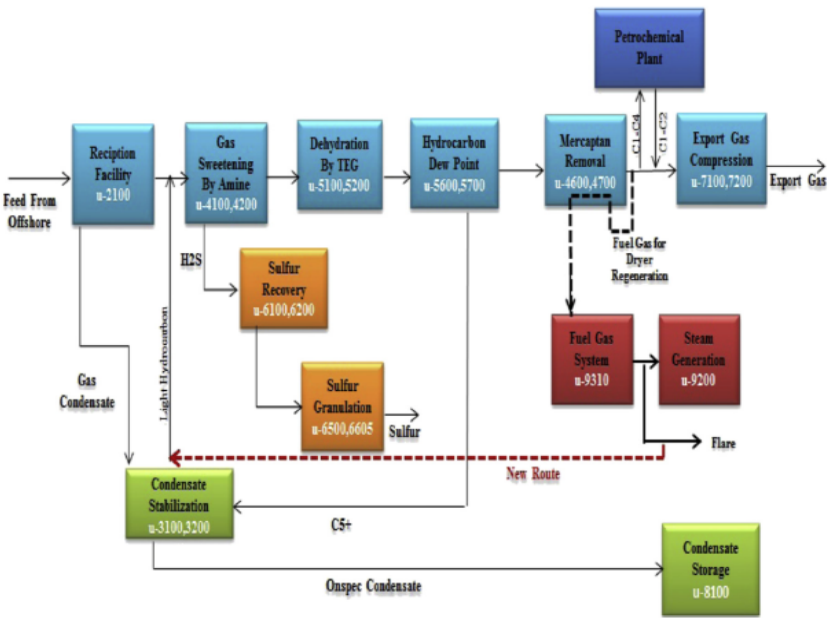

Figure 1: Process block diagram of Phase 1 [10].

2. History of flaring

History of flaring along by 2010 to 2012 in Phase 1 refinery in Assaluyeh, south of Iran which represents the large quantities of gas sent to flare at refinery's start up. Important parameters such as H_2S of sweet gas, H_2S Loading and MDEA Content are indicators which based on these parameters sending the gas to the next unit (Dehydration unit) can be approved or rejected. Therefore, according to these parameters and the way to put them in range, we can provide optimized operational procedure which by using them sweet gas can be transmitted to dehydration unit without sending to flare.

3. Tuning of sweetening parameters:

The history of the sweetening units start ups during 2010 to 2012 reveals this fact that the flaring average duration in order to reduce H_2S of sweet gas less than 3ppm was about 4 hours which is equal to 749000 Nm^3/hr/Train. However in that situation circulating amine was not in suitable situation for use (H_2S Loading was high). Simulation of refinery's units with Aspen Plus® was performed and the results were presented. According to the schematic illustrated in Figure 2, sour gas entering to sweetening unit enters to the first stage of absorption column which will be in contact with the amine (MDEA). Acidic compounds including H_2S absorbed to less than 3ppm and also CO_2 partially absorbed. Absorption column diameter is 4.1m which consists of two sections; packed tower with a height of 4 m at the bottom section and 16 trays (valve type) in the upper section of the column. ELEC-NRTL property method was used which has been developed for non-ideal solutions and electrolytes and also all the reaction equations were introduced.

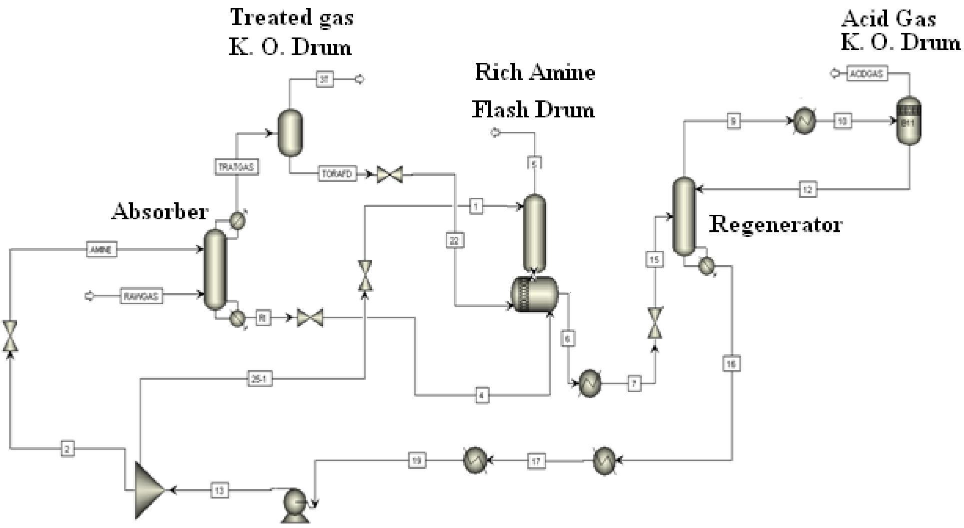

Figure 2: Schematic diagram of sweetening unit

Sour gas inlet temperature and pressure conditions to sweetening unit set on 27°C and 70.5 barg respectively. Also 5560 ppmv H_2S of inlet gas feed was determined according to Rich Summer Case design condition. As can be seen from the simulation results, with turn down sour gas flow rate, by increasing of the amine flow rate from $102m^3/h$ to about $135m^3/h$, H_2S of sweet gas and H_2S Loading rate will increase. The effects of increasing CO_2 and H_2S loading are predominant on the amount of amine flow rate and lead to increasing of the H_2S in sweet gas.

With increasing of sour gas inlet flow rate, the flow rate of amine should be increased accordingly. At higher flow rates of sour gas (greater than $400000Nm^3/h$) two influential factors exist. First one is lean amine residuals (H_2S and CO_2 Loading) and the second one is the level of acid gases along with the sour gas. This means that the H_2S of sweet gas would increase because of two reasons: (1) at low amount of amine flow rates, the high level of acidic components in natural gas would be predominant factor and (2) at high levels of amine flow rate which would be inconsistence with sour gas flow rate, the residual loading of lean amine returned from regeneration package will increase (these effects have been illustrated in Figure 3).

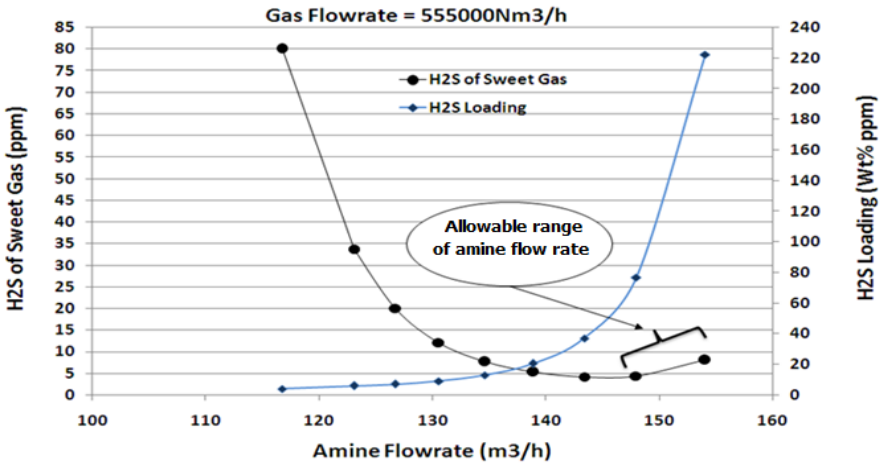

Figure 3: H_2S of sweet gas and residual loading of lean amine vs. Amine flow rate and full load gas flow rate 555000Nm3/h

3.1 Effect of inlet flow rate of sour gas:

As expected, increasing of sour gas inlet flow rate into the absorption column, increase the H_2S of sweet gas. At amine flow rate equal to $140m^3/h$ and a range of inlet sour gas flow rate of $350000\text{-}450000Nm^3/h$, an increasing of H_2S level of sweet gas occurs but does not exceed from the spec. range (3 ppm mol).

3.2 Effect of inlet gas temperature

At the range of turn down inlet gas flow rate and amine flow rate of $130m^3/h$, temperature of inlet sour gas from 20 to 40°C has no significant effect on the amount of H_2S in sweet gas which is much less than the spec range (about 0.8-0.9 ppm mol). By increasing of sour gas and amine flow rates, H_2S in sweet gas changed according to Figure 4. As can be deduced from the corresponding graphs, increasing the temperature from 40°C upwards, leads to increasing of H_2S in sweet gas, so that in the gas flow rate proportional to the amount of amine flow rate, the temperature of sour gas from 20-40°C would be appropriate.

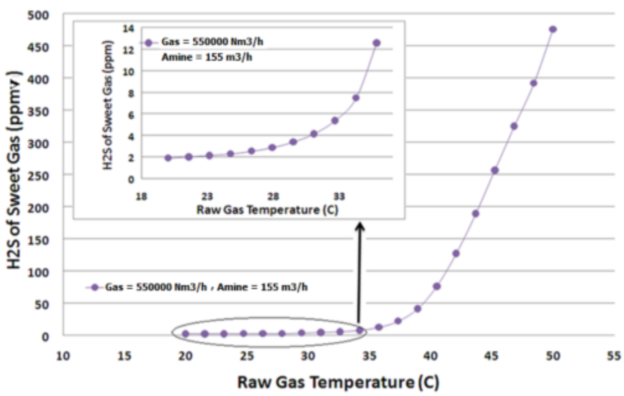

Figure 4: Sour gas temperature effect on H_2S of sweet gas at full capacity flow rate

3.3 Effect of lean amine concentration

According to simulation results decreasing of amine concentration from spec. range (44.5-46.5% wt) increased the H_2S of sweet gas. At the flow rate of 250000Nm^3/h of sour gas different amine concentrations (35%wt to 55% wt) have been investigated. As shown in Figure 5, by increasing the amine concentration, H_2S of sweet gas reduces, but with amine concentrations less than 42% wt and also the amine flow rate at the range of 127-130m3/h, H_2S of sweet gas will exceed from spec. range (< 3 ppm mol).

Moreover at the gas flow rate of 550000Nm^3/h and the appropriate flow rate of lean amine, a decrease in amine concentration to less than spec. range (<44.6 % wt) leads a significant increase of H_2S in the sweet gas and consequently sending sour gas to the flare.

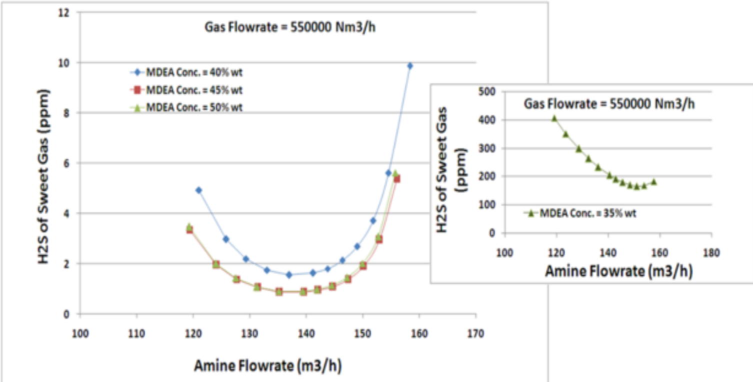

Figure 5: Lean amine concentration effect on H_2S of sweet gas

3.4 Effect of regeneration top temperature

Increase in reboiler duty and also increase in regeneration column top temperature. With turn down sour gas flow rate, the desired top temperature of regeneration column to reach sweet gas H_2S spec. is in the range of 107-111°C. also at lower temperatures, increasing the lean amine residual loading will result poor performance in separating acid gases (H_2S and CO_2) from sour gas in absorption column. As can be seen in Figure 6 the top temperature range should be kept at 100-110°C.

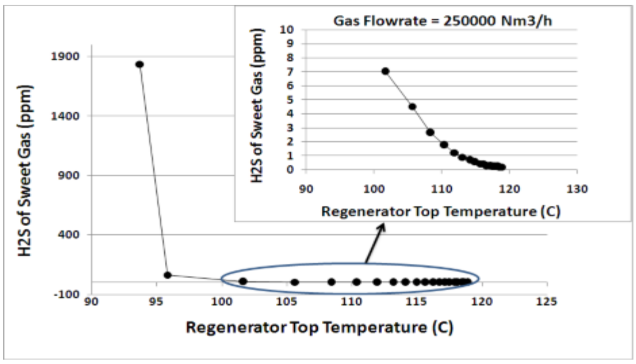

Figure 6: Limitation of regeneration top temperature

3.5 Effect of amine feed tray number

One of the most important parameters in sweetening unit in order to approach the product specification is the amine feed tray in absorption column. Eight inputs considered for amine absorption column in which each entrance is assigned to two trays and the column has a total of 16 trays. Simulation results show that increasing the number of trays, increases the amount of contact between the gas and liquid phases and consequently the absorption of acid gases by amine will be too high. At gas and amine flow rates according to Table 1 the effect of gas temperature increasing and consequently the decision of amine feed tray change summarized in Table 2 and Table 3.

Table 1: Sour gas and amine conditions

Sour gas Conditions	Amine Conditions
Gas flow rate ≈ 560000 Nm^3/h Gas inlet temperature = 21.5-25 °C Gas inlet pressure = 69.5 bar	Amine flow rate = 150 m^3/h Amine temperature = 37 °C Amine pressure = 69.5 bar Feed amine tray = 3[th] inlet feed tray

Table 2: Sour gas inlet temperature increase and its effects on sweet gas and acid gas concentrations

Gas inlet Temperature (°C)	H_2S Sweet gas (ppm)	CO_2 Sweet gas (mol %)	H_2S SRU (mol %)	CO_2 SRU (mol %)
21.5	1.93	1.00	29.61	67.51
22	2.03	1.00	29.68	67.91
23	2.44	1.01	29.87	67.62
24	3.30	1.02	30.08	67.51
25	5.38	1.04	30.30	67.30
26	11.18	1.05	30.52	67.08

Table 3: Amine feed tray effect on the sweet gas and acid gas (SRU) concentration

Feed Amine Tray 3 → 4 Raw gas temperature (°C)	H_2S Sweet gas (ppm)	CO_2 Sweet gas (mol %)	H_2S SRU (mol %)	CO_2 SRU (mol %)
21.5	3.65	1.14	36.27	61.32
22	4.11	1.14	36.34	61.25
23	5.63	1.15	36.57	61.02
24	8.25	1.16	36.74	60.85

But at the goal of this project because of the low SRU flow rate in comparison of the sweet gas flow rate, choosing of that amine feed tray which makes the H_2S of sweet gas lower, is preferential.

4 Pipeline standard for H_2S containing streams

Standard BS EN ISO 15156-2:2003 entitled as "Petroleum, petrochemical and natural gas industries Materials for use in H_2S-containing environments in oil and gas production Part 2: Cracking-resistant carbon and low alloy steels, and the use of cast irons" Section 7 specifies the selection criterion for lines in contact with H_2S. If the partial pressure of H_2S was less than 0.3Kpa or (0.05Psi) any corrosion precautions were not considered. With respect to the permissible level of H_2S (3ppm) and gas pressure of 70bara, the calculated H_2S partial pressure equal to 0.0031psi is less than the criteria considered in this standard. Moreover in order to achieve H_2S partial pressure of 0.05Psi at a total pressure of 70bara, the amount of H_2S can be handled up would be $(0.05/((70\times 14.7)))\cong 50$ppm without any cautions. Also the connecting lines between the sweetening and dehydration units according to Piping Material Specification is

“P-20"-1F2A” which explains it has been made of carbon steel. The next unit’s pipeline specifications have the following characteristics demonstrated in Table 4.

Table 4: Pipeline specifications in the refinery and H_2S limitation criterion

Stream line	Line specification	H_2S limit
Sweetening to Mercaptan Removal Unit pipe lines	P-X”-1F2A*	50 ppmv
Heating gas in MRU regeneration line	P-X”-1G2H	50 ppmv
Export gas	P-X”-1F2C	50 ppmv

5 Dehydration Unit

After sweetening unit, sweet gas enters to dehydration unit which firstly enter into the TEG contactor. This contactor is a packed column with a diameter of 3m and a height of 4m. Sweet wet gas enters from the bottom and TEG enters from the top of the column and contact counter currently, so the dry gas exits the column and rich TEG transferred to the regeneration package with a cold finger design and a concentration criterion of min 99.7wt%. Schematic diagram of dehydration unit demonstrated in Figure 7. For the reason that there are no corresponding equipments in the simulator which simulate performance of the real term equipments we had to build some equivalents.

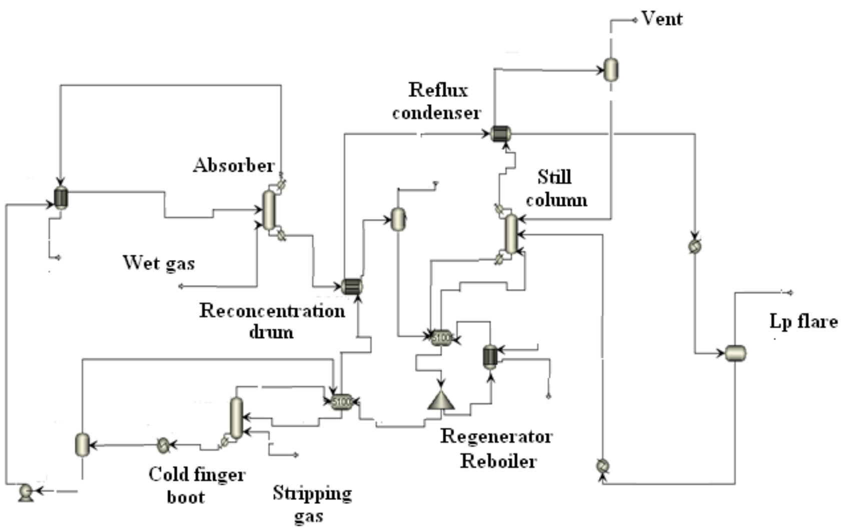

Figure 7: Schematic diagram of Dehydration unit

The criteria of this unit is the moisture concentration of dry gas (max 60ppmv) which more than this value causes pressure drop and undesirable performance in subsequent unit (Hydrocarbon Dew Pointing) and consequently deactivation of molecular sieves in Mercaptan Removal Unit (MRU).

The main parameters in dehydration units include: TEG contactor temperature and pressure, inlet gas flow rate, inlet TEG flow rate, lean TEG purity, reboiler duty, stripping gas flow rate and still column temperature. On the other hand the amount of TEG loss from the top of the still column is another important factor which has to be considered.

5.1 Contactor inlet gas flow rate:

TEG contactor inlet gas temperature and pressure set on 30°C and 69.5 barg respectively. By increasing the wet gas flow rate into the contactor (250000-555000 Nm^3/h) and also TEG inlet flow rate (8500-11000kg/h), the moisture content of dry gas would not exceed from the spec. according to Figure 8.

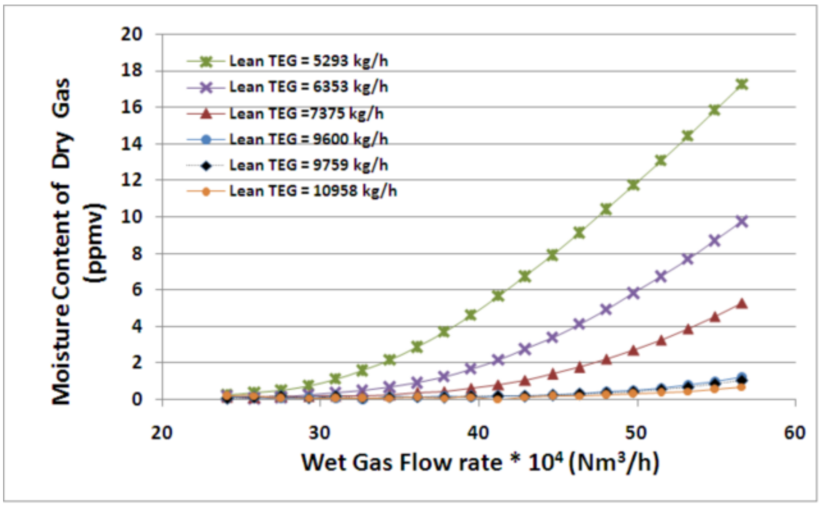

Figure 8: Moisture content of dry gas vs. wet gas flow rate

5.2 Reflux condenser temperature effect on TEG loss:

With increasing of outlet temperature of still column, TEG loss will increase so that with the reflux condenser temperature about 100°C the value of TEG loss would be about $5m^3$/month (Figure 9 and 10). According to simulation results, decreasing of the still column temperature can lead to decreasing TEG loss, but there are some limitations. One of these restrictions is the lean TEG concentration. More investigations show that reflux condenser temperature decrease, causes increasing of return water to the still column and consequently leas to decreasing of semi lean concentration. But because of existence of Re-concentration drum, Cold finger and Blow down drum and moreover the stripping gas as the most effective parameter, there is enough time to re-concentrate the lean TEG to the acceptable range. According to the results, decreasing of the reflux condenser temperature will decrease the TEG loss without negative effects on the lean TEG concentration.

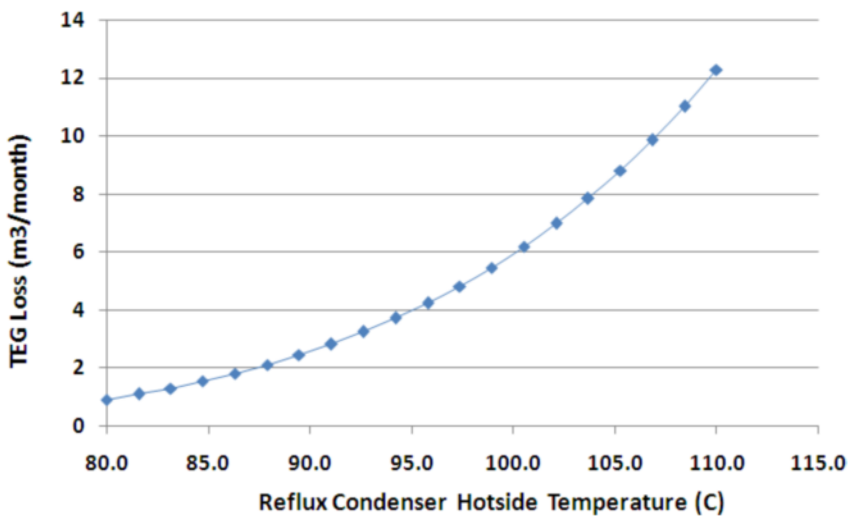

Figure 9: Outlet temperature of still column causes increasing of TEG loss from top of still column

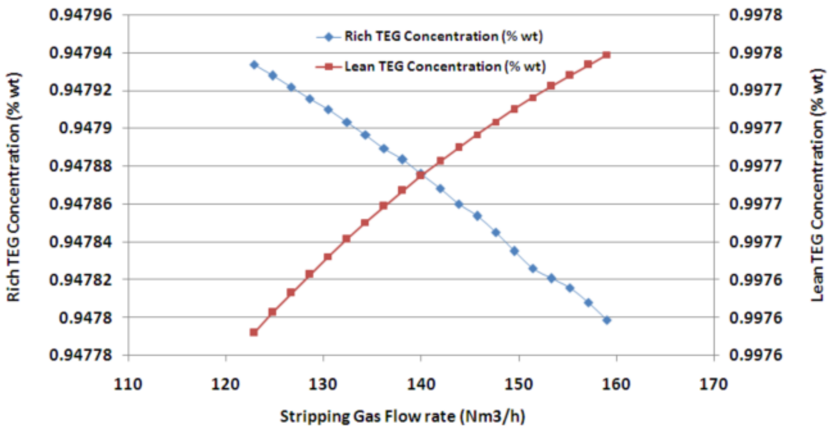

Figure 10: Decreasing of the reflux condenser temperature will decrease the TEG loss without negative effects on the lean TEG concentration

5.3 Reboiler temperature:

According to Table 5 with lean TEG concentration of 99.63 wt%, dew pointing happened on -20°C, so propane compressor temperature in Hydrocarbon Dew Pointing Unit must be set at -20°C for natural gas chilling. If the dew pointing temperature decreased less than this value the risk of hydrate formation increased inside the gas chiller.

Table 5: TEG concentration vs. Dew point temperature

Lean TEG concentration (wt %)	**Dew point (°C)**	**Water content @ dew point (ppm)**
99.5	-15.6	50.5
99.6	-18.9	41.1
99.63	-20	37.9
99.7	-22.2	3.6
99.8	-28.3	21.7

Conclusion:

The most important actions which must be considered at refinery's unit start up include:

1- Adjust the amine feed tray on the 4th tray from the top of the column.
2- Before receiving the sour gas ensure of the suitable amine concentration and lean amine loading. Establishing a hot cycle of amine with a flow rate of 200m^3/h for two hours before start up can be very useful but with consideration of pump sealing and packing from the standpoint of temperature limitation. According to design criteria if the H_2S Loading was in the range of 100-150 ppm wt so it would be in an acceptable range.
3- After establishing a hot cycle of amine, amine flow rate has to decrease stepwise down to the flow rate of 130m^3/h.
4- Adjust sour gas and amine flow rates proportionally according to Table 6:

Table 6: proportional flow rates of sour gas and amine flow rate

Sour gas flow rate (Nm^3/h)	**Amine flow rate (m^3/h)**
250000	127-130
350000	135-140
450000	137-145
555000	148-155

5- In turn down flow rates (below 535000Nm^3/h); inlet sour gas temperature in the range of 20-40°C would be acceptable. Whereas at full load case (100% design) inlet sour gas temperature should not exceed 28-29°C.
6- Lean amine concentration should not lower less than 40% wt.
7- Regenerator top temperature should be in the range of 100-110°C.
8- At start up, amine feed tray could be 3th to 6th tray (4th tray recommended).
9- At start up conditions if H_2S content of sweet gas is less than 30ppm, transferring of sweet gas to the subsequent unit could be allowed.
10- TEG flow rate should be kept at the range of 8500-1100kg/h.
11- Stripping gas flow rate could be at the range of 120-150m^3/h and the pressure set on 2barg.
12- Establishing hot glycol cycle before sweet gas receiving at duration of 1h if possible and set the reboiler temperature at the range of 200-205 °C.
13- According to design criteria, the minimum TEG concentration for declining the hydrate formation risk is 99.7wt% but in order to decrease flaring, the TEG concentration of 99.4 wt% for a short time would be sufficient.
14- At startups and just for short times, propane compressor temperature set on maximum -15°C or less to avoid hydrate formation.

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