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Contribution to the thermal and catalytic oxidation of hydrogen sulphide

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ABSTRACT

The present study was undertaken in order to investigate the thermal and the catalytic depuration of hydrogen sulphide (H₂S) using the Claus experimental method with an initial molar concentration of 12 % in the gaseous mixture. The thermal and catalytic transformation of H₂S has been investigated between 350-700°C and 250-600°C respectively. Thermostability verification of H₂S indicates that H₂S remains stable during the experiment. In addition to the oxidation of H₂S by oxygen, the oxidation of H₂S by SO₂ is equally undertaken. The yield depends on the concentration of O₂ in the gaseous mixture and the contact time. The interaction of sulphur with water vapour is not possible. The oxidation of sulphur by O₂ gives a low concentration of SO₂. Results obtained show a possibility to replace the Claus thermal phase by a catalytic one in view to transform the acid gas into elementary sulphur and to extend the field of utilization of this process for catalytic depuration of sulphurous gas. © 2010 Trade Science Inc. - INDIA

KEYWORDS

Hydrogen sulphide;
Thermal oxidation;
Catalytic oxidation;
Claus method;
Temperature.

INTRODUCTION

The aim of this study is to highlight the fight against the pollution of the environment. Industrial sewage transports and energetic setting-ups wastes entail a considerable pollution of the environment. Atmospheric and water pollution generate changes of micro-climate, soil acidification, animal and plant poisoning as well as noxious effects on human health.

Chemical industries constitute the main source of pollution. The greatest danger comes from the siderurgy

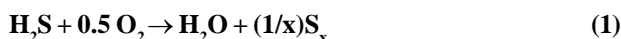
and metallurgy of non-iron metals, from thermal power-stations and from car transports. Toxic substances found in sulphur containing gaseous wastes such as hydrogen sulphide (H₂S) have an impact on the health of living creatures^[1,2]. There are several methods through which the concentration of H₂S in sulphur containing gaseous wastes can be reduced. However the best and most used of these methods is catalytic filtering. Among the catalytic filterings, the simplest and most practical is the H₂S catalytic oxidation through O₂. This method is attractive because the result of its use helps both to

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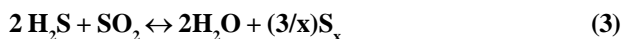
TABLE 1 : Thermal oxidation of H₂S by O₂; O₂/H₂S= 0.45; concentration of H₂S=3 moles %; O₂=1.35 moles %; N₂= 95.65 moles %

Speed of gas feed, ml/mm	Gas concentration at reactor outlet, moles % at temperature, °C					
	350		450		700	
	H ₂ S	SO ₂	H ₂ S	SO ₂	H ₂ S	SO ₂
100	3.00	0.00	1.94	0.35	0.70	0.42
200	3.00	0.00	2.05	0.16	0.84	0.30
300	3.00	0.00	2.10	0.10	0.95	0.21
Equilibrium concentration, mole %	0.17	0.07	0.85	0.37	0.76	0.33

eliminate H₂S and to obtain a non-toxic substance which is elemental sulphur. Generally, H₂S sulphur is obtained through the Claus method. The current modification of this method involves thermal and catalytic stages. Thermal transformation of H₂S by O₂^[3-6] or SO₂^[7,8] or thermal dissociation of H₂S^[9] helps to easily transform part of H₂S into elemental sulphur and SO₂ through the following reactions:



These reactions are usually carried out within temperature intervals oscillating between 200-350°C and 800-1200°C. Meanwhile to the best of our knowledge, not many studies have been carried out within the interval 350-700°C^[10,11]. A stable combustion of H₂S at a gaseous stage is one of the requirements of this process. The thermal process is followed by a subsequent one (H₂S/SO₂ relation = 2) in which there is a catalytic reaction, involving the SO₂ produced. It is worth noting that such a reaction does not happen during the 1st stage.



Besides, there is a forming of such reactions as:



When H₂S < 15 moles %, the combustion of H₂S with air becomes impossible. The transformation of such a gas requires a modernization of the Claus method. One of the possibilities through which that gas can be transformed is the replacement of the thermal stage by catalytic oxidation. The main difficulties encountered during the realization of such a transformation lie in the choice of a catalyst that has a high capacity of converting

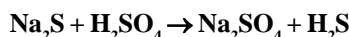
TABLE 2 : Thermal oxidation of H₂S by O₂; O₂/H₂S= 0.6-0.7; concentration of H₂S=3 moles %; O₂=1.99 moles %; N₂=95.02 moles %

Speed of gas feed, ml/mm	Gas concentration at reactor outlet, moles % at temperature, °C					
	350		450		700	
	H ₂ S	SO ₂	H ₂ S	SO ₂	H ₂ S	SO ₂
100	3.00	0.00	1.30	0.53	0.58	0.50
200	3.00	0.00	1.64	0.39	0.60	0.47
300	3.00	0.00	1.71	0.38	0.62	0.45
Equilibrium concentration, mole %	0.13	0.12	0.66	0.58	0.57	0.50

H₂S into sulphur and which has a high stability in situations of highly exothermic reactions. The main criteria for choosing such a catalyst are: chemical activity, stability and cost value. It should have pores with diameters that do not limit the progress of the reaction^[12]. Finally, the catalyst should have a high mechanical stability^[13,14]. Natural bauxites were the first catalysts used in the Claus method^[15,16]. However, they had a low mechanical stability and a variable composition, and this led to the implementation of more efficient catalysts. Among the partial oxidation catalysts of H₂S, the multiple composition systems like those composed of iron, chromium and zinc oxides^[17] are the most appraised; for they are endowed with a great stability and a good chemical activity in the Claus method. Furthermore, these catalysts show a great mechanical resistance and their preparation is very simple.

MATERIALS AND METHODS

H₂S is obtained from the reaction:



H₂S oxidation reactions by SO₂, O₂ and the basic oxidation of sulphur with steam were carried out in the laboratory using a quartz reactor (diameter: 20 mm, length: 180 mm). The analysis of raw materials and chemicals was done with an LXM-8MD chromatograph equipped with a calorie conductivity detector. Two chromatographic columns were used for these analyses. The first column (diameter: 3mm, length: 2m) used to analyse SO₂ and O₂ was filled with silicagel of ASKG brand (0.25-0.50 mm fraction). The second column (diameter: 3mm, length: 1m) used for the analysis of oxygen was filled with CaA zeolites (0.25-0.50 mm

fraction). The carrier gas was hydrogen. Thermatographic columns were thermostated at 70°C each had an output of 1.5 l/h. The catharometer's temperature was 100°C. The analysis sensitivity is 0.01 mol %. The method used for the catalyst synthesis was that cited in the literature^[6]. For the radiographic analysis of the catalyst using x-rays, the light source was provided by a copper-anode ($k\alpha = 1.54 \text{ \AA}$). The device is endowed with a nickel filter (1mm thick). The analysis of the catalyst through infrared is done by using a UR-20 spectrophotometer within the co pass of 450-1400 cm^{-1} and 1600-3800 cm^{-1} .

RESULTS

H₂S thermal oxidation

To verify the thermo stability of H₂S, it was been passed through the reactor of a gaseous mixture made of 3 moles% of H₂S, 97 moles% of helium and within temperatures oscillating between 350 and 700°C. The flow rate of the gas vector was gradually increased from 100, 200 to 300 ml/mn. No trace of hydrogen and sulphur was detected at the exit of the reactor. Besides, the H₂S concentration remained constant. This showed that H₂S was stable under the same experimental conditions.

The influence of O₂ concentration

The thermal oxidation of H₂S by O₂ at temperatures between 350 and 700°C has been done was carried in 2 gas mixtures of different concentrations. In the 1st mixture, the O₂ concentration is 1.35 moles%.

(O₂/H₂S = 0.45) and in the 2nd one, the concentration may go up to 2 moles% (O₂/H₂S = 0.7). The results obtained are recorded in TABLE 1 and 2.

The thermal oxidation of H₂S by O₂ begins at $t > 350^\circ\text{C}$. The conversion of H₂S increased with an increase in temperature. An increase in the flow rate of the gas vector increased the difference between the experimental and theoretical data as far as the H₂S conversion is concerned. Chemicals used for the thermal oxidation of H₂S were: sulphur, water and sulphur dioxide. The conversion H₂S depends mainly on the concentration of O₂ in the gaseous mixture. For O₂/H₂S = 0.45, at temperatures between 550-650°C and a gas flow rate of 100 ml/mn, the conversion of H₂S into basic sulphur reaches 60%. The increase of the ratio

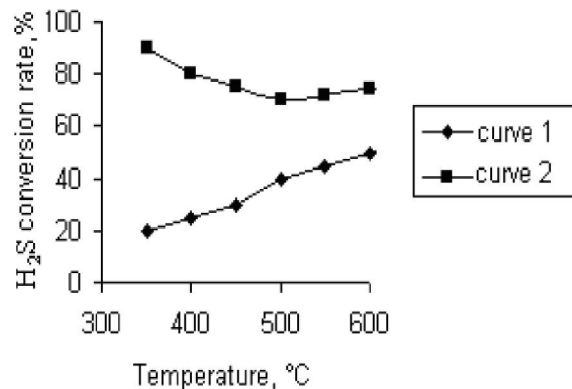


Figure 1 : The thermal oxidation of H₂S by SO₂. Gas concentration in moles %: H₂S=3.0; SO₂=1.5; H₂=95.5. Gaseous flux speed=100ml/mn. Curve 1: experimental data; curve2: theoretical equilibrium

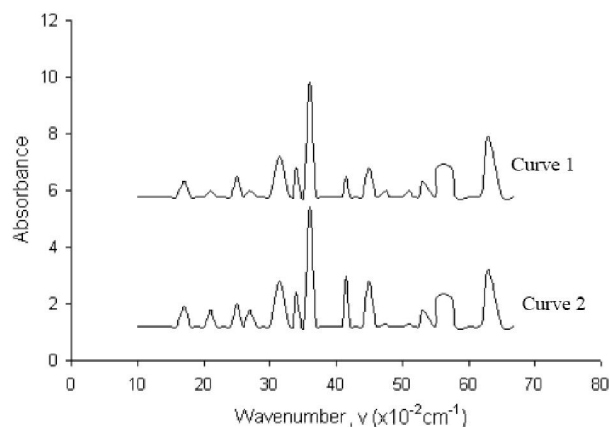


Figure 2 : Diffraction patterns of the catalyst before (curve 1) and after (curve 2) its use

O₂/H₂S = 0.6-0.7 was followed by an increase of the amount of SO₂ that corresponded to a 67% conversion rate of H₂S into sulphur. At $t = 700^\circ\text{C}$, the influence of O₂ decreases and the conversion is equal to the percentage of the theoretical equilibrium which of 70%.

The influence of SO₂ concentration

H₂S conversion rate, as compared to the values of the theoretical equilibrium (Figure 1), shows that as the temperature increases, the conversion rate also increases. When the temperature reaches 700°C, the conversion rate is 50%.

Thermal oxidation of sulphur

The mixture of nitrogen and oxygen with the sulphur vapour passes through the empty reactor. The obtained results are recorded in TABLE 3. We notice that SO₂ appears in the gas as it comes out from the reactor, at $t = 400^\circ\text{C}$ and its concentration increases as temperature

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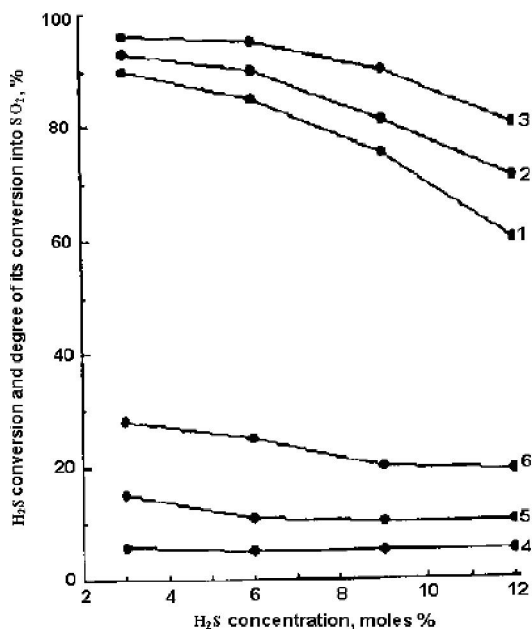


Figure 3 : Dependence of H_2S conversion (1, 2, 3) and its transformation level into SO_2 (4, 5, 6) on H_2S concentration. Flow rate = 6000 h^{-1} ; $O_2/H_2S=0,7$; temperature, $^{\circ}C$: curves 1 and 4 = $250^{\circ}C$; curves 2 and 5 = $450^{\circ}C$ and curves 3 and 6 = $600^{\circ}C$

raises. At $t = 700^{\circ}C$, its concentration is not very high and it does not go beyond 0.10 moles %.

H_2S catalytic oxidation

Physico-chemical study of the catalyst

This study was carried out with a catalyst containing metallic oxides (Cr-Fe-Zn) with the following % composition by mass; $Fe_2O_3 = 24.65$; $ZnO = 26.40$; $Cr_2O_3 = 48.30$; $Co_2O_3 = 0.15$; $SiO_2 = 0.5$.

Initially, the catalyst used for the experiment was like a system made up of spinel structures of $ZnCr_2O_4$ and $FeCr_2O_4$ and of a small amount of non-bonded ferric and chromic oxides. The specific area of the catalyst was equal to $36\text{ m}^2/\text{g}$. The diffractogram shows that the structure of the catalyst remained the same during its stay inside the reactor.

Influence of oxygen concentration

The results were obtained under the following conditions: H_2S concentration of 3 moles%, vector gas flow rate of $6,000\text{ h}^{-1}$ and temperatures $250\text{-}600^{\circ}C$. Sulphur dioxide (SO_2) was produced at all selected oxygen concentrations. When the concentration of O_2 was lower than that of the stoichiometry in the oxidation reaction of H_2S to sulphur (up to 3 moles %), the conversion of H_2S did not go above 86 % at $t = 600^{\circ}C$.

TABLE 3 : Thermal oxidation of sulphur by O_2 . Composition of the gaseous mixture in moles %: $S_8 = 6.3$; $O_2 = 12.6$; $N_2 = 81.1$. Gaseous flux speed = $100\text{ ml}/\text{mn}$

Temperature, $^{\circ}C$	350	400	450	550	700
SO_2 concentration at the reactor leaving, mole %	0.00	0.02	0.03	0.06	0.10

TABLE 4 : Influence of initial concentration of O_2 on the gas composition at the reactor outlet. H_2S initial concentration = 3 moles, flow rate = 6000 h^{-1}

O_2 concentration, mol, %	Gas concentration at the reactor outlet (mol %) as a function of O_2 concentration and temperature								
	250			450			600		
	H_2S	SO_2	O_2	H_2S	SO_2	O_2	H_2S	SO_2	O_2
2.7	2.22	0.15	0.43	1.68	0.24	0.30	1.20	0.30	0.00
3.0	1.89	0.18	0.76	1.44	0.27	0.45	0.78	0.39	0.00
4.2	0.92	0.31	1.35	0.65	0.67	0.86	0.30	1.35	0.00
6.0	0.29	0.56	2.59	0.14	1.82	1.25	0.00	3.60	0.60
9.0	0.04	1.16	4.86	0.02	3.20	2.81	0.00	4.99	1.52

The composition of the gas at the outlet of the reactor is recorded in TABLE 4. The complete interaction of oxygen occurs at $600^{\circ}C$ for an initial O_2 concentration not more than 4.2 moles % (relation $O_2/H_2S = 0.7$). At $t < 600^{\circ}C$ and the ratio $O_2/H_2S > 0.7$, the O_2 concentration in the gas at the outlet of the reactor was high. These results could be due to the insufficient retention time of the vector gas in the catalyst zone. With an increase of the contact time, a complete reaction of O_2 was obtained with the remaining gaseous compounds.

Influence of H_2S concentration

The influence of H_2S concentration was experimented in the temperature range $250\text{-}600^{\circ}C$. The vector gas mixture had a ratio of $O_2/H_2S = 0.7$. The yield of SO_2 , as a function of initial concentration H_2S , may vary from 3 to 12 moles% for a gas flowrate of $6,000\text{ h}^{-1}$ (picture n°3). The increase of the H_2S concentration within the afore-mentioned temperature interval entails the decrease of the H_2S conversion rate. This was especially obvious when $H_2S > 6$ moles %. For concentrations between 3 to 6 moles %, the decrease of the H_2S conversion rate did not go above 4% and it does not depend on the temperature of the process. The H_2S conversion rate into SO_2 also decreases as temperature increased. At temperatures equal to $600^{\circ}C$ and H_2S concentrations ranging from 3 to 12 moles% entail a decrease in the conversion of H_2S

into SO₂ from 25 to 14% and, when the temperature is 450°C, the decrease was from 15 to 8%.

The O₂ conversion rate, as a function of concentration of H₂S in the gaseous mixture, is estimated from the remaining concentration of the compounds which reacted. A decrease in the conversion of H₂S and an increase in its concentration led to a decrease in the conversion of O₂. The oxygen fully reacts at t = 600°C for H₂S concentrations between 3 and 6 moles. H₂S oxidation by oxygen produced chemicals such as sulphur, water and sulphur dioxide. Thus, it is not advisable to neglect the reactions of H₂S with SO₂, of sulphur with steam and of sulphur with oxygen, within the system.

Oxidation reaction of H₂S by SO₂

The composition of the gaseous mixture (in moles %) used in this study was as follows: H₂S = 3.0; SO₂ = 1.5; He = 95.5. The flow rate of the vector gas ranged from 3,000 - 9,000 h⁻¹. The process temperature varied from 250 - 600°C. Results show the influence of temperature on the catalytic oxidation of H₂S by SO₂ is given in TABLE 5. The oxidation H₂S by SO₂ with different volumical speeds is presented in the TABLE 6. When the flow rate increased from 3000 to 9000 h⁻¹, there was a slight decrease (3%) of the (H₂S + SO₂) conversion at t = 450°C.

TABLE 5 : Effect of temperature on the H₂S oxidation by SO₂. Concentration, mole %: H₂S = 3; SO₂ = 1.5; He = 95.5. Volumical speed = 3000 h⁻¹

Temperature, °C	Remaining concentration, mole %		Sum of conversion (SO ₂ +H ₂ S), %
	H ₂ S	SO ₂	
250	0.68	0.35	77.10
450	0.51	0.28	82.00
600	0.83	0.46	71.10

TABLE 6 : Volumical speed influence on the H₂S oxidation by SO₂. Concentration, mol %: H₂S = 3; SO₂ = 1.5; He = 95.5. Temperature = 450°C

Volumical speed, h ⁻¹	Remaining concentration, mole%		Sum of conversion (SO ₂ + H ₂ S), %
	H ₂ S	SO ₂	
3000	0.51	0.28	82.00
6000	0.57	0.30	80.50
9000	0.60	0.32	79.30

Reaction of sulphur with steam

The supply of sulphur solution which was melted by steam was carried out in a stream of helium. The

volumetric flow rate of the gas and the temperature under which the experiment were carried out were: 3000 to 9000 h⁻¹, 250 to 600°C respectively. The reaction rate was estimated as a function of H₂S and SO₂ concentration in the gas at the reactor outlet. The results obtained are recorded in TABLE 7. An increase in temperature and contact time led to an increase in the yield of the reaction between sulphur and steam. However, H₂S and SO₂ concentrations were not high and did not go above 0.27 and 0.14 moles % respectively.

TABLE 7 : Influence of process conditions on the yield reaction between sulphur with steam: S₈ = 6.3 mole %; steam = 5 mole %

Temperature, °C	Gas composition at the reactor outlet (mole %) as a function of flow rate, h ⁻¹					
	3000		6000		9000	
	H ₂ S	SO ₂	H ₂ S	SO ₂	H ₂ S	SO ₂
250	0.04	0.02	0.02	0.01	0.01	traces
450	0.10	0.05	0.09	0.04	0.03	0.02
600	0.27	0.14	0.09	0.05	0.07	0.04

Reaction of sulphur with oxygen

The oxidation reaction of sulphur by oxygen was carried under the same conditions as that of sulphur with steam except that in the latter, water was replaced by oxygen. The reaction's speed was measured using the concentration of SO₂ at the reactor outlet (TABLE 8).

TABLE 8 : Influence process conditions on the yield of SO₂ coming from sulphur oxidation by O₂; S₈ = 6.3 mole %; O₂ = 7 moles %

Temperature, °C	SO ₂ concentration at the reactor outlet (mole %) with flow rate, h ⁻¹		
	3000	6000	9000
250	0.08	0.06	0.02
450	0.10	0.09	0.06
600	0.22	0.20	0.17

As in the previous reaction, the output of the sulphur reaction with oxygen increases with temperature and contact time. For a flow rate of 3000 h⁻¹, H₂S and SO₂ concentration did not go above 0.22 moles %.

DISCUSSION AND CONCLUSION

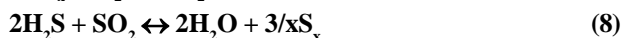
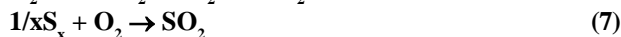
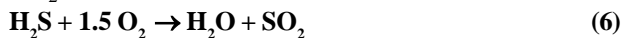
The performances of the Claus method depend on the concentration in H₂S. To the basic reaction H₂S + 0.5 O₂ → H₂O + (1/x)S_x, was added the forming of

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TABLE 9 : Temperature effect of catalyst burning on its activity in H₂S oxidation. Volumical speed= 6000 h⁻¹, time= 10h; H₂S concentration=3mol % ; O₂/H₂S=0,70 ; temperature=600°C

Calcination temperature °C	650	700	800	900	1000
H ₂ S Conversion %	95	94	95	80	60

SO₂ within the system through the following reactions :



All these exothermic reactions take place in contact with a catalyst made up of metallic oxides as well as in a gaseous stage at a high temperature. The thermal oxidation of H₂S by O₂ starts at t > 350°C and that of H₂S by SO₂ at t = 350°C. Thus, for a contact time of 9 seconds and at t = 350°C, H₂S oxidation by SO₂ reaches 12%. This shows that the H₂S thermal oxidation is easier than that H₂S by O₂. At t = 700°C and for a contact time of 9 seconds, H₂S conversion reaches 70–80% if the oxidation occurs in the presence of O₂ and it is at 50% when it occurs in the presence of SO₂. The conversion in sulphur depends on the O₂ concentration. The limitation of O₂ in the initial mixture (O₂/H₂S=7) helps obtain, during the thermal stage, 70% of elemental sulphur at temperatures ranging from 350 to 700°C.

One of the problems that one encounters in using a catalyst made up of metallic oxides (Cr–Fe–Zn) during the thermal stage of the Claus process is that of choosing the temperature interval. The catalyst chosen for this experiment was active at t = 200°C. The upper limit of temperature indicates the thermostability of the catalyst used. 10 hours calcinations at a temperature ranging from 650 to 800°C do not cause obvious changes of the catalytic activity.

When the calcinations temperature was raised to 900°C, H₂S conversion decreased by 15%. An increase in temperature from 700 to 800°C for a short period of time did not cause a notable change of the H₂S conversion rate. The increase in the temperature of the gaseous mixture in the adiabatic reactor depends on the quantity of H₂S used and on the selectivity of its oxidation in basic sulphur or in SO₂. This increase in temperature depends very slightly on the number of atoms of the molecule of sulphur (S_x) formed. Sulphur trioxide of sulphur (SO₃) is not formed during the experiment. Although H₂S has increased in the gaseous mixture, SO₂ yield decreased (Figure 3). The temperature and the oxygen

concentration in the gaseous mixture are important factors for the regulation of oxidation chemicals and H₂S conversion. For a ratio O₂/H₂S > 1, H₂S conversion is close to 100%. This conversion is independent of the experimental temperature and in this case, the SO₂ yield increased (Figure 3).

Indeed, it is only when the oxygen concentration is lowered that one can get a better selectivity in sulphur. The temperature change in the reactor does not go beyond 400°C for a H₂S conversion of 46 to 49%. The results obtained justify the use of a catalyst made up of metallic oxides (Cr–Fe–Zn) in the 1st stage of the Claus process. It permits realising the oxidation of H₂S with a high selectivity and obtaining a high levelled output in basic sulphur.

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