

Table2.1 Comparison between Sulphur concrete and cement concrete

Properties	Unit	Sulphur concrete	Cement concrete
Density	kg/m ³	2400	2200
Compressive strength	MPa	60-115	15-60
Bending strength	MPa	10-16	6-7
Modulus of elasticity	GPa	35-50	25-28
Contraction	mm/m	0.5-1.0	0.6
Linear coefficient of thermal expansibility	10 ⁻⁶ /K	8-12	8-10
Porosity	%	1-4	9-15
Absorptivity	%	0-1	5
Frost resistance	cycles	500	50
Minimal period for forming an element	Hour	0.1-0.4	48
Minimal period for nominal strength	hours	2-24	28 days
Corrosive durability in aggressive surroundings	-	resistant	partly resistant
Bond content	%	10-15	20-30

2.4 Environmental Impacts

There are a lot of different consequences from oil refineries, be it from direct discharge from the various equipment or operations, or the changing of the landscape around it, although there are numerable impacts, there are two which are most common to the general population and are usually associated with oil refineries and those are global warming and acid rain.

Acid rain is a broad term used to describe several ways that acids fall out of the atmosphere. A more precise term is acid deposition, which has two parts: wet and dry. Wet deposition refers to acidic rain, fog, and snow. As this acidic water flows over and through the ground, it affects a variety of

plants and animals. Dry deposition refers to acidic gases and particles. About half of the acidity in the atmosphere falls back to earth through dry deposition. The wind blows these acidic particles and gases towards buildings, cars, homes and trees.

Dry deposited gases and particles can also be washed from trees and other surfaces by rainstorms. When that happens, the runoff water adds those acids to the acid rain, making the combination more acidic than the falling rain alone. Precipitation that has a pH value of less than seven may contain acidic rain. This is due to the presence of acidic oxide emissions in the atmosphere from industries and vehicles. However, a rainfall that has a pH value of less than 5.6 is considered as acid rain. It is formed when sulphur dioxides and nitrogen oxides, as gases or fine reacts with rain water. Particles in the atmosphere combine with water vapor and precipitate as sulphuric acid or nitric acid in rain, snow, or fog.

2.4.1 Components of Acid rain

The major components of acid rains are sulphur dioxide/sulphur trioxide, carbon dioxide and nitrogen dioxide dissolves in rain water. These components are deposited as dry and wet depositions. When these pollutants are dissolved in water during rain it forms various acids. The chemical reactions of these pollutants are discussed as follows.

- $\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3$ (carbonic acid)
- $\text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3$ (sulphurous acid)
- $\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_2$ (nitrous acid) + HNO_3 (nitric acid)

2.4.2 Causes of Acid Rain formation

Natural sources and human activities are the main causes for the formation of acid rain in the world. Natural source causes are emissions from volcanoes and biological processes that occur on the land, in wetlands, and in the oceans contribute acid-producing gases to the atmosphere; and Effects of acidic deposits have been detected in glacial ice thousands of years old in remote parts of the globe. Whereas, activities of human beings are burning of coal, using Oil and natural gas in power stations to produce electricity, cooking purpose and to run their vehicles are giving off oxide of sulphur, oxides of carbon, oxides of

nitrogen, residual hydrocarbons and particulate matters to the environment. These emissions mix with water vapor and rainwater in the atmosphere producing weak solutions of sulphuric and nitric acids, which fall back as acid rain to the ocean, lake and land.

2.4.3 Impacts of Acid Rain

- Harmful to aquatic life: This is due to increasing the acidity character in water bodies that Stops eggs of certain organisms (e.g. fish) to stop hatching, Changes population ratios and affects their ecosystem.
- Harmful to vegetation: Vegetables are destructed due to increased acidity in soil, Leeches nutrients from soil, and slowing plant growth, poisoning plants, creates brown spots in leaves of trees, impeding photosynthesis, allows organisms to infect through broken leaves.
- Affects human health: Causes respiratory problems, asthma, dry coughs, headaches and throat irritations; Leeching of toxins from the soil by acid rain can be absorbed by plants and animals. When consumed these toxins it affects human's life severely, which cause brain damage, kidney problems and Alzheimer's disease have been linked to people who eat meat of toxic animals/plants by these pollutants.
- Effect on transport: Currently, both the railway industry and the airplane industry have to spend a lot of money to repair the corrosive damage done by acid rain. Furthermore, bridges have collapsed in the past due to acid rain corrosion. Acid rain dissolves the stonework and mortar of buildings (especially those made out of sandstone or limestone). It reacts with the minerals in the stone to form a powdery substance that can be washed away by rain.

2.4.4 Future of Acid Rain

Acid deposition penetrates deeply into the fabric of an ecosystem, changing the chemistry of the soil as well as the chemistry of the streams and narrowing, sometimes to nothing, the space where certain plants and animals can survive. Because there are so many changes, it takes many years for ecosystems to recover from acid deposition, even after emissions are reduced and the rain becomes normal again.

For example, while the visibility might improve within days, and small or episodic chemical changes in streams improve within months, chronically acidified lakes, streams, forests, and soils can take years to decades or even centuries (in the case of soils) to heal. However, there are some things that people do to bring back lakes and streams more quickly. Limestone or lime (a naturally-occurring basic compound) can be added to acidic lakes to cancel out the acidity. This process, called liming. Liming tends to be expensive, has to be done repeatedly to keep the water from returning to its acidic condition, and is considered a short-term remedy in only specific areas rather than an effort to reduce or prevent pollution. Furthermore, it does not solve the broader problems of changes in soil chemistry and forest health in the watershed, and does nothing to address visibility reductions, materials damage, and risk to human health. However, liming does often permit fish to remain in a lake, so it allows the native population to survive in place until emissions reductions reduce the amount of acid deposition in the area.

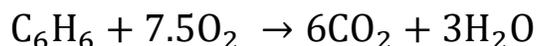
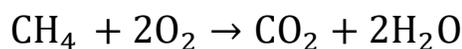
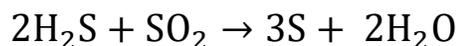
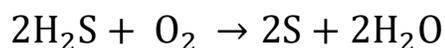
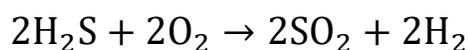
CHAPTER 3

METHODOLOGY

3.1 Selection of case study

Our case study is to attach a sulfur recovery unit to Khartoum refinery in order to increase sulfur production and most importantly, to decrease the harmful emissions that come from the burning of hydrogen sulfide.

3.2 Reaction chemistry



3.3 Process Description

A simplified process flow diagram for the SRU is shown in figure 3.1 the acid gas and air are mixed and fed to the burner at conditions of 21.1°C 273.7 kPa, then sulfur is separated from the burner through a cooler and splitter, afterwards the feed is passed through a conversion reactor to further increase the efficiency of sulfur recovery two reactors are used then in both cases the stream is split to separate the Sulphur.



On average, about 70% of H₂S and SO₂ will react via this reaction, are exothermic and a cooling stage is needed following these steps in order to condense the sulfur produced. The condensed phase is then separated from the gas stream by draining it into container. An interesting property of liquid sulfur is its increase in viscosity with temperature.

This is due to polymerization of sulfur at around 430 K. Therefore, the temperature of condensed sulfur should be closely monitored to prevent polymerization and clogging of pipes used in the process. Care must also

be taken in order not to pass condensed sulfur through the catalyst, which would become fouled and inefficient, liquid sulfur adsorbs to the pores and deactivates the catalytic surface.

A typical Claus process involves one thermal stage followed by multiple catalytic stages in series to maximize efficiency. And the thermal process can be used anymore that's because the insufficient amount of H₂S needed for the reaction to efficiently produce sulphur.

This technology process can possibly provide about 90-97% conversion of the influent sulfur in H₂S to S, which is great efficiency the both recover the economical sulphur and remove the hazardous H₂S and the SO₂ by-product.

This depends on the number of reactors which in case if one reactors is used the efficiency reached by the operation usually ranges between 90%-95% when the second reactor is used the efficiency increases to reach 96-97% when a third reactor is used it becomes 98%; the other remaining 2% can be nearly achieved using a tail gas unit.

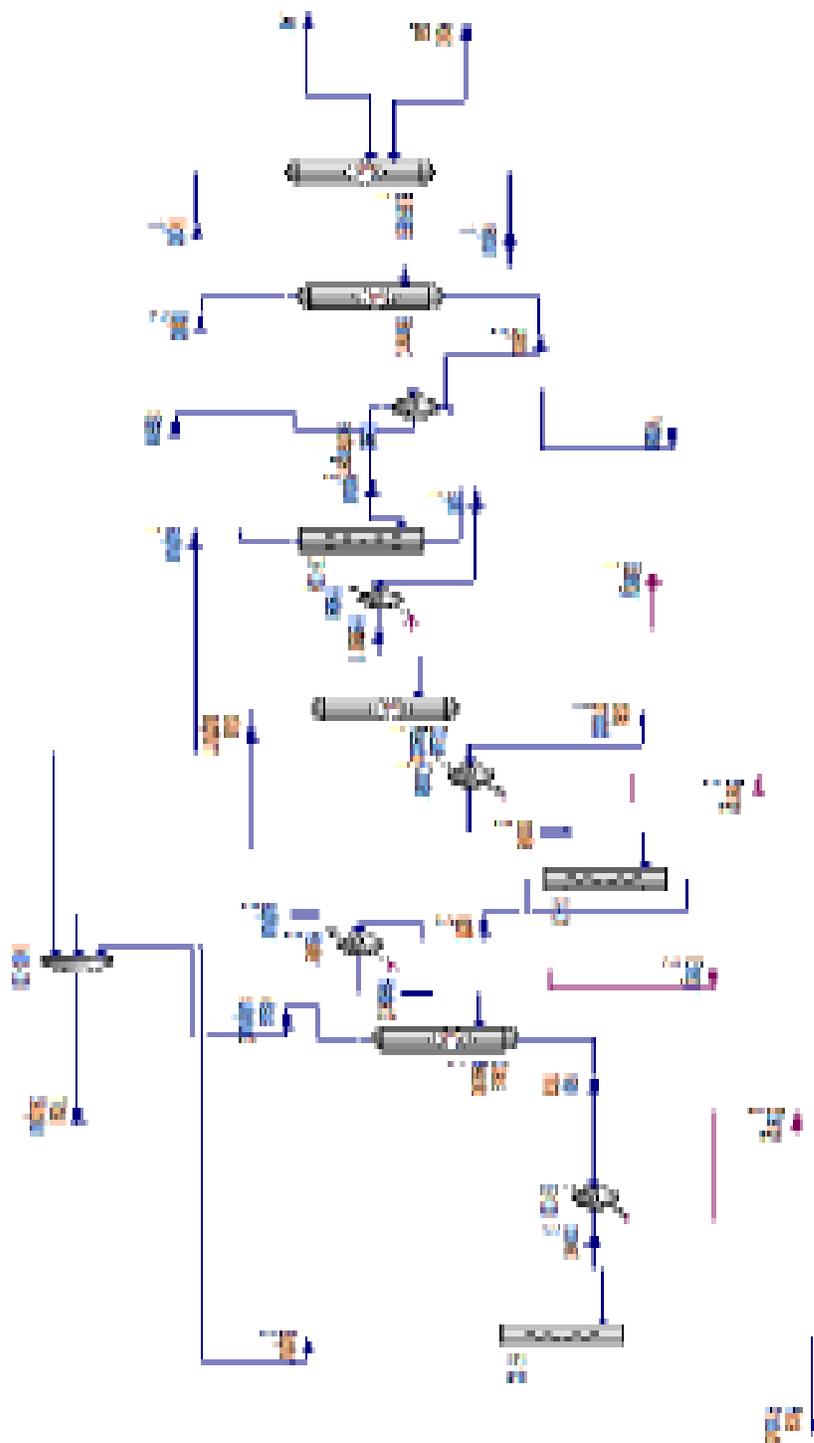


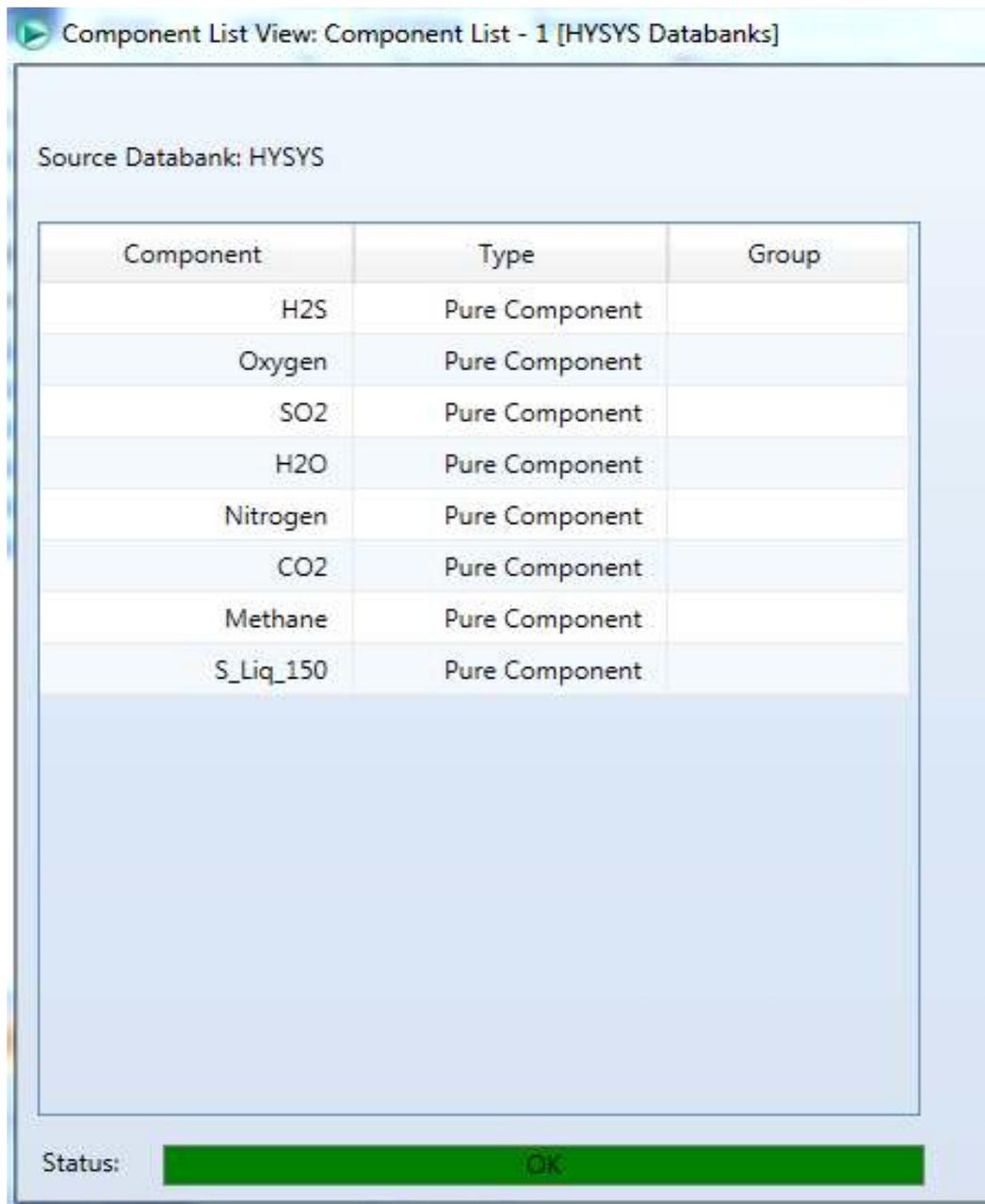
Figure3.1 Flowsheet for the claus process

3.4 Aspen HYSYS process simulator

Aspen HYSYS is a process simulation environment designed to serve many processing industries. It is an interactive, intuitive, open and extensible program. It also has many add-on options to extend its capabilities into specific industries. With this program, rigorous steady state and dynamic models for plant design can be created. Apart from that, monitoring, troubleshooting, operational improvement, business planning and asset management can be performed with the aid of the process simulator. Through its completely interactive interface, process variables and unit operation topology can be easily manipulated.

3.4.1 Simulations steps

First we have to select all the components that are in the main feed or are expected to be produced.



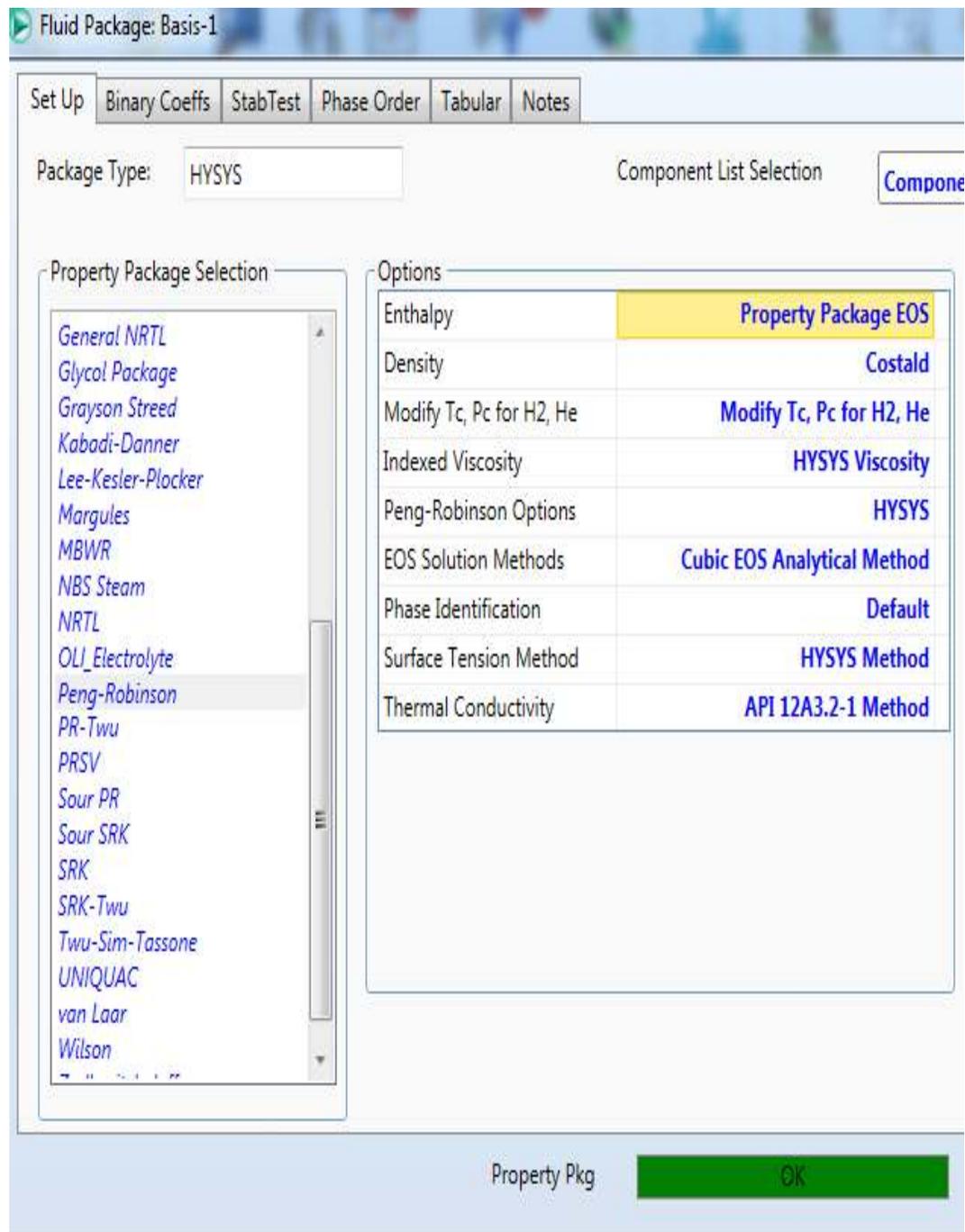
Component List View: Component List - 1 [HYSYS Databanks]

Source Databank: HYSYS

Component	Type	Group
H2S	Pure Component	
Oxygen	Pure Component	
SO2	Pure Component	
H2O	Pure Component	
Nitrogen	Pure Component	
CO2	Pure Component	
Methane	Pure Component	
S_Liq_150	Pure Component	

Status: OK

Then the selection of the Fluid package



Adding the Acid gas condition and composition

Material Stream: Acid gas

Worksheet Attachments Dynamics

Worksheet

- Conditions
- Properties
- Composition
- Oil & Gas Feed
- Petroleum Assay
- K Value
- User Variables
- Notes
- Cost Parameters
- Normalized Yields

Stream Name	Acid gas
Vapour / Phase Fraction	0.9183
Temperature [C]	21.11
Pressure [kPa]	273.7
Molar Flow [kgmole/h]	45.35
Mass Flow [kg/h]	1607
Std Ideal Liq Vol Flow [m3/h]	1.999
Molar Enthalpy [kJ/kgmole]	-1.566e+005
Molar Entropy [kJ/kgmole-C]	169.5
Heat Flow [kJ/h]	-7.104e+006
Liq Vol Flow @Std Cond [m3/h]	1.875
Fluid Package	Basis-1
Utility Type	

OK

Delete Define from Stream... View Assay

Material Stream: Acid gas

Worksheet Attachments Dynamics

Worksheet

- Conditions
- Properties
- Composition
- Oil & Gas Feed
- Petroleum Assay
- K Value
- User Variables
- Notes
- Cost Parameters
- Normalized Yields

	Mole Fractions
H2S	0.6000
Oxygen	0.0000
SO2	0.0000
H2O	0.0900
Nitrogen	0.0000
CO2	0.3000
Methane	0.0100
S_Liq_150	0.0000

Total 1.00000

Edit... View Properties... Basis...

OK

Delete Define from Stream... View Assay

Adding the air stream

Material Stream: Air

Worksheet Attachments Dynamics

Worksheet

Stream Name	Air
Vapour / Phase Fraction	1.0000
Temperature [C]	21.11
Pressure [kPa]	273.7
Molar Flow [kgmole/h]	105.5
Mass Flow [kg/h]	3042
Std Ideal Liq Vol Flow [m3/h]	3.517
Molar Enthalpy [kJ/kgmole]	-136.0
Molar Entropy [kJ/kgmole-C]	143.0
Heat Flow [kJ/h]	-1.434e+004
Liq Vol Flow @Std Cond [m3/h]	2492
Fluid Package	Basis-1
Utility Type	

OK

Delete Define from Stream... View Assay

Material Stream: Air

Worksheet Attachments Dynamics

Worksheet

	Mole Fractions
H2S	0.0000
Oxygen	0.2100
SO2	0.0000
H2O	0.0000
Nitrogen	0.7900
CO2	0.0000
Methane	0.0000
S_Liq_150	0.0000

Total 1.00000

Edit... View Properties... Basis...

OK

Product from the burner

Material Stream: vapour 2

Worksheet	Attachments	Dynamics
Worksheet		
Conditions	Stream Name	vapour 2
Properties	Vapour / Phase Fraction	1.0000
Composition	Temperature [C]	1088
Oil & Gas Feed	Pressure [kPa]	263.6
Petroleum Assay	Molar Flow [kgmole/h]	159.0
K Value	Mass Flow [kg/h]	4649
User Variables	Std Ideal Liq Vol Flow [m3/h]	5.039
Notes	Molar Enthalpy [kJ/kgmole]	-4.478e+004
Cost Parameters	Molar Entropy [kJ/kgmole-C]	209.6
Normalized Yields	Heat Flow [kJ/h]	-7.118e+006
	Liq Vol Flow @Std Cond [m3/h]	6.770
	Fluid Package	Basis-1
	Utility Type	

Buttons: Delete, Define from Stream..., View Assay

Product from the first Claus reactor

Material Stream: claus product 1

Worksheet	Attachments	Dynamics
Worksheet		
Conditions	Stream Name	claus product 1
Properties	Vapour / Phase Fraction	1.0000
Composition	Temperature [C]	366.6
Oil & Gas Feed	Pressure [kPa]	250.5
Petroleum Assay	Molar Flow [kgmole/h]	143.2
K Value	Mass Flow [kg/h]	4038
User Variables	Std Ideal Liq Vol Flow [m3/h]	4.631
Notes	Molar Enthalpy [kJ/kgmole]	-8.087e+004
Cost Parameters	Molar Entropy [kJ/kgmole-C]	183.5
Normalized Yields	Heat Flow [kJ/h]	-1.158e+007
	Liq Vol Flow @Std Cond [m3/h]	3366
	Fluid Package	Basis-1
	Utility Type	

Buttons: Delete, Define from Stream..., View Assay

Finally, the products leaving the operation

Material Stream: Final Product

Worksheet Attachments Dynamics

Worksheet	Stream Name	Final Product
Conditions	Vapour / Phase Fraction	1.0000
Properties	Temperature [C]	149.4
Composition	Pressure [kPa]	242.2
Oil & Gas Feed	Molar Flow [kgmole/h]	137.6
Petroleum Assay	Mass Flow [kg/h]	3818
K Value	Std Ideal Liq Vol Flow [m3/h]	4.481
User Variables	Molar Enthalpy [kJ/kgmole]	-9.244e+004
Notes	Molar Entropy [kJ/kgmole-C]	169.3
Cost Parameters	Heat Flow [kJ/h]	-1.272e+007
Normalized Yields	Liq Vol Flow @Std Cond [m3/h]	3239
	Fluid Package	Basis-1
	Utility Type	

OK

Delete Define from Stream... View Assay

Material Stream: Total Sulphur

Worksheet Attachments Dynamics

Worksheet	Stream Name	Total Sulphur
Conditions	Vapour / Phase Fraction	0.0000
Properties	Temperature [C]	144.2
Composition	Pressure [kPa]	242.2
Oil & Gas Feed	Molar Flow [kgmole/h]	25.93
Petroleum Assay	Mass Flow [kg/h]	831.3
K Value	Std Ideal Liq Vol Flow [m3/h]	0.4594
User Variables	Molar Enthalpy [kJ/kgmole]	-6.711e+004
Notes	Molar Entropy [kJ/kgmole-C]	43.42
Cost Parameters	Heat Flow [kJ/h]	-1.740e+006
Normalized Yields	Liq Vol Flow @Std Cond [m3/h]	0.4594
	Fluid Package	Basis-1
	Utility Type	

OK

Delete Define from Stream... View Assay

3.4 Material balance

Material balances are important first step when designing a new process or analyzing an existing one. They are almost always prerequisite to all other calculations in the solution of process engineering problems.

Material balances are nothing more than the application of the law of conservation of mass, which states that mass can neither be created nor destroyed. Material balance is an accounting for material. Thus, material balances are often compared to the balancing of current accounts. They are used in industry to calculate mass flow rates of different streams entering or leaving chemical or physical processes.

3.4.1 Overall material balance equation

$$\text{Input} = \text{Output} + \text{Consumption}$$

$$\text{Consumption} = \text{Input} - \text{Output}$$

This is used to find out the total efficiency of the process

3.5 Energy balance

Energy takes many forms such as heat, kinetic energy, chemical energy, potential energy but because of interconversions it is not always easy to isolate separate constituents of energy balances. However, under some circumstances certain aspects predominate. In many heat balances, other forms of energy are insignificant; in some chemical situations, mechanical energy is insignificant and in some mechanical energy situations, as in the flow of fluids in pipes, the frictional losses appear as heat but the details of the heating need not be considered. We are seldom concerned with internal energies.

3.5.1 Heat Balances

The most common important energy form is heat energy and the conservation of this can be illustrated by considering operations such as heating and drying. In these, enthalpy (total heat) is conserved. As with the material balances, so enthalpy balances can be written round the various items of equipment, or process stages, or round the whole plant, and it is assumed that no appreciable heat is converted to other forms of energy such as work.

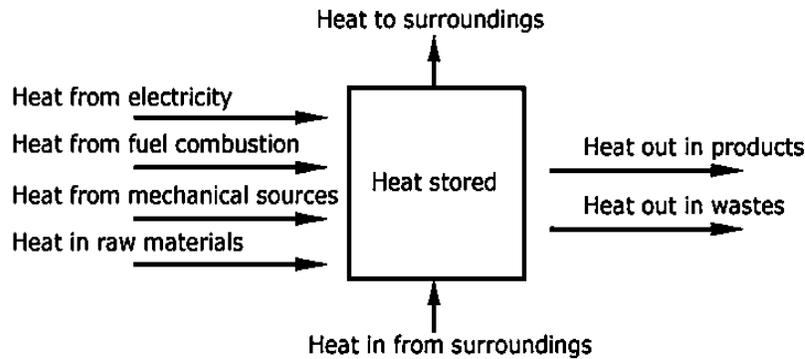


Figure3.2 heat balance

Enthalpy (H) is always referred to some reference level or datum, so that the quantities are relative to this datum. Working out energy balances is then just a matter of considering the various quantities of materials involved, their specific heats, and their changes in temperature or state (as quite frequently, latent heats arising from phase changes are encountered).

Heat is absorbed or evolved by some reactions in feed processing but usually the quantities are small when compared with the other forms of energy entering into food processing such as sensible heat and latent heat. Latent heat is the heat required to change, at constant temperature, the physical state of materials from solid to liquid, liquid to gas, or solid to gas. Sensible heat is the heat which when added or subtracted from feed materials changes their temperature and thus can be sensed.

The units of specific heat (c) are $\text{J kg}^{-1} \text{ } ^\circ\text{C}^{-1}$ and sensible heat change is calculated by multiplying the mass by the specific heat and the change in temperature, $m c \Delta T$ and the unit is J. The unit of latent heat is J kg^{-1} and total latent heat change is calculated by multiplying the mass of the material, which changes its phase, by the latent heat. Having determined those factors that are significant in the overall energy balance, the simplified heat balance can then be used with confidence in industrial energy studies. Such calculations can be quite simple and straightforward but they give a quantitative feeling for the situation and can be of great use in design of equipment and process.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Material balance

All data used was collected using Aspen HYSYS.

4.1.1 Overall material balance

An overall material balance is done for the entire process.

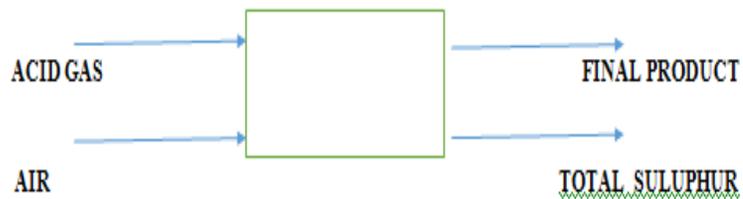


Table4.1 overall material balance

Component	Acid gas (Kg/hr)	Air (Kg/hr)	Final product (Kg/hr)	Total sulphur (Kg/hr)
H2S	964.2	0.000	23.671	0.000
O2	0.000	638.82	211.517	0.000
SO2	0.000	0.000	12.217	0.000
H2O	144.63	0.000	869.62	0.498
N	0.000	2403.18	2311.417	0.000
CO2	482.1	0.000	500.199	0.000
Hydrocarbon As C1	16.07	0.000	0.000	0.000
Sulphur	0.000	0.000	0.000	830.80

4.1.2 Material balance for Hydrogen Sulfide

Determine the efficiency of the process and for the individual process such as the burner and the two Claus reactors.

Table4.2 H2S material balance

Process	Molar Flow (Kg/hr)	Mass Flow (Kgmole/hr)
Burner 1	8.159	236.634
Burner 2	5.437	158.995
Claus Reactor 1	2.162	60.973
Claus Reactor 2	0.859	23.876

The efficiency for the burner is calculated by the calculations:

(Total mass-Mass flow out from the burner) / Total mass

$$(964.2 - 158.995) / 964.2 = 0.73$$

The Efficiency was found to be 73%

The efficiency after the first Claus reactor is found using the equation

(Total mass – Mass leaving the reactor) / Total mass

$$(964.2 - 60.973) / 964.2 = 0.93$$

The Efficiency was found to be 93%

The Efficiency after the second Claus reactor is:

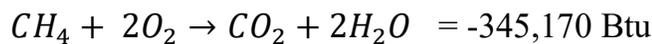
(Total mass – Mass leaving the second reactor) / Total Mass

$$(964.2 - 23.876) / 964.2 = 0.975$$

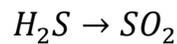
The efficiency was found to be = 97.5%

4.1.3 Material balance for Oxygen

The amount of oxygen needed for the combustion of the acid gas inside the burner is calculated using the following reactions.



Air for first reaction



$$(1/3) * (3/2) * (\text{moles of } H_2S) \quad = 14.17 \text{ kgmole/hr } O_2$$

Hydrocarbons (as C1)

$$2 * (\text{moles of } CH_4) \quad = 2.009 \text{ kgmole/hr } O_2$$

Total air required that reacts with a third of the H₂S and with all of the methane

$$= 16.179 \text{ kgmole/hr}$$

4.1.4 Material balance for Steam

Steam is generated from the heating of the water using the heat exchanger in order to quench the hot gases coming out of the burner.

Table4.3 relationship between temperature and mass flow

Temperature of feed exiting the Heat Exchanger in (°C)	Mass Flow of Steam exiting the HeatExchanger in (kg/hr)
135	2612
140	2596
145	2581
150	2566
155	2552
160	2539
165	2526
170	2513

We found out that when the temperature of the exiting stream needs to be cooled more water is needed to quench the feed so more steam is generated in the process.

The desired temperature is 150 centigrade so the amount of steam generated from this cooling was =2566kg/hr.

4.2 Energy balance

4.2.1 Energy balance around heat exchanger

Table4.5 Energy balance for heat exchanger

Component	Heat flow for burner products at 1080°C (KJ/hr)	Heat flow for cooled products at 150°C (KJ/hr)
H2S	-243435.6	-468882
Oxygen	-341664	- 658080
SO2	-122429.6	- 235812
H2O	-1198671.2	-2308764
CO2	-629231.2	- 1211964
Sulphur	-852736.8	-1642458
Nitrogen	-3730543.8	-7185411

It was found out that the inlet heat flow was the summation of the different components. = 7118711.8 KJ/hr

It was found out that the outlet cooled heat flow which is the summation of the components is equal to = 13711371 KJ/hr

So the total Heat Flow was found out to be equal :

= 6592659.2 KJ/hr

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusion

This thesis is concluded from the study of a sulfur recovery unit using Claus process, using two reactors that in the end resulted in a efficiency of over 97% which is pretty remarkable, and generated near 2.5 tons of steam which can be used for many industrial operations, last but not least the sulfur which was recovered successfully, this helps to prove how valuable and instrumental this unit has become for a modern day oil refinery to reduce the harmful effects that accompany the burning of acid gas, and aims to rectify even if slightly the significant damage done by humans since the industrial revolution era. Even though for some countries this process may not be economically be feasible, but now is time to think about our future generations and the environment all which costs pale in comparison to them.

5.2 Recommendations

There are some recommendation and improvement which can be added to the unit such as:

- The addition of a third reactor to further increase the efficiency and enhance the sulfur yield
- Use of a tail gas unit in order to further treat the products of the SRU
- Use of pure oxygen instead of air increases the burner efficiency

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