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Modelling and Simulation of Claus Furnace by Optimizing Basic Two Claus Reactions for Analysis of Percentage of Sulphur Recovery

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***Abstract*:- Sulphur-bearing compounds are extremely detrimental to the environment and to the industrial process equipments. Sulphur containing compounds are usually found in oil and natural gas deposits and, in some mineral rocks. Sulphur containing hydrogen sulphide, occur in crude petroleum, but 90% of it is found in natural gas. Hydrogen sulphide (H_2S) and sulphur dioxide (SO_2) are the two sulphur containing compounds that needs special attention. Hydrogen sulphide is a highly corrosive gas, and sulphur dioxide is also toxic both for environment and industrial equipments.**

Recovery of elemental sulphur from acid gas, during sour natural gas processing and refinery upgrading, is carried out using different processes. The Claus process is the most efficient and popular process employed worldwide for converting toxic hydrogen sulphide to sulphur in the hydrocarbon processing industries. The Claus process can be operated for higher hydrogen sulphide concentration and feed capacities, and has higher H_2S conversion with respect to other processes. Maximum conversion of hydrogen sulphide to elemental sulphur takes place in Claus furnace and remaining H_2S is converted by using catalytic converters.
The objective of this work is to design Claus Furnace and to achieve maximum recovery of sulphur by using only the basic two Claus reactions. The other several side reactions have been neglected in this work. The aim is to model a furnace which can recover maximum sulphur percentage by using only the main Claus reactions. Modelling of equations were done using Runge – Kutta fourth order method for simultaneous differential equations. Simulation part is done using MATLAB.

Result obtained shows a feasible model which results in 47% conversion of hydrogen sulphide to sulphur by utilizing only the two Claus reactions, which is comparable with other models that are designed using several hundreds of side reactions taking place in the furnace.

Keywords* : *Hydrogen sulphide, Sulphur, H_2S, SO_2, Claus, furnace, reactor.

INTRODUCTION

Sulphur is used in various industries, major consumer being the fertilizer industry. Sulphur bearing compounds especially hydrogen sulphide and sulphur dioxide are highly corrosive in nature and thus needs special attention. Small amounts of hydrogen sulphide occur in crude petroleum, but 90% of it is found in natural gas. The refinery feedstock contains wide range off. Hydrogen sulphide is both an irritant and a chemical asphyxiant. H_2S gas level at or above 100ppm is extremely dangerous to life and health. It is flammable and extremely hazardous gas. It is dangerous to equipments too in the presence of moisture. The damage can lead to pitting and step-wise cracking. Burning of H_2S gives off sulphur dioxide which is toxic in nature. Thus sulphur needs to be recovered from refineries for the safety aspects of human being as well as instruments

There are various methods of reducing pollutants containing sulphur, but the most prevalent method is Claus process. The Claus process has been well known and used in industry for over 100 years. The Claus process is applicable for feeds with H_2S composition greater than 30 mole % (in dry basis) and especially in large scale units with sulphur production greater than 2 tons/day [4]. For the sulphur recovery process, the main focus is on the Claus catalytic conversion reactor, but some studies have identified the Claus furnace as one of the most important part of this process. In the furnace the combustion reaction and initial sulphur conversion (through endothermic reaction) takes place.

- ACID GAS BYPASS : Bypassing a portion of the feed around the furnace results in insufficient combustibles in a lean acid gas feed.. The bypassed gas is mixed with the burner effluent prior to the waste heat boiler. At temperature below 1200°F, SO_2 and H_2S will not react to form elemental sulphur without a suitable catalyst [1].

- AMINE EXTRACTION: Gas containing H_2S is passed through an absorber containing an amine solution (Monoethanolamine(MEA)), where the hydrogen sulphide is absorbed along with carbon dioxide. A typical amine gas treating process includes an absorber unit and a regenerator unit as well as accessory equipment.

The traditional Claus process has been a reliable and relatively efficient way of removing H_2S from the fuel gas and converting it into elemental sulphur. The first step is the thermal stage, where one-third of the H_2S is oxidized, producing H_2S and SO_2 in a 2:1 ratio. This process is carried out in a reaction furnace at high temperature. Some sulphur is formed but the remaining unreacted H_2S proceeds to the next step i.e. catalytic step. In catalytic stage the remaining H_2S is reacted with the SO_2 formed in the thermal stage at lower temperatures over a catalyst bed to make over sulphur. Two to four catalytic stages are needed to obtain 94 to 98% conversion [21]. The reactions are:

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$$3\ H_2S + 3/2O_2 \leftrightarrows 2\ H_2S + SO_2 + H_2O$$
$$2H_2S(g) + SO_2 \rightarrow (3/n)S_n(g) + 2H_2O$$

The thermal reaction furnace is the most important element. Oxidation of one-third of hydrogen sulphide to sulphur dioxide using air is done in the thermal furnace. Temperatures are usually in order of 1000 - 1400°C [15]. The oxidizing reaction is exothermic in nature and without any thermodynamic restriction.

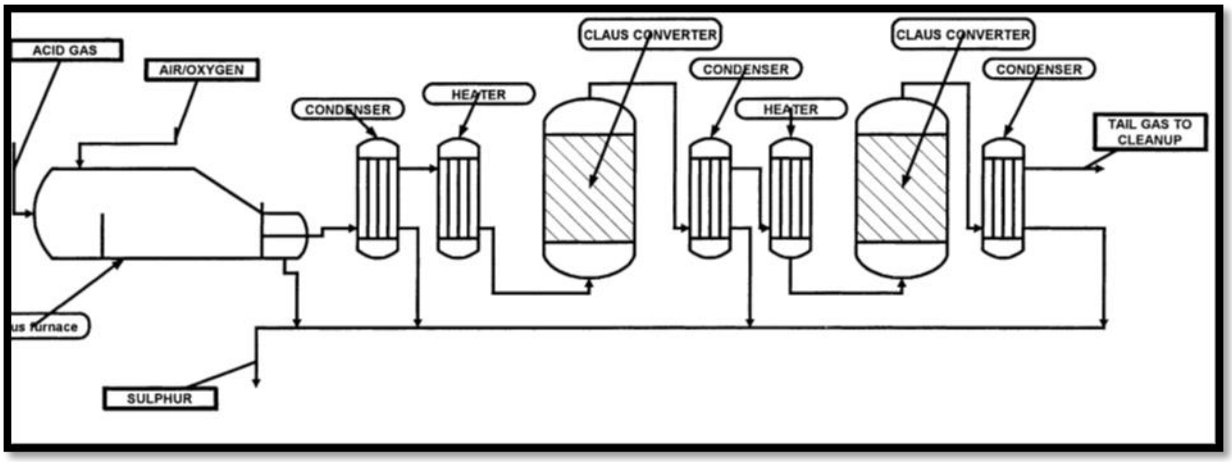

Fig1 : Schematic representation of Claus Process[23]

Two-third of the unreacted hydrogen sulphide reacts with sulphur dioxide to produce elemental sulphur through the so-called Claus reaction:

$$2H_2S(g) + SO_2 \rightarrow (3/n)S_n(g) + 2H_2O$$

The off-gas leaving the furnace enters the waste heat boiler, where it is quenched to about 300°C, so as to prevent recombination reactions. The first separation of liquid elemental sulphur is carried out in the first condenser [17]. The hydrogen sulphide conversion goes on in the catalytic region, where further separation is carried out resulting in 99% recovery of sulphur. It is the main part of the sulphur recovery unit. Reaction furnace has two primal targets. First: Burning 1/3 of existent H_2S in feed and product SO_2 for Claus equilibrium process, catalytic process and preparation H_2S / SO_2 = 2/1 relation for doing Claus equilibrium process with predicting conversion. Second: Destruction and burning any type of component that may damage the downstream equipment's operation.

Claus furnace plays an important role in the unit. Many other factors are dependent on the performance of the furnace, from process efficiency to other equipment operations [22].

MODELLING & SIMULATION

A mathematical model is developed for the furnace used in Claus process for sulphur recovery. Claus furnace can be modelled using a non-ideal reactor, so the furnace can be represented by a plug flow reactor. There are multiple reactions taking place simultaneously in the furnace. In this work maximum amount of available kinetics has been used, but to avoid complexity, free radicals and complex reactions have been ignored.

ASSUMPTIONS

Following assumptions have been taken to model the Claus furnace:

- Reynolds number is greater than 2100, so plug flow pattern is considered.
- Prandtl number is much greater than1, radial diffusion of mass and energy is negligible.
- Axial dispersion is negligible compared to mass transfer by convection in axial direction.
- Due to low pressure and high temperature condition, the gas mixture is an ideal gas.

MODELLING

The furnace is considered to be an adiabatic plug flow reactor. Reactor length is broken into small elements, and mass and energy balances are written for each element.

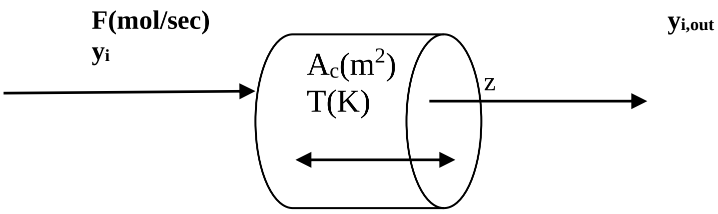

Figure 2: Differential element of plug flow reactor

Consider a small element of the plug flow reactor, of length 0.5 m. Mass balance for each component and energy balance are formed.

Here, F is the molar flow rate of feed

y_i - is the mole fraction of feed

$y_{i,out}$ - is the mole fraction of outlet stream

z - is the length of the elemental section

A_c - is the cross- sectional area of the element and T is temperature in Kelvin scale.

The equations are solved using Runge – Kutta fourth order method for simultaneous differential equations.

MASS BALANCE

Mass balance along the axial direction in a differential element of the reactor for *'i'* component:

here N= 5

$$(-F/A) * (dy_i / dz) + \Sigma_{i=1}^{N} (r_i) = 0$$

ENERGY BALANCE

Energy balance along the axial direction in the differential element of the reactor:

$$(-F/A) * C_p*(dT/dz) + \Sigma_{i=1}^{N} (r_i)*(-\Delta H_{f,i}) = 0$$

CHEMICAL REACTIONS

There are many reactions taking place in the furnace. But, it is difficult to consider all the reactions. Nearly 1500 reactions, take place in the Claus furnace with about 150 molecules and radicals. To avoid complexity only the main reactions have been considered in this work neglecting free radicals and complex reactions. The reactions with their respective rate kinetics have been extracted from the references [18, 19, 22].

Claus reactions in the thermal section:

$H_2S + 1.5\ O_2 \rightarrow SO_2 + H_2O$ .... (1)

$H_2S + 0.5SO_2 \leftrightarrow 3/2\ S_2 + H_2O$ .....(2)

RATE KINETICS FOR THE TWO REACTIONS

$(-r_{H2S,1}) = 14*10^6*e^{-(11/RT)}*\text{þ}_{H2S}*\text{þ}_{O2}^{1.5}$

$(-r_{H2S,2}) = 10^7* e^{-(10.6/RT)}* \text{þ}_{H2S}*\text{þ}_{SO2}^{0.5} - 0.5*10^6* e^{-(5.1/RT)}* \text{þ}_{H2S}* \text{þ}_{S2}$

Initially the feed containing acid gas stream and air is supplied from an external source. The feed consists mainly of hydrogen sulphide gas, water vapour. On entering the furnace, reactions take place and sulphur dioxide is formed, further from which elemental sulphur is extracted out in form of S_2 liquid. The initial conditions of the input stream are as follows:

Table 1: Initial feed conditions

Feed stream	**Stream Composition**	**Air Composition**
Temperature(K)	640	210
F(mol/s)	200	200
Pressure (atm)	0.1747	
Feed	**Mole Fraction**	
H_2S	0.45	----
H_2O	0.08	0.037
O_2	----	0.21
SO_2	0	-----
S_2	0	----
N_2	----	0.753
CO_2	0.4699	
NH_3	0.0001	

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Table 2: Initial feed conditions on N_2, CO_2, NH_3 free basis

Feed stream	**Stream Composition**
T(K)	850
Feed	**Mole Fraction**
H_2S	0.5828
H_2O	0.1451
O_2	0.2719
SO_2	0
S_2	0
N_2	0.379
CO_2	0.2249
NH_3	0.00005

The above table shows the feed contents taking N_2, CO_2 and NH_3 on free basis. These components are present in the input feed.

RESULT AND DISCUSSION

The main objective of this work is to attain sulphur recovery from sulphur containing compounds. The focus is on the variation in sulphur compounds i.e. mole fraction of S_2 and SO_2 at the outlet stream.

Initially the temperature taken is 850K. By burning combustible substances in the beginning, temperature rises to 1500K. Then, the temperature starts decreasing and after reaching 750K it nearly becomes constant. The exothermic reaction and the increasing temperature provide suitable condition for other reactions to occur. The ratio H_2S/SO_2 starts decreasing as sulphur dioxide is formed and finally 2.29 ratio is reached.

The thermal section gives nearly 40% to 60% sulphur at outlet. For 90% recovery catalytic reactors should be added. Since, **only two main reactions** are considered in this work, all the side reactions have been neglected so the **40% recovery is optimum**, that suggests that on considering all the side reactions recovery will reach to 90~95% as the other reactions are supporting reactions that will enhance sulphur recovery.

The table shown below gives a comparative chart of both input feed and the output stream values for each component.

Table 3: Output feed stream

Feed Composition	**Input Feed stream**	**Output Feed stream**
T(K)	850	879.5191
H_2S(mole fraction)	0.5828	0.1133
H_2O	0.1451	0.2266
O_2	0.2719	0.1752
SO_2	0	0.0493
S_2	0	0.4695

Table 3 gives a comparative chart of the input and output feed stream. H_2S concentration decreased from 0.528 to 0.1133 which shows its consumption and thus formation of SO_2. Temperature initially increased to 1400K, as SO_2 starts forming, and finally temperature of the outlet stream was 879.5K.

Figure 2 represents the variation of temperature with the mole fraction of S_2. It is the desired product and its final recovery is 47% that is comparable with that of plant.

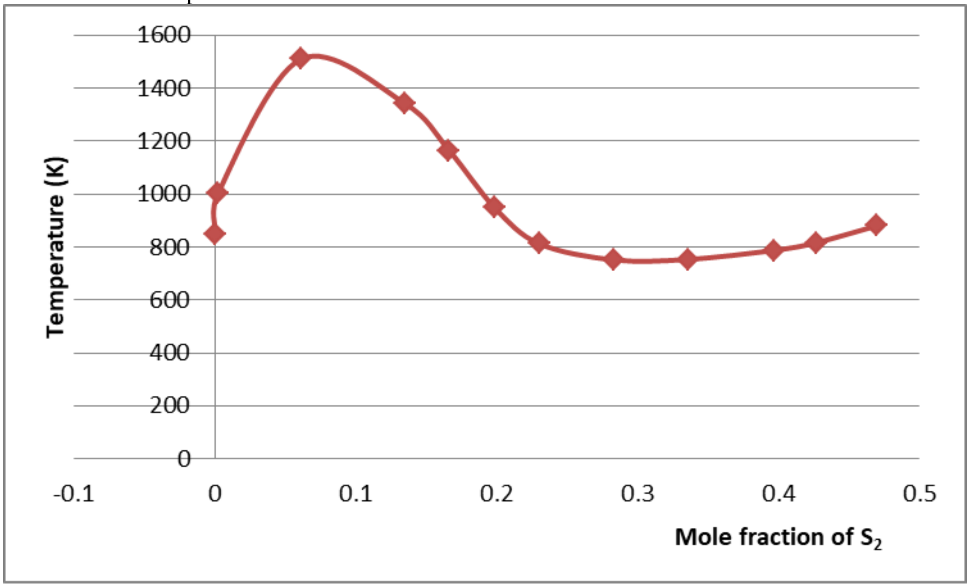

Figure 2: Temperature profile against mole fraction of S_2

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Figure 3 represents the temperature profile with respect to SO_2. Initially as the input feed enters the furnace temperature starts increasing and SO_2 starts forming, so its value keeps on increasing at the desired ratio SO_2 becomes 0.0493.

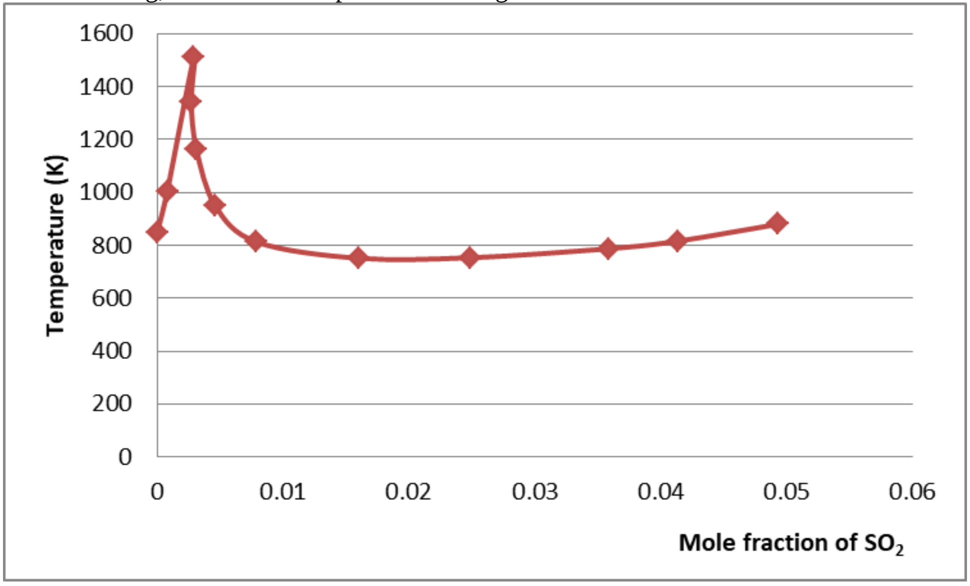

Figure 3: Temperature profile against SO_2

The temperature v/s H_2S plot represents the variation of temperature with the H_2S concentration. Initially the temperature taken at 850 K, increases to 1200 K and then to 1509 K, since the reactions are exothermic in nature. On increasing the length of the reactor temperature starts decreasing and concentration of H_2S also starts dropping to lower concentration as it is getting consumed.

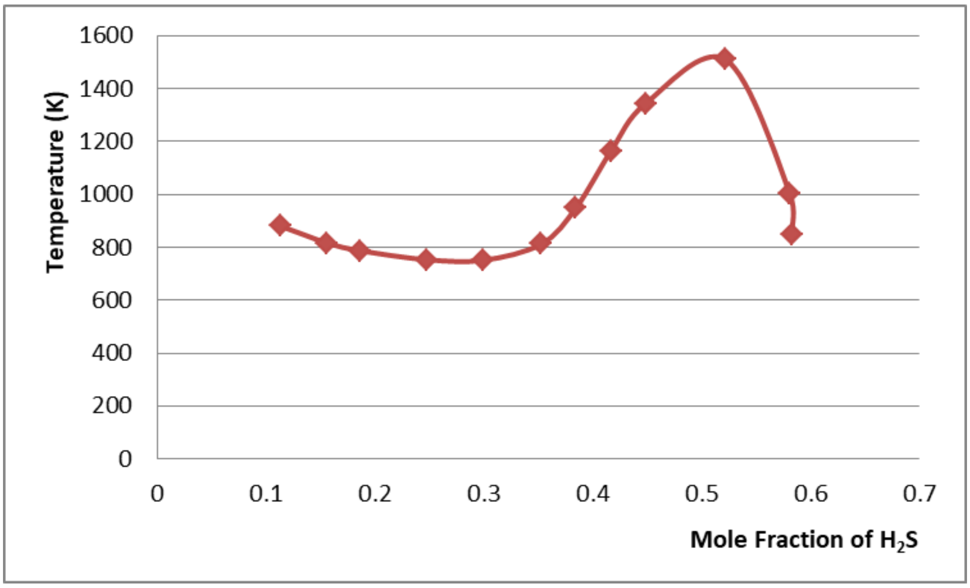

Figure 4: H_2S profile against temperature

CONCLUSION & RECOMMENDATION

In this work modelling and simulation of Claus Furnace was performed using a kinetic model. There is a slight deviation in values, since this work consists of only two main reactions and not the other reactions. The aim was to first study the nature of temperature and, the nature of ratio decrement with respect to temperature and sulphur recovery which can result in maximum recovery of sulphur. Secondly, to avoid complexity, while the works [18, 19 , 22,21] includes 12 to 15 reactions.

Effect of furnace outlet temperature to inlet temperature, fuel concentrations at outlet, H_2S/SO_2 ratio, sulphur recovery, H_2S consumption were investigated in this work. Maximizing sulphur recovery was the main aim of this work, and H_2S/SO_2 ratio parameter should be as close to 2 for better performance. The equations were solved using Runge – Kutta method for simultaneous differential equations. Sulphur was recovered to 0.4695 mole
fraction from zero, that is 47% that suggests that on considering all the other side reactions recovery will reach to 90~95% as the other reactions are supporting reactions.

Thus, the Claus furnace is a good candidate for increasing sulphur recovery and to eliminate contaminant emission.

Recommendations that can be given after this work are: Firstly, if only few more reactions are taken into account it would decrease the furnace length, since furnace length should also be as small as possible taking cost into account, and if few other reactions are taken into consideration, then ratio of H_2S/SO_2 could be reached earlier, with higher percentage of sulphur recovery in thermal stage.

The model thus obtained gives 47% sulphur recovery. Hence it is proved, that only Claus reactions are sufficient to eliminate sulphur, but since refineries have thousand tons of feed stream containing H_2S.Origin of these streams are from different process reactors, so they usually contain many different species and radicals, which while reacting in the Claus furnace results in different complex reactions. These radicals finally have to be taken into account for elimination process and maximum sulphur recovery.

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