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PROCESS OPTIMIZATION FOR THE CATALYTIC OXIDATION OF LOW CONCENTRATIONS OF HYDROGEN SULPHIDE IN NATURAL GAS OVER ACTIVATED CARBON

by

AIMIN YANG

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "Process Optimization of the Catalytic Oxidation of Low Concentrations of Hydrogen Sulphide in Natural Gas Over Activated Carbon" submitted by Aimin Yang in partial fulfilment of the requirements for the degree of Master of Science in Chemical Engineering.

uch.

Dr. E.L. Tollefson (Supervisor) Department of Chemical and Petroleum Engineering

Dr. B.B. Pruden Department of Chemical and Petroleum Engineering

Dr. A. Badakhshan Department of Chemical and Petroleum Engineering

Dr. P. Clark / Department of Chemistry

br 16, 19, 96

Dr. A.H. Younger

Department of Chemical and Petroleum Engineering

ABSTRACT

Low concentrations (e.g. < 3%) of H₂S in natural gas can be selectively oxidized over "granular Hydrodarco" activated carbon catalyst to elemental sulphur, water and a small fraction of by-product of sulphur dioxide, SO₂. Efforts have been made to extend the life of the activated carbon catalyst by removing heavy hydrocarbons from the feed gas. To increase H₂S conversion and maintain it for a longer period of time and to minimize SO₂ in the product gas, the process has been performed at elevated pressures up to 3200 kPa.

To optimize the H_2S catalytic oxidation process, the process was conducted in the temperature range 125 - 200°C, at pressures 230 - 780 kPa, with the O_2/H_2S ratio being varied from 1.05 to 1.20 and using different types of sour and acid gases as feed. The optimum temperature was determined to be approximately 175°C for high H_2S conversion and low SO₂ production with an O_2/H_2S ratio 1.05 times the stoichiometric ratio. The effects of water vapour with different types of feed gases were investigated. The process is not impeded with water vapour up to 10 mol% present in the feed gas containing low concentrations of CO₂. A decrease in H_2S conversion and an increase in SO₂ production were obtained with an increase in water vapour present in the feed gas containing a high percentage of CO₂. The process works well with both sour and acid gases. It gives somewhat higher H_2S conversion and low SO₂ production with feed gas containing low concentrations of CO₂.

A kinetics study on the rate-controlling step for the H₂S catalytic oxidation

reaction over "granular Hydrodarco" activated carbon has been conducted. It was concluded from the experimental data that either adsorption of O_2 or H_2S from the bulk phase on to the catalyst surface is the rate-controlling step for the H_2S catalytic oxidation reaction. The reaction mechanism appears to follow the Oxidation-Reduction model.

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NOMENCLATURE

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| а | Constant, min·(g·cat.)·(mmol) ⁻¹ | | |
|-------------------------------|---|--|--|
| b | Constant, min·(g·cat.)·(mmol) ⁻¹ ·(kPa) ^{-1/2} | | |
| с | Constant, mmol·(min) ⁻¹ ·(g·cat.) ⁻¹ ·(kPa) ⁻¹ | | |
| C _{<i>H</i>2O-X} | Concentration of water on the active sites of the catalyst. | | |
| | mmol·(g·cat.) ⁻¹ | | |
| C _{H_rS-X} | Concentration of H_2S on the active sites of the catalyst, mmol | | |
| | $(g \cdot cat.)^{-1}$ | | |
| C _{O-x} | Concentration of oxygen atom chemisorbed on the active sites of | | |
| | the catalyst, $mmol \cdot (g \cdot cat.)^{-1}$ | | |
| C_{v} C_{M} | Concentration of total active sites on the catalyst, $mmol \cdot (g \cdot cat.)^{-1}$ | | |
| C _{S-x} | Concentration of sulphur sorbed on the catalyst, $mmol \cdot (g \cdot cat.)^{-1}$ | | |
| C _v | Concentration of unoccupied active sites on the catalyst, mmol | | |
| | $(g \cdot cat.)^{-1}$ | | |
| D _p | Particle diameter, cm | | |
| e | Constant, (min) ⁻¹ ·(kPa) ^{-1/2} | | |
| f | Constant, mmol ^{1/2} ·(g·cat) ^{-1/2} | | |
| G _o | Mass flow rate of gas, g/s | | |
| g | Constant, mmol ^{1/2} ·(g·cat) ^{-1/2} ·(kPa) ^{-1/2} | | |
| I.D. | Inside diameter | | |
| K _{adH2} S | H_2S adsorption equilibrium constant | | |
| K _{dH,O} | H ₂ O desorption equilibrium constant | | |

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| K _{adO} | O ₂ chemisorption equilibrium constant |
|----------------------|--|
| K _{dS} | Sulphur desorption equilibrium constant |
| K _{sh,s} | Surface reaction constant of H ₂ S |
| k _{adH,S} | H_2S adsorption rate constant |
| k_adH ₁ S | H ₂ S desorption rate constant |
| k _{adO} , | O ₂ chemisorption rate constant |
| k- <i>adO</i> , | O ₂ desorption rate constant |
| k _{dH,O} | H ₂ O desorption rate constant |
| k | H ₂ O adsorption rate constant |
| k _{dS} | Sulphur desorption rate constant |
| k _{-dS} | Sulphur adsorption rate constant |
| k _{sHr} s | Surface reaction rate constant of H ₂ S, adsorption |
| k _{-sH,S} | Surface reaction rate constant of H_2S , desorption |
| L | Length of the reactor, cm |
| mmol | millimol |
| Р | System operating pressure, kPa |
| ΔΡ | Pressure drop, psig |
| P _{H,O} | Partial pressure of water vapour in bulk of gas, kPa |
| P _{H,S} | Partial pressure of H_2S in bulk of gas, kPa |
| Po | Partial pressure of O_2 in the bulk of gas, kPa |
| Ps | Partial pressure of sulphur in the bulk of gas, kPa |
| Q | Gas flow rate at STP, mL/min |

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| 0.D. | Outside diameter |
|------------------------------|---|
| R | Universal gas constant, 8.314 Pa·m ³ /mol·K |
| r | Overall rate of the H_2S oxidation reaction, mmol·min ⁻¹ ·(g cat.) ⁻¹ |
| T _{adH} S | Rate of H ₂ S adsorption |
| r _{adO} , | Rate of O_2 adsorption |
| Г _{dH_iO} | Rate of H ₂ O desorption |
| r _{dS} | Rate of sulphur desorption |
| r _{sHz} s | Rate of surface reaction of H_2S |
| Т | Temperature, K |
| W _d | Mass of dried activated carbon catalyst, g |
| W _f | Weight of fresh activated carbon catalyst, g |
| Х | Active sites on the activated carbon catalyst |
| x | Concentration of H ₂ S, mol% |
| у | H ₂ S conversion, % |
| θο | Concentration of occupied active sites by O atom, $mmol \cdot (g \cdot cat.)^{-1}$ |
| $\boldsymbol{\theta}_{SH}$ | Concentration of occupied active sites by SH dissociated from H_2S , |
| | $mmol \cdot (g \cdot cat.)^{-1}$ |
| ρ | Density of the feed gas, g/cm ³ |
| μ | Viscosity of the fluid, Pa |
| ε | Void fraction |
| Φ | Friction factor |

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CHAPTER 1

INTRODUCTION AND SCOPE OF THE PROBLEM

Many sour gas reservoirs were found in the 1960's and early 1970's. The occurrence of sour gas is worldwide and H_2S concentrations present range from a few parts per million to 98% [Hyne et al., 1986]. When raw natural gas produced from an underground reservoir contains more than the allowable limit of H_2S for sale in gas (4 ppm), in most cases, it has to be treated to remove the H_2S . The process is called "gas sweetening".

The conventional Claus process is employed to treat H_2S recovered from sour natural gas containing concentrations of H_2S above 20% [Royan and Wichert, 1994]. It consists of a thermal combustion stage followed by two or three catalytic reaction stages. When the acid gas stream contains less than 10% H_2S , it is difficult to operate the facilities and achieve the necessary sulphur recovery efficiency in a split flow Claus plant as the flame in the reaction furnace becomes unstable [Royan and Wichert, 1994]. In this case, the sour gas is sweetened by extraction and the H_2S is incinerated and vented as SO_2 or is flared if the procedure is environmentally acceptable.

As emission limits continue to tighten, processors seek ways to maximize the sulphur recovery efficiency and to minimize SO_2 emissions. It was realized that activated carbon could be used as a catalyst for the oxidation of H_2S with air to elemental sulphur. "Granular Hydrodarco" activated carbon was selected as the catalyst to promote H_2S oxidation reaction because of its high sulphur capacity and activity. The purpose of this research was to determine the life of the "granular Hydrodarco" activated carbon catalyst, to produce the elemental sulphur in a saleable form and to maintain the process at high performance for a longer period of time by varying the parameters of temperature, pressure, O_2/H_2S ratio, mass of the catalyst, water vapour in the feed gas and type of the feed gases.

The process parameters influence not only H_2S conversion but also SO_2 production. The presence of water is very common in the case of natural gas production. Therefore, the effects of its presence in the feed gas on the H_2S conversion and SO_2 production should be established. It is important to establish the process conditions at which high H_2S conversion and low SO_2 production could be achieved.

So far, different types of mechanism on H_2S catalytic oxidation reaction have been reported by various researchers. The results are contradictory. One mechanism was postulated that both H_2S and O_2 were chemisorbed on the catalyst surface followed by the reaction between these two molecules which was considered to be the rate controlling step [Sreeramurthy and Menon, 1975]. An Oxidation-Reduction model was proposed that based on the autocatalytic effect on the produced sulphur [Steijn et al., 1976]. The Langmuir-Hinshelwood surface reaction model has been proposed by most of researchers which described that the H_2S oxidation reaction occurred between a H_2S molecule which was physically adsorbed and an atomic O which came from an O_2 chemisorbed and dissociated on the catalyst surface. The surface reaction was considered to be the rate controlling step [Ghosh and Tollefson, 1986]. To clarify the H_2S catalytic oxidation reaction mechanism and establish a model of it, calculations to determine the rate controlling step of the catalytic oxidation of H₂S over Hydrodarco activated carbon were conducted.

The Ergun equation was used to calculate the pressure drop across the catalyst bed. The result agrees well with the actual pressure drop which was determined to be 0.25 psig with the runs performed at 230 kPa for 15 hours in a fixed-bed reactor having an internal diameter of 12.5 mm I.D. and a length of 25 cm. The pressure drop throughout the bed was constant and not affected by the sulphur deposition in the catalyst pores during the run.

CHAPTER 2

LITERATURE REVIEW

2.1 Scope of Search

The literature survey was divided into three general areas. The first encompassed the experimental work which has been done and published on H_2S catalytic oxidation with air over activated carbon. This included work on the catalytic oxidation mechanism and the parameters which affect the reaction. The second search investigated liquid redox processes used in the oxidation of H_2S involving sulphur recovery methods and their application in industry. The third dealt with other processes for the removal of H_2S from streams.

2.2 Studies of the Catalytic Oxidation of Hydrogen Sulphide with Air over Activated Carbon

The raw sour natural gas is first sent to an extraction unit containing monoethanolamine ("MEA", HO-CH₂-CH₂-NH₂) or diethanolamine ("DEA", (HO-CH₂-CH₂)₂-NH). The H₂S and CO₂ are adsorbed forming a complex. The complex solution is heated to separate the H₂S and CO₂ from the amine solution. The product gas containing H₂S and CO₂ is sent to the Claus plant to convert the H₂S to elemental sulphur and water.

2.2.1 The Conventional Claus Process

The conventional Claus process consists of three stages. There is a combustion

chamber in the first stage in which one third of H_2S in the feed gas is oxidized by air at a temperature range of 926 - 1327°C to produce SO_2 and water:

$$H_2S + 1.5O_2 \longrightarrow SO_2 + H_2O$$
 (2 - 2.1)

The remaining two thirds of the H_2S is reacted subsequently with the SO₂ to form S in catalytic stages according to:

$$2H_2S + SO_2 \implies S + 2H_2O$$
 (2 - 2.2)

Sulphur recovery in traditional Claus plants varies from 90 -96% for a two-stage plant and from 95-98% for a three-stage plant [Lagas et al., 1989].

It is impossible to reach very high sulphur recoveries for three reasons[3]:

- (a) The Claus reaction is an equilibrium reaction and thus complete conversion of H_2S and SO_2 to sulphur is impossible.
- (b) Process water, produced in the Claus reaction and not practically removable from the Claus process gas, hinders the conversion and limits total sulphur recovery.
- (c) The critical $H_2S:SO_2$ ratio of 2:1 is, in practice, difficult to achieve with accuracy.

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2.2.2 Work Which Done by Researchers Other Than That Done in This Laboratory on

the Oxidation of H_2S Over Activated Carbon

The earliest paper [Puri et al., 1971] reported that the use of charcoals, coconut shells and carbon black as catalysts to oxidize H₂S. They pointed out that H₂S is a highly stable gas and does not react with oxygen to any noticeable extent without catalyst present. Less than 1% is reacted at temperatures of 120-240°C. By employing 3 g of charcoal catalyst and running purified and dried H₂S and O₂ through it at 180°C for one hour, they found that 25% of H₂S was removed and small amount of SO₂ was formed. By increasing the amount of catalyst to 10 g, more than 90% H₂S removal was achieved. They found that most of the sulphur was fixed irreversibly on the charcoal and concluded there were some strong valence forces operating along the charcoal surface. Most of the sulphur appeared as free sulphur in the case of carbon black. By comparing the results of original and degassed samples, they concluded that some active sites rather than the surface area exposed in the degassed samples were responsible for the capacity to fix a large fraction of the sulphur. They regenerated the used samples by passing H₂ at 800°C over it and restored the catalytic activity to a considerable extent.

M. Steijns and P. Mars [1974] reported their research on the role of sulphur trapped in the micropores during catalysis. In one case, they performed an experiment in a reactor which contained 1000 cc of glass beads with an external surface area of 3 m² which proved to have no catalytic activity. Liquid sulphur was formed on the surface by condensation of the sulphur vapour on the glass beads. They found that liquid sulphur has some catalytic activity in the oxidation of H₂S with O₂. By performing the experiments

on a kind of activated carbon, Norit RBWI, (washed with diluted acid to remove iron oxide) and molecular sieve 13X, they observed that the oxidation rate of H_2S showed a maximum as a function of the amount of sulphur deposited in the pores. They explained that at the first stage of H₂S oxidation the surface area of the liquid sulphur increased as the amount of sulphur deposited in the micropores increased until it reached a maximum. They observed that small amounts of iron oxide(0.2%) could raise the initial oxidationrate to such an extent that the maximum rate was hidden. They also observed a large decrease in the BET [Emmett, 1954] surface area of a catalyst during the reaction and concluded that sulphur deposited in the micropores. By ESR measurement, they found a signal from the sulphur trapped in the micropores and attributed it to polysulphur biradicals, These biradicals could catalyze cracking reactions. In the absence of H_2S , the ESR signal disappeared when molecular O2 was present and this was attributed to the reaction of O₂ with the sulphur radicals. From the experimental data they concluded the reaction order in terms of H_2S was 0.5 and this was caused by the fact that the oxidation rate was proportional to the concentration of SH-groups(polysulphide). The mechanism might be connected with the reaction of adsorbed oxygen with the hydrogen of these SHgroups on the surface.

O. C. Carioso and P. L. Walker [1975] reported their studies on the oxidation of H_2S over microporous carbons. Their major work included the preparation of activated, carbonized Saran, a kind of carbon with high surface area and high purity, at atmospheric pressure in CO₂ at 900°C, O₂ at 300°C and air at 425°C. They then conducted the H_2S

oxidation over them at 140°C.

They found that microporous carbons of high purity had a significant catalytic activity for the oxidation of H_2S to elemental sulphur. During a long run conducted over a five-day period, they observed that the instantaneous rate of sulphur build-up on the carbon was directly proportional to the concentration of H_2S in the gas phase. They suggested that H_2S oxidation at 140°C was first order with respect to the H_2S concentration. The addition of 1% of water to the reaction mixture had no detectable effect on the oxidation rate. By changing the H_2S and O_2 pressure independently, they found that the reaction was first order with respect to H_2S but zero order with respect to O_2 .

Carioso and Walker indicated that carbons activated in O_2 or air had both a higher initial catalytic activity as well as a higher activity in the "constant-rate" regime than samples activated with CO_2 . By comparing H_2S oxidation rates with rates of adsorption of O_2 and H_2S , they found that the O_2 and air-activated carbons show identical rates for both the oxidation and O_2 adsorption processes. In addition, the rates and conversions were significantly greater than those of the Saran carbons which had not been activated as well as those samples activated in CO_2 . In marked contrast to the rate of O_2 adsorption, the rate of H_2S adsorption was unaffected by the activation process. They concluded that O_2 was chemisorbed on the activated carbon and this chemisorption was strongly sensitive to the geometry of the carbon sites on the surface. Those activated in O_2 or air create a template more susceptible to the subsequent O_2 chemisorption than the template created by CO_2 activation. On the other hand, H_2S adsorption was physical in nature. In discussing the effect of temperature, they found that the rate of H_2S oxidation was affected by the physical form of the product sulphur on the surface when the temperature was above 115°C, the monoclinic sulphur melting point. For the O₂-activated carbon, a reduction in total pressure resulted in a rate increase. For a first order reaction, it has been shown that the reaction rate per unit of external area of the particles can be expressed as:

$$Rate = C_0 \sqrt{kaD_{eff}} \qquad (2 - 2.1.1)$$

where C_0 is the reactant H₂S concentration outside of the particles, k is a constant, "a" is the total of the internal surface area, and D_{eff} is the effective diffusion coefficient in the pore system in which mass transport is the limiting reaction rate.

A reduction of total pressure while keeping the pressure of H_2S and O_2 constant would change C_o or k, but D_{eff} might be inversely proportional to the total pressure. There would be a possibility that a change in total pressure could affect "a". Both the rate of O_2 chemisorption and the subsequent H_2S oxidation decreased with an increase of total pressure.

From activity studies using commercial activated carbons of significant ash contents and acid-treated samples in which most of the impurities were removed, they concluded that silica and alumina appeared to have negligible activity for H_2S oxidation while sodium oxide and iron oxide had significant activity.

R. Sreeramamurthy and P. G. Menon [1975] reported a study on the air oxidation

of H_2S to sulphur on activated coconut shell charcoal at 65-100°C. Their experiments showed:

- (a) no sulphur was deposited on the walls of the reaction tube;
- (b) sulphur products in the catalyst had no catalytic activity for H_2S oxidation;
- (c) no SO_2 was formed at these temperatures;
- (d) the adsorption of water on the catalyst at these temperatures was negligibly small.

Since the oxidation of H_2S was highly exothermic, the temperature of the catalyst rose rapidly during the reaction. They also observed that at a fixed flow rate the rise in temperature of the catalyst depended on the amount of carbon employed. In a fixed catalyst bed with 10 g carbon and without diluent nitrogen, even at a furnace temperature of 100°C the catalyst temperature rose abruptly within a few minutes to over 350°C, the carbon started to burn and the whole catalyst mass became red hot. It was therefore imperative:

- (a) to dilute the gas stream considerably with N_2 and
- (b) to take only a small quantity of catalyst so as to reduce this temperature rise of the catalyst.

They found that both the temperature of the catalyst and the catalytic activity showed a steep maximum within 30 min of starting the reaction but the maximum in the rate curve was reached 5-20 min before that in the temperature-time curve. They explained this phenomenon as the time lag involved in the measurement of temperature. By the time the catalyst reaches the maximum temperature, part of its surface was already covered by the deposited sulphur and the reaction rate decreased considerably. They suggested that part of the carbon surface was extremely active and the vigorous reaction on this part raised the catalyst temperature, which in turn accelerated the reaction. However, the sulphur formed as product of the reaction soon covered this highly active surface and the catalytic activity decreased rapidly, thereby lowering the catalyst temperature.

By exposing several catalyst samples of the same mass to the H_2S-N_2 -air mixture at 100°C so that different amounts of sulphur were deposited, they observed that with the deposition of the first 160 mg S/g catalyst the surface area was reduced by about 5% but the catalytic activity was reduced to about 30% of the original. The first sulphur deposited occurred in the relatively large pores. It was this 5% of the total surface that raised the catalyst temperature which in turn accelerated the reaction. Thereafter, the reaction proceeded slowly and the deposition of sulphur progressively filled up the micropores of the carbon. They did not find physically-adsorbed H_2S remaining on the catalyst surface.

An x-ray study of the sulphur deposited on the catalyst surface showed no sulphur pattern, so the deposited sulphur was in an amorphous state. They conducted an electron probe microanalysis (EPMA) study of sulphur on the carbon catalyst. The EPMA photographs showed the concentration of sulphur in a 1 μ m thick layer of the catalyst surface after exposure to the H₂S-N₂-air mixture for half hour. Sulphur formed in the early stages in lumps or as "islands" - not as a continuous film. Sreeramamurthy and Menon suggested that the rate of H₂S oxidation was inversely proportional to the amount of sulphur deposited on the catalyst.

$$r = A/C_c$$
 (2 - 2.1.2)

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where r was the rate of H_2S oxidation, C_c is the amount of sulphur on the carbon catalyst, and A is a constant.

The data on the H_2S oxidation in the temperature range 70-100°C with 1-4% H_2S in the gas stream could be expressed in terms of a Langmuir-Hinshelwood model.

M. Steijns and P: Mars [1976] reported their further research on the mechanism of the catalytic oxidation of H_2S . The kinetic experiments were conducted with a 0.5 mole percent concentration of H_2S on different porous materials including activated carbon but also different sulphur contents of these materials. For materials which had a low intrinsic oxidation activity, the characteristic course of the activity as a function of sulphur uptake by the material was given as in Fig 2.1.



Sulphur Content on Catalyst



There were three distinct ranges, A, B, and C. In range A, the activity increase with reaction time was due to the autocatalytic activity of the sulphur deposited in the pores. In range B, a decrease in the activity was observed because the pores became filled with sulphur which resulted in a considerable decrease of the specific surface area of sulphur. A stationary activity level was reached in range C, when the amount of sulphur formed equalled to the amount of sulphur desorbed from the large pores left unfilled and from the outer surface of the particles. For a material possessing a high intrinsic activity and branch A was not observed. For experiments in the regions A or B where the activity did not attain a stationary level, the desorption rate of sulphur was much smaller than the oxidation rate. At temperatures below 200 °C, the selectivity towards sulphur was always above 90% and the main by-product was SO₂.

For activated carbon, M. Steijns and P. Mars observed that the reaction order in terms of O_2 varied from zero to one and in terms of H_2S it varied from approximately 0.5 at low H_2S concentrations to zero at high concentrations. The amount of sulphur adsorbed on the catalyst did not affect the reaction order significantly. The oxidation rate of H_2S was, however, a function of the sulphur deposited on the catalyst. On the other hand, the oxidation rate of H_2S on zeolite 13X showed a first order dependence on the concentration of O_2 over wide concentration and temperature ranges. An "oxidation-reduction mechanism" was suggested based on the assumption of autocatalytic oxidation of sulphur. This mechanism involved two reactions in series:

$$H_2S$$
 + oxidized site \longrightarrow $S + H_2O$ + reduced site (2 - 2.1.3)
reduced site + oxygen \longrightarrow oxidized site (2 - 2.1.4)

The maximum half order dependence on H_2S concentration observed for activated carbon was in accordance with a reduction step (2 - 2.1.4) which was a surface reaction between adsorbed oxygen and dissociatively adsorbed H_2S . Assuming that the rate of this reduction reaction was proportional to the degree of occupation of the specific sites on the carbon surface with oxygen and dissociated hydrogen sulphide, respectively, θ_0 and θ_{SH} , then

$$-\frac{dP_{H_s}}{dt} = k_{red} \cdot \theta_{sH} \cdot \theta_o \qquad (2 - 2.1.5)$$

This rate could be related to the partial pressure of H_2S if there were an equilibrium between H_2S in the gas phase and dissociatively adsorbed H_2S :

$$H_2S(g) = H_2S_{ads} = S_xH.$$
 (2-2.1.6)

The equilibrium constant K for reaction (2 - 2.1.6) is given by:

$$K = \frac{\theta_{SH}^2}{P_{HS} (1 - \theta_{SH})}$$
(2 - 2.1.7)

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If $\theta_{SH} \ll 1$ the equilibrium established is then:

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$$\theta_{SH} = K \cdot P_{H,S}^{0.5} \tag{2 - 2.1.8}$$

Substituting Eq. (2 - 2.1.8) in (2 - 2.1.5):

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$$-\frac{dP_{H_2S}}{dt} = k_{red} \cdot P_{H_2S}^{0.5} \cdot \theta_0$$
 (2 - 2.1.9)

For the oxidation step, the rate of oxidation of sites reduced by H_2S was proportional to the oxygen partial pressure and the fraction of sites not covered by oxygen, i.e.,

$$-\frac{dP_{o_2}}{dt} = k_{OX} \cdot P_{O_2} (1 - \theta_O) \qquad (2 - 2.1.10)$$

For the oxidation of one mole of H_2S to sulphur a half mole of oxygen is required, see (2 - 2.2):

$$-0.5 \frac{dP_{H_2S}}{dt} = -\frac{dP_{O_2}}{dt}$$
(2 - 1.11)

In the steady state:

$$0.5 \cdot k_{red}^{,} \cdot P_{H_2S}^{0.5} \cdot \theta_O = k_{OX}^{,} \cdot P_{O_2}^{,} (1 - \theta_O) \qquad (2 - 2.1.12)$$

Solving Eq. (2 - 2.1.12) for θ_0 and substituting in (2 - 2.1.9) gives:
$$-\frac{dP_{H_2S}}{dt} = \frac{1}{(1/k_{red}^{,} \cdot P_{H_2S}^{0.5}) + (1/2 \cdot k_{OX}^{,} \cdot P_{O_2})}$$
(2 - 2.1.13)

The general expression relating the oxidation rate of H_2S , expressed as mmol H_2S g⁻¹ hr⁻¹ to the partial pressures of H_2S and O_2 is:

$$V_{H_2S} = -A \cdot \frac{dP_{H_2S}}{dt} = \frac{1}{(1/k_{red}^{'} \cdot P_{H_2S}^{0.5}) + (1/2 \cdot k_{OX}^{'} \cdot P_{O_2})}$$
(2 - 2.1.14)

in which A is a constant.

The rate constants k_{ox} and k_{red} were calculated for some materials under various conditions. From the temperature dependence of these rate constants, Steijins and Mars derived $E_{ox} = 37 \pm 4$ kJ mol⁻¹ and $E_{red} = 52 \pm 5$ kJ mol⁻¹ for the activated carbon employed.

Steijins and Mars also observed the oxidation of H2S according to the reaction,

$$2H_2S + O_2 \xrightarrow{400 \text{ K}} 1/4 \text{ S}_8 + 2H_2O$$

for which: $K_P = 2 \times 10^{48}$ (2 - 2.1.15)

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It was not the only reaction which may occur at the catalyst surface. Especially at high temperatures (T>200°C) and with an excess of oxygen, a consecutive reaction may occur:

$$1/8 S_8 + O_2 \xrightarrow{400 \text{ K}} SO_2$$
 (2 - 2.1.16)

for which $K_p = 4 \times 10^{39}$

The SO_2 will react with unconverted H_2S via the fast reaction:

$$400 \text{ K}$$

$$2H_2S + SO_2 = 3/8 S_8 + 2H_2O$$
(2 - 2.1.17)
for which
$$K_P = 6 \times 10^7$$

From the equilibrium constant calculated for the different reactions, it was concluded that the possibility existed that SO_2 was an intermediate. This was because the energy of activation for S oxidation (125 ± 10 kJ mol⁻¹) was much higher than that for H_2S oxidation (40 kJ mol⁻¹).

Steijns and Mars [1977] reported further work on the influence of pore structure and chemical compositions of various porous substances on the catalytic oxidation of H_2S . The materials involved in their research were divided into five groups according to their chemical compositions:

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(1) carbonaceous solids;

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- (2) zeolite;
- (3) silica;
- (4) alumina;
- (5) other oxides.

They observed that microporous materials with micropore sizes of 0.5 nm $< d_p < 1.0$ nm adsorbed appreciable amounts of product sulphur and combine a high activity with a high selectivity not withstanding the low surface area in the stationary state. Micropores with pores smaller than 5 nm in diameter were less active for the oxidation of H₂S.

Within one group of materials an increase of the average pore size yielded a less active catalyst. Some metal oxides showed another behaviour:

- (a) iron oxide had high activity, low selectivity towards sulphur product and micropores were absent;
- (b) titanium oxide showed high activity, high selectivity and micropores were absent;
- (c) aluminum oxide had high activity, high selectivity and micropores were absent;
- (d) zirconium oxide showed high activity and high selectivity and micropores were absent.

Industrial active charcoals were the most active catalysts among the carbonaceous materials. The activity of wide pore carbon blacks was rather low, especially if the activity per square meter of surface area were considered. This fact suggested that micropores were essential for an active carbonaceous material. At relative sulphur pressures above 0.25, the condensation in cylindrical pores with $d_p > 3.0$ nm could be described in terms of the Kelvin equation.

$$\ln\left(\frac{P}{P_o}\right) = -\frac{\gamma V_m \cos\theta}{rRT} \qquad (2 - 2.1.18)$$

where P is the vapour pressure above the curved surface in a pore with radius r, P_o is the vapour pressure of the sulphur above the planar surface, γ is the surface tension of the liquid sulphur, V_m is the molar volume of the liquid, θ is the angle of contact, R is the gas constant, and T is the absolute temperature.

This equation clearly demonstrates that the influence of both the pore structure parameter (r) as well as the adsorbate and adsorbent interaction parameter ($\gamma \cos\theta$) determine capillary condensation. In the case of the micropores ($d_p \sim 1.0$ nm). The Kelvin equation does not apply because the pores are commensurate with the adsorbed molecules, which leads to a substantial increase in the adsorption energy. The authors stated that Swinarski and Siedlewski [1961] had studied the influence of the pore structure of active carbon on the activity in H₂S oxidation. They found that the catalytic activity was proportional to the surface area of the pores with a diameter between 3.5 and 8.0 nm.

Data on the influence of the surface composition of materials with $d_p > 1.0$ nm showed that there were remarkable differences in activity between the oxide materials. The catalytic behaviour of iron oxide combined high activity and low selectivity. Under Steijns and Mars's experimental conditions, all the available oxygen was consumed and the primary product was SO₂. The important reactions in this case were:

$$H_2S + 3O_2 \xrightarrow{\text{iron oxide}} 2SO_2 + 2H_2O$$
 (fast) (2 - 2.1.19)

$$SO_2 + 2H_2S \longrightarrow 3S + 2H_2O$$
 (slow) (2 - 2.1.20)

The iron oxide was partly converted into sulphide. The autocatalytic reaction on sulphur did not play a predominant role because the selectivity toward elemental sulphur was too small.

Steijns and Mars's research showed that the catalyst activity was reduced due to the presence of moisture in the feed gas. They explained this phenomenon by suggesting that the sorption changed the character of the surface of the porous material, which led to a decrease in the amount of sorbed sulphur.

Kaliva and Smith [1983] reported their research on the oxidation of low concentrations of H_2S by the oxygen in air over a fixed activated carbon bed. They performed their experiments in a glass reactor which was 7 cm in diameter and 48 cm in length and packed with a bed of granular activated carbon from 5-15 cm deep. The oxidation was conducted at room temperature and ambient pressure with inlet gas H_2S concentrations of 1000 ppm and 2000 ppm and with the humidity varying from 30 to 90%.

The data from their experiments fitted a Langmuir-Hinshelwood mechanism including catalyst fouling and a "steady state" regime. By changing the air stream humidity from 30-40% to 80-90%, the oxidation rate increased by a factor of 6. Based

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on the strong effect of water vapour on the oxidation rate they made an assumption that water vapour was involved in the oxidation mechanism. They suggested that the reaction may occur on the activated carbon surface between adsorbed H_2S and the complex, formed between oxygen and water vapour or that the reaction may occur in the liquid phase in the pores of the carbon at lower temperature.

Choi et al. [1991] published a paper on a similar project. The experiment was conducted in a glass column which was 5 cm in diameter and 50 cm in height and was packed with Activated Carbon Fiber (ACF) which had a surface area, micropore radius, and micropore volume of 1500 m²/g, 0.9 nm and 0.8 cm³/g, respectively. The inlet gas was a mixture of H₂S, N₂ and air with an H₂S concentration of 200 ppm.

In one case the experiment was conducted at room temperature and ambient pressure on the ACF with a moisture content of 80% and without moisture. They found that with a moisture content of 80% the H_2S conversion was 100% for a period of 45 days. Without moisture, the breakthrough point of H_2S appeared to come after two days at 100% conversion. By washing the used ACF from the experiment with a moisture content of 80% with distilled water until no sulphate ion was detected in the mother liquid they brought the ACF activity back to the original level which maintained 100% conversion for another 45 days. When the moisture content was reduced to less than 30%, the conversion began to decrease and SO₂ by-product appeared. They conducted the experiment on the GAC at the same conditions as on the ACF and they found that 100% conversion was obtained for only 20 days and SO₂ production accompanied the reaction

right from the beginning. When the moisture content was lower than 10%, the SO_2 production was significant.

The oxidation mechanism of H₂S suggested was as follows:

$$H_2S \xrightarrow[(a)]{[O]} S^0 \xrightarrow{[O]} SO_2 \xrightarrow{[H_2O]} H_2SO_3 \xrightarrow{[O]} H_2SO_4 \qquad (2 - 2.1.21)$$

The authors explained their data with this mechanism as follows: In the initial oxidation step, the sulphur product deposits in micropores of the ACF and the deposited sulphur accelerates step (a); the water-retaining capacity of the ACF promotes a rapid reaction in steps (b) and (c) and this results in complete oxidation of H_2S to H_2SO_4 . By removal of the sulphate ion with water, the catalytic activity was recovered. This indicated that sulphate ion in water inhibited oxidation steps (b) and (c). The difference in SO_2 production between ACF and GAC may be due to the poor water-retaining capacity of GAC and the iron content and/or other unknown catalytic compounds within the ash components of the GAC.

Turk et al.[1989] did some work aimed at enhancing the capacity of activated carbon for H_2S oxidation. Ammonia was found to be a catalyst for H_2S oxidation. Granular activated carbon, caustic-containing carbon made by impregnating granular activated carbon with KOH or NaOH and granular activated carbon in conjunction with a small side stream of ammonia gas were used in laboratory, pilot plant and full scale studies to assess the efficacy of the ammonia/GAC process. Sulphur capacity of the

activated carbon in g sulphur/cm³ carbon was used as a criterion for the removal of H₂S.

In bench-scale tests, a vertical glass cylinder, 2.54 cm in diameter and 15.24 cm in height, was packed with carbon. The gas used was a mixture of 1% H_2S by volume at 80% relative humidity prepared by mixing of a 290 mL/min stream containing 5% H_2S (vol/vol) in dry nitrogen, a 1150 mL/min stream of purified air saturated with moisture, and a stream of NH₃ of 10 mL/min. The contact time between gas and carbon in the reactor was 3.2 s. The carbon sample was removed and analyzed when the concentration of H_2S in the outlet reached 50 ppm.

The results indicate that by introducing a small amount of ammonia into the reaction system, the sulphur removal capacity of the carbon catalyst was increased by a factor of 3 or greater than that of the caustic-containing carbon. But the reaction system was found not to be sensitive to the concentration of NH_3 in the range of 0-10 ppm. In practice, the concentration of NH_3 should be maintained at its threshold point in the effluent stream.

In pilot-scale tests, an effluent gas mixture from a wastewater treatment plant containing 500 ppm H_2S was split into two streams. They were then introduced into two reactors each of 7.62 cm in diameter and 30.48 cm in height at flow rates of 69 L/min, the contact time being 1.2 s. One reactor was packed with the carbon containing caustic which content was mentioned in the paper. The other was packed with virgin carbon operated with a side stream of 50 ppm NH_3 . Samples were taken from the reactor at depths of 7.62, 15.24 and 22.86 cm after 50 hours of oxidation.

The data indicated that the ammonia system provided at least double the life for

 H_2S removal that was provided by the caustic-containing carbon system at a bed depth of 15.24 cm of the reactors. The advantage of ammonia was much greater at a bed depth of 7.26 cm. When the useful life of the caustic carbon bed was reached at a depth of 22.86 cm, the breakthrough point was not reached at the same depth in the system being fed ammonia system. The advantage of ammonia at this depth was not quantified. The results showed that the addition of ammonia to the system provided much longer life than that provided by the carbon containing caustic on carbon.

In full-scale tests two reactors of 3.66 m in diameter were installed in which one was packed with caustic-containing carbon and the other was packed with virgin carbon operated with a side stream of 7 ppm NH₃. The feed gas was the same as that used in the pilot-scale tests but the flow rate was much higher at 7550 L/s. Samples were removed from the reactor at depths of 5.1 to 6.6 cm and 23 to 30 cm after the oxidation had been continued for 6 months.

Data at depths of 5.1 to 6.6 cm showed that the sulphur capacity of both reactors was very small. Because of such a high gas flow rate with a lot of impurities assumed to be organic matter, the top layer from 5.1 to 6.6 cm of carbon picked up the majority of the particulate matter. At depths of 23 to 30 cm, the ammonia system retained a capacity of 0.21 g of H_2S/cm^3 of carbon but the caustic-containing carbon bed had lost its capacity.

Analysis of the carbon from the system fed with ammonia showed the ratio of NH_3/S in the exhausted carbon was 1:25.

The oxidation mechanism with ammonia was assumed to be as follows:

$$xH_2S + 2NH_3 + [\frac{(x-1)}{2}]O_2 \rightarrow (NH_4)_2S_x + (x-1)H_2O$$

(2 - 2.1.22)

Analysis of the samples showed the value of x was approximately 50.

A possible sequence that does not require the formation of polysulphide is as follows:

| $3NH_3 + 3H_2S \implies 3NH_4HS$ | (fast equilibrium) | (2 - 2.1.23) |
|---|-------------------------------|--------------|
| $NH_4HS + 1.5O_2 \longrightarrow NH_4HSO_3$ | (rate controlling) | (2 - 2.1.24) |
| $NH_4HSO_3 \longrightarrow NH_3 + SO_2 + H_2O$ | (fast equilibrium) | (2 - 2.1.25) |
| $2NH_3SH + SO_2 \longrightarrow 3S + 2NH_3 + 2$ | H ₂ O (fast redox) | (2 - 2.1.26) |

Overall

$$3H_2S + 1.5O_2 \xrightarrow{NH_3} 3S + 3H_2O$$
 (2 - 2.1.27)
Catalyst

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Introducing a side stream of NH_3 not only lengthened the life of the carbon catalyst for the removal of H_2S but also extended the life of the exhausted causticcontaining carbon for both the physical adsorptive capacity for H_2S and the capacity for sulphur from H_2S oxidation. It also provided a methyl mercaptan sorptive capacity 3-4 times higher than caustic-containing carbon and eight times higher than virgin carbon.

2.2.2 The Work Which Has Been Done in This Laboratory on the Oxidation of H_2S

Over Activated Carbon

Research on the oxidation of low concentrations of H_2S over activated carbon has been conducted in this laboratory over the past 18 years under the supervision of Dr. Eric L. Tollefson for about 18 years. The first researcher I. Coskun, published a paper on this project [Coskun and Tollefson, 1980]. The catalyst he used was an activated carbon made from semi-anthracite coal, supplied by Aqua Tech. Ltd., Calgary, Canada. The activated carbon had a surface area of 700 m²/g, a porosity of 0.337 cm³/g and the particle size range from 20 to 40 mesh. The experiments were performed over the temperature range 24-200°C using both fixed and fluid bed reactors. The fixed bed reactor was constructed from a 7.0 mm I.D., 316 stainless steel tube, 150 mm long. The fluid bed was constructed from a 52.5 mm I.D., 316 stainless steel pipe, 0.9 m long.

It was observed that below 100°C the loss of activity in the initial oxidation stage was more rapid than was observed of above 100°C. This phenomenon was explained by the fact that the product H_2O was adsorbed on the surface of the catalyst and played a role by reduction of the activity. At temperatures of 50, 80 and 110°C, the activated carbon adsorbed small amounts of water so its activity was affected. The author suggested that there might be two different modes by which the reaction took place depending on the extent of water deposition on the catalyst. In one mode with little water vapour present, the reaction occurred on the surface with more and more sulphur and water being deposited, so that the rate of reaction decreases with time. In the other mode, with higher relative humidity and lower temperature, the reaction might occur in the water phase in the pores of the catalyst causing the rate of the reaction to increase. After two to three hours of operation, an almost constant conversion stage was observed. During this stage the amount of sulphur carried out of the reactor was the same as the amount formed in the reaction. This makes it possible for the H_2S to be oxidized to sulphur in a continuous process.

The order of the reaction was estimated to be 0.5 with respect to the H_2S concentration. The apparent activation energy determined varied from 20.5 to 26.4 kJ/mol and the frequency factor from 1.2 to 2.9 mmol $H_2S(min)^{-1}$ (g C)⁻¹ (L/molH₂S)^{0.5} for sulphur loadings ranging from 5 to 15% by weight based on the carbon.

Pure sulphur was used to determine its catalytic activity. The experiment was conducted at 115°C. No catalytic activity was observed.

Further research work was done by Tushar K. Ghosh on a continuous process for recovery of sulphur from natural gas containing low concentrations of H_2S [Ghosh and Tollefson, 1986]. Several parameters which influence the H_2S conversion and SO_2 production were investigated as follows:

- (a) temperature $(125-300^{\circ}C)$;
- (b) pressure (100-300 kPa);
- (c) oxygen concentration (one to four times the stoichiometric ratio with respect to H_2S concentration present in the gas mixture);
- (d) concentration of H_2S in the feed gas (300-3000 ppmv), (0.0126-0.126 moles/m³);
- (e) superficial linear gas velocity (0.0658-0.395 m/s);

- (f) water content of the feed gas;
- (g) different active carbons;
- (h) bed height (25-145 mm).

To gain a better knowledge of the oxidation system, a gas mixture of nitrogen, air and H_2S was first used, then the nitrogen was replaced by commercial methane. Finally, dried wellhead gas was employed. The fixed bed reactor was constructed from a stainless steel tube 12.5 mm in diameter and 250 mm long.

An increase in the conversion of H_2S to elemental sulphur was observed with an increase of reaction temperature. Surface area also played an important role in achieving high H_2S conversion. As the temperature increased, the vapour pressure of the sulphur also increased, and more sulphur was vaporized from the catalyst surface thus freeing some of the surface for further reaction. The rate of SO₂ production became significant at and above 175°C. This limited the reaction temperature at which it was feasible to operate to study the influence of the other parameters on the conversion of H_2S to sulphur.

The conversion of H_2S was found to increase with increases in the oxygen concentration in the feed gas. However, the conversion of H_2S at steady state increased with the decrease of H_2S concentration in the feed gas. The surface area measured at steady state also increased but the sulphur loading on the catalyst surface decreased. Since the mass of the catalyst was the same for all the runs, as the H_2S concentration decreased the number of the active sites on the catalyst per mol of H_2S was increased. Therefore the percentage conversion increased. It was found that the presence of H_2O in the feed gas decreased the H_2S conversion. The principle reaction may be represented by:

$$H_2S + 0.5O_2 \longrightarrow S + H_2O$$
 (2 - 2.2.1)

The presence of water tends to drive the reaction to the reverse side so that the conversion was decreased.

An increase in conversion was observed with an increase in residence time. Since there would be more surface area available per mole H_2S with an increase in the mass of the catalyst, the number of collisions of the molecules with the surface would be increased thus enhancing the extent of the rate of the reaction. When the concentration of H_2S in the feed gas was decreased, the conversion was less affected by changing the superficial linear velocity. This may be due to the presence of a sulphur film at the inlet of the micropores which hindered the diffusion of H_2S from the bulk stream to the micropores. With a decrease in the H_2S concentration in the feed gas, the amount of sulphur produced in the reaction for the same degree of conversion decreased thus decreasing the sulphur film and diminishing the effects of superficial linear velocity of the feed gas on H_2S conversion.

With an increase of pressure, the conversion of H_2S was increased. This was because the residence time was increased as pressure was increased while keeping the flow rate constant. The partial pressure of sulphur in the gas phase during the reaction calculated from the experimental data was less than that calculated from the reaction temperature. Therefore, the gas phase was not saturated with sulphur. Increased pressure would force more molecules into the micropores of the catalyst so that they could react. Hence the conversion tended to increase.

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By replacing the nitrogen in the feed gas by commercial methane gas, the conversion of H_2S at steady state was a little lower than that of the nitrogen based mixture. The difference may be due to the heavy hydrocarbons present in commercial methane gas absorbed on the surface of the carbon. The product sulphur was light brown in colour when field gas was used. The heavy hydrocarbons C_4 , C_5 , C_6 and heavier may have exhibited some cracking at the reaction temperature and condensed on the product sulphur. It was suggested that these heavy hydrocarbons should be removed prior to the reaction, when bright yellow sulphur is desired.

Ghosh and Tollefson published a paper [1986] on the kinetics and reaction mechanism of H_2S oxidation over activated carbon in the temperature range 125-200°C. The data used were taken from the runs in which "granular Hydrodarco" activated carbon was used as a catalyst. Several assumptions were made before the Langmuir-Hinshelwood surface reaction model could be employed to derive the rate expression. They are given below:

1. The reaction which took place in the temperature range 125-200°C was

$$H_2S + \frac{1}{2}O_2 = \frac{1}{8}S_8 + H_2O$$
 (2 - 2.2.2)

- 2. SO_2 production was very low in the experimental temperature range.
- 3. In the first step of the reaction, O₂ was chemisorbed and dissociated on the catalyst surface while H₂S was physically adsorbed.

- 4. Surface reaction occurred between a dissociated oxygen atom and an H_2S molecule. This reaction step controlled the reaction rate.
- 5. Water was adsorbed on the catalyst surface.
- 6. The internal and external diffusion resistances were negligible.
- 7. Catalyst deactivation was caused by the deposition of product sulphur.

The Langmuir-Hinshelwood surface reaction model contains three steps:

(a) Sorption

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$$O_2 + 2X = O - X + O - X$$
 (2 - 2.2.3)

$$H_2S + X$$
 (2 - 2.2.4)

(b) Surface reaction

$$H_2S - X + O - X$$

 $H_2O - X + S - X \downarrow$ (2 - 2.2.5)

(c) Desorption of water

$$H_2O - X \longrightarrow H_2O \uparrow + X$$
 (2 - 2.2.6)

The rate expression for the temperature range 125-200°C was given by the equation:

$$r = \frac{k_s C_M K_{H_s} K_O^{0.5} p_{H_s} p_o^{0.5}}{|1 + K_{H_s} p_{H_s} + K_O^{0.5} p_O^{0.5}|^2} |1 - \frac{W_{su}}{W_{su}}|^2$$
(2 - 2.2.7)

This equation fitted the experimental data within 15%[15].

By plotting the rate constants against the reciprocal of the absolute reaction temperature, the relationships between them were expressed as follows:

$$\ln(k_s C_m) = 5.46 - \frac{23,600}{RT} \qquad (2 - 2.2.8)$$

$$\ln K_o = -18.02 + \frac{73,800}{RT} \qquad (2 - 2.2.9)$$

$$\ln K_{H_2S} = -3.71 + \frac{16,000}{RT} \qquad (2 - 2.2.10)$$

The activation energy as shown above was 23.6 kJ/mol. The heat of adsorption of oxygen was 73.8 kJ/mol. This relatively high value might be due to the fact that the oxygen was chemisorbed on the catalyst surface. However, the heat of adsorption of H_2S was lower at 16.0 kJ/mol which indicates that the H_2S was physically sorbed.

The experimental data on the water produced in the reaction did not fit the rate expression (2 - 2.2.9). It indicated that water was not adsorbed on the catalyst surface and did not take part in the reaction in the experimental temperature range 125-200°C.

The role of sulphur in the reaction was also discussed by Ghosh and Tollefson in their paper. The surface area covered by sulphur decreased with an increase in the temperature since more sulphur vaporized from the catalyst surface at higher temperature and exposed more active sites. On the other hand, the reaction rate increased with the increase in temperature. This strongly suggested that it was the surface area of the catalyst that played an important role in the catalytic oxidation rather than sulphur on the catalyst surface. The experimental data from different activated carbon catalysts also supported this conclusion.

"Hydrodarco", compared with "Calgon-SGL" and "Nuchar-WVL", had a larger total pore volume and larger pore volume in the range 5-7500 nm. The properties of these catalysts are listed in Table 2.1. In Ghosh and Tollefson's view, the sulphur deposited on the "Hydrodarco" had a larger surface area. However, at unsteady state the conversion, in the case of "Hydrodarco", decreased sharply compared with the conversions of the other two activated carbons. It was concluded that sulphur did not act as a catalyst for the reaction.

Chowdhury and Tollefson [1990] studied the effects of modified catalysts on H_2S conversion and SO_2 production. In these experiments, the Hydrodarco catalyst was saturated with $(NH_4)_2SO_4$. In another case, Hydrodarco was degassed by heating it at a temperature of 800°C in a nitrogen flow for 2.5 hours. It was found that there was no improvement in either case in terms of simultaneously increasing H_2S conversion and decreasing SO_2 production. This may mean that iron oxides and iron sulphates formed during the sulfidation have equal catalytic activities. In the other case, degassing increased the pore volume and decreased the number of pores due to the collapse of pores resulting in decreasing surface area [Ghosh and Tollefson, 1986].

A sulphur of bright yellow colour was recovered by putting a guard bed upstream to remove C_6 hydrocarbons from the natural gas feed stream.

| | Hydrodarco | Calgon SGL | Nuchar WVL | |
|--|------------|------------|------------|--|
| Initial surface area, m²/g | 487 | 1250 | 1122 | |
| Iodine number | 550 | 972 | 1041 | |
| Moisture content, % | 7.9-8.81 | 2.0 | 2.0 | |
| Particle density, g/cm ³ | 0.4 | 0.72 | 0.86 | |
| Mean pore radius, nm | 2.9 | 1.4 | 1.2 | |
| Total pore volume, cm ³ /g | 0.75 | 0.85 | 0.682 | |
| Pore volume in the range 5-7500 nm, cm ³ /g | 0.441 | 0.251 | 0.291 | |
| Particle size, (diameter) mm | 2.38×0.841 | 2.38×0.841 | 2.38×0.841 | |

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Table 2.1Properties of the Catalysts

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Dalai, Tollefson et al.[1993] published a paper on the effects of pressure and temperature on the catalytic oxidation of H_2S in natural gas and regeneration of the catalyst to recover the sulphur produced. The catalyst used in his study was Hydrodarco activated carbon. Methane-enriched gas containing 1.3% H_2S was employed to conduct the experiments at temperatures of 160-175°C and pressures from 3463 to 5600 kPa. A fixed bed reactor constructed from a 12.5 mm I.D., stainless steel tube, 250 mm long, was used with the feed gas and air concurrently flowing through it to oxidize the H_2S to elemental sulphur and water.

In discussing the effects of pressure on the oxidation of H_2S , some experimental data from Chowdhury and Tollefson were taken into account. These data were from runs in a fixed bed reactor operated at pressures of 98, 502, 640 kPa at 175°C with an H_2S concentration of 1.1% and using 1.2 times the stoichiometric ratio of O_2/H_2S required to oxidize H_2S to sulphur and water. The results showed that by operating at higher pressure there was increased conversion of H_2S and this higher conversion persisted for a longer period of time. At the same time, SO_2 production was reduced. Based on these results, higher pressure runs up to 5600 kPa were designed and conducted at 175°C. It was found that virtually 100% conversion of H_2S lasted about 800 minutes at 502 kPa, while at 5600 kPa, it was 1150 minutes. By increasing the pressure from 98 kPa to 5600 kPa, the SO_2 production was reduced to 0.30% from 3.2%. It may therefore be concluded that the oxidation of H_2S to produce sulphur is more selective at higher pressure. This phenomenon may be explained on the basis that higher pressure causes the sulphur to penetrate more deeply into the smaller pores of the catalyst thus causing greater utilization

of the available pore volume. Based on the hypothesis that the initial fraction of sulphur deposits in the micropores d<100 nm and later in the macropores, d>100 nm, it was estimated that approximately 74% sulphur was loaded in the micropores. When all of the micropores became filled with sulphur, the capillary effect gradually decreased as the macropores were loaded.

To study the effects of temperature on regeneration of the activated carbon catalyst, the catalyst was loaded with a known amount of sulphur by conducting a controlled certain amount of H_2S oxidation. A constant flow of 90 mL/min (STP) of N_2 was maintained through the reactor during the period of regeneration. A "U" tube made of stainless steel was connected to the outlet of the reactor to trap the sulphur carried by the N_2 out of the reactor. It was found that at a given sulphur loading, the amount of sulphur desorbed was higher at a higher temperature and this difference tended to diminish for smaller concentrations of deposited sulphur, there being less decrease of sulphur deposition because of the capillary effect. There is a logarithmic effect of temperature on the time required to remove a given fraction of sulphur. According to the paper by Dalai et al.[1993], as the temperature was increased from 175 to 327°C, the time required to recover 45% of the sulphur was reduced from 2570 to 13 minutes, while to recover 85%, the time decreased from 4900 to 37 minutes. This relationship of temperature with time was fitted to an equation as follows:

$$y = \exp(a + bx + cx^2)$$
 (2 - 2.2.11)

where y is the time in minutes and x is the temperature in °C. For different percentages of sulphur recovery, a,b and c have different values. Some values are given in Table 2.2. It was concluded that to get a rapid removal of sulphur from the catalyst at atmospheric pressure, higher temperature was essential to overcome the capillary effect.

The kinetics study of the oxidation of H_2S over Hydrodarco activated carbon catalyst in the temperature range of 110-240°C, and in the pressure range of 712-3436 kPa, was conducted in 1992 using a fixed-bed reactor. The rate equation from which H_2S was oxidized by O_2 to yield elemental sulphur and water was suggested to be:

$$r_{H_2S} = Aexp(-E/RT)[H_2S][O_2]$$
 (2 - 2.2.12)

This equation indicated that the reaction order was independent of operation pressure. Dalai et al.[1993] suggested that the reaction was diffusion controlled at temperatures above 130°C while it was surface reaction controlled below 130°C.

The rate equation of product SO₂ formation was suggested to be:

$$r_{SO_2} = Aexp(-E/RT)[S]^m[O_2]^n \qquad (2 - 2.2.13)$$

where $0.3 \ge m \ge 0$, $1.0 \ge n \ge 0.7$, m+n=1

| Percentage of sulphur | | | | Temperature | Pressure | |
|-----------------------|--------|----------|------------------------|-------------|----------|--|
| recovery % | a | Ъ | c | °C | kPa | |
| 45 | 7.0551 | -0.02465 | 2.011×10 ⁻⁵ | | | |
| 65 | 7.7482 | -0.02867 | 2.784× ⁻⁵ | 175-327 | 502-5600 | |
| 85 | 6.4281 | -0.01732 | 8.446× ⁻⁶ | | | |

Table 2.2 Values of a, b and c at Different Percentages of Recoveries of Sulphur

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2.3 Liquid Redox of H₂S to Elemental Sulphur

Liquid redox processes for the removal of H_2S can be used in a wide variety of applications where sulphur recovery is required [Dalrymple and Trofe, 1989]. They can be used to desulfurize:

- 1) natural gas;
- 2) refinery and chemical plant fuel gases and sour off gases;
- 3) process and off-gas streams in coal gasification plants;
- 4) geothermal vent gas;
- 5) Claus tail gas;
- 6) shale oil plant and underground coal gasification plant gases;
- 7) enhanced oil recovery vent gas.

Liquid redox processes possess the following advantages:

They can

- a. reduce H_2S levels to below 10 ppm.
- b. absorb H_2S from the gas stream and converting it to sulphur in one step.
- c. be used at ambient temperature and pressure.
- d. handle fluctuating inlet gas flow rates and H_2S concentrations;
- e. treat both low and high H_2S gas streams;
- f. use of regenerable catalysts.

Examples of such processes follow hereafter.

2.3.1 Processes Using Vanadium Catalyst

2.3.1.1 The Stretford Process

The Stretford process uses first redox process which was developed jointly by the North Western Gas Board and the Clayton Aniline Co., Ltd in the United Kingdom during 1950s [Dalrymple and Trofe, 1989]. It consists of the sulphur reactions with anthraquinone disulfonic acid (ADA) using vanadium as the primary catalyst to catalyze oxygen transfer in the regeneration of the reduced vanadium. The Stretford process consists of a series of complex, oxidation-reduction reactions in the liquid phase containing oxygen, bisulphide ion, vanadium species, and ADA. The overall reaction is:

Vanadium Catalyst

$$H_2S + 1/2O_2 \longrightarrow S + H_2O$$
 (2 - 2.3.1)

This reaction can be split into several steps. First, H_2S is absorbed in a solution containing carbonate and biocarbonate. It then hydrolyses and dissociates to form bisulphide ion (HS⁻).

$$H_2S(g) \longrightarrow H_2S(l) \longrightarrow H^+ \longrightarrow HS^-$$
 (2 - 2.3.2)

Then, the HS⁻ is oxidized to elemental sulphur by vanadium (V), which is reduced to vanadium (IV) thus:

$$4VO_3 + 2HS + H_2O$$
 \sim $V_4O_9^2 + 2S + 4OH^2$ (2 - 2.3.3)

In the next vessel, the vanadium (IV) is oxidized back to vanadium (V) by dissolved molecular oxygen transferred by ADA.

$$V_4 O_9^{2-} + O_2 + 20H^- \longrightarrow 4VO_3^- + H_2O$$
 (2 - 2.3.4)

Organic compounds in the gas can be absorbed into the Stretford solution and accumulated there and thus causing foaming, sulphur flotation, and odour problems. Some of the absorbed H_2S is converted to by-product sulphur salts rather than the desired product of elemental sulphur. When excessive amounts of sulphur salts are formed, the entire solution inventory must be discarded. Discharge of the solution containing significant vanadium levels is not environmentally acceptable. As a consequence, the vanadium-based processes are concentrating on optimizing the process to minimize the formation of sulphur salts.

2.3.1.2 The Unisulf Process

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The Unisulf process was commercialized in 1985 [Dalrymple and Trofe, 1989]. It is a vanadium-based process, which is similar to the Stretford process, but also contains thiocyanate, a carboxylic acid (usually citrate), and an aromatic sulphonate complexing agent. This process has been modified to eliminate the by-product formation since it eliminates the need for a sulphur melter in which the high temperature operation results in by-product salt formation.

2.3.1.3 The Sulfolin Process

The Sulfolin Process [Dalrymple and Trofe, 1989] is similar to the Unisulf process

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in that it is a modified Stretford process. Besides vanadium, the solution contains organic nitrogen compounds. It is claimed that by-product salt formation is low.

2.3.2 Processes Using Metal Complexes

2.3.2.1 The LO-CAT Process

The LO-CAT process was commercialized in the late 1970s [Royan and Wichert, 1994]. The LO-CAT reaction solution contains ferric iron and organic chelating agents, which are proprietary compounds that maintain iron ions in solution and prevent the precipitation of $Fe(OH)_3$ and FeS, a biocide, and a surfactant to ensure that the product sulphur will sink to the bottom of the reactor where it is removed as a slurry. As it is applied in a gas sweetening plant, the LO-CAT process is introduced downstream from the conventional Claus process to take off the small amount of H_2S in the effluent gas from Claus process. It is also applied directly to clean up natural gas which contains low concentrations of H_2S .

The dilute aqueous solution, typically has a concentration of 500-1500 ppm of H_2S which is ionized:

$$H_2S \longrightarrow H^+ + HS^- \longrightarrow 2H^+ + S^-$$
 (2 - 2.3.5)

Then the ferric iron is reduced to ferrous iron via a redox reaction with sulphur ions in the absorber to form elemental sulphur:

$$2Fe^{+++} + S^{-} \longrightarrow 2Fe^{++} + S^{0} \downarrow$$
 (2 - 2.3.6)

The used LO-CAT solution is then transferred to a regenerator in which the ferrous ions are regenerated to ferric ions by oxidation in air.

$$2Fe^{++} + \frac{1}{2}O_2 + H_2O \longrightarrow 2Fe^{+++} + 2(OH)^-$$
 (2 - 2.3.7)

The overall reaction is:

$$H_2S + 1/2O_2 \xrightarrow{\text{Catalyst}} H_2O + S^0 \downarrow \qquad (2 - 2.3.8)$$

An improved LO-CAT process [Royan and Wichert, 1994] contains an autocirculation unit in which the acid gas is introduced through the solution at one end of the reactor where H_2S is converted to sulphur and air is introduced into the solution at the other end where the used solution is regenerated. By utilizing fluid density differences resulting from different ratios within the vessel, autocirculation is achieved. Hence the autocirculator combines the absorber, pump and regenerator in one unit so that both capital and operating costs are reduced. In the LO-CAT process, complete conversion of H_2S is achieved. Therefore, eliminating the need for an incinerator and stack. The tail gas coming off the vessel can be vented to atmosphere directly. This process gives a poor quality of sulphur and the solution is very corrosive.

2.3.2.2 The Hiperion Process

The Hiperion process [Royan and Wichert, 1994], which is a modified LO-CAT process, was developed and widely used in Japan. In this process, chelated iron is combined with naphthaquinone resulting in great reduction in residence times required, and thus permitting the use of a smaller size of equipment. The advantage of this process

is: "the removal of sulphur by a plate-and-frame filter and gas/liquid contactors featuring beds which have been designed to be resistant to plugging".

2.3.3 The SulFerox Process

The SulFerox process was introduced in 1987 by the Shell Oil Company and now operated by Dow Chemical [Royan and Wichert, 1994]. The SulFerox scrubbing solution contains a different chelating agent from the LO-CAT solution, which permits the concentration of iron up to 2-4% in solution and thus results in a higher H_2S removal ability for a given volume of solution. As a result, the equipment sizes of the system employed are reduced and circulation rates are lower. The high H_2S absorption capacity is achieved using a cocurrent contactor, which is adjusted for the lower circulation rates. There is no fouling of the scrubbing solution. The SulFerox process is capable of treating the sour natural gas at high operating pressures in an absorber. The quality of the product sulphur is low and it needs to be melted and purified for sale.

2.3.4 The Bio-SR Process

The Bio-SR process was developed in Japan in 1984 [Royan and Wichert, 1994]. The reaction media is a solution containing ferric sulphate $(Fe_2(SO_4)_3)$ in an absorber. H₂S is oxidized to elemental sulphur by the ferric sulphate which is reduced to ferrous sulphate (FeSO₄).

bacteria

$$H_2S + Fe_2(SO_4)_3 \longrightarrow S^0 \downarrow + 2FeSO_4 + H_2SO_4$$
 (2 - 2.3.9)

The sulphur produced from the above reaction is suspended in the solution. It is

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transported to a filter where it is separated from the solution. The solution is then transported to a regenerator where the ferrous sulphate is oxidized back to ferric sulphate by the oxygen in air in the presence of bacteria.

 $2\text{FeSO}_4 + \text{H}_2\text{SO}_4 + 1/2 \text{ O}_2 \longrightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O}$ (2 - 2.3.10)

The regenerated solution is then recirculated back to the absorber. The following advantages of this process are claimed:

There is

1) no degradation of the solution;

2) no waste;

3) no catalyst;

4) and no special chemistry.

2.3.5 The Sulfa-Scrub Process

The Sulfa-scrub process uses a novel class of alkanolamines known as "triazines" as the reactant to remove H_2S in natural gas [Dillon, 1991]. The preferred reagent, hexahydrotriazine, is a liquid,

1,3,5 tri-(hydroxyethyl)-hexhydro-N-triazine

These reagents react with H_2S and do not react with CO_2 . The byproducts of the process are liquids rather than solids so the equipment for the removal of solid slurry is eliminated from downstream. These byproducts are not only excellent water-soluble corrosion inhibitors but also nonhazardous and of low toxicity so that they are environmently safe. Since triazines also react with water and hydrocarbon, before the triazine treatment, water and hydrocarbons should be removed from gas stream.

Examples of products are:



Bis-dithiazine



:

Dithiazine

2.4 Other Processes for the Removal of H₂S

There are several other processes for removal of H_2S from natural gas and for obtaining different valuable products.

2.4.1 The ATS Process

The ATS process was developed by Coastal States Gas Corp. in 1980 [Reginald, 1980]. This process is used to purify Claus tail gas. In the process, Claus tail gas is first incinerated thereby generating a stream containing SO₂. After being cooled, it is sent to an absorption tower where SO₂ is absorbed into an aqueous ammonia solution to form $(NH_4)_2SO_3$ and NH_4HSO_3 . Clean gas is vented to the atmosphere. The solution from the bottom of absorber containing $(NH_4)_2SO_3$ and NH_4HSO_3 enters a reactor and contacts H_2S to form $(NH_4)_2S_2O_3$ which is a type of fertilizer and has a higher value than elemental sulphur.

$$H_2S + NH_4HSO_3 + (NH_4)_2SO_3 \rightarrow \frac{3}{2}(NH_4)_2S_2O_3 + \frac{3}{2}H_2O$$

(2 - 2.3.11)

The drawback of the process is that the market for the fertilizer is small because it is only suited to areas, such as the west and southwest, where the soil is deficient in sulphur.

2.4.2 Copper Desulphurization

Copper can be used to remove H_2S for obtaining both H_2 and elemental sulphur [Chen and Hepler, 1991]. Cu-containing carbon fibers and Cu-containing activated carbon fibers are found to be most efficient materials for the removal of small amounts of H_2S in the temperature range of 298-1173K at ambient pressure.

$$2Cu + H_2S = Cu_2S + H_2$$
 (2 - 2..3.12)

The degree of H_2S removal varies from 30 to 90% with increasing temperature from 473 to 773K. Part of the H_2S adsorbed is decomposed and the H_2 is released. The maximum amount of H_2 formed could reach 50%. The drawback of the process is that: "only partial regeneration of the used Cu-containing carbon fibers is possible".

CHAPTER 3

EXPERIMENTAL METHODS

3.1 Materials Preparation

3.1.1 Activated Carbon Catalyst [Chowdhury and Tollefson, 1990]

| Tab | le | 3.1 | [] | Properties | s and | Analysi | s of | the | "Hydrodarco" | Activated | Carbon | Catalyst |
|-----|----|-----|-----|------------|-------|---------|------|-----|--------------|-----------|--------|----------|
|-----|----|-----|-----|------------|-------|---------|------|-----|--------------|-----------|--------|----------|

| Initial surface area, m²/g | 487 |
|---------------------------------------|-----------|
| Iodine number | 550 |
| Moisture content, % | 6.29 |
| Particle density, g/cm ³ | 1.3-1.5 |
| Total pore volume, cm ³ /g | 1.0 |
| Mean pore radius, nm | 2.9 |
| Particle size, mm | 0.85-2.38 |
| Metal contents, wt.% | |
| Aluminum | 1.43 |
| Calcium | 0.42 |
| Iron | 0.73 |
| Magnesium | 0.12 |
| Sodium | 0.15 |
| Silicon | 0.28 |
| Titanium | 0.23 |
| | |

The activated carbon used in all the experiments was "Granular Hydrodarco" manufactured by ICI America Inc. Ghosh and Tollefson (1986a) found that this activated carbon catalyst was a very suitable catalyst for the removal of H_2S from natural gas[15]. The activated carbon was graded by sieves. The carbon ranging from 0.85 to 2.38 mm (20 - 8 mesh) was used in these experiments. The properties and metal contents of "Granular Hydrodarco" activated carbon catalyst are listed in Table 3.1.

3.1.2 Gas Supplies

The gas mixtures containing about 1 mol% H_2S and no heavy hydrocarbons were supplied by Matheson Gas Products, Canada. One gas mixture was largely methane with a small amount of CO_2 while the other was largely CO_2 with a small amount of methane. The compositions of these gases are listed in Table 3.2.

The "field gas" employed in this study was obtained from a well-head after dehydration and was supplied by Petrogas Processing Ltd., Balzac, Alberta, Canada. The composition of this gas as supplied by the company is listed in the Table 3.3.

Compressed air of medical grade (purity 99.9%) was used to oxidize H_2S in the reactor and was supplied by Medigas, Calgary, Alberta.

Nitrogen, N_2 , with purity above 99.9 % was used for preheating the reactor before H_2S oxidation and in the regeneration of used activated carbon catalyst, was supplied by Medigas, Calgary, Alberta.

| Component | CH₄-Enriched Gas | CO ₂ -Enriched Gas | | |
|------------------|------------------|-------------------------------|--|--|
| | Mol% | Mol% | | |
| H ₂ S | 1.12 | 1.15 | | |
| CH_4 | 97.69 | 1.07 | | |
| CO ₂ | 1.19 | 97.78 | | |

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Table 3.2 Compositions of CH_4 -Enriched Gas and CO_2 -Enriched Gas
| Component | Mol. % |
|------------------|--------|
| N ₂ | 0.43 |
| CO ₂ | 6.00 |
| $\rm H_2S$ | 1.27 |
| Methane | 80.40 |
| Ethane | 7.22 |
| Propane | 2.50 |
| Isobutane | 0.57 |
| N-Butane | 0.84 |
| Isopentane | 0.33 |
| N-Pentane | 0.28 |
| C ₆ + | 0.16 |

Table 3.3 Typical Analysis of Elkton Field Gas

3.2 Apparatus Description

3.2.1 Fixed-Bed Reactor

The reactor used for this study was constructed from a stainless steel tube 12.5 mm ID and 250 mm in length with a screen fitted 2 cm from the bottom end of the tube to support the catalyst. The reactor was snugly fitted into a hole drilled through an aluminum block, 55 mm in diameter and having the same length as the reactor. The aluminum block was externally heated by a beaded electrical resistance wire, coiled in grooves on the outside surface of the block to provide an uniform temperature throughout the reactor. The aluminum block coiled with beaded wire was insulated with a layer of insulator to prevent the loss of heat.

3.2.2 Sulphur Condenser

The sulphur condenser used for the regeneration of catalyst was constructed from a 9.5 mm O.D. stainless steel tube (see Figure 3.1). Its purpose was to trap the sulphur carried out by the inert hot N_2 . It consisted of three parts with each part shaped as a "U". The first and third were filled with glass wool and were cooled to trap sulphur while the second part was inverted as a connector to link the first and third part. The sulphur condenser was connected to the reactor outlet by means of a 5 cm long connecting tube coated with copper coil plate to permit uniform heat transfer. The connecting tube was heated by means of a piece of beaded, resistance wire to approximately 130°C to prevent the sulphur from condensing in it. The outlet of the sulphur condenser was linked to the vent by a piece of Tygon tubing. The "U" tubes were designed to measure precisely the small quantities of desorbed sulphur which were collected in them.



Figure 3.1 Sulphur condenser

3.2.3 Temperature Measurement

The temperatures of the reactor, downstream sulphur condenser and the connector between them were measured by means of chromel-alumel thermocouples which were linked to a microprocessor thermometer, Model HH22 supplied by OMEGA Engineering, Inc., CT, USA. Its calibration was checked with distilled water at its boiling point. Its output was within 0.5°C. The temperature was read on the screen of the microprocessor thermometer. The reactor temperature was measured by placing a thermocouple placed in a thermowell which was a piece of 0.315 mm O.D. stainless steel tubing located in the reactor. The thermocouple and the thermowell were immersed in the catalyst bed from the top. The temperatures along the reactor axis were measured by moving the thermocouple

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to the desired point along the thermowell.

3.2.4 Pressure Control and Measurement

The system pressure was increased by supplying pressure from a reducing pressure gauge at the top of the gas cylinder. The system pressure was maintained by means of a back pressure regulator, Model 26-1765-24-069, obtained from Tescom Corporation, Elk River, Minnesota. The system pressure was measured by means of pressure gauges. When operating at a lower pressure, a type 103 pressure gauge, ranging from 0 to 500 kPa, obtained from Marsh Instrument Company, Skokie, Ill., U.S.A., was used. When operating at higher pressure (~4225 kPa), a Permagage pressure gauge was used.

3.2.5 Gas Flow Measurements

A mass flow meter, Model 8100, ranging from 0 to 2000 mL/min, was used to measure natural gas and nitrogen flows. Another mass flow meter, Model 8100, ranging from 0 to 200 mL/min was used to measure air flow rate. Both of the mass flow meters were obtained from Matheson Products and were calibrated at STP by passing gas through a bubble-flow meter [Rittenhouse and Tait, 1992]. Figure 3.2 and 3.3 give the calibration data of the meters for the natural gas flow rate and nitrogen flow rate respectively, whereas Figure 3.4 gives the calibration of air flow meter at STP.



Figure 3.2 Calibration of the mass flowmeter for sour gas



Figure 3.3 Calibration of the mass flowmeter for nitrogen

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Figure 3.4 Calibration of the mass flowmeter for air

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3.2.6 Process Flow Diagram

A schematic flow diagram of the process is shown in Figure 3.5. Sour gas was supplied from a gas cylinder through a guard bed containing activated carbon to remove any trace amounts of heavy hydrocarbons present in the feed gas and through a CaCl, column to absorb the trace amounts of moisture present in the gas. Before the sour gas passes through the mass flow meter, it was passed through a gas filter which removed the particulates in the gas to protect the flow meter. There was a micro-valve downstream for the mass flowmeter. Gas mixed with air coming from the compressed air cylinder was cleaned by means of a particulate filter and the flow adjusted by means of a micro-valve (see Figure 3.5). The mixture of feed gas was pre-heated by means of a beaded resistance wire heater wound around the inlet tube to bring its temperature up to the reaction temperature as it entered the reactor. H₂S was oxidized by the O₂ in the air over an activated carbon catalyst packed in the reactor to form sulphur and water. The pressure drop was measured by means of a pressure gauge connected to both ends of the reactor. The sulphur condenser downstream from the reactor, and which was connected with the reactor by a connecting tube, was heated to above 160°C to prevent the sulphur from condensing. On cooling the condenser collected the sulphur present in the product gas coming from the reactor. A back pressure regulator, protected from contamination by a gas filter, was installed downstream from the reactor to maintain the pressure of the reaction system at the desired level. There were three exit gas lines downstream from the back pressure regulator. The released product gas flowed to gas chromatograph analysing for hydrocarbons and sulphur compounds. One was connected to the GC for analysing

 H_2S and hydrocarbons in the product gas. One was connected to a gas sampler from which samples were taken by a 50 μ l syringe and then were injected into an SRI GC analysing for SO₂ in the product gas. One was turned on during the sampling intervals to introduce the product gas through a scrubber containing sodium hydroxide solution in which H_2S and SO₂ in the product gas were absorbed before the residual gas was vented.

A by-pass line was installed between the preheating line and the equipment for feed gas analysis. Another by-pass line incorporating a water bubbler upstream from the reactor was used to saturate the sour gas with water vapour when the effects of water vapour in the feed gas on H_2S conversion and SO_2 production were being investigated.

3.2.7 Total Pore Volume of Activated Carbon Measurement

Total pore volume of fresh and used activated carbon samples were measured by means of a AUTOSCAN-60 porosimeter supplied by QUANTACHROME Corporation, New York. It compresses mercury into the pores of a weighed sample at an elevated pressure. The volume difference of mercury before and after pressurization is the total pore volume of the activated carbon sample.



Figure 3.5 Schematic diagram of the apparatus for the experiments

3.3 Analytical Methods

3.3.1 Gas Analysis

3.3.1.1 Hydrogen Sulphide (H₂S) and Hydrocarbons

A Varian-Aerogragh (Hansenway, Palo Alto, CA), series 1700 Gas Chromatograph (GC) and a HP 3396 Series II Integrator (Hewlett Packard, Avondal, PA) were used to determine H_2S and hydrocarbon concentrations in the feed and product gases. A stainless steel tube of 6.25 mm ID and 1.828 m long packed with Poropark Q, 50-80 mesh, was used as a chromatographic column. High purity helium (Medigas) was used as a carrier gas. A six-way valve was used as a sample injector with which the sample volume was set at 1.0 mL. The operating conditions for this GC were set as follows:

| Column temperature: | 85°C |
|-----------------------|-----------|
| Detector temperature: | 200°C |
| He flow rate: | 30 mL/min |
| Attenuation: | 1 |
| Filament current | 150 mA |

At these conditions, H_2S retention time was calibrated to be 4.5 minutes, CH_4 at 1.3 minutes, C_2H_6 at 2.0 minutes and C_3H_8 at 5.5 minutes.

3.3.1.2 Sulphur Dioxide (SO₂)

A SRI 8610 Gas Chromatograph (WSC Wennick Scientific Corporation, Las Vegas, Nevada) and a Packard Bell 286 computer loaded with a software PEAKSAMPLE system controlling the analytical program were used to determine SO_2 and H_2S

concentrations in the product gas. A flame photometric detector was used in which a flow of hydrogen produced a hydrogen-rich flame in which sulphur compounds were burned to release photons of discrete frequencies which passed through a 393 nanometer filter. The output was picked up by the detector as electronic signals. A 0.32 mm I.D. and 30 m long fused silica capillary was used as the chromatographic column. High purity helium (Medigas) was used as the carrier gas. A 50 μ m syringe was used as a sample injector in which the 10 μ m sample volume was used. The operating conditions for this GC were set as follows:

| Primary hydrogen flow rate: | 30 mL/min |
|-------------------------------|----------------|
| Secondary hydrogen flow rate: | 30 mL/min |
| Air flow rate: | 100 mL/min |
| He flow rate: | 50 mL/min |
| FPD voltage: | 500 millivolts |
| Initial temperature: | 27°C |
| Final temperature: | 100°C |
| Ramp time | 4 minutes |

At the above conditions SO_2 and H_2S retention times were calibrated to be approximately 2.6 and 2.4 minutes respectively using gases containing known concentrations of these components. These gases were prepared by Praxair, Calgary.

3.4 Experimental Procedure

3.4.1 Preparation of the Activated Carbon Catalyst

3.4.1.1 Screening the Activated Carbon Catalyst

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"Granular Hydrodarco" activated carbon was graded with sieves in the range between 20 and 8 mesh (0.85 mm and 2.38mm). Particles with sizes between 0.85 mm and 2.38 mm were obtained and stored for use.

- 3.4.1.2 Analysis for the Moisture Content of the Activated Carbon Catalyst
 - a: Samples of activated carbon catalyst were taken and were weighed in a crucible, which had been weighed before hand, using a microbalance.
 - b: The samples was dried in the oven at 140°C for 4 hours.
 - c: The samples were transferred to a desiccator for cooling until the ambient temperature was reached.
 - d: The samples contained in the crucibles were weighed precisely as soon as they were taken from the desiccator.
 - f: The moisture content of the activated carbon was calculated by the following equation:

Moisture Content (%) =
$$\frac{W_f - W_d}{W_f} \times 100$$
 (3 - 4.1)

where:

W_f: the weight of fresh activated carbon catalyst

W_d: the weight of dried activated carbon catalyst

3.4.2 H₂S Oxidation Experiments Using Five Grams of Activated Carbon Catalyst

- 3.4.2.1 H₂S Oxidation Procedure
 - a: Five grams (dry base) "Granular Hydrodarco" activated carbon was weighed precisely.
 - b: The catalyst was carefully loaded on a piece of glass wool support at the bottom of the reactor.
 - c: The reactor with its packed activated carbon catalyst was installed in the reaction system.
 - d: The electrical system was turned on to bring the temperatures of each part of the system to the levels required for H_2S oxidation with a small amount of nitrogen flowing through the reactor bed.
 - e: The sour gas was turned on while the system pressure and the gas flow rate were adjusted as required for the H_2S oxidation.
 - f: The process of H_2S oxidation was started by the addition of the air which was adjusted as required for the H_2S oxidation.
 - g: Samples were taken from the product gas every half hour and were injected into both gas chromatographs to analyze for the H_2S and SO_2 concentrations.
 - h: The H_2S oxidation process was stopped after it had been continued for 1000 minutes when the sulphur loading was up to approximately 120% of the mass of the activated carbon.

3.4.2.2 Procedure for Regeneration of the Spent Activated Carbon Bed

- a: Each part of a set of sulphur condensers, constructed from 9.525 mmO.D. stainless steel, was weighed precisely with a microbalance.
- b: The downstream sulphur condenser and the connector were disconnected from the outlet port of the reactor.
- c: Three parts of the sulphur condenser were linked in series and its input was connected to the output of the reactor by means of a connector.
- d: A "variac" power transformer for controlling the reactor temperature was turned on to raise the temperature of the activated carbon bed while a small flow of nitrogen passed through the activated carbon to carry out the vaporized sulphur from the activated carbon. The connector linking the reactor and the sulphur condenser was heated by a piece of beaded resistance wire to prevent the sulphur in the gas from condensing.
- e: The regeneration process was continued by increasing the reactor temperature slowly until the sulphur condenser was plugged by condensed sulphur.
- f: The power was turned off and the system was cooled to the ambient temperature.
- g: The sulphur condenser was detached from the reactor and each part was weighed accurately to within 1.0 mg. The difference in mass before and after it trapped the sulphur was the amount of sulphur recovered.
- h: Another set of sulphur condensers was connected to the reactor to

continue the regeneration process until the reactor temperature reached 350°C at which it was maintained for more than eight hours.

- i: An alternate procedure in the case of the H_2S oxidation process, the reaction was conducted with sour gas containing no heavy hydrocarbons, the regeneration temperature was maintained at approximately 300 °C for eight hours and then the regeneration process was pursued under partial vacuum for seven hours at an absolute pressure of 260 mm Hg until the activated carbon bed was free of sulphur and ready for the next H_2S oxidation cycle.
- 3.4.3 Procedure for the Kinetics Study of H_2S Oxidation on the Activated Carbon Catalyst
 - a: One or two grams of "Granular Hydrodarco" activated carbon catalyst (dry base) was weighed precisely on a microbalance.
 - b: The activated carbon then was mixed with white sand so that the total volume was approximately 12.8 mL. The sand itself was shown to have a low level of catalytic activity which decreased with time on stream so no correction was made.
 - c: The mixture was packed into the reactor carefully.
 - d: The reactor with its packing was installed in the reaction system.
 - e: The electrical system was turned on to bring the temperature of each part of the reaction system to the levels required for the H_2S oxidation while

a small stream of nitrogen was flowing through the activated carbon bed.

- f: The nitrogen was switched to sour gas, the pressure and the gas flow rate were adjusted to levels required for H_2S oxidation.
- g: The H_2S oxidation process was started as soon as the air was turned on and its flow rate was adjusted to the amount required for the oxidation process.
- h: Samples were taken from the exhausted gas every half hour and injected into both gas chromatographs for the analyses of H_2S and SO_2 .
- i: The oxidation process was stopped after it had been conducted for three hours.
- 3.4.4 Procedure for Determining the Effects of Water Vapour on H₂S Oxidation
 - a: Two grams of "Granular Hydrodarco" activated carbon catalyst was weighed precisely by means of a microbalance.
 - b: The activated carbon was mixed with white sand so that its total volume was approximately 12.8 mL.
 - c: The mixture was packed into the reactor carefully.
 - d: The reactor with its packing was installed in the reaction system.
 - e: The electrical system was turned on to bring the temperature of each part of the system to that required for H_2S oxidation.
 - f: The sour gas was turned on and the reaction system was pressurized to 230 kPa while the gas flow rate was adjusted to 527 mL/min.

- g: The sour gas was introduced by bubbling it through a column of water to saturate it. The product sour gas was passed through a $CaCl_2$ column via a bypass line for 15 minutes so that the water vapour in the gas was removed.
- h: The sour gas flow was then switched to the reactor. The oxidation process was started as soon as the air was turned on and its flow rate was adjusted as required for H_2S oxidation.
- i: Samples were taken from the product gas every half hour and injected into both GCs for the analysis of H_2S and SO_2 .
- j: The oxidation process was stopped after it had been continued for 3 hours.
- k: The sour gas was switched to the $CaCl_2$ column to absorb the water vapour in the saturated sour gas for 15 minutes. The water content was determined by the weight difference of the column before and after it had absorbed water.
- 3.5 Experimental Conditions
- 3.5.1 Long Runs for Determining Catalyst Life

Two series of long runs were performed to determine the life of the catalyst. In each series of long runs, 5 grams catalyst was used.

The first series of twelve long runs was performed at 230 kPa using dried natural gas from the Elkton gas field containing an H₂S concentration ranging from 0.7 - 1.3% and 3% of heavy hydrocarbons(C_5^+). Feed gas was maintained at 500 mL/min. The first

ten runs were conducted at 175°C, while Run 11 was done at 190°C and Run 12 at 205°C. The activated carbon catalyst was regenerated by heating it up to 350°C with nitrogen flowing through it at 90 mL/min(STP). Prior to Run 4, the catalyst was regenerated by heating it up to 450 °C so that the vapour pressure of the sulphur was increased from 133 to 780 mm Hg [West and Menzies, 1919] to remove more sulphur from the micropores of the catalyst. The experimental conditions are listed in Table 3.4.

The second series of 10 runs was performed at elevated pressures up to 3200 kPa, a reaction temperature of 175°C with methane-enriched gas containing 0.9% H₂S and no heavy hydrocarbons. Feed gas was maintained at 527 mL/min. and the air flow was maintained for the oxidation reaction in such a way that the O₂/H₂S stoichiometric ratio was varied from 1 to 1.20. The activated carbon catalyst was regenerated by heating it up to 300°C and then using a absolute pressure of 260 mm Hg for seven hours at the same time flowing nitrogen through it at 90 mL/min(STP). The experimental conditions for each of these run are listed in Table 3.5.

3.5.2 Short Runs for the Study of Kinetics on H_2S Oxidation

Short runs were also performed for three hours each in which the mass of the catalyst, reaction temperature, reactor pressure, water content present in the feed gas, and O_2/H_2S ratio were varied. These experiments were conducted to study the kinetics of the H₂S oxidation process. The operation conditions for the experiments with methane-enriched gas are given in Table 3.6 and 3.7. The conditions of runs with CO₂-enriched acid gas are given in Table 3.8.

| Run No. | T ℃ | P kPa | O ₂ /H ₂ S mol ratio | H ₂ S mol% | FGF [*] mL/min | t min | S Loaded g | S Recovered g | R.T** ℃ |
|------------|--------|----------|---|--------------------------|----------------------------|-------------------|---------------|---------------------|------------|
| 1 | 175 | 230 | 1.2 | 0.84 | 500 | 1100 | 4.958 | 4.851 | 325 |
| 2 | 175 | 230 | 1.2 | 0.74 | 500 | 915 | 4.338 | 4.028 | 338 |
| 3 | 175 | 230 | 1.2 | 0.71 | 500 | 1006 | · 3.783 | 3.862 | 350 |
| 4 | 175 | 230 | 1.2 | 0.68 | 500 | 942 | 3.212 | 3.392 | 332 |
| 5 | 175 | 230 | 1.2 | 1.21 | 500 | 900 | 4.233 | 3.507 | 380 |
| 6 | 175 | 230 | 1.2 | 1.07 | 500 | 910 | 4.243 | 2.892 | 339 |
| 7 | 175 | 230 | 1.2 | 1.16 1.11 1.15 | 500 | 460 670 900 | 4.407 | 3.133 | 336 |
| 8 | 175 | 230 | 1.2 | 1.18 1.14 | 500 | 450 900 | 4.121 | 3.285 | 324 |
| 9 | 175 | 230 | 1.2 | 1.14 | 500 | 900 | 4.086 | 3.065 | 325 |
| 10 | 175 | 230 | 1.2 | 1.14 | 500 | 900 | 3.291 | 2.873 | 325 |
| 11 | 190 | 230 | 1.2 | 1.07 | 500 | 900 | 4.580 | 3.586 | 325 |
| 12 | 205 | 230 | 1.2 | 1.13 | 500 | 900 | 5.587 | 4.372 | 407 |

Table 3.4 Reaction Conditions for Each Long Run with Feed Gas Containing Heavy Hydrocarbons

*FGF=Feed gas flow at STP. **R.T=Regeneration Temperature.

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| Run No. | T ℃ | P kPa | O ₂ /H ₂ S mol ratio | H ₂ S mol% | FGF* mL/min | t min | S Loaded g | S Recovered | R.T** ℃ |
|------------|--------|----------|---|--------------------------|----------------|----------|---------------|-------------|------------|
| 1 | 175 | 1470 | 1.03 | 0.9 | 527 | 1120 | 7.629 | 7.770 | 250 |
| 2 | 175 | 1470 | 1.03 | 0.9 | 527 | 1115 | 6.827 | 6.779 | 300 |
| 3 | 175 | 1470 | 1.03,1.08 | 0.9 | 527 | 1025 | 6.601 | 6.072 | 310 |
| 4 | 175 | 1470 | 1.08 | 0.9 | 527 | 1040 | · 6.661 | 6.056 | 300 |
| 5 | 175 | 1470 | 1.10 | 0.9 | 527 | 1040 | 6.546 | 5.916 | 300 |
| 6 | 175 | 1470 | 1.05 | 0.9 | 527 | 1045 | 6.575 | 6.081 | 300 |
| 7 | 175 | 3200 | 1.05 | 0.9 | 527 | 1180 | 7.761 | 6.724 | 300 |
| 8 | 175 | 2330 | 1.05 | 0.9 | 527 | 1100 | 7.133 | 6.319 | 300 |
| 9 | 175 | 1470 | 1.05 | 0.9 | 527 | 1030 | 6.631 | 6.006 | 300 |
| 10 | 175 | 230 | 1.05 | 0.9 | 527 | 815 | 4.056 | 3.275 | 300 |

Reaction Conditions for Each Long Run with Feed Gas Containing No Heavy Hydrocarbons Table 3.5

*FGF=Feed gas flow at STP. **R.T=Regeneration Temperature. Mass of catalyst used=5.0 g

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| Run No. | T ℃ | P kPa | O ₂ /H ₂ S mol ratio | Cat.Wt g | H ₂ S mol% | FGF [*] mL/min | H ₂ O mol% |
|------------|--------|----------|---|-------------|--------------------------|----------------------------|--------------------------|
| 1 | 125 | 230 | 1.05 | 1.0 | 1.12 | 527 | 0.0 |
| 2 | 125 | 230 | 1.10 | 1.0 | 1.12 | 527 | 0.0 |
| 3 | 150 | 230 | 1.05 | 1.0 | 1.12 | 527 | 0.0 |
| 4 | 150 | 230 | 1.10 | <u>1.0</u> | 1.12 | 527 | 0.0 |
| 5 | 175 | 230 | 1.05 | 1.0 | 1.12 | 527 | 0.0 |
| 6 | 175 | 230 | 1.10 | 1.0 | 1.12 | 527 | 0.0 |
| 7 | 200 | 230 | 1.05 | 1.0 | 1.12 | 527 | 0.0 |
| 8 | 200 | 230 | 1.10 | 1.0 | 1.12 | 527 | 0.0 |
| 9 | 125 | 230 | 1.05 | 2.0 | 1.12 | 527 | 0.0 |
| 10 | 150 | 230 | 1.05 | 2.0 | 1.12 | 527 | 0.0 |
| 11 | 175 | 230 | 1.05 | 2.0 | 1.12 | 527 | 0.0 |
| 12 | 200 | 230 | 1.05 | 2.0 | 1.12 | 527 | 0.0 |
| 13 | 125 | 500 | 1.05 | 1.0 | 1.12 | 527 | 0.0 |
| 14 | 150 | 500 | 1.05 | 1.0 | 1.12 | 527 | 0.0 |
| 15 | 175 | 500 | 1.05 | 1.0 | 1.12 | 527 | 0.0 |
| 16 | 200 | 500 | 1.05 | 1.0 | 1.12 | 527 | 0.0 |
| 17 | 125 | 780 | 1.05 | 1.0 | 1.12 | 527 | 0.0 |
| 18 | 150 | 780 | 1.05 | 1.0 | 1.12 | 527 | 0.0 |
| 19 | 175 | 780 | 1.05 | 1.0 | 1.12 | 527 | 0.0 |
| 20 | 200 | 780 | 1.05 | 1.0 | 1.12 | 527 | 0.0 |
| 21 | 125 | 230 | 1.20 | 1.0 | 1.12 | 527 | 0.0 |
| 22 | 150 | 230 | 1.20 | 1.0 | 1.12 | 527 | 0.0 |
| 23 | 175 | 230 | 1.20 | 1.0 | 1.12 | 527 | 0.0 |

 Table 3.6
 Reaction Conditions for Short Runs With Methane-Enriched Sour Gas

*FGF=Feed gas flow at STP.

| Run No. | T ℃ | P kPa | O ₂ /H ₂ S mol ratio | Cat.Wt g | H ₂ S mol% | FGF [*] mL/min | H ₂ O mol% |
|------------|--------|----------|---|-------------|--------------------------|----------------------------|--------------------------|
| 24 | 200 | 230 | 1.20 | 1.0 | 1.12 | 527 | 0.0 |
| 25 | 125 | 230 | 1.05 | 2.0 | 1.12 | 527 | 1.0 |
| 26 | 125 | 230 | 1.05 | 2.0 | 1.12 | 527 | 8.0 |
| 27 | 150 | 230 | 1.05 | 2.0 | 1.12 | 527 | 0.6 |
| 28 | 150 | 230 | 1.05 | 2.0 | 1.12 | 527 | 8.6 |
| 29 | 175 | 230 | 1.05 | 2.0 | 1.12 | 527 | 1.7 |
| 30 | 175 | 230 | 1.05 | 2.0 | 1.12 | 527 | 5.6 |
| 31 | 200 | 230 | 1.05 | 2.0 | 1.12 | 527 | 0.6 |
| 32 | 200 | 230 | 1.05 | 2.0 | 1.12 | 527 | 10.5 |

Table 3.7Continuation of Reaction Conditions for Short Runs With Methane-
Enriched Sour Gas

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*FGF=Feed gas flow at STP.

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| Run No. | T ℃ | P kPa | O ₂ /H ₂ S mol ratio | Cat.Wt g | H ₂ S mol % | FGF [*] mL/min | H ₂ O mol % |
|------------|--------|----------|---|-------------|---------------------------|----------------------------|---------------------------|
| 33 | 175 | 230 | 1.05 | 1.0 | 1.15 | 527 | 0.0 |
| 34 | 175 | 500 | 1.05 | 1.0 | 1.15 | 527 | 0.0 |
| 35 | 175 | 780 | 1.05 | 1.0 | 1.15 | 527 | 0.0 |
| 36 | 125 | 230 | 1.05 | 1.0 | 1.18 | 527 | 0.0 |
| 37 | 125 | 435 | 1.10 | 1.0 | 1.18 | 527 | 0.0 |
| 38 | 125 | 640 | 1.10 | 1.0 | 1.18 | 527 | 0.0 |
| 39 | 150 | 230 | 1.10 | 1.0 | 1.18 | 527 | 0.0 |
| 40, | 150 | 435 | 1.10 | 1.0 | 1.18 | 527 | 0.0 |
| 41 | 150 | 640 | 1.10 | 1.0 | 1.18 | 527 | 0.0 |
| 42 | 175 | 230 | 1.05 | 2.0 | 1.15 | 527 | 0.0 |
| 43 | 175 | 230 | 1.05 | 2.0 | 1.15 | 527 | 1.1 |
| 44 | 175 | 230 | 1.05 | 2.0 | 1.15 | 527 | 6.9 |

 Table 3.8
 Reaction Conditions for Short Runs With CO₂-Enriched Sour Gas

*FGF=Feed gas flow at STP.

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CHAPTER 4

RESULTS AND DISCUSSION

4.1 Activated Carbon Catalyst Life

It was considered desirable to study the life of the activated carbon catalyst for the oxidation of H_2S in order to evaluate this process for possible use in industry.

Ghosh and Tollefson [1986] stated in their study of the oxidation of H_2S that an increase in the conversion of H_2S to elemental sulphur was obtained with an increase of reaction temperature. One drawback of the process is that it also yields a by-product, SO_2 the yield of which increases with an increase of temperature. It was found that SO_2 production increases dramatically when the reaction temperature is above 175°C. Therefore, SO_2 production limits the reaction temperature to about 200°C at which it is feasible to operate and necessitates the study of the influence of the other parameters to be described on the conversion of H_2S to sulphur. At 175°C, the extent of increase of H_2S conversion is small as the O_2/H_2S ratio varies from 1.05 to 1.20 while SO_2 production increases significantly. Therefore, 1.05 was selected as being close to the optimum O_2/H_2S mol ratio for high H_2S conversion and low SO_2 production.

The first series of 10 runs was performed at 175°C, at 230 kPa with dried sour natural gas containing H_2S in the range 0.71 - 1.21 mol% and 1.0 mol% C_5^+ heavy hydrocarbons. Each of these runs was continued for more than 900 minutes on stream. After each cycle, the catalyst was regenerated by heating the catalyst up to 350°C so that the sulphur is vaporized and removed by a small flow of nitrogen. H_2S conversion as a function of time-on-stream for the 10 cycles of operation at 175°C is plotted in Figure

4.1. The results of the 10th cycle at 175°C, the 11th cycle at 190°C and the 12th cycle at 205°C are plotted in Figure 4.2 to describe the effects of temperature on the process.

Figure 4.1 and 4.2 indicate that there are three stages in the oxidation process in an experimental run under the conditions chosen. In the initial stage, H₂S is converted completely and most of the elemental sulphur produced is deposited in the micropores of the activated carbon catalyst, resulting in a reduction of the catalyst surface area. As a result, H₂S conversion slowly decreases. It has been suggested that some of the sulphur at reaction temperature would be in the vapour phase. According to Steijns and Mars [1974], the deposition of sulphur in the micropores of the activated carbon causes a decrease in its vapour pressure by a factor of 1000 as a result of the "capillary effect" of micropores. In the second stage of the oxidation process, H_2S conversion decreases with more sulphur being deposited resulting in less catalyst surface area being available. During this stage, the amount of sulphur depositing on the catalyst is more than the amount vaporized from the catalyst surface. In the third stage, H₂S conversion is almost constant due to the amount of sulphur being deposited being equal to the amount of sulphur being vaporized. This leads to a constant catalyst surface area. Therefore, H₂S conversion at this stage is maintained constant at a certain level.



Figure 4.1 Percentage of H₂S conversion as a function of time-on-stream with Elkton field gas;



Figure 4.2 Percentage of H₂S conversion as a function of time-on-stream with Elkton field gas;

It is observed that the conversion of H_2S decreases during each cycle. it was maintained at virtually 100% for 600 minutes in the first cycle and decreased to 75% over 100 minutes in the tenth cycle. The H_2S conversion at the "steady state" also decreased from 75% to 45% during the first cycle to the tenth cycle. By increasing the temperature to 190 and 205°C respectively, H_2S conversion in the first stage was increased from 78% to 93% and 95%, from 45% to 70% and 85% at the "steady state" stage. This is due to the fact that at higher temperatures more sulphur is vaporized leaving more available surface area for H_2S oxidation reaction.

The average conversion of H_2S within the process when conducted for 15 hours versus the cycle number is plotted in Figure 4.3. The decrease of H_2S conversion after each cycle is stated explicitly.



Figure 4.3 Average conversion of H_2S within the process when conducted for a 15-hour period as a function of cycle number with Elkton field gas;

| cycle number: | 1 - 12; |
|-------------------|-------------------------------------|
| type of gas: | Elkton field gas; |
| H_2S conc.: | 0.706 - 1.210 mol%; |
| temperature: | $175 - 205 \pm 1.5^{\circ}C;$ |
| pressure: | 230 kPa; |
| O_2/H_2S ratio: | $1.2 \times \text{stoichiometric};$ |
| feed gas flow: | 500 mL/min (STP); |
| catalyst: | 5.0 g dry Hydrodarco. |

In another series of 10 runs, the H_2S oxidation process was conducted for more than 1000 minutes in each cycle using 5 g catalyst. The same amount was used in the previous series at 175°C, and at elevated pressure up to 3200 kPa, with O_2/H_2S mol ratios ranging from 1.03 to 1.20 using a prepared methane-enriched sour gas mixture containing 0.9% H_2S and no heavy hydrocarbons. In these ten runs the yield of byproduct SO_2 was measured while H_2S conversion was monitored. After each cycle, the catalyst was regenerated by heating it to 300°C (which was much lower than the regeneration temperature in the previous series which was 350°C) and maintained at this temperature for 8 hours. It was then subjected to an absolute pressure of 260 mm Hg for 7 hours for further regeneration. H_2S conversion versus time-on-stream in these 10 cycles is plotted in Figure 4.4, 4.5 and 4.6. The plots were drawn with the aid of a French curve.

Figure 4.4, 4.5 and 4.6 indicate that there are three stages in the SO₂ production curve. In the initial stages of the oxidation process, H_2S conversion is virtually complete and SO₂ production is relatively low. At this stage the elemental sulphur produced is deposited in the smaller micropores or it covers part of the surface of the activated carbon catalyst possibly as a monolayer. The attractive forces between the sulphur and the surface of the catalyst are relatively strong, especially in the micropores. When further sulphur is deposited on the surface, the attractive forces are lower and hence the sulphur vapour pressure tends to increase making the reaction with excess oxygen faster thereby producing SO₂.



Figure 4.4 Percentage of H_2S conversion and percentage of H_2S fed converted to SO_2 as a function of time-on-stream with CH_4 -enriched gas;

| cycle number: | 1 - 4; |
|---|--|
| type of gas: | methane-enriched sour gas; |
| H_2S conc.: | 0.9 mol%; |
| temperature: | $175 \pm 1.5^{\circ}C;$ |
| pressure: | 1470 kPa; |
| O ₂ /H ₂ S ratio: | $1.03 - 1.08 \times \text{stoichiometric}$ |
| feed gas flow: | 527 mL/min (STP); |
| catalyst: | 5.0 g dry Hydrodarco. |

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Figure 4.5 Percentage of H_2S conversion and percentage of H_2S fed converted to SO_2 as a function of time-on-stream with CH_4 -enriched gas;

| cycle number: | 5 - 6; |
|---|---|
| type of gas: | methane-enriched sour gas; |
| H_2S conc.: | 0.9 mol%; |
| temperature: | $175 \pm 1.5^{\circ}C;$ |
| pressure: | 1470 kPa; |
| O ₂ /H ₂ S ratio: | $1.05 - 1.10 \times \text{stoichiometric};$ |
| feed gas flow: | 527 mL/min (STP); |
| catalyst: | 5.0 g dry Hydrodarco. |

;



Figure 4.6 Percentage of H_2S conversion and percentage of H_2S fed converted to SO_2 as a function of time-on-stream with CH_4 -enriched gas;

| cycle number: | 7 - 10; |
|---|-------------------------------------|
| type of gas: | methane-enriched sour gas; |
| H_2S conc.: | 0.9 mol%; |
| temperature: | $175 \pm 1.5^{\circ}C;$ |
| pressure: | 230 - 3200 kPa; |
| O ₂ /H ₂ S ratio: | $1.05 \times \text{stoichiometric}$ |
| feed gas flow: | 527 mL/min (STP); |
| catalyst: | 5.0 g dry Hydrodarco. |

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During the second stage, the elemental sulphur produced in the reaction accumulates in the micropores or covers the catalyst surface to such an extent that there is not sufficient surface area available for a complete oxidation of the H_2S . The attractive forces between the sulphur and the catalyst surface decrease allowing more free sulphur atoms to react with oxygen thereby resulting in an increase in SO₂ production. During this stage, H_2S conversion also decreases somewhat. During the third stage, when H_2S conversion decreases dramatically, the residual H_2S in the vapour phase increases to such an extent that it allows the Claus reaction to occur in which H_2S reacts with SO₂ to produce sulphur and water. Therefore, the SO₂ content in the vapour phase decreases during this stage of the oxidation process.

There are three reactions occurring in the oxidation process:

$$x H_2S + x/2 O_2 \longrightarrow x S \downarrow \uparrow + x H_2O$$
 (4 - 1.1)

$$S_x + x O_2$$
 $(4 - 1.2)$

:

$$x SO_2 + 2x H_2S$$
 $=$ 3 $S_x + 2x H_2O$ (4 - 1.3)

Since part of the elemental sulphur produced in the reaction is deposited on the surface of the activated carbon catalyst and part of it is in the vapour phase, the production of sulphur is expressed as S $1\downarrow$ in the reaction equation 4 - 1.1. The first reaction is the principal reaction which produces elemental sulphur. The second reaction

produces a by-product SO_2 which is undesirable. The third reaction is the reversible Claus reaction. The product of sulphur in the Claus reaction at these conditions is considered to be in the liquid form [Moore, 1992].

4.1.1 Effects of Pressure

H₂S conversion and SO₂ production versus time-on-stream at pressures of 3200, 2330, 1470 and 230 kPa are plotted in Figure 4.6 in order to express the effects of pressure on H₂S conversion and SO₂ production clearly. It has been observed that higher H_2S conversion and lower SO₂ production were achieved for longer periods of time at higher reaction pressures. With the reaction pressure increased from 230 to 1470 and 3200 kPa, the average conversion of H_2S increased from 78.0% to 97.6% and 99.2% while the average conversion of H_2S converted to SO_2 decreased from 1.25 to 0.44 over 900 minutes of operation. This is due to the fact that the residence times for H_2S and oxygen were increased with the increase of pressure in the reaction system. The flow of gas through the reactor was maintained constant as measured at STP. Therefore, the chance of collision and reaction for both molecules was increased. Meanwhile, H₂S was forced into the smaller pores of the catalyst at elevated pressure and more surface area became available for the reaction. The elemental sulphur produced at higher pressure was strongly fixed on the surface of the catalyst due to the "capillary effect" so that less sulphur was available to react with oxygen to produce SO₂. This was supported by the evidence that the sulphur vapour pressure was higher when the system was plugged at higher temperature during the regeneration of the catalyst after runs conducted on the
oxidation of H_2S at higher pressure.

4.1.2 Effects of Heavy Hydrocarbons in the Feed Gas

The average conversion of H_2S and the SO_2 production when the process was continued for 900 minutes with a methane-enriched gas mixture containing no heavy hydrocarbons are plotted in Figure 4.7. Figure 4.3 and 4.7 show that H_2S conversion decreases after each cycle. This means that the activity of the catalyst decreases after each cycle. It is found by comparing Figure 4.3 and 4.7 that the extent of decrease after each cycle is much less with a methane-enriched gas mixture than the decrease in the previous series with Elkton field gas. Heavy hydrocarbons play a role in the decrease of the catalytic activity due to the formation of coke on the surface of activated carbon, during regeneration of the activated carbon catalyst at temperatures above 300°C. This may be due to some of the heavy hydrocarbons being adsorbed on the catalyst surface during H_2S oxidation process, being cracked when the regeneration temperature is raised to above 300°C causing coke formation on the catalyst surface and blocking some of the micropores thereby reducing the available surface area of the catalyst. This is supported by the observation that the elemental sulphur produced with the gas containing heavy hydrocarbons shows a dark brown colour while the sulphur produced with the gas mixture containing no heavy hydrocarbons is bright yellow. This contention is also supported by the scanning electron micrographs taken of the used and the freshly activated carbon samples as shown in Figure 4.8. (The magnification of these pictures is around 1000). "A" is the freshly activated carbon sample; "B" is the sample after 12

cycles with the gas containing heavy hydrocarbons; "C" is the sample after 10 cycles with the gas containing no heavy hydrocarbons. There appears to be a number of large lumps on the surface of the catalyst "B". They are considered to be coke resulting from the heavy hydrocarbons. The fibres of sample "C" are more uniform and look more like the fresh sample.

A partial vacuum was used for 7 hours during the regeneration period and the activated carbon was heated to 300°C. The objective of using reduced pressure was to reduce the partial pressure so that the sulphur deposited in the smaller pores would be more easily vaporized. By keeping the temperature below 300°C, the trace amounts of heavy hydrocarbon adsorbed were prevented from cracking.



Figure 4.7 Average conversion of H_2S and average percentage of H_2S fed converted to SO_2 within the process when conducted for 15 hours as a function of cycle number with CH_4 -enriched gas;

| cycle number: | 1 - 10; |
|------------------|---|
| type of gas: | methane-enriched sour gas; |
| H_2S conc.: | 0.9 mol%; |
| temperature: | $175 \pm 1.5^{\circ}C;$ |
| pressure: | 230 - 3200 kPa; |
| O_2/H_2 ratio: | $1.03 - 1.10 \times \text{stoichiometric};$ |
| feed gas flow: | 527 mL/min (STP); |
| catalyst: | 5.0 g dry Hydrodarco. |



Figure 4.8 Scanning electron micrographs taken from used and fresh catalyst

- A: Fresh sample (1040)
- B: Sample after 12 cycles with heavy ends (1020)
- C: Sample after 10 cycles without heavy ends (1040)

It has been observed from Figure 4.7 that the average conversion of H_2S in Run 9 was a little higher than that in Run 6 while SO_2 production was a little lower from Figure 4.5 and 4.6. Both cycles were conducted under the same conditions i.e. 175°C, 1470 kPa and with an O_2/H_2S ratio 1.05 but Run 9 was performed after two high pressure cycles. It would appear that some of the "dead pores" were activated by increasing the operating pressure resulting in a small increase in H_2S conversion and a small decrease in SO_2 production in Run 9 cycle. At high pressure the H_2S may penetrate the blocked pores causing an increase in the active sites on the surface of the catalyst. It suggests a way to recover the catalytic activity of a used catalyst by increasing the operating the H_2S oxidation reaction process.

By increasing the operating pressure with feed gas containing no heavy hydrocarbons and regenerating the catalyst after each cycle at lower temperature with a partial vacuum, higher catalyst activity was maintained. The results of characterization of the used and fresh of the activated carbon samples with respect to the surface area, pore volume and the other properties are listed in Table 4.1. Compared to the freshly activated carbon catalyst, which possessed a surface area of 487 m²/g, the surface area of the activated carbon obtained from the sample with which 10 runs were done on H₂S oxidation was 296 m²/g. On the other hand, the surface area of the sample obtained after conducting 12 runs with the feed gas containing heavy hydrocarbons decreased to 50 m²/g showing that the heavy hydrocarbon fraction had cracked yielding coke which plugged the pores so that they were no longer available in terms of surface area.

Pore structure of the activated carbons was analyzed by means of the porosimeter.

The total pore volume of the freshly activated carbon was 0.75 mL/g. It decreased to 0.06 mL/g after 12 cycles of H_2S oxidation being conducted using feed gas containing heavy hydrocarbons. This indicates that most of the pores of the activated carbon collapsed or were plugged resulting in a decrease of total pore volume. Support for the suggestion that the pores of activated carbon may be plugged by coke from the cracking of heavy hydrocarbons or by sulphur may be reasons why the loss of activity is seen in the density of the used activated carbon which was at least twice that of the freshly activated carbon. The densities of elemental sulphur (2 g/cm³) [Kirk et al.] and coke are much higher than that of carbon. The significant increase in the density may be due to the elemental sulphur blocked inside the micropores by the formation of coke so that sulphur could not be vaporized during the regeneration process.

After conducting the H_2S oxidation process using feed gas containing no heavy hydrocarbons the total pore volume of the used activated carbon was 0.69 cc/g, which is close to the value of 0.75 cc/g for freshly activated carbon. The small decrease in the total pore volume may be due to the collapse of some of the micropores or to the change of structure of the catalyst during the oxidation and regeneration process or due to the formation of coke resulting from a trace amount of heavy hydrocarbons being present in the feed gas. The fraction of the micropores which collapsed is considered to be small as the amount of decrease in surface area which accounts for about half of that of the fresh carbon is much higher compared with the amount of decrease of total pore volume which accounts for one eleventh of that of the fresh carbon. Some of these pores are capable of being activated by elevating the operating pressure.

| Item of analysis | Fresh | Used | Used |
|---------------------------------|---------------------|----------------------------|---------------------|
| | catalyst | catalyst* | catalyst** |
| Surface area, m ² /g | 487 | 50 | 296 |
| Particle density, g/cc | 0.4 | >> 0.4 | > 0.4 |
| Moisture content, % | 6.9 | 2.2 | 4.8 |
| Total pore volume, cc/g | 0.75 | 0.06 | 0.69 |
| Particle size, (diameter) mm | 2.38×0.595 | 88% in 2.38 \times 0.595 | 88% in 2.38 × 0.595 |

 Table 4.1
 Characterization of Fresh and Used Hydrodarco Catalysts

* Used catalyst had been regenerated 12 times - after each cycle of operation.

Feed gas contained 1% C_5^+ hydrocarbons.

** Used catalyst had been regenerated 10 times - after each cycle of operation.

Feed gas contained no C_5^+ hydrocarbons.

4.2 Optimization of the H₂S Oxidation Process

A continuous process for H_2S oxidation over an activated carbon catalyst has been developed. In this process, a small fraction of by-product SO_2 is present in the product gas. To make this process as simple and economical as possible to operate, work on the process optimization has been done by varying the temperature, pressure, O_2/H_2S ratio, water vapour content in the feed gas and the type of feed gas as well so minimizing production of SO_2 and at the same time achieving high conversion of H_2S to sulphur and water.

4.2.1 Effects of Temperature

To study the effects of temperature on H_2S conversion and SO_2 production in the H_2S oxidation process over the activated carbon catalyst, a series of short runs were conducted at temperatures ranging from 125 - 200°C with different amounts of activated carbon, varying pressures and O_2/H_2S stoichiometric ratios. The results are plotted in Figure 4.9 - 4.14. The plots are fitted with the aid of a French curve.

Figure 4.9 and 4.10 indicate that both H_2S conversion and SO_2 production increase with an increase of reaction temperature using 1 g and 2 g of the activated carbon catalyst.

Figure 4.9, 4.11 and 4.12 indicate that both H_2S conversion and SO_2 production increase with an increase of reaction temperature when the process is conducted at pressures of 230, 500 and 780 kPa.



Figure 4.9 Effects of temperature on H_2S conversion and SO_2 production with 1.0 g catalyst;

| catalyst: | 1 g dry Hydrodarco; |
|-------------------|--------------------------------------|
| temperature: | $125 - 200 \pm 1.5^{\circ}C;$ |
| pressure: | 230 kPa; |
| O_2/H_2S ratio: | $1.05 \times \text{stoichiometric};$ |
| type of gas: | methane-enriched sour gas; |
| H_2S conc.: | 1.12 mol%; |
| feed gas flow: | 527 mL/min (STP). |
| | |



Figure 4.10 Effects of temperature on H_2S conversion and SO_2 production with 2.0 g catalyst;

| catalyst: | 2 g dry Hydrodarco; |
|-------------------|--------------------------------------|
| temperature: | $125 - 200 \pm 1.5^{\circ}C;$ |
| pressure: | 230 kPa; |
| O_2/H_2S ratio: | $1.05 \times \text{stoichiometric};$ |
| type of gas: | methane-enriched sour gas; |
| H_2S conc.: | 1.12 mol%; |
| feed gas flow: | 527 mL/min (STP). |

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Figure 4.11 Effects of temperature on H_2S conversion and SO_2 production at 500 kPa;

| catalyst: | 1 g dry Hydrodarco; |
|-------------------|--------------------------------------|
| temperature: | $125 - 200 \pm 1.5^{\circ}C;$ |
| pressure: | 500 kPa; |
| O_2/H_2S ratio: | $1.05 \times \text{stoichiometric};$ |
| type of gas: | methane-enriched sour gas; |
| H_2S conc.: | 1.12 mol%; |
| feed gas flow: | 527 mL/min (STP). |



Figure 4.12 Effects of temperature on H_2S conversion and SO_2 production at 780 kPa;

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| catalyst: | 1 g dry Hydrodarco: |
|---|--------------------------------------|
| temperature: | $125 - 200 \pm 1.5^{\circ}C;$ |
| pressure: | 780 kPa; |
| O ₂ /H ₂ S ratio: | $1.05 \times \text{stoichiometric};$ |
| type of gas: | methane-enriched sour gas: |
| H_2S conc.: | 1.12 mol%; |
| feed gas flow: | 527 mL/min (STP). |

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Effects of temperature on H_2S conversion and SO_2 production at 230 kPa with an O_2/H_2S ratio of 1.10; Figure 4.13

| catalyst: | 1 g dry Hydrodarco; |
|-------------------|--------------------------------------|
| temperature: | $125 - 200 \pm 1.5^{\circ}C;$ |
| pressure: | 230 kPa; |
| O_2/H_2S ratio: | $1.10 \times \text{stoichiometric};$ |
| type of gas: | methane-enriched sour gas; |
| H_2S conc.: | 1.12 mol%; |
| feed gas flow: | 527 mL/min (STP). |





| catalyst: | 1 g dry Hydrodarco; |
|-------------------|--------------------------------------|
| temperature: | $125 - 200 \pm 1.5^{\circ}C;$ |
| pressure: | 230 kPa; |
| O_2/H_2S ratio: | $1.20 \times \text{stoichiometric};$ |
| type of gas: | methane-enriched sour gas; |
| H_2S conc.: | 1.12 mol%; |
| feed gas flow: | 527 mL/min (STP). |

Figure 4.9, 4.13 and 4.14 indicate that both H_2S conversion and SO_2 production increase with an increase of reaction temperature when the process is conducted at 1.05, 1.10 and 1.20 times the O_2/H_2S stoichiometric ratio.

There are three reactions occurring in the H_2S oxidation system when the process is conducted over activated carbon catalyst.

$$x H_2S + x/2 O_2 - x H_2O + S_x$$
 (4.2 - 1)

$$S_x + x O_2$$
 (4.2 - 2)

$$x SO_2 + 2x H_2S$$
 \longrightarrow $3 S_x + 2x H_2O$ (4.2 - 3)

Since the reaction rates of both 4.2 - 1 and 4.2 - 2 are increased with an increase in temperature, H₂S conversion and SO₂ production increase although the equilibrium constants are reduced because of the nature of the exothermic reaction. On the other hand, the elemental sulphur produced in the reaction possesses higher energy at high temperature, so it overcomes the attractive forces to be vaporised from the surface of the catalyst leaving more surface area for further reaction capable of reacting with the excess oxygen to yield more SO₂.

In each of these short runs listed in Table 3.6, 3.7 and 3.8, the H_2S conversion decreased rapidly in the initial stages indicating that the elemental sulphur produced in the reaction was deposited in the smaller pores resulting in a large decrease in the

available surface area of the catalyst. Meanwhile, because of the capillary effects most of the elemental sulphur was fixed in the smaller pores less free sulphur being available to yield SO₂. As each of these runs proceeded further, H_2S conversion decreased gradually since the elemental sulphur produced in the reaction was deposited on the surface of the catalyst gradually resulting in less surface area being available to maintain H_2S conversion. At this stage of the process as the amount of elemental sulphur accumulated on the surface of the catalyst increases, the attractive forces between the sulphur and the surface area decrease gradually resulting in an increase in the amount of free elemental sulphur available to react with excess oxygen in the air to yield more SO₂. As H_2S conversion decreases further, the residual H_2S reacts with the SO₂ to yield elemental sulphur and water resulting in a decrease in SO₂ production. (See Figure 4.9 -4.14).

It is observed for a particular set of conditions that the reduction in H_2S conversion in the initial stages is higher at lower temperatures than that at higher temperatures and that the extent of increase of SO₂ production was less. (See Figure 4.9 - 4.14). This is due to the fact that more extensive adsorption occurs at lower temperatures so that more of the sulphur produced in the reaction is deposited and less free sulphur is released.

The average conversion of H_2S and average of H_2S fed converted to SO_2 in three hours as a function of temperature at different pressures 230, 500 and 780 kPa with an O_2/H_2S stoichiometric ratio 1.05 using 1 g of catalyst are plotted in Figure 4.15. These plots indicate that there is a critical temperature of approximately 175°C, below which H_2S conversion is rapid compared with the rate above this point. The production of SO_2 increases dramatically when the temperature is above this point. To achieve high H_2S conversion and low SO_2 production, 175°C was selected as an optimum temperature for the H_2S oxidation process over the activated carbon catalyst. This result is in accord with the results of other researchers, Coskun and Tollefson [1980] and Ghosh and Tollefson [1986].

4.2.2 Effects of Pressure

Effects of pressure on H_2S conversion and SO_2 production were studied and reported by other researchers, Ghosh and Tollefson [1986], Dalai and Tollefson [1993]. An increase in H_2S conversion and decrease in SO_2 production with an increase in pressure in the reaction system has been demonstrated. In the Ghosh and Tollefson study, the increase in H_2S conversion with an increase in pressure was due in part to the increase in the residence time of H_2S and O_2 molecules in the reactor. Dalai and Tollefson reported that higher pressure causes increased conversion of H_2S and decreased SO_2 production. The high H_2S conversion level and low SO_2 production level persist for longer periods of time at higher pressures. The results of the work done on catalyst life at elevated pressures are in accord with these results.



Figure 4.15 Average percentage of H_2S conversion and average percentage of H_2S fed converted to SO_2 as a function of temperature within the process when conducted for three hours with CH_4 -enriched gas;

| catalyst: | 1 g dry Hydrodarco; |
|-------------------|--------------------------------------|
| temperature: | $125 - 200 \pm 1.5^{\circ}C;$ |
| pressure: | 230 - 780 kPa; |
| O_2/H_2S ratio: | $1.05 \times \text{stoichiometric};$ |
| type of gas: | methane-enriched sour gas; |
| H_2S conc.: | 1.12 mol%; |
| feed gas flow: | 527 mL/min (STP). |
| | |



Figure 4.16 Effects of pressure on H_2S conversion and SO_2 production at 125°C;

| catalyst: | 1 g dry Hydrodarco; |
|-------------------|--------------------------------------|
| temperature: | $125 \pm 1.5^{\circ}C;$ |
| pressure: | 230, 500 and 780 kPa; |
| O_2/H_2S ratio: | $1.05 \times \text{stoichiometric};$ |
| type of gas: | methane-enriched sour gas; |
| H_2S conc.: | 1.12 mol%; |
| feed gas flow: | 527 mL/min (STP). |

:



Figure 4.17 Effects of pressure on H_2S conversion and SO_2 production at 150°C;

| catalyst: | 1 g dry Hydrodarco; |
|-------------------------|--------------------------------------|
| temperature: | $150 \pm 1.5^{\circ}C;$ |
| pressure: | 230, 500 and 780 kPa; |
| O_2/H_2S ratio: | $1.05 \times \text{stoichiometric};$ |
| type of gas: | methane-enriched sour gas; |
| H ₂ S conc.: | 1.12 mol%; |
| feed gas flow: | 527 mL/min (STP). |



Figure 4.18 Effects of pressure on H_2S conversion and SO_2 production at 175°C;

| catalyst: | 1 g dry Hydrodarco; |
|-------------------|--------------------------------------|
| temperature: | $175 \pm 1.5^{\circ}C;$ |
| pressure: | 230, 500 and 780 kPa; |
| O_2/H_2S ratio: | $1.05 \times \text{stoichiometric};$ |
| type of gas: | methane-enriched sour gas; |
| H_2S conc.: | 1.12 mol%; |
| feed gas flow: | 527 mL/min (STP). |



Figure 4.19 Effects of pressure on H_2S conversion and SO_2 production at 200°C;

| catalyst: | 1 g dry Hydrodarco; |
|-------------------|--------------------------------------|
| temperature: | $200 \pm 1.5^{\circ}C;$ |
| pressure: | 230, 500 and 780 kPa; |
| O_2/H_2S ratio: | $1.05 \times \text{stoichiometric};$ |
| type of gas: | methane-enriched sour gas; |
| H_2S conc.: | 1.12 mol%; |
| feed gas flow: | 527 mL/min (STP). |

 H_2S conversion and SO_2 production at three different pressures and at temperatures of 125, 150, 175 and 200°C are plotted in Figure 4.16, 4.17, 4.18 and 4.19. At each of these temperatures the process was conducted at 230, 500 and 780 kPa, respectively. The other conditions such as the H_2S concentration in the feed gas, the O_2/H_2S ratio, the mass of catalyst and feed gas flow were held constant.

The results shown in the above figures indicate that H_2S conversion was enhanced and SO₂ production was suppressed by increasing the pressure in the reactor from 230 to 780 kPa. This is due to the fact that residence time is proportional to the system pressure. At high pressure, the residence times of H_2S and O_2 are longer and as a result the chance of collisions of these molecules with the active sites of the catalyst is enhanced resulting in an increase in H_2S conversion. It is observed that the peaks denoting SO₂ production get smaller with increasing pressure in the runs conducted at 230, 500 and 780 kPa. This indicates that at high pressure less free sulphur is available to react with excess O_2 to yield SO₂. This is due to the fact that at higher pressure H_2S and O_2 molecules are compressed into the smaller pores of the catalyst making more surface area or active sites effective. The elemental sulphur produced in the reaction occurring in those smaller pores is more tightly bound. Hence, less free sulphur is available to yield SO₂.

It is concluded from the fact that the peaks denoting SO_2 production were getting smaller at higher operating pressures that at a particular temperature the Claus reaction is feasible at elevated pressures for this process. See Figure 4.16 - 4.19. According to Le Chatelier's Principle, the reversible Claus reaction would shift to the left hand side at higher pressure (see Equation 4.2 - 3) resulting in a higher content of SO₂ in the system if all the components involved in the reaction were in the vapour phase. Since H₂O produced in the reaction at such temperatures and pressures is not adsorbed on the catalyst [Ghosh and Tollefson, 1986], it would appear that the elemental sulphur produced from the reversible Claus reaction is in liquid phase. This result is in accord with that of B. J. Moore [1992] who stated that the product sulphur in the converter (315 - 345°C) in the Claus process is in liquid form.

The results of the average H_2S conversion and the average H_2S fed converted to SO_2 as a function of operating pressure at temperatures ranging from 125 - 200°C are plotted in Figure 4.20. It is interesting to observe that at lower temperatures, pressure effects on increasing H_2S conversion are significant. This means that if the process is conducted at lower temperature, H_2S conversion could be brought to a high level, which is not much less than that at higher temperature by conducting the process at an elevated pressure. (See Figure 4.20). This is due to the fact that H_2S and O_2 molecules are more easily adsorbed onto the surface of the catalyst at lower temperature than at higher temperatures and that at higher pressure (longer residence time) greater utilization of the available pores and surface area of the catalyst results.



Figure 4.20 Average percentage of H_2S conversion and average percentage of H_2S fed converted to SO_2 as a function of pressure within the process when conducted for 3 hours with CH_4 -enriched gas;

| catalyst: | 1 g dry Hydrodarco; |
|-------------------|--------------------------------------|
| temperature: | $125 - 200 \pm 1.5^{\circ}C;$ |
| pressure: | 230 - 780 kPa; |
| O_2/H_2S ratio: | $1.05 \times \text{stoichiometric};$ |
| type of gas: | methane-enriched sour gas; |
| H_2S conc.: | 1.12 mol%; |
| feed gas flow: | 527 mL/min (STP). |

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Figure 4.21 Effects of the mass of catalyst on H_2S conversion and SO_2 production at 125°C;

| catalyst: | 1 and 2 g dry Hydrodarco; |
|-------------------|--------------------------------------|
| temperature: | $125 \pm 1.5^{\circ}C;$ |
| pressure: | 230 kPa; |
| O_2/H_2S ratio: | $1.05 \times \text{stoichiometric};$ |
| type of gas: | methane-enriched sour gas; |
| H_2S conc.: | 1.12 mol%; |
| feed gas flow: | 527 mL/min (STP). |



Figure 4.22 Effects of the mass of catalyst on H_2S conversion and SO_2 production at 150°C;

| catalyst: | 1 and 2 g dry Hydrodarco; |
|-------------------|--------------------------------------|
| temperature: | $150 \pm 1.5^{\circ}C;$ |
| pressure: | 230 kPa; |
| O_2/H_2S ratio: | $1.05 \times \text{stoichiometric};$ |
| type of gas: | methane-enriched sour gas; |
| H_2S conc.: | 1.12 mol%; |
| feed gas flow: | 527 mL/min (STP). |



Figure 4.23 Effects of the mass of catalyst on H_2S conversion and SO_2 production at 175°C;

| catalyst: | 1 and 2 g dry Hydrodarco; |
|-------------------|--------------------------------------|
| temperature: | $175 \pm 1.5^{\circ}C;$ |
| pressure: | 230 kPa; |
| O_2/H_2S ratio: | $1.05 \times \text{stoichiometric};$ |
| type of gas: | methane-enriched sour gas; |
| H_2S conc.: | 1.12 mol%; |
| feed gas flow: | 527 mL/min (STP). |



Figure 4.24 Effects of the mass of catalyst on H_2S conversion and SO_2 production at 200°C;

| catalyst: | 1 and 2 dry Hydrodarco; |
|-------------------|--------------------------------------|
| temperature: | $200 \pm 1.5^{\circ}C;$ |
| pressure: | 230 kPa; |
| O_2/H_2S ratio: | $1.05 \times \text{stoichiometric};$ |
| type of gas: | methane-enriched sour gas; |
| H_2S conc.: | 1.12 mol%; |
| feed gas flow: | 527 mL/min (STP). |

4.2.3 Effects of the Mass of the Catalyst

Increased H_2S conversion was observed by increasing the mass of the catalyst from 1 g to 2 g. The results obtained from these short runs conducted over 1 g and 2 g catalyst at temperatures of 125, 150, 175 and 200°C are plotted in Figure 4.21, 4.22, 4.23 and 4.24. Other conditions including feed gas concentration, feed gas flow rate, pressure in the reactor and O_2/H_2S ratio were held constant. The results show that H_2S conversion increases with the mass of the catalyst increased from 1 g to 2 g. This is due to the fact that there are more active sites of the catalyst available per molecule of H_2S and O_2 so that they have more chance to collide with the surface of the catalyst resulting in an increased chance of them being adsorbed onto the catalyst surface and for reaction occurring.

It is observed that at a particular temperature, SO_2 production was somewhat higher when the mass of the catalyst was increased from 1 g to 2 g while other conditions were maintained constant. This would be due to the fact that at a higher level of H₂S conversion, the amount of residual H₂S in the vapour phase would be lower and that it is balanced by higher concentrations of products of elemental sulphur and water. Hence, the Claus reaction 4.2 - 3 tends to shift the equilibrium in the reverse direction causing a increase in SO₂ production.

It also would be due to the fact that oxidation of elemental sulphur is a catalytic process so that SO_2 production tends to be high when there is an excess of surface area of the catalyst. The mechanism may involve elemental sulphur on the catalyst surface reacting with O_2 in the vapour phase or with atomic O chemisorbed on the surface of the

catalyst (see Figure 4.25).



Figure 4.25 Partial surface catalytic oxidation of S to sulphur dioxide

This hypothesis does not conflict with that of lower SO_2 production with more surface area available with an elevated pressure. The elemental sulphur produced at an elevated pressure is deposited in smaller pores of the catalyst so that the attractive force between sulphur and the surface of the catalyst is relatively strong hence SO_2 would not be released to the vapour phase.

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4.2.4 Effects of O₂/H₂S Molar Ratio

 H_2S conversion was increased by increasing the partial pressure of O_2 from the air supplied in the feed gas during a long run study of catalyst life. The results from the long Run 6 without heavy hydrocarbons in the feed gas are plotted in Figure 4.5. Run 6 was conducted at 175°C and a pressure of 1470 kPa. At the time when this run was continued for 170 minutes the air supply in the feed gas was varied so that O_2/H_2S ranged from 1.00, 1.10 to 1.15. The response obtained in terms of H_2S conversion and the percentage of H₂S fed converted to SO₂ indicated that the H₂S conversion fed decreased from 98.12% to 95.93% and the percentage of H_2S fed converted to SO_2 decreased from 0.21% to 0.16% when O_2/H_2S ratio was reduced from 1.05 to 1.00. Upon increasing the O_2/H_2S ratio to 1.10, H_2S conversion increased to virtually 100%. Meanwhile, the percentage of H_2S fed converted to SO_2 increased significantly to 1.17%. After 250 minutes on stream, the O_2/H_2S in the feed was increased to 1.15. H_2S conversion was maintained 100% while the percentage of H_2S fed converted to SO_2 increased to 2.47%. The O_2/H_2S ratio was then reduced to 1.05 causing H_2S conversion to decrease and the percentage of H_2S fed converted to SO_2 to be reduced to 0.5%.

The results of the short runs made in which the O_2/H_2S ratio was varied from 1.05 to 1.20 at different temperatures of 125, 150, 175 and 200°C are plotted in Figure 4.26, 4.27, 4.28 and 4.29. The pressure was maintained at 230 kPa and 1 g of catalyst was employed. The curves obtained show that H_2S conversion did not vary much with an increase of O_2/H_2S ratio from 1.05 to 1.20 at each temperatures of 125, 150, 175 and 200°C. At temperatures of 125 and 150°C, SO₂ production did not vary much



Figure 4.26 Effects of O_2/H_2S ratio on H_2S conversion and SO_2 production at 125°C;

| catalyst: | 1 g dry Hydrodarco; |
|-------------------|--|
| temperature: | $125 \pm 1.5^{\circ}C;$ |
| pressure: | 230 kPa; |
| O_2/H_2S ratio: | 1.05, 1.10 and 1.20 \times stoichiometric; |
| type of gas: | methane-enriched sour gas; |
| H_2S conc.: | 1.12 mol%; |
| feed gas flow: | 527 mL/min (STP). |

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Figure 4.27 Effects of O_2/H_2S ratio on H_2S conversion and SO_2 production at 150°C;

| catalyst: | 1 g dry Hydrodarco; |
|-------------------|--|
| temperature: | $150 \pm 1.5^{\circ}C;$ |
| pressure: | 230 kPa; |
| O_2/H_2S ratio: | 1.05, 1.10 and $1.20 \times$ stoichiometric; |
| type of gas: | methane-enriched sour gas; |
| H_2S conc.: | 1.12 mol%; |
| feed gas flow: | 527 mL/min (STP). |

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| catalyst: | 1 g dry Hydrodarco; |
|-------------------|--|
| temperature: | $175 \pm 1.5^{\circ}C;$ |
| pressure: | 230 kPa; |
| O_2/H_2S ratio: | 1.05, 1.10 and 1.20 \times stoichiometric; |
| type of gas: | methane-enriched sour gas; |
| H_2S conc.: | 1.12 mol%; |
| feed gas flow: | 527 mL/min (STP). |

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| catalyst: | 1 g dry Hydrodarco; |
|-------------------|--|
| temperature: | $200 \pm 1.5^{\circ}C;$ |
| pressure: | 230 kPa; |
| O_2/H_2S ratio: | 1.05, 1.10 and 1.20 \times stoichiometric; |
| type of gas: | methane-enriched sour gas; |
| H_2S conc.: | 1.12 mol%; |
as the O_2/H_2S ratio varied from 1.05 to 1.20. At temperature 175°C, however, SO_2 production increased significantly as the O_2/H_2S ratio increased from 1.05 to 1.20. At 200°C, both H₂S conversion and SO₂ production increased quite significantly as the O_2/H_2S ratio increased from 1.05 to 1.20. This phenomenon is due to the fact that at lower temperatures the reaction rate constant is low so that the conversion is not affected greatly with a small scale variation in the O_2/H_2S ratio in the feed. With the temperature being increased up to 175 °C, the reaction rate constant for elemental sulphur oxidation increases significantly causing SO_2 production to increase significantly.

The effects of O_2/H_2S ratio on H_2S conversion and SO_2 production in these short runs are relatively small compared with the results obtained by varying O_2/H_2S ratio during the long run. The difference may be due to the fact that the surface area of the catalyst is dominant for the long run over 5 g activated carbon catalyst. Hence, the effects of O_2/H_2S ratio on H_2S conversion and SO_2 production would be enhanced by maintaining the other conditions constant.

The average H_2S conversion and percentage of H_2S converted to SO_2 as a function of O_2/H_2S ratio in the feed at temperatures ranging from 125 to 200°C at a pressure of 230 kPa are plotted in Figure 4.30. The plots indicate that both H_2S conversion and SO_2 production increase with an increase of O_2/H_2S ratio in the feed gas. At 175°C, the increase of H_2S conversion is small while SO_2 production increased significantly. Therefore, the optimum O_2/H_2S ratio is approximately 1.05 times the stoichiometric value in order to maximize H_2S conversion and to minimize SO_2 production. The results are in accord with those of Ghosh and Tollefson [1986].



Figure 4.30 Average percentage of H_2S conversion and average percentage of H_2S fed converted to SO_2 as a function of O_2/H_2S ratio within the process when conducted for three hours;

| 1 g dry Hydrodarco; | | |
|----------------------------|--|--|
| | | |
| | | |
| × | | |
| methane-enriched sour gas; | | |
| 1.12 mol%; | | |
| | | |
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4.2.5 Effects of Water Vapour in the Feed gas

The effects of water vapour in the feed gas on H_2S conversion have been discussed by many researchers. Chowdhury and Tollefson [1990] stated that the presence of water decreased the activity of the catalyst by introducing the feed gas as bubbles through water to saturate it. Their results are in agreement with those of early researchers Steijn and Mars [1977]. Some researchers such as Kaliva and Smith [1983] as well as Choi and Hirai [1991] got increased H_2S conversion by increasing the humidity of the feed gas.

Water vapour effects on H_2S conversion and SO_2 production were investigated by bubbling the feed gas through water at different temperatures to saturate it to different extents. The pressure was maintained at 230 kPa, temperatures at 125, 150, 175 and 200°C using 2 g catalyst with an O_2/H_2S ratio of 1.05. The results from these experiments are plotted in Figure 4.31, 4.32, 4.33 and 4.34.

The results from Figure 4.31 - 4.34 indicate that H_2S conversion is not affected to a significant extent by increasing the water vapour content up to 10% present in the feed gas. SO₂ production, however is enhanced significantly. This implies that in the temperature range 125 - 200°C, water molecules are not adsorbed on the activated carbon catalyst. Hence, the active sites of the catalyst remain effective for H_2S oxidation. The increased SO₂ production could be due to the fact that since the Claus reaction is reversible, the presence of water in the vapour phase tends to shift the equilibrium in the reverse direction hence increasing SO₂ and H_2S production (see equation 4.2 - 3).



Figure 4.31 Water vapour effects on H_2S conversion and SO_2 production at 125°C;

| catalyst: | 2 g dry Hydrodarco; |
|-------------------|--------------------------------------|
| temperature: | $125 \pm 1.5^{\circ}C;$ |
| pressure: | 230 kPa; |
| O_2/H_2S ratio: | $1.05 \times \text{stoichiometric};$ |
| type of gas: | methane-enriched sour gas; |
| H_2S conc.: | 1.12 mol%; |
| feed gas flow: | 527 mL/min; |
| water vapour: | 0.0, 1.0 and 8.9 mol%. |
| | |



Figure 4.32 Water vapour effects on H_2S conversion and SO_2 production at 150°C;

| catalyst: | 2 g dry Hydrodarco; |
|-------------------|--------------------------------------|
| temperature: | $150 \pm 1.5^{\circ}C;$ |
| pressure: | 230 kPa; |
| O_2/H_2S ratio: | $1.05 \times \text{stoichiometric};$ |
| type of gas: | methane-enriched sour gas; |
| H_2S conc.: | 1.12 mol%; |
| feed gas flow: | 527 mL/min; |
| water vapour: | 0.0, 0.6 and 8.6 mol%. |
| | |

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Figure 4.33 Water vapour effects on H_2S conversion at 175°C;

| catalyst: | 2 g dry Hydrodarco; |
|-------------------|--------------------------------------|
| temperature: | 175 ± 1.5℃; |
| pressure: | 230 kPa; |
| O_2/H_2S ratio: | $1.05 \times \text{stoichiometric};$ |
| type of gas: | methane-enriched sour gas; |
| H_2S conc.: | 1.12 mol%; |
| feed gas flow: | 527 mL/min; |
| water vapour: | 0.0, 1.7 and 5.6 mol%. |



Figure 4.34 Water vapour effects on H_2S conversion and SO_2 production at 200°C;

| catalyst: | 2 g dry Hydrodarco; |
|-------------------|--------------------------------------|
| temperature: | $200 \pm 1.5^{\circ}C;$ |
| pressure: | 230 kPa; |
| O_2/H_2S ratio: | $1.05 \times \text{stoichiometric};$ |
| type of gas: | methane-enriched sour gas; |
| feed gas flow: | 527 mL/min; |
| water vapour: | 0.0, 0.6 and 10.5 mol%. |

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This result is in accord with that of Cariaso and Walker [Cariaso and Walker, 1975]. The contradiction with the results of Kaliva and Smith, Choi and Shoda may be due to the fact that they conducted their experiments at temperatures lower than 100°C with the carbon in the liquid phase. Water may be adsorbed by the catalyst at the temperature lower than its boiling point. With the simultaneous high humidity, a water film could be formed on the surface of the catalyst enabling the reaction to occur in the liquid phase. With the high volumetric flow of more than 1000 mL/min and a short bed height from 5 to 15 cm, more H_2S and O_2 in the air would be absorbed by this water film and transferred to the active sites on the surface of the catalyst causing a significant increase in H_2S conversion. Since the solubility of elemental sulphur in water is extremely low and with a water film covering the surface, the elemental sulphur would be fixed in a stable manner on the surface of the catalyst so that no SO_2 was detected during their experiments.

The results are partly in conflict with those of Chowdhury and Tollefson in terms of the effect of water vapour on H_2S conversion. It could be due to the difference in the experimental conditions. They used 6 g of catalyst, which is more than the 2 g of catalyst which we used in our experiments. Hence there would be a greater probability that the water vapour would be adsorbed on the increased surface of the catalyst causing decreased H_2S conversion.

4.2.6 CO₂-Enriched Sour Gas

A series of short runs was performed using CO2-enriched acid gas as feed in order

to make use of the process of H_2S oxidation over the activated carbon catalyst more widely applicable. The compositions of CH_4 -enriched gas and CO_2 -enriched sour gas are listed in Table 3.2.

The results from the runs conducted with CO_2 -enriched acid gas are plotted in Figure 4.35, 4.36, 4.37.

Figure 4.35 shows the results of three runs conducted at a temperature 125° C, at pressures of 230, 435, 640 kPa and with an O₂/H₂S ratio of 1.05 and 1.10. It indicates that at elevated pressures from 230 to 640 kPa with a simultaneous increase in the O₂/H₂S ratio from 1.05 to 1.10, the initial H₂S conversion increases from 47% to 93%, H₂S conversion at "steady state" increases from 27% to 40% and 54% while the peak value of SO₂ decreases from 0.2% to 0.1%. The reason that the same level of SO₂ production was obtained in both runs conducted at 230 and 435 kPa is that there was an increase of O₂/H₂S ratio from 1.05 to 1.10. Hence, it compensated for the effect of the increase in pressure on SO₂ production.

Figure 4.36 show results of three runs conducted at 150°C with an O_2/H_2S ratio of 1.10 and pressures of 230, 435 and 640 kPa, respectively. The Run at 640 kPa was continued for 50 minutes because of a system problem. Figure 4.36 indicates that the initial H_2S conversion was increased from 72%, to 87% to 95% by increasing pressure from 230 to 435 and 640 kPa. H_2S conversion at "steady state" increased from 42% to 52% and the SO₂ peak value decreased from 1.26% to 0.79% when the pressure was increased from 230 to 435 kPa.



Figure 4.35 Effects of pressure on H_2S conversion and SO_2 production with CO_2 enriched gas at 125°C;

| catalyst: | 1 g dry Hydrodarco; |
|-------------------|--|
| temperature: | $125 \pm 1.5^{\circ}C;$ |
| pressure: | 230, 435 and 640 kPa; |
| O_2/H_2S ratio: | 1.05 and 1.10 \times stoichiometric; |
| type of gas: | CO ₂ -enriched acid gas; |
| H_2S conc.: | 1.18 mol%; |
| feed gas flow: | 527 mL/min. |

;



Figure 4.36 Effects of pressure on H_2S conversion and SO_2 production with CO_2 -enriched gas at 150°C;

| 1 g dry Hydrodarco; |
|--------------------------------------|
| $150 \pm 1.5^{\circ}C;$ |
| 230, 435 and 640 kPa; |
| $1.10 \times \text{stoichiometric};$ |
| CO ₂ -enriched acid gas; |
| 1.18 mol%; |
| 527 mL/min. |
| |

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Figure 4.37 Effects of pressure on H_2S conversion and SO_2 production with CO_2 enriched gas at 175°C;

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| catalyst: | 1 g dry Hydrodarco; |
|-------------------|--------------------------------------|
| temperature: | 175 ± 1.5℃; |
| pressure: | 230, 500 and 780 kPa; |
| O_2/H_2S ratio: | $1.05 \times \text{stoichiometric};$ |
| type of gas: | CO ₂ -enriched acid gas; |
| H_2S conc.: | 1.15 mol%; |
| feed gas flow: | 527 mL/min. |

Figure 4.37 shows the results of three runs conducted at 175° C, with an O₂/H₂S ratio of 1.05, and pressures of 230, 500 and 780 kPa respectively. It indicates that the initial H₂S conversion increased from 96% to 100% and that H₂S conversion at "steady state" increased from 50% to 62% and 68% while SO₂ peak value decreased from 2.7% to 2.4% and 1.7%.

In general, the effects of temperature, pressure, O_2/H_2S ratio on H_2S conversion and SO_2 production with CO_2 -enriched sour gas are similar to those with methaneenriched gas. This suggest that by increasing pressure and temperature and reducing the O_2/H_2S ratio, high H_2S conversion and low SO_2 production can be obtained for feed gas containing high CO_2 content.

The average H_2S conversion and the average H_2S fed converted to SO_2 in three hours at a temperature of 175°C, with an O_2/H_2S ratio of 1.05, and pressures of 230, 500 and 780 kPa using CO_2 -enriched sour gas as feed gas are plotted and compared in Figure 4.38 with those runs conducted at the same conditions using CH_4 -enriched gas as feed gas. The plots indicate that H_2S conversion using CO_2 -enriched sour gas is somewhat lower than that using CH_4 -enriched gas while SO_2 production is higher. It could be due to CO_2 adsorption on the activated carbon catalyst being somewhat stronger than that of CH_4 and that it is feasible for the reaction to occur in micropores [Gray and Do 1991]. Hence, there would be less surface area and larger size of pores available for H_2S oxidation. The sulphur in the larger pores would yield a higher sulphur vapour pressure causing a higher SO_2 production because there would be less "capillary effect" exerted.

The effects of water vapour on the H_2S oxidation process with CO_2 -enriched acid

gas were also investigated. The experiments were conducted at a temperature of 175° C, with a pressure of 230 kPa using 2 g catalyst with an O₂/H₂S ratio of 1.05 in the feed gas. Feed gas was passed through a water container at different temperatures to saturate it with water vapour to different levels. The results are plotted in Figure 4.39. They indicate that H₂S conversion decreases from 92.5 to 91.1 and to 89.8% extrapolated to zero time in each run and that the peak value of SO₂ production increases from 2.35 to 3.90 and 4.45% with an increase of water vapour present in the feed gas combining with water vapour may produce H₂CO₃ which may be readily adsorbed on the catalyst surface resulting in a decrease of the surface area and hence causing a decrease of H₂S conversion. The sulphur vapour produced with less sorptive surface area available is likely to be greater and could react with oxygen to produce more SO₂.



Figure 4.38 Comparison of H_2S conversion and SO_2 production using methaneenriched sour gas versus using CO_2 -enriched acid gas;

| catalyst: | 1 g dry Hydrodarco; |
|-------------------|---|
| temperature: | $175 \pm 1.5^{\circ}C;$ |
| pressure: | 230, 500 and 780 kPa; |
| O_2/H_2S ratio: | $1.05 \times \text{stoichiometric};$ |
| type of gas: | methane-enriched sour gas and CO ₂ -enriched acid gas; |
| H_2S conc.: | 1.12 and 1.15 mol%; |
| feed gas flow: | 527 mL/min. |



Figure 4.39 Water vapour effects on H_2S conversion and SO_2 production with CO_2 enriched gas at 175°C;

| 2 g dry Hydrodarco; |
|--------------------------------------|
| 175 ± 1.5℃; |
| 230 kPa; |
| $1.05 \times \text{stoichiometric};$ |
| CO ₂ -enriched acid gas; |
| 1.15 mol%; |
| 527 mL/min; |
| 0.0, 1.1 and 6.9 mol%. |
| |

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4.2.7 Process Optimization

The process of removal of low concentrations of H_2S over activated carbon catalyst can be applied in industry to remove H_2S in product gases in order to meet special specifications or environmental regulations. In the sour gas processing industry, natural gas containing H_2S must be sweetened so that it meets pipeline specifications. Five sources of pipeline gas specifications from Trans Canada, Canadian Western, Westcoast for US use, Westcoast for BC use and Nova are listed in Table 4.2.

In recent years, many wells containing low concentrations of H₂S have been drilled and because the amounts of H₂S are relatively small it is economical and simple to apply this H₂S oxidation on the activated carbon catalyst process to remove H₂S. Usually, the product of natural gas from well head is in the pressure range 5600 - 20760 kPa and temperature is in the range 60 - 180°C. Figure 4.20 indicates that at a relatively low temperature the effect of pressure on H₂S conversion is more significant. It would be more economical for the sake of energy conservation if the H₂S oxidation process were conducted at an elevated pressure and relatively low temperature. Figure 4.40 indicates that by increasing pressure up to 1470 kPa H₂S complete conversion is continued for 400 minutes over 5 g catalyst at temperature 160°C while SO₂ production is lower than 0.04% of the fed H_2S or 4 ppm, which meets the pipeline gas specifications for total sulphur content. It would be more optimized if the process of H₂S oxidation were performed at a temperature lower than 160°C and a pressure above 5600 kPa. The product gas should meet the requirements of pipeline gas specifications as required by of Trans Canada, Canadian Western, Westcoast for US use, Westcoast for BC use and

Nova. By using an pressure above 3540 kPa, pump required for shipping and for pressurizing along with a storage vessel would be eliminated.

Application of the Process in Sewage Treatment Plants

In recent years, more and more wastewater treatment plants have been facing a problem that the sewage water to be treated is coupled with a "dirty" gas containing about 2000 ppm H_2S at ambient temperature and somewhat about ambient pressure. It appears to be more difficult to increase the operating pressure than to increase the temperature in the plant. In this case, by increasing reaction the temperature at the low pressure available, it is possible to achieve high H_2S conversion. Figure 4.20 indicates that at relatively low pressure the temperature effect on H_2S conversion is more significant. Therefore, by selecting the critical temperature 175°C and using the pressures 130 - 145 kPa available in the plant, relatively high H_2S conversion and low SO_2 production can be achieved when the process is applied to treat sewage gas.

| Table 4.2 | Pipeline | Gas S | pecifications |
|-----------|----------|-------|---------------|
|-----------|----------|-------|---------------|

| Specification item | Trans Canada | Canadian Western | Westcoast for US Use | Westcoast for BC Use | Nova |
|-------------------------------------|----------------|---|-------------------------|-------------------------|--------------------------------|
| H ₂ S content | 16 ppm | 16 ppm | 4 ppm | 16 ppm | 16 ppm |
| Total sulphur | 320 ppm | 160 ppm | 320 ppm | 320 ppm | 80 ppm |
| CO ₂ content, volume% | 2 | No spec. | 1 | No spec. | 2 |
| O₂ content, volume% | No spec. | No spec. | 0.2 | 1 | 0.4 |
| Delivery Temperature, °F | 120 | 120 | No spec. | No spec. | 120 |
| Delivery pressure, psig | 900 | 500 | Varies | Varies | Varies |
| Minimum Heating Value BTU/CF | 950 | 950 | 1000 | 1000 | 990 |
| Hydrocarbon Dewpoint °F | 15 800 psia | 15 500 psia | Free from Liquid | Free from Liquid | 15 at operating pressure |
| Water Content lbs/MMSCF | 4 | Equivalent to 15°F dewpoint at 500 psia | 4 | 4 | 4 |
| Mercaptan content | No spec. | No spec. | 80 ppm | No spec. | No spec. |

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Figure 4.40 H_2S conversion and SO₂ production versus time-on-stream at temperature 160°C and 1470 kPa with an O₂/H₂S ratio of 1.05;

| catalyst: | 5 g dry Hydrodarco; |
|-------------------|--------------------------------------|
| temperature: | $160 \pm 1.5^{\circ}C;$ |
| pressure: | 1470 kPa; |
| O_2/H_2S ratio: | $1.05 \times \text{stoichiometric};$ |
| type of gas: | methane-enriched sour gas; |
| feed gas flow: | 527 mL/min (STP). |

;

CHAPTER 5

KINETICS STUDY

A series short runs were conducted with different oxygen contents in the feed gas at a pressure of 230 kPa, and temperature ranging from 125 - 200°C over 1 - 2 g of activated carbon catalyst (0.84 × 2.38 mm) to determine the H₂S oxidation rate. The catalyst bed was diluted with Ottawa sand to maintain 12.8 mL (\sim 50 g) of the bed. The gas used in the experiments was a prepared methane-enriched gas mixture in which H₂S concentration was 1.12 mol% balanced with approximately 99% methane and a small amount of CO₂.

In the early stages of the H_2S oxidation, the rate of H_2S oxidation decreased rapidly with reaction time. Later on, it became constant because the deposition of sulphur was balanced by the amount of sulphur being vaporized.

5.1 Assumptions

Several assumptions were made to derive formulas for the determination of the rate controlling step of the H_2S oxidation reaction.

1. The principal reaction considered in the H_2S oxidation system at temperatures ranging from 125 to 200°C is given by:

$$H_2S + 1/2 O_2 \longrightarrow S + H_2O$$
 (5 - 1.1)

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- 2. SO_2 production is small compared with H_2S conversion.
- 3. H_2S is physically adsorbed on the surface as molecules while O_2 molecules is chemisorbed and dissociated into atoms on the active sites of the catalyst.
- 4. Reaction occurs between an oxygen atom and an H_2S molecule adjacent to it on the active sites.
- 5. The external mass transfer resistance and pore diffusion resistance are negligible.
- 6. The gases follows the ideal gas law.
- 7. Initially all of the sulphur produced in the reaction at the unsteady state deposits in the pores because of the "capillary effect" causing deactivation of the catalyst.

5.2 Development of the Rate Equations

The overall rate of the H_2S oxidation reaction is calculated from the data on H_2S conversion and has units of mmoles of H_2S converted per minute per gram of catalyst [Ghosh and Tollefson, 1986].

$$r = Q \frac{P}{RT} \frac{x}{100} \frac{y}{100} \frac{1000}{W_d}$$
(5 - 2.1)

where:

r = overall rate of H₂S oxidation in mmoles·min⁻¹·g catalyst⁻¹ Q = gas flow rate at STP, mL/min P = operating pressure, kPa T = Temperature, K x = concentration of H₂S, mole % y = H₂S conversion, % W_d = weight of catalyst, g

Assuming that the reaction mechanism follows the Langmuir-Hinshelwood surface reaction model, the reaction mechanism is represented as given below:

Adsorption Processes

H₂S adsorption on surface site, X

 $H_2S + X = H_2S - X$ (5 - 2.2)

$$r_{adH_2S} = k_{adH_2S} P_{H_2S} C_{\nu} - k_{-adH_2S} C_{H_2S-X} = k_{adH_2S} (P_{H_2S} C_{\nu} - \frac{C_{H_2S-X}}{K_{adH,S}})$$

(5 - 2.3)

where
$$K_{adH_2S} = \frac{k_{adH_2S}}{k_{-adH_2S}}$$
 (5 - 2.3a)

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O₂ adsorption on two surface sites, X

$$O_2 + 2X = O - X + X - O$$
 (5 - 2.4)

$$r_{adO_2} = k_{adO_2} P_{O_2} C_{\nu}^2 - k_{-adO_2} C_{O-X}^2 = k_{adO_2} (P_{O_2} C_{\nu}^2 - \frac{C_{O-X}^2}{K_{adO_2}})$$

where
$$K_{adO_2} = \frac{k_{adO_2}}{k_{-adO_2}}$$
 (5 - 2.5)
(5 - 2.5a)

Surface Reaction

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$$H_2S - X + O - X = H_2O - X + S - X$$
 (5 - 2.6)

$$r_{sH_{2}S} = k_{sH_{2}S}C_{H_{2}S-X}C_{O-X} - k_{-sH_{2}S}C_{H_{2}O-X}C_{S-X} = k_{sH_{2}S}(C_{H_{2}S-X}C_{O-X} - \frac{1}{K_{sH_{2}S}}C_{H_{2}O-X}C_{S-X})$$
(5 - 2.7)

where
$$K_{sH_2S} = \frac{k_{sH_2S}}{k_{-sH_2S}}$$
 (5 - 2.7a)

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Desorption Processes

Water desorption

$$H_2O - X \longrightarrow H_2O + X$$
 (5 - 2.8)

$$r_{dH_2O} = k_{dH_2O}C_{H_2O-X} - k_{-dH_2O}P_{H_2O}C_{\nu} = k_{dH_2O}(C_{H_2O-X} - \frac{1}{K_{dH_2O}}P_{H_2O}C_{\nu})$$
(5 - 2.9)

where
$$K_{dH_2O} = \frac{k_{dH_2O}}{k_{-dH_2O}}$$
 (5 - 2.9a)

Sulphur desorption

$$S - X = S + X$$
 (5 - 2.10)

$$r_{dS} = k_{dS}C_{S-X} - k_{-dS}P_SC_{\nu} = k_{dS}(C_{S-X} - \frac{1}{K_{dS}}P_SC_{\nu})$$
(5 - 2.11)

where
$$K_{dS} = \frac{k_{dS}}{k_{-dS}}$$
 (5 - 2.11a)

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5.2.1 Development of the Rate Equation When the Rate is Controlled by the Rate of Physical Adsorption of H_2S .

If it is assumed that the reaction is controlled by the rate of physical adsorption of H₂S, then k_{adH_2S} is small while k_{adO_2} , k_{dH_2O} , k_{dS} and k_{sH_2S} are relatively large. At steady state, r_{adH_2S} is small and:

$$r_{adH_2S} = r_{adO_2} = r_{sH,S} = r_{dH,S} = r_{dS}$$

Therefore,

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$$\frac{r_{adO_2}}{k_{adO_2}} \approx 0 \tag{5 - 2.12a}$$

Equation (5 - 2.5) becomes:

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$$P_{O_2}C_{\nu}^2 - \frac{C_{O-X}^2}{K_{adO_2}} = 0$$
 (5 - 2.12b)

Solving equation (5 - 2.12b) for C_{0-x} :

$$C_{O-X} = C_{\nu} \sqrt{K_{adO_{2}}} \sqrt{P_{O_{2}}}$$
(5 - 2.12)

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$$\frac{r_{dH_2O}}{k_{dH_2O}} \approx 0 \qquad (5 - 2.13a)$$

Equation (5 - 2.9) becomes:

$$C_{H_2O-X} - \frac{1}{K_{dH,O}} P_{H_2O} C_v = 0$$
 (5 - 2.13b)

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Solving equation (5 - 2.13b) for C_{H_1O-X} :

$$C_{H_2O-X} = \frac{1}{K_{dH_2O}} P_{H_2O} C_{\nu}$$
(5 - 2.13)

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From the above assumption,

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$$\frac{r_{dS}}{k_{dS}} \approx 0 \qquad (5 - 2.14a)$$

Therefore, equation (5 - 2.11) becomes,

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$$C_{s-x} - \frac{1}{K_{ds}} P_s C_v = 0$$
 (5 - 2.14b)

Solving equation (5 - 2.14b) for C_{s-x} :

$$C_{S-X} = \frac{1}{K_{dS}} P_S C_{\nu}$$
(5 - 2.14)

$$\frac{r_{sH_2S}}{k_{sH_2S}} \approx 0 \tag{5-2.15a}$$

Therefore, equation (5 - 2.7) becomes:

$$C_{H_2S-X}C_{O-X} - \frac{1}{K_{sH_2S}}C_{H_2O-X}C_{S-X} = 0$$
 (5 - 2.15b)

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Solving equation (5 - 2.15b) for C_{H_xS-x} :

$$C_{H_{2}S-X} = \frac{C_{H_{2}O-X}C_{S-X}}{K_{SH,S}C_{O-X}}$$
(5 - 2.15)

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Combining (5 - 2.12), (5 - 2.13), (5 - 2.14) and (5 - 2.15):

According to the assumption,

$$C_{H_2S-X} = \frac{P_{H_2O}P_SC_{\nu}}{K_{dH_2O}K_{dS}K_{sH_2S}\sqrt{K_{adO_2}}\sqrt{P_{O_2}}}$$
(5 - 2.16)

The total active sites is the sum of the active sites occupied by H_2S , O atom, H_2O , S and unoccupied active sites.

$$C_{t} = C_{v} + C_{H_{2}S-X} + C_{O-X} + C_{H_{2}O-X} + C_{S-X}$$
(5 - 2.17)

Combining (5 - 2.12), (5 - 2.13), (5 - 2.14), (5 - 2.16) and (5 - 2.17):

$$C_{t} = C_{v} + \frac{P_{H_{2}O}P_{S}C_{v}}{K_{dH_{2}O}K_{dS}K_{sH_{2}S}\sqrt{K_{adO_{2}}}\sqrt{P_{O_{2}}}} + C_{v}\sqrt{K_{adO_{2}}}\sqrt{P_{O_{2}}} + \frac{1}{K_{dH_{2}O}}P_{H_{2}O}C_{v} + \frac{1}{K_{dS}}P_{S}C_{v}$$
(5 - 2.18a)

or,

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$$C_{v} = \frac{C_{t}}{1 + \frac{P_{H_{2}O}P_{S}}{K_{dH_{2}O}K_{dS}K_{SH_{2}S}\sqrt{K_{adO_{2}}}\sqrt{P_{O_{1}}} + \sqrt{K_{adO_{2}}}\sqrt{P_{O_{2}}} + \frac{P_{H_{2}O}}{K_{dH_{2}O}} + \frac{P_{S}}{K_{dS}}}$$
(5 - 2.18)

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Combining (5 - 2.12), (5 - 2.13), (5 - 2.14), (5 - 2.16), (5 - 2.18) and (5 - 2.3), the rate expression for the H_2S catalytic oxidation, assuming that H_2S adsorption is the rate controlling step, is:

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$$r_{adH_2S} = k_{adH_2S} C_{\nu} \{ P_{H_2S} - \frac{P_{H_2O} P_S}{K_{adH_2S} K_{dH_2O} K_{dS} K_{sH_2S} \sqrt{K_{adO_2}} \sqrt{P_{O_2}} \}$$

$$r_{adH_2S} = k_{adH_2S}C_t \frac{\{P_{H_2S} - \frac{P_{H_2O}P_S}{K_{adH_2S}K_{dH_2O}K_{dS}K_{sH_2S}\sqrt{K_{adO_2}}\sqrt{P_{O_2}}\}}{\{1 + \frac{P_{H_2O}P_S}{K_{dH_2O}K_{dS}K_{sH_2S}\sqrt{K_{adO_2}}\sqrt{P_{O_2}} + \sqrt{K_{adO_2}}\sqrt{P_{O_2}} + \frac{P_{H_2O}}{K_{dH_2O}} + \frac{P_S}{K_{dS}}\}}$$
(5 - 2.19)

. At time zero, no reaction has occurred, therefore,

$$P_{H,O} = P_S = 0$$

Equation (5 - 2.19) becomes,

$$r_{adH_2S} = k_{adH_2S} C_t \frac{P_{H_2S}}{1 + \sqrt{K_{adO_2}} \sqrt{P_{O_2}}}$$
(5 - 2.20)

On inversion, equation (5 - 2.20) becomes,

$$\frac{1}{r_{adH_2S}} = \frac{1}{k_{adH_2S}C_tP_{H_2S}} + \frac{\sqrt{K_{adO_2}}}{k_{adH_2S}C_tP_{H_2S}}\sqrt{P_{O_2}}$$
(5 - 2.20a)

Partial pressure of H_2S in the feed gas is constant. Therefore,

$$\frac{1}{k_{adH_2S}C_tP_{H_2S}} = a \; ; \quad \frac{\sqrt{K_{adO_2}}}{k_{adH_2S}C_tP_{H_2S}} = b \tag{5 - 2.20b}$$

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$$\frac{1}{r_{adH,S}} = a + b\sqrt{P_{o_1}}$$
(5 - 2.21)

The rate adsorption of H_2S was calculated by the equation (5 - 2.1). By plotting $1/r_{adH_2S}$ versus $\sqrt{P_{o_1}}$, a straight line should be obtained if H_2S adsorption is the rate-controlling step. The experimental data and the calculations are given in Appendix A. The results are discussed along with the other results in Section 5.3.

5.2.2 Development of the Rate Equation When the Reaction

is Controlled by the Rate of Oxygen Chemisorption

If it is assumed that the reaction is controlled by the rate of O_2 chemisorption, then k_{adO_2} is small while k_{adH_2S} , k_{dH_2O} , k_{dS} and k_{sH_2S} are relatively large.

At steady state, r_{adO_2} is small and

$$r_{adO_2} = r_{adH_2S} = r_{sH_2S} = r_{dH_2S} = r_{dS}$$

Therefore,

$$\frac{r_{adH_sS}}{k_{adH,s}} \approx 0 \tag{5 - 2.22a}$$

Then equation (5 - 2.3) becomes,

$$P_{H_2S}C_{\nu} - \frac{C_{H_2S-X}}{K_{adH,S}} = 0$$
 (5 - 2.22b)

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Solving equation (5 - 2.22b) for $C_{H,S-X}$:

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$$C_{H_{2}S-X} = K_{adH_{2}S}C_{\nu}P_{H_{2}S}$$
(5 - 2.22)

According to the above assumption, solving equation (5 - 2.7) for C_{o-x} :

$$C_{o-x} = \frac{C_{H_2 o-x} C_{s-x}}{K_{sH,s} C_{H,s-x}}$$
(5 - 2.23)

Combining (5 - 2.13), (5 - 2.14), (5 - 2.22) and (5 - 2.23):

$$C_{O-x} = \frac{\frac{1}{K_{dH_{2}O}} C_{v} P_{H_{2}O} \cdot \frac{1}{K_{dS}} C_{v} P_{s}}{K_{sH_{2}S} K_{adH_{2}S} C_{v} P_{H_{2}S}} = \frac{P_{H_{2}O} P_{s} C_{v}}{K_{adH_{2}S} K_{sH_{2}S} K_{dH_{2}O} K_{dS} P_{H_{2}S}}$$

(5 - 2.24)

Combining (5 - 2.13), (5 - 2.14), (5 - 2.17), (5 - 2.22) and (5 - 2.24):

$$C_{t} = C_{v} \left\{ 1 + K_{adH_{2}S}P_{H_{2}S} + \frac{P_{H_{2}S}P_{S}}{K_{adH_{2}S}K_{dH_{2}O}K_{dS}P_{H_{2}S}} + \frac{P_{H_{2}O}}{K_{dH_{2}O}} + \frac{P_{s}}{K_{dS}} \right\}$$

$$(5 - 2.25a)$$

$$C_{v} = \frac{C_{t}}{1 + K_{adH_{2}S}P_{H_{2}S} + \frac{P_{H_{2}O}P_{S}}{K_{adH_{2}S}K_{sH_{2}S}K_{dH_{2}O}K_{dS}P_{H_{2}S} + \frac{P_{H_{2}O}}{K_{dH_{2}O}} + \frac{P_{S}}{K_{dS}}}$$

(5 - 2.25)

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Combining (5 - 2.24) and (5 - 2.25) with (5 - 2.5), the rate expression for the oxidation of H_2S , assuming O_2 chemisorption if the rate-controlling step, is:

$$r_{adO_{2}} = k_{adO_{2}} \left\{ \frac{C_{t}}{1 + K_{adH_{2}S}P_{H_{2}S} + \frac{P_{H_{2}O}P_{S}}{K_{adH_{2}S}K_{sH_{2}S}K_{dH_{2}O}K_{dS}P_{H_{2}O}} + \frac{P_{H_{2}O}}{K_{dH_{2}O}} + \frac{P_{S}}{K_{dS}} \right\}^{2}$$

$$\times \{ P_{O_2} - \frac{P_{H_2O}^2 P_S^2}{K_{adO_2} K_{adH_2S}^2 K_{sH_2S}^2 K_{dH_2O}^2 K_{dS}^2 P_{H_2S}^2} \}$$
(5 - 2.29)

At time zero, no reaction has occurred, therefore,

$$P_{H,O} = P_S = 0$$

Equation (5 - 2.19) becomes,

$$r_{adO_2} = k_{adO_2} \left(\frac{C_t}{1 + K_{adH_s} P_{H_s}} \right)^2 P_{O_2}$$
 (5 - 2.27a)

Partial pressure of H₂S in the feed gas is constant. Therefore,

$$k_{adO_2} \left(\frac{C_t}{1 + K_{adH_2S} P_{H_2S}} \right)^2 = c$$

$$r_{adO_2} = c P_{O_2}$$
(5 - 2.27)

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The rate of adsorption of oxygen was calculated by the equation (5 - 2.1). By plotting r_{adO_1} versus P_{O_2} , a straight line should be obtained if O_2 chemisorption is the ratecontrolling step. The experimental data and the calculation are given in Appendix A. The results are discussed along with other results in Section 5.3.

5.2.3 Development of the Rate Equation When the Reaction

is Controlled by the Rate of the Desorption of Water

If it is assumed that the reaction is controlled by the rate of the desorption of H_2O , then k_{dH_2O} is small while k_{adH_2S} , k_{adO_2} , k_{dS} and k_{sH_2S} are relatively large. Therefore, at steady state, r_{dH_2O} is small and

$$r_{dH_2O} = r_{adH_2S} = r_{adO_2} = r_{sH_2S} = r_{dH_2S} = r_{dS}$$

$$\frac{r_{sH_2S}}{k_{sH_2S}} \approx 0 \qquad (5 - 2.28a)$$

Then, equation (5 - 2.7) becomes:

$$C_{H_{x}S-X}C_{O-X} - \frac{1}{K_{sH,S}}C_{H_{x}O-X}C_{S-X} = 0$$
 (5 - 2.28b)

Solving equation (5 - 2.28a) for C $_{H_2O-X}$:

$$C_{H_2 O-X} = \frac{C_{H_2 S-X} C_{O-X} K_{S H_2 S}}{C_{S-X}}$$
(5 - 2.28)

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Combining equations (5 - 2.12), (5 - 2.14), (5 - 2.22) with (5 - 2.28):

$$C_{H_2O-X} = \frac{P_{H_2S}C_v K_{adH_2S} \sqrt{K_{adO_2}} C_v \sqrt{P_{O_2}} K_{sH_2S}}{\frac{1}{K_{dS}} C_v P_S}$$
(5 - 2.29a)

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or,

$$C_{H_2O-X} = \frac{K_{adH_2S}K_{sH_2S}K_{dS}P_{H_2S}\sqrt{K_{adO_2}}\sqrt{P_{O_2}}C_{\nu}}{P_S}$$
(5 - 2.29)

Combining equations (5 - 2.12), (5 - 2.14), (5 - 2.22), (5 - 2.29) with (5 - 2.17) for C_t :

$$C_{t} = C_{v} \{ 1 + K_{adH_{2}S}P_{H_{2}S} + \sqrt{K_{adO_{2}}}\sqrt{P_{O_{2}}} + \frac{P_{S}}{K_{dS}} + \frac{K_{adH_{2}S}K_{sH_{2}S}K_{dS}P_{H_{2}S}\sqrt{K_{adO_{2}}}\sqrt{P_{O_{2}}}}{P_{S}} \}$$

$$(5 - 2.30a)$$

$$C_{v} = \frac{C_{t}}{1 + K_{adH_{2}S}P_{H_{2}S} + \sqrt{K_{adO_{2}}}\sqrt{P_{O_{2}}} + \frac{P_{s}}{K_{dS}} + \frac{K_{adH_{2}S}K_{sH_{2}S}K_{dS}P_{H_{2}S}\sqrt{K_{adO_{2}}}\sqrt{P_{O_{2}}}}{P_{s}}$$
(5 - 2.30)

Combining equations (5 - 2.29), (5 - 2.30) with (5 - 2.9):

$$r_{dH_{2}O} = k_{dH_{2}O} \left\{ \frac{C_{t}}{1 + K_{adH_{2}S}P_{H_{2}S} + \sqrt{K_{adO_{2}}}\sqrt{P_{O_{2}}} + \frac{P_{S}}{K_{dS}} + \frac{K_{adH_{2}S}K_{sH_{2}S}K_{dS}P_{H_{2}S}\sqrt{K_{adO_{2}}}\sqrt{P_{O_{2}}}}{P_{S}} \right\}$$

$$\times \left\{ \frac{K_{adH_{2}S}K_{sH_{2}S}K_{dS}\sqrt{K_{adO_{2}}}P_{H_{2}S}\sqrt{P_{O_{2}}}}{P_{S}} - \frac{P_{H_{2}O}}{K_{dH_{2}O}} \right\}$$
(5 - 2.31a)

$$r_{dH_{2}O} = \frac{k_{dH_{2}O}C_{t} \{K_{adH_{2}S}K_{sH_{2}S}K_{dS}P_{H_{2}S}\sqrt{K_{adO_{2}}}\sqrt{P_{O_{2}}} - \frac{P_{S}P_{H_{2}O}}{K_{dH_{2}O}}\}}{P_{S} + P_{S}K_{adH_{2}S}P_{H_{2}S} + P_{S}\sqrt{K_{adO_{2}}}\sqrt{P_{O_{2}}} + \frac{P_{S}^{2}}{K_{dS}} + K_{adH_{2}S}K_{sH_{2}S}K_{dS}P_{H_{2}S}\sqrt{K_{adO_{2}}}\sqrt{P_{O_{2}}}}$$

$$(5 - 2.31)$$

At time zero, no reaction has occurred,

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$$P_{S} = P_{H,O} = 0$$

Therefore, equation (5 - 2.31) becomes,

$$r_{dH_2O} = \frac{k_{dH_2O}C_t K_{adH_2S} K_{sH_2S} K_{dS} P_{H_2S} \sqrt{K_{adO_2}} \sqrt{P_{O_2}}}{K_{adH_2S} K_{sH_2S} K_{dS} P_{H_2S} \sqrt{K_{adO_2}} \sqrt{P_{O_2}}}$$
(5 - 2.32a)

Which on simplification gives:

$$r_{dH_2O} = k_{dH_2O}C_t = constant$$
 (5 - 2.32)

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The reaction rate should be constant if H_2O desorption is the rate-controlling step. The experimental data and the calculation are given in Appendix A. The results are discussed along with other results in Section 5.3.

5.2.4 Development of the Rate Equation When the Reaction
is Controlled by the Rate of Desorption of Sulphur
<u>If it is assumed that the reaction is controlled by the desorption of sulphur.</u>
r_{ds} is derived by the similar procedure as r_{dH,O}.

$$\mathbf{r}_{ds} = \mathbf{k}_{ds} \mathbf{C}_{t} = \text{Constant}$$
 (5 - 2.33)

The reaction rate should be constant if sulphur desorption is the rate-controlling step. The experimental data and the calculation are given in Appendix A. The results are discussed along with other results in Section 5.3.

5.2.5 Development of the Rate of Equation When the Reaction

is Controlled by the Rate of Surface Reaction

If it is assumed that the reaction is controlled by surface reaction, then k_{sH_2S} is small while k_{adH_2S} , k_{adO_2} , k_{dH_2O} and k_{dS} are relatively large.

At steady state, $r_{sH,S}$ is small and

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$$r_{sH_2S} = r_{adH_2S} = r_{adO_2} = r_{dH_2S} = r_{dS}$$

Combining equations of (5 - 2.12), (5 - 2.13), (5 - 2.14), (5 - 2.22) with (5 - 2.17),

$$C_{t} = C_{v} \left\{ 1 + K_{adH_{2}S}P_{H_{2}S} + \sqrt{K_{adO_{2}}P_{O_{2}}} + \frac{P_{H_{2}O}}{K_{dH_{2}O}} + \frac{P_{S}}{K_{dS}} \right\}$$

(5 - 2.34a)

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$$C_{v} = \frac{C_{i}}{1 + K_{adH_{2}S}P_{H_{2}S} + \sqrt{K_{adO_{2}}P_{O_{2}}} + \frac{P_{H_{2}O}}{K_{dH_{2}O}} + \frac{P_{s}}{K_{dS}}}$$
(5 - 2.34)

Combining equations (5 - 2.12), (5 - 2.13), (5 - 2.14), (5 - 2.22), (5 - 2.34) with (5 -
$$r_{sH_2S} = k_{sH}C_v^2 \{ K_{adH_2S}\sqrt{K_{adO_2}}P_{H_2S}\sqrt{P_{O_2}} - \frac{P_{H_2O}P_S}{K_{sH_2S}K_{dH_2O}K_{dS}} \}$$

$$r_{sH_2S} = k_{sH_2S} \left\{ \frac{C_t}{1 + K_{adH_2S}P_{H_2S} + \sqrt{K_{adO_2}P_{O_2}} + \frac{P_{H_2O}}{K_{dH_2O}} + \frac{P_S}{K_{dS}}} \right\}^2$$

$$\times \{ K_{adH_2S} P_{H_2S} \sqrt{K_{adO_2}} \sqrt{P_{O_2}} - \frac{P_{H_2O} P_S}{K_{sH_2S} K_{dH_2O} K_{dS}} \}$$
(5 - 2.35)

At time zero, no reaction has occurred, therefore,

$$P_{H_2O} = 0; \qquad P_S = 0$$

Equation (5 - 2.35) becomes,

$$r_{sH_2S} = k_{sH_2S} K_{adH_2S} \sqrt{K_{adO_2}} C_t \frac{P_{H_2S} \sqrt{P_{O_2}}}{(1 + K_{adH_2S} P_{H_2S} + \sqrt{K_{adO_2} P_{O_2}})^2} (5 - 2.36)$$

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Partial pressure of H_2S in the feed gas is constant, therefore,

$$\frac{1 + K_{adH_2S}P_{H_2S}}{k_{sH_2S}K_{adH_2S}\sqrt{K_{adO_2}}C_tP_{H_2S}} = f; \qquad \frac{\sqrt{K_{adO_2}}}{k_{sH_2S}K_{adH_2S}\sqrt{K_{adO_2}}C_tP_{H_2S}} = g$$

Then, equation (5 - 2.36) becomes:

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$$r_{sH_2S} = \frac{\sqrt{P_{O_2}}}{(f + g\sqrt{P_{O_2}})^2}$$
(5 - 2.37a)

$$\frac{\sqrt{P_{o_1}}}{r_{sH_2S}} = f + g\sqrt{P_{o_2}}$$
 (5 - 2.37)

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The rate of surface reaction of H₂S was calculated by the equation 5 - 2.1. By $plotting \sqrt{\sqrt{P_{O_2}} / r_{sH_2S}}$ versus $\sqrt{P_{O_2}}$, a straight line should be obtained if surface reaction is the rate-controlling step. The experimental data and the calculation are given in Appendix A. The results are discussed along with other results in Section 5.3.



Figure 5.1 $\frac{1}{r_{adH_s}}$ as a function of $\sqrt{P_{o_s}}$ at 125°C



Figure 5.2 $\frac{1}{r_{adH,S}}$ as a function of $\sqrt{P_{o_1}}$ at 150°C



Figure 5.3 $\frac{1}{r_{adH_{2}S}}$ as a function of $\sqrt{P_{O_{2}}}$ at 175°C



Figure 5.4 $\frac{1}{r_{adH,S}}$ as a function of $\sqrt{P_{o_1}}$ at 200°C



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Figure 5.5 r_{adO_2} as a function of P_{O_2} at 125°C



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Figure 5.6 r_{adO_1} as a function of P_{O_1} at 150°C



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Figure 5.7 r_{adO_2} as a function of P_{O_2} at 175°C

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FIgure 5.8 r_{ado_2} as a function of P_{o_2} at 200°C



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Figure 5.12
$$\int \frac{\sqrt{P_{O_1}}}{r_{sH_1S}}$$
 as a function of $\sqrt{P_{O_1}}$ at 200°C

5.3 Discussion

Table 5.1 gives the data of P_{o_1} , $\sqrt{P_{o_1}}$, r, 1/r and $\sqrt{\sqrt{P_{o_2}}/r_{sH,S}}$ for plotting. Table 5.2 gives the correlation coefficients for different types of fittings (Figure 5.1 - 5.12) of H_2S adsorption control, O_2 adsorption and surface reaction control at temperatures 125, 150, 175 and 200°C. Since the H₂S oxidation reaction rate is not constant, it is certainly not control by desorption of either one of the products. Table 5.2 indicates that the correlation coefficients of O2 adsorption control and H2S adsorption control are quite close and both of them are higher than those of surface reaction control at temperatures 125, 150, 175 °C. Therefore, at temperatures 125, 150 and 175 °C, either O_2 adsorption or H_2S adsorption is the controlling step for H_2S oxidation reaction. This conclusion is conflict with one of the assumptions which states that the surface reaction is the rate controlling step. As a result, the mechanism of H_2S oxidation would be Oxidation-Reduction Model which is in accordance with the results of Steijns and Mars [1975]. The results are in conflict with those of Ghosh and Tollefson who stated that surface reaction was the rate controlling step for H₂S oxidation reaction and the reaction mechanism followed Langmuir-Hinshelwood model.

| | 125°C | | |
|-------------------------------------|-------|-------|-------|
| O ₂ /H ₂ S | 1.05 | 1.10 | 1.20 |
| <i>P₀</i> , | 1.315 | 1.377 | 1.503 |
| $\sqrt{P_{o_i}}$ | 1.147 | 1.173 | 1.226 |
| I | 0.166 | 0.158 | 0.202 |
| 1/r | 6.024 | 6.329 | 4.950 |
| $\sqrt{\sqrt{P_{O_2}}} / r_{sH_2S}$ | 2.629 | 2.725 | 2.464 |
| | 150°C | | |
| r | 0.259 | 0.256 | 0.278 |
| 1/r | 3.861 | 3.906 | 3.597 |
| $\sqrt{\sqrt{P_{O_2}} / r_{sH_2S}}$ | 2.105 | 2.141 | 2.100 |
| | 175°C | | |
| r | 0.324 | 0.317 | 0331 |
| 1/r | 3.090 | 3.150 | 3.020 |
| $\sqrt{P_{o_1}} / r_{sH_1S}$ | 1.883 | 1.922 | 1.925 |
| | 200°C | | |
| r | 0.320 | 0.330 | 0.330 |
| 1/r | 3.125 | 3.030 | 3.030 |
| $\sqrt{\sqrt{P_{o_1}}} / r_{sH_1S}$ | 1.914 | 1.936 | 1.927 |

Table 5.1Data for the Determination of H2S Oxidation Reaction ControlOver Hydrodarco Catalyst

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| Temperature ℃ | O_2 adsorption control | H_2S adsorption control | Surface reaction control | |
|------------------|--------------------------|---------------------------|-----------------------------|--|
| 125 0.88 | | 0.86 | 0.76 | |
| 150 | 150 0.90 | | 0.29 | |
| 175 | 175 0.86 | | 0.78 | |
| 200 0.75 | | 0.75 | 0.43 | |

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Table 5.2Correlation Coefficients of Different Rate Equations Developed for the
Reaction Control Steps at Temperatures 125, 150, 175 and 200°C.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

In this thesis a semi-continuous H_2S catalytic oxidation process on a small laboratory scale was well established. The life of "granular Hydrodarco" activated carbon was determined. The H_2S catalytic oxidation process under different conditions at temperatures of 125 - 200°C, pressures of 230 - 3220 kPa, O_2/H_2S ratios of 1.05 -1.20 and over 1 and 2 g of catalyst with sour and acid gas as feed was well examined. The effects of water present in different types of feed gas on the process were investigated. The kinetics study of the rate-controlling step on the H_2S catalytic oxidation reaction was conducted which suggested an Oxidation-Reduction mechanism for the H_2S oxidation reaction.

The optimum temperature for high H_2S conversion and low SO_2 production at a particular pressure was determined to be approximately 175°C.

Increased operating pressure at the same gas throughput for a given set of operating conditions causes increased conversion of H_2S to sulphur and water for a longer period of time and reduces SO_2 concentrations in the product gases.

The optimum O_2/H_2S ratio at a given set of conditions for high H_2S conversion and low SO_2 production is 1.05 times the stoichiometric ratio.

The process works well with both sour and acid gases. It gives somewhat higher H_2S conversion and lower SO₂ production with the feed gas containing low CO₂.

Water vapour present in the feed gas containing low concentrations of CO_2 does not affect H₂S conversion to a significant extent while it enhances SO₂ production somewhat. On the other hand, with a high CO₂ concentration present in the feed gas H₂S conversion is reduced somewhat and SO₂ production is increased.

With more activated carbon catalyst employed at a given sets of operating conditions, both H_2S conversion and SO_2 production are increased.

"Granular Hydrodarco" activated carbon catalyst can be used for at least 10 cycles with the regeneration temperature being lower than 300°C and a partial vacuum 620 mm Hg being employed and with the feed gas containing no heavy hydrocarbons.

The conditions investigated may not represent the optimum set for commercial operation. However, they demonstrate that by combining of the parameters such as low temperature with an elevated pressure, the process can provide a high H₂S conversion (99.9%). Therefore, it can satisfy pipeline gas specifications. For gases containing low concentrations of H₂S, the process should reduce the capital and operating costs compared with the Claus process because it is a dry process and provides a good quality of sulphur (>99%). This may eliminate the need for equipment for sulphur purification.

RECOMMENDATIONS

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To apply the H_2S catalytic oxidation process on a pilot scale, natural gas containing high concentrations of H_2S (5 - 10 mol%) should be investigated to establish its effects on the catalyst life and control of the reactor temperature. Since there may be poor heat transfer present in a big reactor on a pilot scale, partial product gas recycling should be considered as a means of controlling the temperature rise in the reactor when the process is applied to deal with low concentrations of H_2S (< 5 mol%). Two or three stage reactors may be a choice to achieve high H_2S conversion when the process is applied to deal with higher concentrations of H_2S . Heat transfer equipment could be installed in the reactor so that the large amount of heat released from the reaction could be removed. Steam and other inert gases may be considered for regenerating the used activated carbon catalyst. The applications of the process in the treatment of sewage gas containing 2000 ppm H_2S should be investigated.

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APPENDIX A

CALCULATION OF RATE OF H₂S OXIDATION REACTION AND PARTIAL PRESSURE OF O₂

Rate of H₂S Oxidation Reaction

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Extrapolating H₂S conversion curve to time zero to get H₂S initial conversion.

| Temperature | O ₂ /H ₂ S Ratio. | | | |
|-------------|---|------|------|--|
| °C | 1.05 | 1.10 | 1.20 | |
| 125 | 41 | 39 | 50 | |
| 150 | 68 | 67 | 73 | |
| 175 | 90 | 88 | 92 | |
| 200 | 94 | 97 | 97 | |

Table A. H₂S initial conversion at temperatures of 125, 150, 175 and 200°C

The rate of H₂S oxidation reaction is calculated by the equation,

$$r = Q \frac{P}{RT} \cdot \frac{x}{100} \cdot \frac{y}{100} \cdot \frac{1000}{W_d}$$
(a)

where

$$\begin{split} &Q = 527 \times 10^{-3} \text{ mL/min} \\ &P = (13 + 20)/14.7 = 2.24 \text{ atm} \\ &R = 0.082 \text{ atm} \cdot \text{L} \cdot \text{K}^{-1} \\ &T_1 = 398.15 \text{ K}, \qquad T_2 = 423.15 \text{ K}, \qquad T_3 = 448.15 \text{ K}, \qquad T_4 = 473.15 \text{ K} \\ &x = 1.12 \\ &y = \text{Initial H}_2\text{S conversion}, ~\%. \text{ They are obtained from Table A}. \end{split}$$

Substituting all the data into equation a to obtain the initial H_2S oxidation reaction rate at different temperatures with different O_2/H_2S ratios.

Partial Pressure of O₂

With O_2/H_2S ratio of 1.05,

 $P_0 = (1.05/2) \times 1.12 \% \times 2.24 = 1.315 \text{ atm}$

With O_2/H_2S ratio of 1.10,

 $P_0 = (1.10/2) \times 1.12 \% \times 2.24 = 1.377 \text{ atm}$

With O₂/H₂S ratio of 1.20,

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 $P_0 = (1.20/2) \times 1.12 \% \times 2.24 = 1.503 \text{ atm}$

APPENDIX B

CALCULATIONS ON THE PRESSURE DROP ACROSS THE CATALYST BED According to Ergun equation,

$$\frac{\Delta P}{G_o^2} \rho \left(\frac{D_P}{L}\right) \left(\frac{\epsilon^3}{1-\epsilon}\right) = 150 \frac{(1-\epsilon)}{D_P G_o/\mu} + 1.75$$

where:

P = Pressure drop, psig

 $G_o = Mass$ flow rate of gas, g/s

 ρ = Density of the feed gas, g/cm³

 D_{p} = Particle diameter, cm

 $V_o =$ Superficial linear velocity, cm/s

L = Length of the reactor, cm

 ϵ = Void fraction

 μ = Viscosity of the fluid, Pa

Gas compositions

Methane-enriched gas mixture has the following composition.

| Component | mol fraction % |
|------------------|----------------|
| H ₂ S | 1 |
| CH_4 | 98.2 |
| CO_2 | 0.8 |

O₂
$$1.05 \times H_2S/2 = 0.55$$
 mols
air $0.55/0.21 = 2.619$ mols

.

Therefore, the feed gas has the following composition.

| H_2S | 0.97 |
|-----------------|-------|
| CH ₄ | 95.69 |
| CO ₂ | 0.78 |
| O ₂ | 0.51 |
| N_2 | 2.04 |

Mol weight of the feed gas,

 $M_{ave} = 16.819 \text{ g/mol}$

Feed gas density

 $\rho = (PM/RT) = 1.0272 \times 10^3 \text{ g/m}^3$

From Perry's Chemical Engineering Hand Book,

$$\mu^o = \sum \frac{y_i \mu_i}{\sum y_j \phi_{ij}}$$

•

where

 μ_i = viscosity of each component, Pa

 $y_i = mol$ fraction of each component

 Φ_{ij} = friction factor between each pair of components

$$\phi_{ij} = \frac{\left[1 + \left(\frac{\mu_i}{\mu_j}\right)^{\frac{1}{2}} \left(\frac{M_j}{M_i}\right)^{\frac{1}{4}}\right]^2}{\left[8\left(1 + \frac{M_i}{M_j}\right)\right]^{\frac{1}{2}}}$$
$$\phi_{ji} = \left(\frac{\mu_j}{\mu_i}\right) \left(\frac{M_i}{M_j}\right) \phi_{ij}$$

From Perry's Chemical Engineering Hand Book,

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| | Component | Viscosity, Pa | |
|---------|-----------------|---------------|--|
| μ_1 | H_2S | 0.19 | |
| μ_2 | air | 0.25 | |
| μ_3 | CO ₂ | 0.22 | |
| μ_4 | CH_4 | 0.15 | |

 $\mu^{o} = 0.2116$ Pa

From Perry's Chemical Engineering Hand book,

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| Component | T _c (K) | P _c (atm) | V _c (cm ³ /g mol) | Z_{c} |
|-----------------|--------------------|----------------------|---|---------|
| H_2S | 373.2 | 88.2 | 98.5 | 0.284 |
| CO ₂ | 304.2 | 72.8 | 94.0 | 0.274 |
| CH_4 | 190.6 | 45.4 | 99.0 | 0.288 |
| O ₂ | 154.6 | 49.8 | 73.4 | 0.288 |
| N_2 | 126.2 | 33.5 | 89.5 | 0.290 |

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$$T_{c \text{ mix}} = 191.74 \text{ K}$$

$$Z_{c \text{ mix}} = 0.2879$$

$$V_{c \text{ mix}} = 98.62 \text{ cm}^{3}/\text{g mol}$$

$$P_{c \text{ mix}} = 45.92 \text{ atm}$$

$$\rho_{c \text{ mix}} = 1.014 \times 10^{3} \text{ g/cm}^{3}$$

$$\varsigma_{\text{mix}} = T_{c \text{ mix}}^{1/6} M_{\text{mix}}^{-(1/2)} P_{c \text{ mix}}^{-(2/3)} = 0.0457$$

$$\rho_{r} = \rho_{\text{mix}} / \rho_{c \text{ mix}} = 6.024 \times 10^{-3}$$

$$(\mu - \mu^{0})\varsigma = 1.08[\exp(1.439\rho_{r, \text{ mix}}) - \exp(-1.11\rho_{r, \text{ mix}}^{1.858})]$$

$$\mu = 0.4154 \text{ Pa}$$

$$V = v_{1} + v_{2} + v_{3}$$

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where

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 v_1 = Activated carbon pore volume, cm³ v_2 = Carbon volume, cm³ v_3 = Void volume, cm³

therefore,

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$$v_3 = 5.68 \text{ cm}^3$$

$$\epsilon = 0.44$$

$$L = 10.4 \text{ cm}$$

$$D_p = 6/a_v$$

For a_v (Total particle surface/Volume of the particle) = 34.144

$$D_p = 0.1757 \text{ cm}$$

 $G_o = v_o \rho = V_o / S \rho = (527/60) / [(\pi/4)D^2] = 73.28 \text{ g/s}$

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Right hand side of Ergun equation,

$$150 \ \frac{(1 - \epsilon)}{(D_p G_o/\mu)} + 1.75 = 2.02$$

Left hand side of Ergun equation,

$$\frac{\Delta P \rho}{G_o^2} \left(\frac{D_P}{L}\right) \left(\frac{\epsilon^3}{1-\epsilon}\right) = 1.383 \times 10^3 \Delta P$$

Therefore, $\Delta P = 0.21$ psig

The actual pressure drop determinations had been performed at 230 kPa and 205°C for 15 hours in a fixed-bed reactor having an internal diameter of 12.5 mm and a length of 25 cm. The pressure drop was 0.25 psig through out the run. The pressure drop was,therefore, due to the catalyst bed and agrees well with the above calculated value. The pressure drop throughout the bed was constant and not affected by the sulphur deposition in the catalyst pores during the run.