SIMULATION OF SEPARATION OF VALUABLE COMPONENTS FROM TEHRAN REFINERY FLARE STACK GASES

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Abstract

In the study separation of hydrogen sulfide in the flare stack gases using alkanolamines solution and the subsequent reduction to elemental sulfur using the CLAUS process has been simulated using Aspen Plus commercial simulator. Additionally hydrogen present in the gases was also separated using a Pressure Swing Adsorption unit. The hydrocarbon constituents consisting mainly of C_1 to C_6 gases were subsequently flash separated. Simulation results show that methyl diethanolamine solution provides the highest amount of absorption of hydrogen sulfide compared to other alkanolamines such mono, di and tri ethanolamines.

Keywords: Clause process; pressure swing adsorption; Aspen Plus; flare stack gases; hydrocarbon recovery.

1. Introduction

Global warming due to the accumulation of greenhouse gases and also increasing fossil flue prices has made separation of valuable gases from refinery flare stacks a commercially viable process. In this study different samples from Tehran refinery were analysed and a typical gas analysis was used as the base sample. The flare gas analysis as shown in Table 1 consist of 40% methane, 17% ethane, 18% propane, 11% butane and about 4% H_2S. Table 2 shows the properties of the flare gas.

Table 1 Analysis of the Tehran refinery flare

Component	Mole %	Component	Mole %
H_2O	0.2	C_3H_8	18.0
H_2	4.7	i-C_4H_{10}	5.3
H_2S	4.0	n-C_4H_{10}	5.2
O_2	0.9	i-C_5H_{12}	0.6
N_2	3.3	n-C_5H_{12}	0.3
CH_4	40.3	C_6H_{14}	0.2
C_2H_6	17.0		

Table 2 Flow properties of the Tehran refinery flare gas

Minimum rate	2180 Ibs/hr
Maximum rate	658179 Ibs/hr
Temperature	235°F
Pressure	13-14.9 psia

2. Outline of the simulation

The first stage of simulation involves the separation of H_2S using amine process and production of elemental sulfur by means of Claus process. Subsequently the hydrocarbon gases are flash separated and the effluent gas stream is sent through a pressure awing absorption system wherein hydrogen is separated. Finally the simulated case is analyzed for its economic viability.

The simulations were carried out in Aspen plus environment and the Aspen Adsim and Aspen Icarus modules were utilized for the different parts of the study.
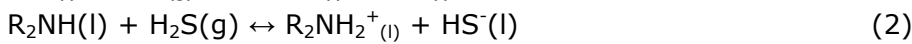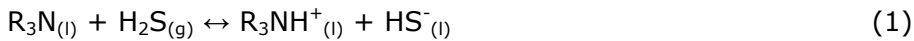
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3. Amine process for H_2S removal

Hydrogen sulfide (H_2S) is a noxious and toxic gas found in crude oils and natural gas. Because it is corrosive to carbon steel and most alloys, it must be removed form processed petroleum products and pipeline-quality natural gas. Furthermore many of the catalysts used for the treatment of hydrocarbons in the petrochemical industry are highly susceptible to poisoning by sulfur compounds.

The amines considered in the simulations were monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA) and methyldiethanolamine (MDEA). The use of blended solutions can produce relevant benefits, joining together the high reactivity of the primary and secondary amines with the low energy requirement for regeneration of tertiary types. Methyl diethanolamine (MDEA) is a tertiary amine that offers the advantage of selective H_2S absorption while allowing a portion of the CO_2 in the sour gas to pass through. This property reduces the solvent solution recirculation rate, thereby using less energy. In this process the flue gas is scrubbed with alkanolamines, an amine based solvent in an absorption column. The alkanolamines solvent is then regenerated in a distillation column thereby releasing a high purity H_2S product

The reactions between alkanolamines and acid gases are believed to proceed in the following sequence:

$$R_3N_{(l)} + H_2S_{(g)} \leftrightarrow R_3NH^+_{(l)} + HS^-_{(l)} \qquad (1)$$

$$R_2NH(l) + H_2S(g) \leftrightarrow R_2NH_2^+_{(l)} + HS^-(l) \qquad (2)$$

$$2RNH_2 + H_2S \leftrightarrow (RNH_3)_2S \qquad (3)$$

$$(RNH_3)_2S + H_2S \leftrightarrow 2RNH_3SH \qquad (4)$$

These reactions are all reversible. The amine complexes can be thermally decomposed to release acid gases, thus effecting regeneration of the solvent. The reaction steps also show that H_2S complexes directly with the amine molecule in one step, whereas CO_2 complexes in two steps. It hydrolyzes to a carbonate first before achieving the final form of complexing in the second step. The two-step process results in a slower reaction rate for CO_2 absorption. Although CO_2 can also react directly with primary and secondary amines to form a corresponding amine salt of a substituted carbamic acid it does not react directly with tertiary amines such as TEA and MDEA. The reaction rate differential between H_2S and CO_2 is useful in controlling the relative degree of absorption for the two acid gases. For example, in an MDEA absorption system, the rate of CO_2 complexing with the amine is much slower than with H2S. As a result, the absorption is more selective towards H_2S. In recent years, this phenomenon has enhanced MDEA's popularity, as a partially selective solvent for H2S removal in applications where a more concentrated H_2S feed gas is desirable or required to increase the throughput of a downstream SRU. Introduced in the 1930s, TEA was the first amine used for industrial gas treatment, but the more stable and reactive MEA and DEA solvents have now largely displaced it. These two primary and secondary amines are particularly effective in reducing moderate concentrations of acid gases (e.g., less than 2.5 mol %) to negligible amounts in the residue gas.

4. Sulfur recovery unit (SRU)

The H_2S lean gas stream from the Amine plant must be treated prior to emission to the atmosphere. The recovery of elemental sulfur is the preferred treatment of the acid gas streams formed from Amine plant. However, in some cases it may be acceptable to oxidize this stream into sulfur dioxide (SO_2). Sulfur recovery typically involves application of the Claus process using the reaction between hydrogen sulfide and sulfur dioxide yielding elemental sulfur and water vapor:

$$2H_2S_{(g)} + SO_{2\,(g)} = (3/n)\,S_{n\,(g)} + 2H_2O_{(g)} \qquad \Delta H\ rxn = -108\ kJ/mol$$
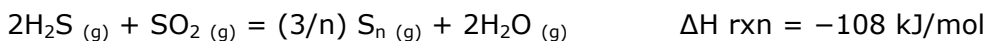
High conversions for this exothermic, equilibrium limited reaction call for low temperatures, the use of which, however, leads to low reaction rates, so that a catalyst must be employed. Even so, high sulfur yields still necessitate a multistage process with interstage cooling and sulfur condensation. According to Le Chatelier's principle, the removal of a reaction product results in an equilibrium displacement to higher conversion. The conventional process is based upon the withdrawal of sulfur by in situ condensation within the reactor. The selective removal of water should, however, be a far more effective technique, as its effect on the equilibrium composition in the mass action equation is much greater:

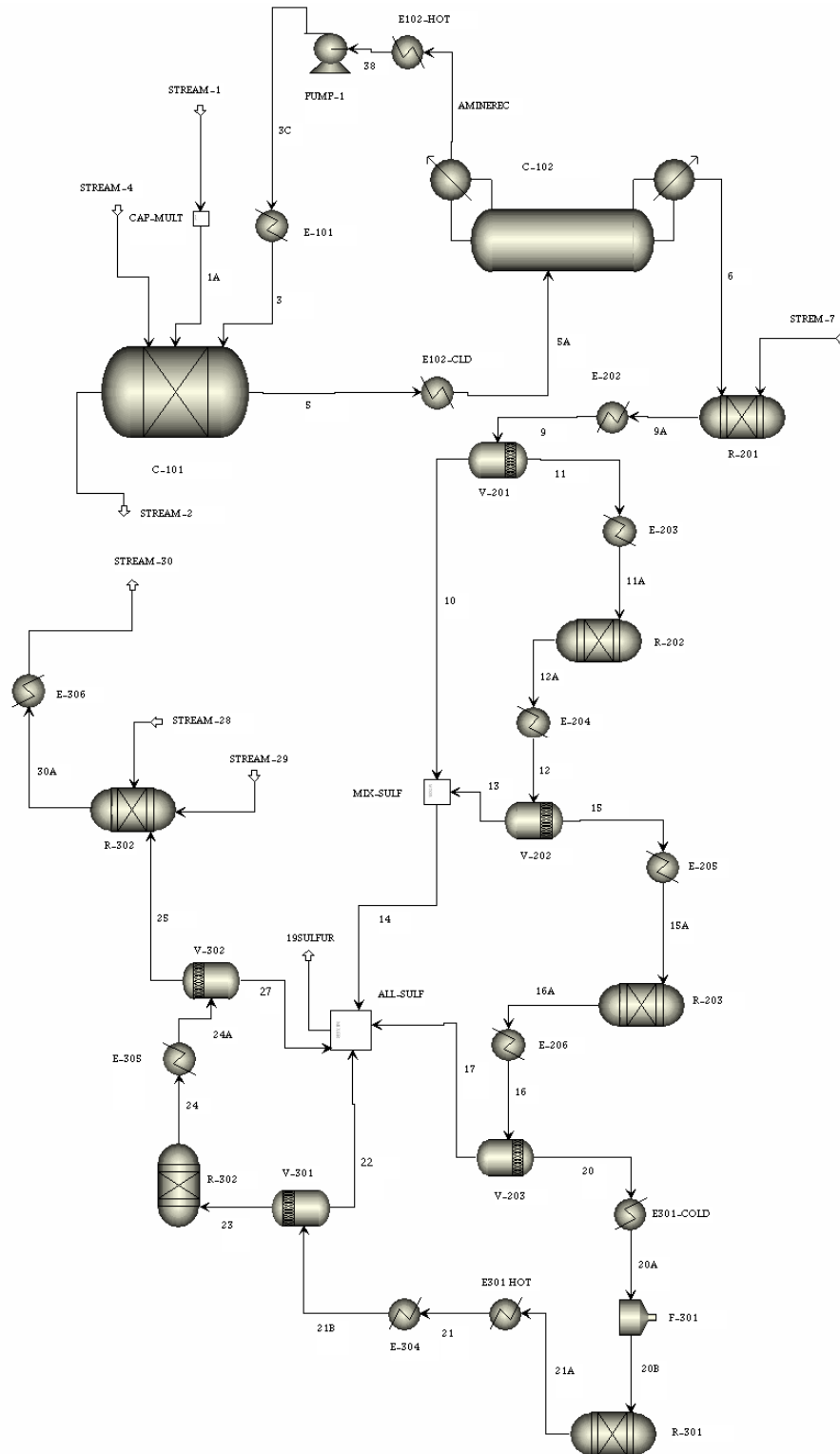$$K_P = \frac{P_{H2O}^2 \; P_{S8}^{\frac{3}{8}}}{P_{H2S}^2 \; P_{SO2}}$$

Figure 1 Process flow diagram for the Amine and SRU plants

The typical Claus process consists of a high-temperature front-end reaction furnace, followed by catalytic reaction stages. A key reaction that occurs in the front-end reaction furnace is the Claus reaction, a two-step sequence, in which H_2S is partially oxidized and then reacts with SO_2 to form the sulfur product. Some other reactions occurring are as follows:

$$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O \qquad\qquad\qquad\qquad (5)$$
$$2H_2S + SO_2 \rightarrow 3S\downarrow + 2H_2O \qquad\qquad\qquad\qquad (6)$$

$$2H_2S + O_2 \rightarrow 2S\downarrow + H_2O \qquad\qquad (7)$$

$$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O \qquad\qquad (8)$$

$$2H_2S + SO_2 \rightarrow 3S\downarrow + 2H_2O \qquad\qquad (9)$$

In terms of these reactions, the primary purpose of the reaction furnace is to provide temperature and residence times such that the exiting gas ratio of H_2S: SO_2, of ideally 2: 1 is maintained. The kinetics of reaction (6) have been well studied at catalytic reactor conditions, however, reaction (6) also occurs at furnace conditions. The ultimate conversion of H_2S via reaction (6) in the furnace can be substantial (over 60% in a straight through configuration) and the extent of this H_2S conversion will have a major impact on downstream processing and ultimately, on overall plant sulfur conversion or conversely environmental emissions. It is therefore important to quantify the extent of reaction (6), at temperature and pressure conditions existing in the reaction furnace.

5. Simulation method details

In the simulations, the ELECNRTL physical property package of Aspen Plus was used. The ELECNRTL property method is the most versatile electrolyte property method. It can handle very low and very high concentrations. It can handle aqueous and mixed solvent systems. The ELECNRTL is fully consistent with the NRTL-RK property method.

Table 1 Listing and operating conditions for equipments used in the Amine plant and SRU

Block name	Block type	Assumptions		
Mult	manipulators	Multiplication factor=1		
E102-CLD	Heater	T=107°C P=27 psia		
C-102	RadFrac	Number of Stages=10 condenser=Partial-vapor, Condenser pressure=1 psia, Reflux Ratio=3 mole, Bottoms to feed ratio= 0.9mole		
E102-HOT	Heater	P=0 Heat Duty=0		
PUMP1	Pump	Discharge Pressure=120 psia		
E-101	Heater	P=-5 psia T=43°C		
R-201	RYield	P=25 psia T=315°C		
E-202	Heater	T=160°C P=0		
V-201	Flash2	T=160°C P=0		
MIX-SULF	Mixer	P=0		
E-203	Heater	T=235°C P=0		
R-202	RYield	T=320°C P=-5 psia		
E-204	Heater	T=160°C P=0		
V-202	Flash2	T=160°C P=0		
E-205	Heater	T=205°C P=0		
R-205	RYield	T=250°C P=21 psia		
E-206	Heater	T=142°C P=0		
V-203	Flash2	T=142°C P=21 psia		
ALL-SULF	Mixer			
E301COLD	Heater	T=280°C P=0		
F-301	Heater FURNACE	T=300°C P=-5 psia		
R-301	Reactor RStoic	T=310°C	Reactions:	$COS + H_2O \rightarrow CO_2 + H_2S$
		P=0		$CS_2 + 2H_2O \rightarrow CO_2 + 2H_2S$
E301HOT	Heater	Heat Duty=0 P=0		
E-304	Heater	T=132°C P=0		
V-301	Flash2	T=132°C P=0		
R-302	Reactor RStoic	T=145°C	Reactions:	$2H_2S + SO_2 \rightarrow 3S\downarrow + 2H_2O$
		P=0		
E-305	Heater	T=132°C P=0		
V-302	Flash2	T=132°C P=0		
F-302	Reactor RStoic	T=450°C	Reactions:	$S + O_2 \rightarrow SO_2$
		P=0		$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
E-306	Heater	T=176°C P=0		

Table 1 shows the process equipments and operating conditions used for the simulation of the amine and SRU plant.

Table 2 shows the exit gas stream from the SRU plant and it can be seen that is rich in hydrocarbon gases but virtually no H_2S is present. This stream is taken through a series of flash separators to separate the hydrocarbon gases and subsequently the resulting gas stream is taken through a pressure swing absorber cycle to separate the hydrogen content. Table 3 shows the exit stream from the SRU plant containing the elemental sulfur produced.

Table 2 Physical property and chemical analysis of stream-2

Component	Flow rate (lb/hr)	Component	Flow rate (lb/hr)
H_2O	1.6933	C_3H_8	1.1847E+05
H_2	3.0934E+04	$i-C_4H_{10}$	3.4883E+04
H_2S	0.00	$n-C_4H_{10}$	3.4225E+04
O_2	5923.6110	$i-C_5H_{12}$	3949.0740
N_2	2.1720E+04	$n-C_5H_{12}$	1974.5370
CH_4	2.6525E+05	C_6H_{14}	1316.3580
C_2H_6	1.1189E+05		
Temperature	233.0330°F	Pressure	14.9 psia

Table 3 Physical property and chemical analysis of stream 19 sulfur

Component	Flow rate (lb/hr)	Component	Flow rate (lb/hr)
H_2O	4180.0487	$i-C_4H_{10}$	0.0
H_2	9.4406E-05	$n-C_4H_{10}$	0.0
H_2S	77.8604	$i-C_5H_{12}$	0.0
O_2	0.1750	$n-C_5H_{12}$	0.0
N_2	0.4856	C_6H_{14}	0.0
CH_4	0.0	CO_2	0.0
C_2H_6	0.0	SO_2	46.4794
C_3H_8	0.0	COS	5.4634
CS_2	13.3876		
S	1.6497E+04		
Temperature	300.4287 °F	Pressure	16.0 psia

6. Pressure swing adsorption

In Figure 2 a typical Pressure Swing Adsorption (PSA) unit is displayed. A PSA cycle consists of the following stages of operation:
1-pressurization and adsorption of hydrogen onto solid adsorber
2-blowdown of remaining of the gas
3-depressurization and evacuation of the adsorbed hydrogen
4- normalization of the unit for the next cycle
The adsorbent used in the simulations was zeolite 5x with the specifications as shown in Table 4. The time settings for the different PSA cycles were maintained at the following:
1) Pressurized adsorption at 1 minute
2) Blowdown of the reminder gas at 1 minute
3) Depressurization and evacuation of hydrogen at 3 minutes
4) Normalization of the system at 1 minute
Table 5 shows the properties of the gas flowing into the PSA unit. Tables 6 and 7 show the properties of the outlet streams after 10 PSA cycles.
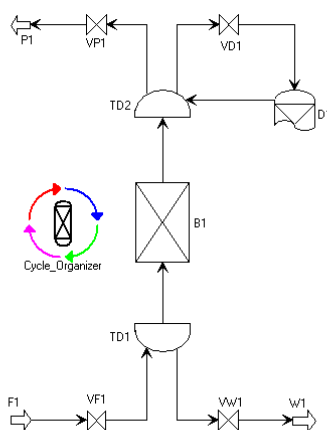
Figure 2 Pressure swing adsorption cycle organizer

Table 4 Specifications of Zeolite 5X type adsorbent used in the simulation

Bulk density	720 Kg/m3
Particule voidage	0.3
Heat capacity	100 J/Kg/K
Particule radius	0.001 meter
Macropore radius	5.000e-09 meter
Micropore radius	1.000e-10 meter
Shaper factor	1

Table 5 Gas stream properties flowing into the PSA unit

Property	Value
H_2 to N_2 ratio	0.364704179 Kmole/Kmole
Temperature	200.9498 K
Pressure	5.0000 atm

Table 6 Hydrogen rich gas stream after 10 PSA cycles

Total Material	0.0938606 Kmole/s
Hydrogen mole fraction	0.572963
Nitrogen mole fraction	0.427063

Table 7 Hydrogen rich gas stream after 10 PSA cycles

Total Material	0.059535 Kmole/s
Hydrogen mole fraction	0.150802
Nitrogen mole fraction	0.849198

7. Conclusion

In this study an attempt has been made to design different processes for the recovery of valuable gases exiting the Tehran flare stack. The first stage the H_2S of the flare gas stream was removed by means of Amine process and then the H_2S rich gas stream was directed into a SRU plant in which a Claus type process was utilized to produce elemental sulfur. The exit gas stream from the SRU plant low in H_2S was used as feed for several stages of flash separations in which the hydrocarbon gases were removed. Finally the exit gas stream was allowed into a PSA unit in which the hydrogen of the gas stream was recovered.

References

[1] Kucka, L., Muller,I., Kenig, Eugeny Y., Gorak, Andrzej: "On the modelling and simulation of sour gas absorption by aqueous amine solutions", Elsevier, Chemical Engineering Science 58 (3571 – 3578), 2003.
[2] Gomez, G., Fueyo, N., Tomas , A.: "Detailed modeling of a flue-gas desulphurization plant" , Elsevier , Computers and Chemical Engineering 31 (1419–1431), 2007.
[3] Alie, C., Backham, L., Croiset, E.,Douglas , P.L.:"Simulation of CO_2 capture using MEA scrubbing : a flowsheet decomposition method", Elsevier, Energy Conversion and Management 46 (475–487), 2005.
[4] Elsner, M.P., Menge, M., Müller, C., Agar, D.W.:"The Claus process: teaching an old dog new tricks" , Elsevier , Catalysis Today 79–80 (487–494), 2003