## Article

# STUDIES ON SULFUR RECOVERY PLANT PERFORMANCE USING ASPEN HYSYS SULSIM SIMULATIONS

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#### Abstract

Sulfur recovery is a core process in both midstream and downstream oil and gas industries. Changing the feed composition, temperature, and pressure, degrading the equipment and catalysts, suboptimal operations due to inadequate control of temperature, pressure and air flow rate are some of the obstacles which reduce the performance of the sulfur recovery units. Low performance of sulfur recovery units creates the issues of safety and environmental problems. The objective of work is improving the performance of sulfur recovery unit in a gas plant. Aspen HYSYS V10 sulsim modified Claus three stage simulation model is used to mimic the behavior of a real sulfur recovery unit and it is considered as the base case. The performance of the base case is 93.89%. Base case process is optimized by controlling the air demand percent and the adjusting the sulfur dew point margin. These changes improved the performance to 98.60%. The performance of the plant is tested for a challenging feed composition case and this change reduced the performance to 96.39%. Arranging the selective oxidation converter improved the performance to 99.14%. Adding the tail gas section with the recycle stream and replacing the alumina catalyst with titania catalyst improved the performance to 99.92%. The simulation procedure developed in this work is useful to process engineers to smoothly handle the sulfur recovery unit in challenging situations.

Keywords: Alumina catalyst; Challenging feed; Sulfur recovery unit; Sulsim; Titania catalyst.

#### 1. Introduction

Natural gas contains  $H_2S$ ,  $CO_2$ ,  $SO_2$ ,  $NH_3$ , mercaptans and other sulfur-containing compounds. Presence of these contaminants in natural gas degrades the quality of sales gas, corrodes the equipment, pipelines and causes acid rains <sup>[1]</sup>. Sulfur-containing natural gas is named as sour gas if it contains ammonia and it is called as acid gas if ammonia is not present. Acid gas must be treated: to meet safety considerations and environmental regulations, to reduce corrosion and protect equipment, to improve quality of liquid products and to improve heating value of sales gas. The most commonly used method for acid gas cleaning is done using regenerative amine solvents. In this process, acid gas is passed through the aqueous amine solution.  $H_2S$  and  $CO_2$  are absorbed by amines and they are separated from the natural gas and the gas is sweetened <sup>[2]</sup>. The mixture of amines and contaminants can then be regenerated with heat, and the amines can be reused in the process.

In gas plants, after the acid gas cleaning, sulfur is removed. Based on  $H_2S$  content in acid gas, acid gas is classified as lean acid gas and rich acid gas.  $H_2S$  content in rich acid gas is greater than 50% and in lean acid gases,  $H_2S$  content is less than 50%. From the inception, Claus process is the most practiced process industrially for recovery of sulfur <sup>[3]</sup>. In Claus process, sulfur recovery from acid gases is a challenging task because of operational parameters and feed stock changes <sup>[4]</sup>. Process challenges can be handled by process modifications.

Process modification studies need the knowledge of thermodynamics and kinetics of chemical species involved in the process. Various studies on process modification and optimization are available to the sulfur recovery. Some of them are: A review for process modification technologies <sup>[5]</sup>, Selectox process for lean acid gases processing <sup>[6]</sup>, studies on effect of reaction parameters on the quality of captured sulfur <sup>[7]</sup>, reaction with adsorption in a reaction furnace itself to overcome the Claus reaction equilibrium limitations <sup>[8]</sup>, super Claus process using selective oxidation catalyst <sup>[9]</sup>, designing new alumina catalysts with specific properties <sup>[10-11]</sup> and structures <sup>[12]</sup>, lanthanum oxide based catalysts <sup>[13]</sup>, ammonia pyrolysis and oxidation technique <sup>[14]</sup>, benzene destruction technique <sup>[15]</sup>, new tubular Claus catalytic reactor heat exchanger unit filled with a heat transfer enhancement medium <sup>[16]</sup>, Claus recycle with double combustion process <sup>[17]</sup>, reaction kinetic studies to reduce CS<sub>2</sub> formation <sup>[18]</sup>, BTX oxidation by SO<sub>2</sub> in a BTX destruction unit placed between Claus furnace and catalytic units <sup>[19]</sup>, toluene destruction using oxygen enriched air <sup>[20]</sup>, maintaining suitable operating conditions in the reaction furnace for the presence of toluene and carbon dioxide <sup>[21]</sup>, feasibility studies for lean acid gas feed containing mercaptans <sup>[22]</sup>, coupled modification of GTU and SRU processes <sup>[23]</sup>, thermal insulation to avoid thermal damage of Claus reaction chamber <sup>[24]</sup>, reducing number of catalytic stages by following guidelines for the design of thermal section <sup>[25]</sup>, introducing high temperature air combustion technology <sup>[26]</sup>.

In the Claus process maximum possible sulfur is recovered from the thermal and catalytic sections. For a two-stage Claus process the maximum sulfur recovery is 95% and for a three-stage Claus process sulfur recovery is 98% <sup>[4]</sup>. These recovery efficiencies are not sufficient to meet the stringent environmental regulations. The new regulations demands, 100% recovery of sulfur from acid gases. To meet the new environmental standards tail gas treatment units are attached to the sulfur recovery units. In tail gas treatment the remaining sulfur is recovered. Various technologies available for tail gas cleaning in literature are Beavon sulfur removal process <sup>[27]</sup>, in which the tail gas is treated in two-steps. Sulfur contaminants are first catalytically hydrolysed and/or hydrogenated to hydrogen sulfide and the hydrogen sulfide is then converted to elemental sulfur and recovered, The Shell Claus Off-gas Treating (SCOT) Process <sup>[28]</sup>, use of Cu- and Ag-exchanged Y zeolites as selective adsorbents for hydrogen sulfide <sup>[29]</sup>, temperature swing adsorption systems for Claus tail gas clean up units <sup>[30]</sup>, use of a re-generable solid sorbent <sup>[31]</sup>.

Performance of the Claus units depends on thermodynamics and kinetic factors of the process <sup>[32]</sup>. Using thermodynamics and kinetic data models for the Claus process can be developped <sup>[25, 33-35]</sup>. These models are useful for the simulation of Claus process and its unit operations <sup>[36]</sup>, Genetic algorithms <sup>[37]</sup>, model-based optimization techniques <sup>[38]</sup>, modeling and multi-optimization of thermal section <sup>[39]</sup> are some the techniques used for the improved performance of sulfur recovery units. The advantage of the simulations is one can predict the response of the process for challenging conditions and for operational changes <sup>[40-42]</sup>.

The above studies motivated the present simulation work to improve the performance of the sulfur recovery plant with tail gas treating section. Results of this work are useful for process modification studies to recover the desired quantity of sulfur from acid gases without changing the process equipment.

#### 2. Process description

Acid gas feed to the modified Claus three- stage process contains  $H_2S$ ,  $CO_2$ ,  $CH_4$ ,  $C_2H_6$ ,  $C_3H_8$ . Feed gas composition is given in Table 1. Acid gas is processed for sulfur recovery using the Aspen HYSYS Sulsim Claus three-stage process with tail gas treatment section and incinerator.

Component	Mole fractions	Component	Mole fractions
CO <sub>2</sub>	0.242	$C_2H_6$	0.002
H₂S	0.75	C₃H <sub>8</sub>	0.001
CH <sub>4</sub>	0.005		

Table 1. Feed gas composition of sour gas

In general the Claus plant contains two sections. Section one is the thermal section by containing the main burner, reaction furnace, and waste heat boiler. Section two is the catalytic section by containing two or three catalytic converters in series. Catalytic converter contains a catalytic reactor with a catalyst layer and a condenser. In between catalytic reactors, re-heaters are present to provide the necessary heat for the catalytic reactions. Schematic diagram for Claus three-stage process is shown in Figure 1. At the entrance of the thermal section main burner is placed. The role of the main burner is to burn the impurities (i.e. hydrocarbons, ammonia and mercaptans) present in the acid gas stream from the acid gas cleaning unit. For this reaction, external air stream is supplied. Adjacent to the main burner, reaction furnace is present. In reaction furnace,  $1/3^{rd}$  of the H<sub>2</sub>S is converted to elemental sulfur. Corresponding reactions are the reaction (1) and reaction (2).



Figure 1. Process flow diagram for the base case three stage Claus process

Remaining  $2/3^{rd}$  of the H<sub>2</sub>S is converted into elemental sulfur in catalytic converters followed by the thermal section. The overall Claus reaction is given by reaction (3).

$$2H_2S + SO_2 \to \frac{3}{n}S_n + 2H_2O$$
 (3)

Due to the combustion reaction at the reaction furnace, some impurities are also formed. Impurities formed are COS and  $CS_2$ . These impurities lower the sulfur recovery efficiency and these can be handled at catalytic converters only by hydrolysis reactions. Hydrolysis reactions are the reaction (4) and reaction (5).

$$COS + H_2O \leftrightarrow CO_2 + H_2S$$
(4)  
$$CS_2 + 2H_2O \leftrightarrow CO_2 + 2H_2S$$
(5)

Reaction (4) and (5) takes place at high temperatures and in the presence of the catalyst. In thermal furnace reactions (1) and reaction (2) takes place in about 2 seconds at 1000<sup>o</sup>C - 1400<sup>o</sup>C. The elemental sulfur formed in the reaction furnace is cooled in the waste heat boiler and it is separated by condensation. By absorbing the heat from the reaction furnace gases, steam is generated from the waste heat boiler. The remaining unconverted gases are sent to the re-heater. Re-heater acts as a link between the thermal section and catalytic section. Reheater outlet stream is connected to the catalytic converter. In catalytic converters, the reaction to form sulfur is continued. This step improves the further sulfur recovery. Catalytic reactors operate at temperatures above the sulfur dew point. From the process gases, at each

catalytic converter, elemental sulfur is condensed and collected in the condensers. In general alumina catalyst and titania catalysts are used as catalysts in catalytic converters. The gaseous effluent from the last catalytic stage condenser is low in sulfur-containing compounds but may require some additional treating to meet flare gas specifications. This gas is sent to tail gas treating processing, which can contain unit operations such as hydrogenation bed, reducing gas generator, quench tower, amine absorber, incinerator, and flare. The amount of sulfur recovery needed depends on the tail gas treating system installed. The recycle gas stream will be recycled back to the reactor furnace. The process gas containing the low sulfur compounds is directed to the incinerator and flare.

#### 3. Process simulation

Acid gas stream from the amine regenerator unit in the acid gas cleaning unit is connected to the sulfur recovery unit as feed gas stream. The tail gas stream is connected to the outlet of the Sulsim sub-flow sheet. After the convergence of the Aspen HYSYS V10 Sulsim, sub-flow sheet cumulative sulfur recovery of the unit is checked. If the initial overall performance is not satisfactory a couple of modifications are performed to improve the performance of the sulfur recovery unit.

In the simulation, the main parameters considered are reaction furnace empirical model,  $H_2S$  to  $SO_2$  ratio, the temperature of catalytic converters, incinerator checker wall kinetic parameters. Base case simulation uses the straight through acid gas empirical model. Selection of the empirical model depends on the percentage of the  $H_2S$  present in the feed gas. Here, straight through amine acid gas empirical model is selected and this option is suitable for feed containing the more than 50% of the  $H_2S$ . For further improvement in sulfur recovery, it can be tested with other empirical models available in Aspen HYSYS. Optimum  $H_2S$  to  $SO_2$  ratio can be maintained by arranging air demand analyzer (ADA) and adjust operations as shown in Figure 2. ADA is connected between the last condenser and the reaction furnace. Air demand analyzer (ADA) is useful in adjusting the air to fuel ratio and Adjust block is useful to adjust the converter temperature. To meet the tail gas specifications air demand analyzer controls air flow to the reaction furnace. To do this, in ADA internal options, tail gas is selected as the sample stream, target variable is selected as air demand percent and air demand target value is set as zero percent (it corresponds to the ratio of  $H_2S$  and  $SO_2$  as 2). For convergence, it needs more iteration. After re-converging, performance will be improved.



Figure 2. Sulfur recovery unit with air demand analyser and adjust operations

Adjust operations are arranged at catalytic converter 2 and catalytic converter 3, these can be seen in Figure 2. Adjust operations are added to decrease the outlet sulfur dew point margin. Initially, it is 24.52°C for the second catalytic converter. For catalytic converter operations, these temperatures should be as low as possible without depositing sulfur on the catalyst. A good target is 10°C. This value can be adjusted using the adjust unit operation. Second catalytic converter target variable is outlet sulfur dew point margin. 10°C is specified as the specified target value of outlet sulfur dew point margin. In parameters specifications, minimum temperature specified as 135°C and the maximum temperature specified as 500°C. Process re-converges and improvements in the performance of sulfur recovery are observed. For further recovery of sulfur selective oxidation section is added.

Selective oxidation converter is connected to the vapor outlet stream from the last condenser attached to the catalytic converter 3. It can be seen in Figure 3.



Figure 3. Sulfur recovery unit with selective oxidation converter

Feed composition fluctuations are common in sulfur recovery units. To handle challenging situations in this study, simulations are performed for low percentage composition of  $H_2S$ in the feed stream. The same optimization procedure is followed as in the above sections to handle the challenging situation to maintain the same sulfur compounds compositions in tail gas without changing the process equipment.

In Figure 4, the tail gas section is attached. It contains the reducing gas generator, hydrogenation bed, quench tower and simple amine absorber. In reducing gas generator mention burn stoichiometry as 85% and Steam to fuel ratio 85 mass%. Similarly RGG Air, RGG Fuel Gas, and RGG Water streams also defined. Adjust block is added (ADJ-3) to adjust RGG Fuel Gas Flow to achieve an RGG Effluent temperature of 285°C. The next the data for hydrogenation bed is given. For quench tower set the pressure drop 3 kPa and the outlet temperature to 35°C. Data for simple amine absorber also provided.

Finally, sulfur recovery efficiency is tested by varying the alumina catalyst with titania catalyst and the improvements in performance are noted.



Figure 4. Sulfur recovery unit with tail gas treating section, incinerator and recycle stream

#### 4. Results and discussion

Acid gas feed composition (mole fractions) to sulfur recovery unit is:  $CO_2 \ 0.242$ ,  $H_2S \ 0.75$ ,  $CH_4 \ 0.005$ ,  $C_2H_6 \ 0.002$ ,  $C_3H_8 \ 0.001$ , Simulations are conducted to improve the cumulative sulfur recovery of the three- stage Claus process. Main parameters concentrated for simulation are  $H_2S/SO_2$  ratio, outlet sulfur dew point temperature, catalytic converter inlet stream temperatures, incinerator temperature. Since improvements in sulfur recovery are possible by improving the hydrolysis reaction (i.e. reactions (4) and (5)) to achieve this at first catalytic converter influence of temperature increase on sulfur recovery is tested while maintaining the second and third catalytic converters at low temperatures (operating the last two stages at low temperatures favours the Claus reaction). For further improvements of cumulative sulfur recovery or to improve the hydrolysis reaction performance Titania catalyst is selected which is available in catalytic converter unit operation.

In sulfur recovery plants (SRUs) sometimes processes are challenging due to changing feed slates. For changing feed conditions current process configurations does not meet the desired specifications. To meet the current process configurations process optimization conducted and the optimum process parameters calculated.

#### 4.1. Effect of H<sub>2</sub>S/CO<sub>2</sub> ratio

Performance of the SRU decreases due to incomplete oxidation, losing catalytic activity and lowering temperatures of the furnace. The base case process cumulative sulfur recovery efficiency obtained is 93.89% (Table 2).

Stage	Thermal reaction furnace	Catalytic converter 1	Catalytic converter 2	Catalytic converter 3
Conversion percent	68.25	47.02	53.85	24.28
Cumulative conversion	68.25	83.17	92.21	94.10
Sulfur recovery percent	99.73	98.76	97.88	89.90
Cumulative sulfur recovery percent	68.08	82.98	92.02	93.89
COS hydrolysis percent		97.37	74.38	60.56
CS <sub>2</sub> hydrolysis percent		93.93	43.98	28.80
Overall recovery efficiency percent				93.89

Table 2. Sulfur recovery efficiency summary for base case process

To increase the sulfur recovery around 98.5% operational changes are needed. To meet the flare specifications, it is also mandatory to maintain the concentration of sulfur-containing compounds in the tail gas less than 1 kmole/hr. These changes (i.e. improving the sulfur recovery percent) can be made with no equipment changes. Adjust block is added to adjust the converter temperature, Air demand analyzer is added to adjust air to fuel ratio. Air demand analyzer targeted the last condenser vapor outlet stream in the catalytic section. First catalytic temperature is at 340°C to ensure  $CS_2$  and COS destruction. Second and third catalytic converters are maintained at minimum sulfur dew point margin of at least 10°C so that no liquid sulfur will not deposit on the catalyst surface. Deposition of liquid sulfur on the catalyst surface decreases the overall recovery percent of sulfur.



 $H_2S/SO_2$  ratios (air demand %) and their effect on sulfur recovery are shown in Figure 5. Based on Claus reaction i.e. reaction (3) more closeness of the  $H_2S/SO_2$  ratio to number 2 leads to better performance and more sulfur recovery efficiency for the catalytic section. At low zero percent air demand (i.e. the ratio between  $H_2S$  to  $CO_2$  is 2:1) the cumulative percent recovery of sulfur is maximum and the value is from the 98.6%. (Table 3)

Figure 5. Variation of cumulative sulfur recovery percent with  $H_2S/SO_2$ 

Table 3. Sulfur reco	overy unit performance	summary for	optimized	process
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Stage	Thermal reaction furnace	Catalytic converter 1	Catalytic converter 2	Catalytic converter 3
Conversion percent	68.56	48.61	80.79	62.73
Cumulative conversion percent	68.56	83.83	96.86	98.80
Sulfur recovery percent	99.75	98.84	98.58	90.61
Cumulative sulfur recovery percent	68.39	83.65	96.67	98.60
COS hydrolysis percent	N/A	97.19	36.05	12.31
CS <sub>2</sub> hydrolysis percent	N/A	94.33	9.974	2.213
Overall recovery efficiency percent				98.60

### 4.2. Effect of outlet sulfur dew point margin

To know the effect of outlet dew point temperature adjust block is added at the second catalytic converter. Outlet sulfur dew point temperature is varied by adjusting the target variable values and the corresponding variations in sulfur recovery are shown in Figure 6. It is observed that at lower sulfur dew point temperature margin, percent sulfur recovery is more. Very low temperatures are also not favorable for catalysts. The temperatures between 5°C and 10°C are identified as favorable dew point temperature margins.

### 4.3. Effect of temperature

At reaction furnace, because of side reactions, by-products like COS and  $CS_2$  are formed. Presence of these compounds reduces the efficiency of sulfur recovery. To destruct these compounds increased temperatures at first catalytic converter are required. From Figure 7 it is evident that the temperature increasing from 250°C to 340°C cumulative percent recovery of sulfur increased from 98.35 to 98.6%. This is because of additional decomposition of COS and CS<sub>2</sub> at first catalytic converter. At very high temperatures percent sulfur recovery is too low this may be due to decreasing activity of catalyst because of deposition of sulfur on the catalyst surface.





Figure 6. Variation of cumulative percent recovery of sulfur with outlet dew point temperature margin at catalytic converter two

Figure 7. Variation of cumulative percent recovery of sulfur with varying temperature of first catalytic converter (for additional destruction of COS and  $CS_2$ )

#### 4.4. Process for challenged feed

In the base case, the sulfur recovery percent obtained is 98.61% corresponding to a flow rate of about 4.2774 kmol/hr of sulfur-containing compounds in the tail gas. However, the refinery is looking to increase the amount of low-cost heavy sour crude in the crude slate, which contains a greater concentration of sulfur. The composition of the new feed in mole fraction is  $H_2S$  0.8,  $CO_2$  0.05 and it is given in Table 4. When the new feed simulated to the SRU in HYSYS, the feed change increased the amount of sulfur -containing compounds in tail gas to 43.377 kmole/hr, which is above the 4.2774 kmol/hr target. To meet the target specifications we need to investigate the options.

The first option is installing a bypass around the WHE at next turnaround. Single-pass option is changed to double pass for the WHE. By-pass split fraction is varied from 0 to 0.15. Zero bypass fraction means we are not bypassing any gas from the WHE to the first stage. Then we are not saving any operational expenses on heater 1 duty. Outlet temperature adjust target value is from 335°C to 355°C. To see the effect of both parameters i.e. bypass fraction and catalytic converter 1 temperature on cumulative sulfur recovery sensitivity analysis is done. With an increase in bypass fraction, the amount of sulfur in tail gas increased. It is shown in Figure 8.

Component	Mole	Component	Mole
	fractions		fractions
CO <sub>2</sub>	0.05	C <sub>2</sub> H <sub>6</sub>	0.02
H₂S	0.80	C <sub>3</sub> H <sub>8</sub>	0.01
SO <sub>2</sub>	0.05	$n-C_4H_{10}$	0.005
$CH_4$	0.06	i-C₅H <sub>12</sub>	0.005

Table 4. Feed Gas Composition of acid gas for challenging case

The increase is very small i.e in the order of about 0.02 kmol/hr for a bypass up to 15%. This can be reduced with the additional efficiency of the selective oxidation converter. If we completely bypass the preheater of the first catalytic converter saved reheater duty costs (up to 29,000 kJ/h) with a minimal impact on increasing sulfur in the tail gas. The second option



Figure 8. Effect of bypass split fraction on tail gas sulfur compounds

is adding an additional catalytic stage with a selective oxidation converter at next turnaround. This will help to improve the overall recovery efficiency. The optimal operating temperature at the first catalytic converter inlet is around 340°C for a bypass fraction of zero. This is due to higher destructions of COS and CS<sub>2</sub> in the first catalytic stage at higher temperatures.

To know the effect of the selective catalytic converter on cumulative sulfur recovery sensitivity analysis was done by varying the inlet temperature of the fourth selective catalytic converter. Temperature range is from 160°C to 340°C. The new recovery efficiency is 99.14% (Table 5).

This corresponds to 0.5548 kmol/hr of sulfur-containing compounds in the tail gas, which should enable us to meet the flare specifications.

Stage	Thermal reac-	Catalytic	Catalytic	Catalytic	Selective catalytic
	tion furnace	converter 1	converter 2	converter 3	oxidation converter
Conversion percent	71.32	34.66	81.12	63.12	59.64
Cumulative conversion percent	71.32	81.25	96.44	98.67	99.45
Sulfur recovery percent	70.76	99.20	98.33	88.88	71.12
Cumulative sulfur recovery	50.47	81.01	96.18	98.39	99.14
COS hydrolysis percent		96.48	33.51	11.34	
CS <sub>2</sub> hydrolysis percent		90.65	8.66	1.96	
Overall recovery efficiency percent					99.14

Table 5. Sulfur recovery unit performance for three stage Claus process with selective catalytic converter

## 4.5. Tail gas treating

The tail gas section further reduces the sulfur content to meet the flare specifications. Recycle stream redirected from the tail gas regenerator to the SRU furnace inlet for further cleaning of the tail gas, this step decreases the overall sulfur recovery. An incinerator is added to investigate the value of installing a checker wall. Benefits of installing checker wall on eliminating breakthrough of  $COS+CS_2+H_2S+SO_2$  to the flare is to be evaluated. Simulation goal is to maintain the target of < 0.8 kmol/hr of sulfur-containing compounds to the tail gas section, including the recycle, and to evaluate the impact of the incinerator upgrade will have on stack composition. Recycle stream arrangement effect can be observed in condenser 5 vapour outlet. In condenser 5 vapor outlet, sulfur compound flow increased from 0.45 kmol/hr to 0.58 kgmol/hr. This is due to additional sulfur is recycled to the furnace. It is still below the 0.8 kmol/hr target from the base case. Incinerator parameters kinetic value 4(a factor of incinerator geometry and it implies good mixing in the existing system), residence time 1.5 seconds, stack value 1 second. Corresponding  $COS + CS_2 + H_2S$  at Exit is 3.94 ppm total, which is fairly low compared to a typical flare spec of 50 ppm.

Effect of installing a checker wall (better mixing in the incinerator) is checked by changing its kinetic value from 4 to 8. Corresponding  $COS+CS_2+H_2S$  concentration is 1.973 ppmmol, this value is exactly half the original value.



Effect of incinerator temperature on sulfur compounds at the exit of incinerator is shown in Figure 9. For increasing temperatures, sulfur compounds concentrations are decreasing at the exit of the incinerator. The optimum temperature observed is 410°C and the corresponding concentration is 49 ppm mol. These results are useful whether or not to invest the additional capital to install a checker wall at the next turnaround.

Figure 9. Variation of concentration of sulfur containing compounds (ppmmol) at incinerator exit with incinerator exit temperature

#### 4.6. COS and CS<sub>2</sub> hydrolysis percentage at each unit operation

When acid gas is burned in the reaction furnace, some undesirable reactants like COS and  $CS_2$  are created due to the side reaction between  $CO_2$ , hydrocarbon and  $H_2S$ . These sulfur compounds reduce the percent sulfur recovery. Their concentrations should be minimized. COS and  $CS_2$  can be reduced by hydrolysis reaction take place at catalytic converters especially at the first catalytic converter. Hydrolysis is the reaction between COS and  $H_2O$  or  $CS_2$  and  $H_2O$  which is turning back that reactant to  $H_2S$ .  $H_2S$  is then can participate in Claus reaction which is a desired main reaction in the sulfur reactor. In Figure 10  $CS_2$  hydrolysis percentages at each unit operation are given. CS2 hydrolysis conversion at converter 1 is 92%, at converter 2 is 5.32% and at converter 3 is 1.24%. These results show that  $CS_2$  hydrolysis conversion is more at converter 1. Similarly, COS hydrolysis conversion at each converter is given in Figure 11. It is observed that at converter 1 hydrolysis conversion is 97% and the conversion values decrease from converter 1 to converter 3. These observations are useful in taking the better process design decisions.





Figure 10. Variation of CS<sub>2</sub> hydrolysis conversion for catalytic converters

Figure 11. Variation of COS hydrolysis percentage with unit operations

## 4.7. Percent sulfur conversion and cumulative percent sulfur recovery at each unit operation

Optimizing the entire Claus process is possible by knowing the percent conversion and percent recovery of sulfur at each stage of the process. To know these effects variation of

percent sulfur conversion at each unit operation and variation of cumulative percent sulfur recovery at each unit operation are shown in Figure 12 and in Figure 13 respectively. From Figure 12 it is evident that percent conversion of sulfur is more at converter two (It is well matched with the statement that  $1/3^{rd}$  of the H<sub>2</sub>S is converted into elemental sulfur at the reaction furnace and the remaining  $2/3^{rd}$  of H<sub>2</sub>S is converted at the remaining stages of the process). In Figure 14 outlet concentrations of sulfur compounds at each unit operation is shown. From Figure 13 cumulative percent recovery of sulfur is increasing progressively. From Figure 14 it is known that the concentration of sulfur compounds are decreasing at the unit operations in the order of furnace to the incinerator.





Figure 12. Stage wise sulfur conversion

Figure 13. Cumulative percent recovery of sulfur for unit operations





## 4.8. Catalyst selection

For alumina catalyst case the overall performance is 99.92% (Table 6). Sulfur recovery percentage for Titania catalyst is given 99.93%. By the selection of titania catalyst for the first stage catalytic converter hydrolysis reaction performance is improved. Catalyst change option improved the performance slightly. Space velocity and catalyst bed volumes are necessary for Titania catalyst. Space velocity is 1000 hr<sup>-1</sup> and catalyst bed volume is 10.42 m<sup>3</sup>. The reason for higher performances of Titania catalyst may be its high hydrolysis reaction while keeping Claus reaction.

Stage	Thermal Reac- tion furnace	Catalytic converter 1	Catalytic converter 2	Catalytic converter 3	Selective catalytic oxidation converter
Conversion percent	70.50	36.71	82.96	62.53	56.69
Cumulative conversion percent	70.50	81.32	96.80	98.79	99.47
Sulfur recovery percent	99.44	96.14	96.98	77.52	45.74
Cumulative sulfur recovery	70.11	80.89	96.32	98.24	98.80
COS hydrolysis percent		97.04	24.19	7.836	
CS <sub>2</sub> hydrolysis percent		92.04	5.33	1.243	
Overall recovery efficiency					99.92
percent					

Table 6. Sulfur recovery performance summary for sulfur recovery unit attached with tail gas section and incinerator

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