ISSN NO. 2320-5407

Journal homepage: http://www.journalijar.com
Journal DOI: 10.21474/IJAR01

INTERNATIONAL JOURNAL OF ADVANCED RESEARCH

RESEARCH ARTICLE

Hydrogen Sulphide (H_2S) Gaseous Control in Claus Process.

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Manuscript Info

Manuscript History:

Received: 10 February 2016
Final Accepted: 19 March 2016
Published Online: April 2016

Key words:
H_2S, pollution; catalyst; Claus process; sulphur; recovery.

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Abstract

The efficiency of the Claus process plant is determined by material balance. A new commercial available catalyst is recommended with contact time 3 seconds. A pilot plant has been designed to optimize temperature and air to gas ratio for maximizing of sulphur recovery in process thus reducing H_2S pollution.

Introduction:-

The Claus process remains to be the extensively used method for the conversion of H2S to sulfur [1].
The mission of Claus processes is to recover elemental sulfur from hydrogen sulfide and, more generally, from byproduct gases originating from physical and chemical gas and oil treatment units in refineries, natural gas processing, and gasification plants [2]. Sulphur is recovered from the Claus plant by the reaction

$$2H_2S\ (g) + SO_2\ (g) \xrightarrow{\text{Bauxite}} 3S\ (s) + 2H_2O\ (g) \quad \ldots\ldots. (1)$$

ΔH = -35 Kcal/g.mole

The process for the recovery of sulphur in Claus plant involves the producing SO_2 in the burner. SO_2 can be produced by the combustion of the H_2S with air in approximate proportion of 1:2.5. The incoming stream to the burner is gas and air through the blower. The reaction in the burner is as follows:

$$H_2S + 3/2\ O_2 \longrightarrow SO_2 + H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

ΔH = -123.97 Kcal/g.mole
H_2S and SO_2 are catalytically reacted in a Claus converter. The reaction is highly exothermic. There are two converters and a condenser after each converter. As elemental sulphur is formed, the reverse dynamic of the reaction starts, according to the Le_chateliers principle. Thus for better yield, we remove the sulphur in the molten form by condensing the gases. Fig.1 gives block diagram of Claus process for sulphur recovery from hydrogen sulphide. The condenser prevents the sulphur from solidifying. Finally, the gases are let off in the atmosphere through the stack.

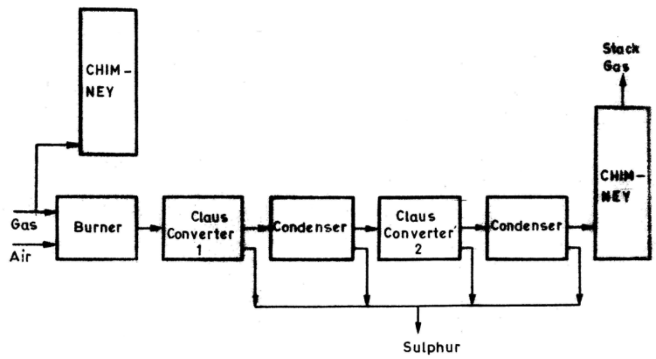

Fig. 1. Block Diagram of Claus Sulphur Recovery Process from Hydrogen Sulphide

The paper deals with the following.

- The gas analysis, in order to find out the variation in the concentration of H_2S in the inlet gas stream.
- The flow rate measurement experiments to quantity the variation in the inlet gas flow rate.
- Increase of the sulphur recovery, for which exact areas of inefficiency are identified. The material balances are done in the various sections of the plant.
- Presence of COS and CS_2 in the inlet gas stream has been a problem, studies of different available commercial catalysts are made and a catalyst which increases hydrolysis of these components was recommended.
- The ratio of air to gas entering to burner affects the yield of sulphur. A catalyst was recommended which gives a higher yield of sulphur in excess of oxygen.

Methodology:-

The problems encountered in the Claus plant are the variations in the H_2S concentration and gas flow rate. The experiments were conducted with a view to establish these variations and hence improved the yields of sulphur. To find the H_2S concentration in the input stream, the gas was sampled at the pressure point of mainline H_2S in the Claus control room. The chemical analysis was done. To estimate the flow rate variation, experiments were conducted with gas holder. The rate gas holder rising or falling was found for each of the gas holder and the pressure of the gas in the holder and the rate of rising or falling of the gas holder gives the flow rate at that time. The pressure drop between the gas holder pressure point and Claus control room point was also found at the same time. A graph of flow rate Vs pressure drop was plotted. From this plot the pressure drop can be found out. In order to increase the sulphur yield, the exact area of inefficiency must be identified. The material balance for sulphur was done for the whole plant. The efficiency of the converter was found to be very low, i.e. (15.47%). In order to increase the efficiency of the converter and hence the Claus plant efficiency, catalyst selection was made and a design of new converter was recommended. With a view to control the H_2S produced in the furnaces, the present rate of charging was found and the optimum number of charges that should be done per hour of the day was established. To obtain kinetic data for the Claus reaction H_2S and air let into a catalytic reactor (2.47 liters). Space time is varied from 3 to 6 seconds, at three temperatures (150^0C, 225^0C, 300^0C). This gives us the rate equation along with the optimum temperature and optimum space time. Next H_2S, CS_2 are fed with varying ratio of air (2.85 to 3.55). This gives us the optimum gas to air ratio.

Gas Analysis (Concentration of H_2S and CS_2):-

The gas was analyzed to find out the variation in the concentration of H_2S and CS_2 in the input stream to the burner. H_2S in the input stream to burner is 60.28% and CS_2 is 15.73%. The difference between the percentage gas absorbed and percentage H_2S and CS_2 present, is the percentage of CO and CO_2 present in the sample taken. Average percentage of CO and CO_2 present in the samples was found to be about 17%.

Sampling Parameters:-

1. Sampling location: The gases were analyzed before gases enter the burner. The sampling point was the pressure point of main line H_2S available in the Claus control room.
2. Period of sampling: For effective results, the period of sampling was established as 1 hour.

3. Size of sample: 500 ml of gas was dissolved in 150 ml of alcoholic KOH.

Description of the equipment:-

Gas samples were taken with the help of Orsat apparatus as described in figure 2. Saturated sodium chloride solution was used for pumping the gas into the absorption town. Water cannot be used the cylinder meant for it. For gas collection, 150 ml of alcoholic KOH was prepared.

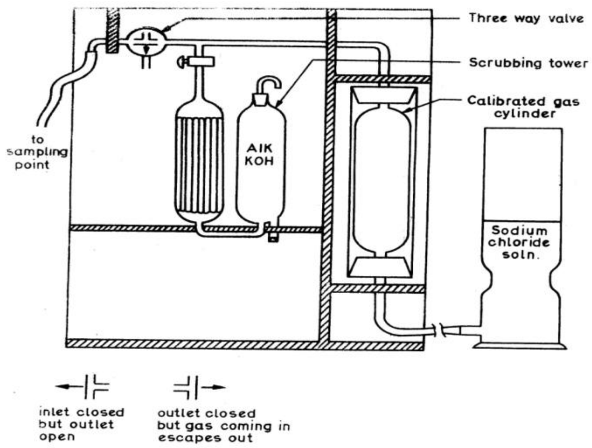

Fig. 2 Orsat Apparatus

Flow rate determination:-

To establish flow rate variation, the pressure drop experiments were conducted with the gas holder. The pressure drop, Δ P Vs Q (flow rate) has been plotted (Fig 3). This can act as a rough guide to ascertain the flow rate of a given pressure drop which can be easily read by installing a u-tube manometer. The flow rate Vs time has indicated that the maximum flow rate around 145 m^3/hr exist at maximum charging to the furnaces. In general the flow rate of the gas to the Claus plant is varying between 50 m^3/hr to 150 m^3/hr. To find out the efficiency of the Claus plant, the material balance of CS_2 plant was done. The efficiency of the Claus plant was found to be 68.7 %. The sulphur input to the Claus plant found from the experiments is within 0.75% error.

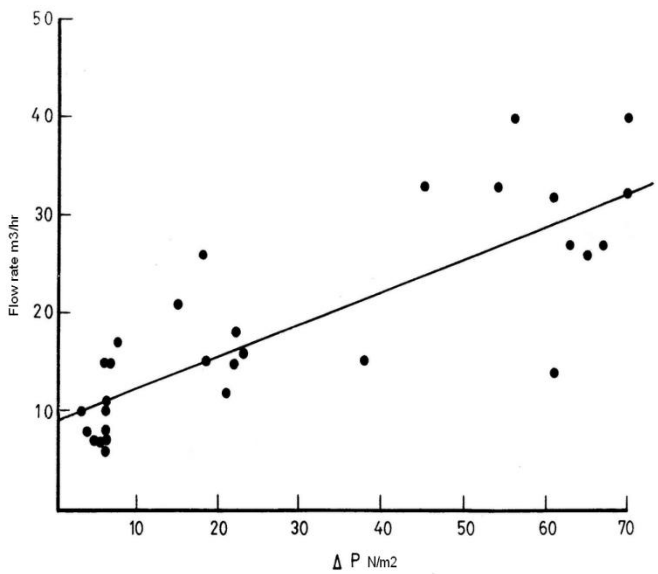

Fig. 3. Flow Rate Vs Pressure Drop Q (m^3/hr) Vs Δ P (N/m^2)

The temperature of Claus burner is around 700^0C. H_2S conversion at this temperature was 63% (Fig. 4).

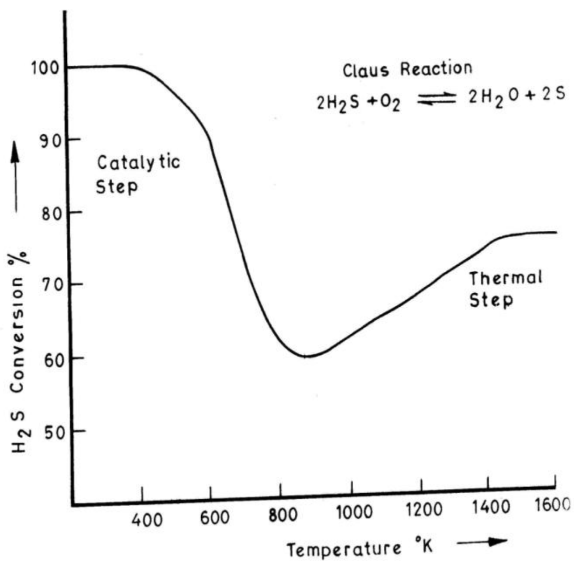

Fig. 4. H_2S Conversion Vs Temperature

If converter efficiency increases, the Claus plant efficiency will also be increases, therefore to improve the efficiency of the converter and hence the Claus plant efficiency, a detailed study of the commercial catalyst was done. To obtain the best conversion of H_2S, the following steps are necessary.

a) Remove the Sulfur product at each step periodically.

b) To use the most effective catalyst i.e. those which provide a rapid reaction rate and obtain thermodynamic balance as quickly as possible. The detailed study of catalysts [6-8],

revealed that CRS-31 is the best catalyst for Claus plant.

Basis for CRS-31 Selection [9-13]:-

Presence of COS and CS2 in the gas mixer:-

The main problem in the converter is the presence of COS and CS_2 which must be hydrolyzed. CRS-31 increases the hydrolysis of COS and CS_2.

Reactions are as follows:

$$COS + H_2O \rightarrow CO_2 + H_2S \quad \ldots\ldots\ldots\ldots (3)$$

$$CS_2 + 2\,H_2O \rightarrow CO_2 + 2\,H_2S \quad \ldots\ldots\ldots\ldots (4)$$

Ratio of H_2S to air entering the burner:

The gas to air ratio is controlled manually. As there are huge variations in the flow rate and concentration, the ratio is not kept proper most of the time. This normally results in excess of air. If air is more than the stoichometric ratio, more of SO_2 will be formed. Further it will react with oxygen and sulphate formation will taken place. Sulphation effect is a major reason for loss of catalyst activity. The total elimination of which is practically impossible. To achieve the highest performance during an extended period of time, CRS-31 is recommended. CRS-31 increases the yield of the Claus reaction in presence of a large excess of oxygen.

$$2\,H_2S + SO_2 \xrightarrow{CRS-31} 2H_2O + 3S \quad \ldots\ldots\ldots\ldots (5)$$

Since CRS-31 increases the hydrolysis of COS and CS_2, H_2S will be formed and this H_2S will react with excess SO_2 to give sulphur. Hence sulphur yield increases. Regeneration of the catalytic bed is not required with loading of CRS-31.

Converter Design [14-16]:-
To increases the converter efficiency to 95% with catalyst CRS-31, a new converter designed proposed.

Specific design approach:-
Less efficiency of converter is because of following reason
(a) The catalyst used, (b) Sulphation, (c) Sulfur deposition.
To avoid sulphation and to increase the activity of catalyst, a new catalyst CRS-31 is recommended. It was suggested that the catalyst to be placed in the tubes and steam to be passed around it. The length of the tube will be determined by allowable pressure across the catalyst bed. The catalyst will be supported by wire mesh fixed at the bottom of the tube. The diameter of tube was optimized w.r.t. number of tube and with steam passing around the tubes, so that the problem of sulfur deposition on the catalyst can be eliminated.

Functional Design:-
Contact time vs. temperature plot for CRS-31 catalyst, has indicated 5 sec as an optimal contact time. The design is been done for maximum flow rate 150 m^3/hr and ratio of air gas to the burner 2.5:1. Only 1/3 of the gas is used for the production of SO_2 in the burner. Therefore 2/3 of the gas goes to the converter as per the reaction in the burner.
$H_2S + 3/2\ O_2 \rightarrow H_2O + SO_2$ SO_2 …………….. (6)
The temperature of convertor is 300^0C. The total flow rate to the convertor is found to be 840.4 m^3/hr. Therefore in view of 5 sec contact time and flow rate 840.4 m^3/hr, the volume of converter is comes to be 1.17 m^3 . 10% over design is done due to aging, channeling and sulphation problems. The maximum allowable pressure drop across the catalyst bed in the converter is 245.166 25 N/M^2. For this design, 49.033 25 N/M^2 is suggested so that due to aging, sulphation and channeling, this does not cross the maximum limit. Table 1 gives the details about the catalyst.

Table 1. Details of catalyst

Parameters	Details
The area of the catalyst	4.2 m^2
Gas velocity	3.33 m/min
The number of tubes	565
Shell ID	3.35 m
Pitch	1.25 times tube diameter (5”)
Bulk density of CRS-31(Rhone Poulenic)	900 kg/m^3 m^3
Volume of catalyst bed	1.28 m^3
Catalyst required	1152 kg

Typical properties of the catalyst CRS-31for Claus plant is given in Table 2.

Table 2. Properties of the catalyst CRS-31

Properties	Details
Shape	Diameter 4mm
Specific surface diameter	120 m^2/gm
Bulk density	0.9 gm/ml
Average crushing strength	9 kg
Composition	TiO2 > 85%

Furnace charging:-
The quantity of H_2S varies with variation in the time of charging. The sulfur is fed continuously to the furnace in the liquid form. Due to non-uniform charging of the charcoal, fed is not in proportion to the sulfur feed when there is less charcoal, more of H_2S is produced in comparison to CS_2 produced. Therefore, charging of charcoal must be done uniformly to the furnaces. To reduce the variation, the average number of chares that should be done every hour of the day, was calculated to be 1.35 charges. Two converters should be used in series, so that efficiency as high as 95% continues for a longer period. In the beginning, the first converter will do most of the conversion (93-95%) and second converter will be a small portion of it (3-5%) but after some years, the efficiency of the second converter will rise to (10-35%).

Recommendations:-

The following recommendations are made to increase the yield of sulfur in the Claus plant.

1. The commercial catalyst CRS-31 (Rhone-Poulenic Us) should be used [17] as
   a. It increases the hydrolysis of COS and CS2.
   b. It increases the sulfur yield even in presence of excess of oxygen.
2. A modified converter should be used with catalyst CRS-31 (Rhone-Poulenic Us) inside the tube and steam passing around, it in order to
   a. Sulfur deposition
   b. Sulphation
3. Two converters should be used in series, so the overall efficiency of the plant will remain at 95%for a longer period of time.
4. The charges to the furnaces should be at uniform rate.

References:-

1. Zare Nezhad, B., An investigation on the most important influencing parameters regarding the selection of the proper catalysts for Claus SRU converters, J. Ind. Eng. Chem. 15,143-147,2009.
2. Signor, S., Manenti, F., Grottoli, M. G., Fabbri, P., and Pierucci, S., Sulfur Recovery Units: Adaptive Simulation and Model Validation on an Industrial Plant, Ind. Eng. Chem. Res. 49 ,5714-5724,2010.
3. John B "Sulphur removal and recovery process" American Chemical Society, Washington D. C., 1975.
4. Smith J M "Chemical Engineering Kinetics" McGraw Hill, New York, Third Edition, 1981.
5. Process Slashes Claus Tail Gas Pollution, Chemical Engineering, McGraw Hill, June, 14, 1971.
6. Alcoa S-100 Claus Catalyst literature supplied by Alcoa, USA.
7. Kaiser Chemicals Catalyst literature supplied by Kaiser Limited, USA.
8. Rhone-Poulenic Specialities Chemiques Catalyst.
9. Sulphur recovery process: compute for loading role. Chemical Engineering, McGraw Hill, December 13, 1971.
10. Rhodia developes quick, simple way to remove H_2S from gases; Chemical Engineering, McGraw Hill, Oct., 1972.
11. Pritchard Process to take sulphur out of tail gas from Claus plant; Chemical Engineering, McGraw Hill, Feb. 7, 1972.
12. Treading Hydrogen Sulphide; Chemical Engineering, Mc Graw Hill, Oct. 6, 1988.
13. Sulphur removal flue gas Desulphurization process, McGraw Hill, 1977.
14. Kern, D Q "Process Heat Transfer" McGraw Hill New York, 1950.
15. Perry, J H "Chemical Engineering Handbook" McGraw Hill, New York, Eight Edition, 2007.
16. J. Welty C.E.Wicks,R.E Wilson and Gregory L.Rorrer, Fundamentals of Momentum, Heat, and Mass Transfer , John Wiley and sons, New York, Fifth Edition,2007.
17. S. Tong et.al. Kinetic modeling of the hydrolysis of carbon disulfide catalyzed by either titania or alumina The Canadian Journal Of Chemical Engineering 73(2):220 - 227 , April 1995