Systematic Design Procedures for Natural Gas Desulphurization

by

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Disertation submitted in partial fulfillment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

JANUARY 2009

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CERTIFICATION OF APPROVAL

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Approved by,

(Dr Shuhaimi Mahadzir)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
January 2009

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

NAWAREE SUVANMANI

ABSTRACT

Natural gas is a mixture of variable hydrocarbons and many contain other contaminants such as nitrogen, carbon dioxide and sulfur. The undesirable compound such as hydrogen sulfide must be removed to prevent corrosion and environmental problems. Sulfur compound also poisons the catalysts and consequently disrupts reactor performance. Reactor systems that have been poisoned by sulphur sees lower the conversion, lower selectivity and higher temperature requirement for a particular lower conversion. While sulfur removal from natural gas stream is necessary, there is insufficient framework to systematically design the removal system. The objective of this project is therefore to develop a framework for the systematic design of H_2S adsorber. The desired design framework will be able to predict the breakthrough curve of the chemisorption reaction and determine the size of the adsorption column. The project will also study the interactions between parameters that affect the system's design. The desulphurization system selected in this project uses zinc oxide adsorbent. Additionally H_2S is chosen as the adsorbate in the natural gas stream. Desulphurization of natural gas is a two step process; firstly the natural gas containing organic sulfur is catalytically hydrogenated to H_2S. Then the natural gas stream containing H_2S is send to a chemisorption column. Zinc oxide adsorbent is converted to zinc sulfide upon contact with H_2S. The shrinking core model is selected to describe the solid gas reaction on the surface of the adsorbent. The model considers chemical reaction coupled with diffusion as the rate limiting step. Solutions of the shrinking core model enable the prediction of breakthrough curve. The shrinking core model was found to give a good description of the sulfur removal process whereby it has been found that the conversion of single solid sorbent increases continuously with time until it completely converted in 8.32min. A single zinc oxide pellet able to adsorb 1.66E-03 moles of H_2S per hour before it reaches its breakthrough limit. Further on, sizing is done to calculate the amount of adsorbent needed for a column. The results obtained are 34,747 kg ZnO needed for an adsorption column with a service lifetime of 6 months and the dimensions of column from calculation deviates less than 5% then the actual industrial equipment. Therefore, the systematic design procedures outlined are applicable for industrial use.

ACKNOWLEDGEMENT

The author wishes to take the opportunity to express her utmost gratitude to the individual that have taken the time and effort to assist the author in completing the project. Without the cooperation of these individuals, no doubt the author would have faced some minor complications through out the course.

First and foremost the author's utmost gratitude goes to the author's supervisor, Dr Shuhaimi Mahadzir. Without his guidance and patience, the author would not be succeeded to complete the project. To the Final Year Research Project Coordinators for providing her all the initial information required to begin the project.

To Mr Mohd Ashraf from Technical Services Department of Petronas Fertilizer Kedah, thank you for assisting the author in completing her project.

To all individuals that has helped the author in any way, but whose name is not mentioned here, the author thank you all.

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ABBREVIATIONS AND NOMENCLATURES

H_2S	Hydrogen Sulfide
CH_4	Methane
C_2H_6	Ethane
C_3H_8	Propane
C_4H_{10}	Butane
CO_2	Carbon Dioxide
O_2	Oxygen
N_2	Nitrogen
A	Argon
He	Helium
Ne	Neon
Xe	Xenon
NG	Natural Gas
HC	Hydrocarbon
ZnO	Zinc Oxide
ZnS	Zinc Sulfide
H_2O	Water
SCM	Shrinking Core Model

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

The desulphurization of sulfur-containing gas streams such as sour natural gas is an important expedient in providing commercially viable and valuable sources of process gas or fuel suitable for a multitude of uses. While natural gas is found in many regions of the world, many of the available sources of natural gas frequently contain sulfur contaminants like hydrogen sulfide, carbonyl sulfide and mercaptans.

Natural gas has its origins in decayed living matter, most likely as the result of the action of bacteria upon dead animal and plant material. Natural gas, like petroleum, is a mixture of many organic substances. The most common substances in natural gas are summarized in the Table 1.1 [1]. Other gases such as oxygen, argon, and carbon dioxide make up the rest of most natural gas composition. The exact composition of different sources of natural gas varies slightly, but in all cases, methane is by far the most common component, followed by higher hydrocarbons.

Depending upon the particular commercial process or end use, the sulfur-containing natural gas stream must be suitably desulfurized to remove substantially all sulfur compounds present therein. Frequently, it is necessary to lower the sulfur concentration to low levels in the range of 0.05 to 0.4ppm. For example, in processes requiring the use of a catalytic reformer for conversion of a natural gas feed to a reducing gas effective for the production of hydrogen, methanol, ammonia, and for other uses, the sulfur content of the natural gas should be less than about 0.2ppm to avoid sulfur poisoning of the reformer catalyst.

Table 1.1: Typical Composition of Natural Gas

Methane	CH_4	70-90%
Ethane	C_2H_6	0-20%
Propane	C_3H_8	
Butane	C_4H_{10}	
Carbon Dioxide	CO_2	0-8%
Oxygen	O_2	0-0.2%
Nitrogen	N_2	0-5%
Hydrogen Sulfide	H_2S	0-5%
Rare Gases	A, He, Ne, Xe	trace

It is noted that the adsorption of sulfur compounds contained in hydrocarbon gas streams by contact with metals or metallic compounds is generally known. Exemplary is U.S. Pat. No. 2,551,905 directed to a process for the desulphurization of a hydrocarbon gas by the countercurrent contact of a sour gas stream with adsorbent ceramic and metal-oxide pellets such as iron oxide at elevated temperatures. In U.S. Pat. No. 3,199,946 a method is disclosed for the removal of hydrogen sulfide from hydrocarbon fuel gases using adsorbent compositions including finely-divided iron metal, moisture and a water soluble alkali metal carbonate, bicarbonate or hydroxide. Further, in U.S. Pat. No. 3,151,973 a method for the production of low sulfur molten iron is disclosed by passing a reducing gas stream through a bed of sponge iron to absorb the sulfur contaminants. Finally, U.S. Pat. No. 3,816,101 discloses the removal of hydrogen sulfide from a stream of process gas at low temperatures.

While the prior art generally recognizes a variety of methods directed to the desulphurization of carbonaceous gases including the use of molecular sieves and metallic compounds such as zinc oxide or even sponge iron, a real need continues to exist for a more economical, efficient and effective method for the desulphurization of natural gas. That is, a method by which a cost-effective, efficient and readily available system can be used to carry out the desulphurization reaction at an acceptable rate of reaction without cracking of components of the natural gas.

1.1.1 Adsorption

A boundary that separates two phases is known as a surface or an interface. Surfaces show special properties that are different from those of the phases themselves. For example, the surface of a solid often shows a strong affinity for molecules that come into contact with it and which are said to be adsorbed [2]. A simple way of visualizing adsorption is in terms of additional valence bonds at the surface, which are available for bonding [2]. However, in reality, the situation is more complex. Adsorption is a process in which atoms or molecules move from a bulk phase of solid, liquid or gas onto a solid or liquid surface. An example is purification by adsorption where impurities are filtered from liquids or gases by their adsorption onto the surface of a high surface area solid such as activated charcoal.

Adsorption is to be distinguished from absorption, a process in which atoms or molecules move into the bulk of a porous material, such as the absorption of water by a sponge [2]. Sorption is more general term that includes both adsorption and absorption. Desorption refers to the reverse of adsorption and is a process in which molecules adsorbed on a surface are transferred back into a bulk phase. The term adsorption is most often used in the context of solid surfaces in contact with liquid or gases. Molecules that have been adsorbed onto solid surfaces are referred to generically as adsorbates and the surface to which they are adsorbed as the substrate or adsorbent.

Adsorption is very different from absorption, distillation and extraction. These three processes typically involve two fluids flowing steadily in opposite directions. In absorption, a gas mixture flows upward through a packed column while an absorbing liquid trickles down. In distillation, a liquid mixture is split into a more volatile liquid distillate and a less volatile bottom stream. In extraction, two liquid streams move counter currently to yield an extract and a raffinate. To be sure, in some cases, the contacting may involve near-equilibrium states, and in other cases it may be described with non-equilibrium ideas like mass transfer coefficients. Still, all three units operations involve two fluids at steady state.

In contrast, adsorption is almost always an unsteady process involving a fluid and a solid. The use of a solid is a major difference. On the one hand, solids can adsorb mere traces of solute, making this method especially useful for dilute solutions, including those streams requiring treatment for pollution control [3]. We must pay for this energy-intensive treatment as adsorption tends to be more expensive than the other separations. On the other hand, solids are hard to move. They abrade pipes and pumps; they break into fines, which are hard to retain [3]. As a result, the feed fluid is usually pumped through the stationary bed of solid particles to effect a separation by adsorption.

It is often convenient to think of adsorption as occurring in three stages, as the adsorbate concentration increases. First, a single layer of molecules builds up over the surface of the solid. This monolayer may be chemisorbed and will be associated with a change in free energy which is characteristic of the forces which hold it. As the fluid concentration is further increased, second, third etc., layers form by physical adsorption; the number of layers which can form may be limited by the size of the pores. Finally, for adsorption from the gas phase, capillary condensation may occur in which capillaries become filled with condensed adsorbate, when its partial pressure reaches a critical value relative to the size of the pore.

Though the three stages are described as taking place in sequence, in practice, all three may be occurring simultaneously in different parts of the adsorbent because conditions are not uniform throughout. Generally, concentrations will be higher at the outer surface of an adsorbent pellet than in the centre, at least until equilibrium conditions have been established. Also, the pore structure will consist of a distribution of pore sizes, the spread of the distribution depending on the origin of the adsorbent and its conditions of manufacture.

1.1.2 Types of Adsorption

There are two main types of adsorption. In the first type, the forces are of a physical nature and the adsorption is relatively weak. The forces correspond to those considered by J. H. van der Waals in connection with his equation of states for gases and are known as van der Waals forces. This type of adsorption is known as physical adsorption, physisorption or van der Waals adsorption. There is no significant redistribution of electron density in either the molecule or at the substrate surface. The heat evolved when a mole of gas becomes physisorbed is usually small, less than 20kJ. This type of adsorption plays only an unimportant role in catalysis, except for certain special types of reactions involving free atoms or radicals [2].

In the second type of adsorption, first considered in 1916 by the American chemist Irving Langmuir (1881-1957), the adsorbed molecules are held to the surface by covalent forces of the same general type as those occurring between atoms in molecules [2]. The heat evolved per mole for this type of adsorption, known as chemisorption is usually comparable to that evolved in chemical bonding, and mainly ranges from 100 kJ mol^{-1} to 500 kJ mol^{-1} [2]. A chemical bond, involving substantial rearrangement of electron density is formed between the adsorbate and substrate. The nature of this bond may lie anywhere between the extremes of virtually complete ionic or complete covalent character. An important consequence of chemisorption is that after a surface has become covered with a single layer of adsorbed molecules, it is saturated. Additional adsorption can occur only on the layer already present and this is generally weak adsorption. Langmuir thus emphasized that chemisorption involves the formation of a unimolecular layer [2]. Many investigations on surfaces of known are have confirmed that chemisorption ceases after a unimolecular layer is formed, but that physisorption may give rise to additional layers.

It was suggested in 1931 by Hugh Stott Taylor (1890-1974) that chemisorption is frequently associated with appreciable activation energy and may therefore be a relatively slow process [2]. For this reason chemisorption is often referred to as activated adsorption. By contrast, van der Waals adsorption requires no activation energy and therefore occurs more rapidly than chemisorption.

Another important concept, suggested in 1925 by H. S. Taylor, is that solid surfaces are never completely smooth and that adsorbed molecules will be attached more strongly to some surface sites than to others. This is particularly important in connection with catalysis, since chemical reaction may occur predominantly on certain sites, which Taylor referred as active centers.

1.1.3 Adsorbents

Molecules adsorb on virtually all surfaces. The amount they adsorb is roughly proportional to the amount of the surface [3]. As a result, commercial adsorbents are extremely porous with surfaces areas typically of several hundred square meters per gram. Indeed, some specialized adsorbents have surface areas as high as 3000 m^2/ gram. The investigation of many porous solid involves the use of gas adsorption methods. Pores are usually classified according to size in the manner originally proposed by Dubinin. Pores having width less than 2nm are termed micropores, those between 2 and 50nm, mesopores and those whose width is larger than 50nm, macropores.

Adsorbents are conveniently divided into three classes which are carbons, inorganic materials and synthetic polymers (Ruthven, 1984; Gembicki, Oroskar and Johnson, 1991). The carbons have nonpolar surfaces that are used to adsorb nonpolar molecules, especially hydrocarbons. They are manufactured from both organic and inorganic sources, including coal, petroleum coke, and wood and coconut shells. Decolorizing carbons tend to be based on a mixture of sawdust and pumice. Carbons used for gas adsorption can be made from vegetable sources like coconut shells and fruit pits. Activated carbons, which are manufacturing conditions to control pore size more exactly, can be used to recover solvents, to filter gases, and to purify water. Overall, carbons make a broad and important class of adsorbents.

Inorganic materials vary widely. Activated alumina, which has a polar surface, is used largely as a dessicant. It is also used for laboratory-scale chromatography [3]. Silica gel, consisting of amorphous silicon dioxide, is also used as a dessicant. Clays are used as inexpensive adsorbents; for some petroleum-based applications, they are used once and discarded.

The most important class of inorganic adsorbents is probably zeolites, a subclass of molecular sieves. These are crystalline aluminosilicates with specific pore sizes located within small crystals. Two common classes have simple cubic crystals (type A) or body-centered cubic crystals (type X). Sometimes, the type is assigned a number equal to a nominal pore size in the crystals [3].

Adsorbents based on synthetic polymers also vary widely. Ion exchange polymers with a fixed negative charge are most commonly made by treating styrene-divinylbenzene copolymers with sulfuric acid. These polymers, as well as acrylic ester polymers, are used for water treatment. Polymers with a fixed positive charge are frequently based on alkylammonium groups. In either case, the adsorbing polymers tend to capture polyvalent ions in preference to monovalent ones. They also surprisingly useful for adsorbing hydrophobic materials, including highly valued solutes like drugs and pigments.

Adsorbents are available as irregular granules, extruded pellets and formed spheres. The size will reflect the need to pack as much surface area as possible into a given volume of bed, at the same time minimizing pressure drop for flow through the bed. Sizes up to about 6 mm are common. To be attractive commercially, an adsorbent should embody a number of features:

(i) It should have a large internal surface area
(ii) The area should be accessible through pores big enough to admit the molecules to be adsorbed. It is a bonus if the pores are also small enough to exclude molecules it is desired not to adsorb.
(iii) The adsorbent should be capable of being regenerated easily.

(iv) It should not age rapidly, that is losing its adsorptive capacity through continual recycling.

(v) It should be mechanically strong enough to withstand the bulk handling and vibration that are part of any industrial unit.

1.2 PROBLEM STATEMENT

Sulfur compound in fuels is one of the major problems in air pollution and catalyst poisoning. As environmental regulation is getting stricter, efficient removal of sulfur compounds from liquid fuel or natural gas becomes highly necessary to minimize the formation of environmentally toxic species such as SO_x. Moreover, sulfur compounds are known as strong poisons to deactivate transition metal catalysts by forming metal-sulfide species on the surface [4]. Currently, there are inadequate methods and procedures to design the H_2S adsorber. Therefore, this project will study the kinetics for non-catalytic solid gas reaction between hydrogen sulphide and zinc oxide which acts as the sorbent in the sulphur desulphurization unit and comes out with the framework to facilitate the systematic design of the unit.

1.3 OBJECTIVES AND SCOPE OF STUDY

1. To develop a framework to facilitate the systematic design of the adsorption column for the process removal of organic sulphur from a natural gas stream.
2. To predict the breakthrough curve of the desulphurization reaction and size the adsorption column.
3. To study the interactions between parameters that affect the system's design.

This study will focus on the desulphurization column which uses zinc oxide pellets as the adsorbent and sulfur compound in the natural gas as the reactant or adsorbate.

CHAPTER 2

LITERATURE REVIEW

2.1 DESULPHURIZATION OF HYDROGEN SULPHIDE (H_2S)

Catalysts are employed in a variety of chemical processes such as synthesis and reforming of hydrocarbons, ammonia synthesis, etc. Many such catalysts consist of or contain metallic, i.e., nickel, iron, copper, chromium, etc., compounds which may be either temporarily deactivated or permanently poisoned by certain contaminants or components in a process stream [5]. Prominent among the permanent poisons are hydrogen sulfide and various organic sulfur compounds. With such catalysts it is essential that the sulfur be removed from the process stream to prevent contact with such catalysts.

Various methods for removing sulfur have been proposed and several are in current use including washing with sulfuric acid, absorption on activated carbon and absorption or chemisorption by various materials. A material found to be particularly effective in reducing sulfur in process streams to an acceptable level, is zinc oxide. This project model and utilizes chemisorption process whereby it is one of the industry preferred method for feed desulphurization in steam reforming plants. Sulfur is removed using two steps whereby firstly sulfur is passed over a hydrogenation reactor where it is converted into H_2S and then the H_2S is removed from the process gas in adsorbent beds.

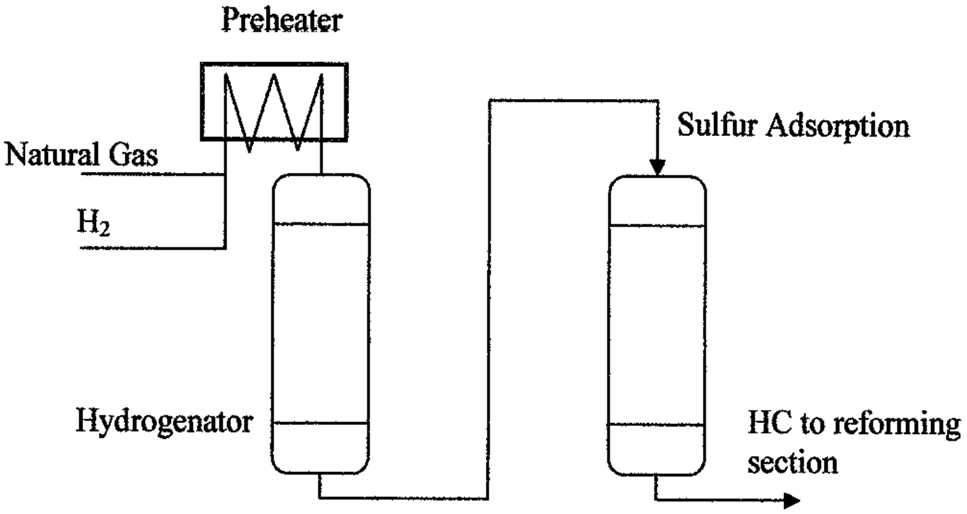


Figure 2.1: Typical Desulphurization Unit

Zinc oxide is known to be used as a highly efficient desulfurizer of natural gas and chemically synthesized gases since the sulfidation of zinc oxide leads to very low concentrations of hydrogen sulfide due to the high equilibrium constant for sulfidation [6]. When used as a desulfurant, zinc oxide is converted to zinc sulfide. The active life of a charge of zinc oxide in a desulfurizing reactor is obviously dependent upon the sulfur content of the feedstock being processed. Nevertheless, maximum utilization of the zinc oxide itself is also of importance. In that regard, the availability of the zinc oxide for the desulfurizing reaction and the quantity of zinc oxide that can be contained within an available reactor volume has important effects upon the active life of the zinc oxide.

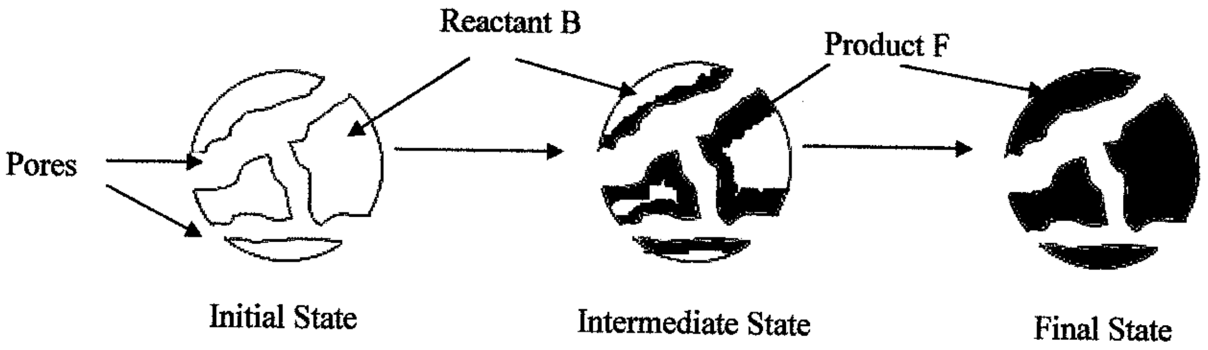
2.2 FLUID-SOLID NONCATALYTIC REACTIONS

Gas-solid reaction has immense applications in metallurgical and chemical industries. Several reaction models have been presented for heterogeneous gas-solid reactions. When solid reactant is nonporous, shrinking particle model and unreacted shrinking core model are commonly used. At the same time, newly developed grain model is also still in the study for application of gas-solid reactions.

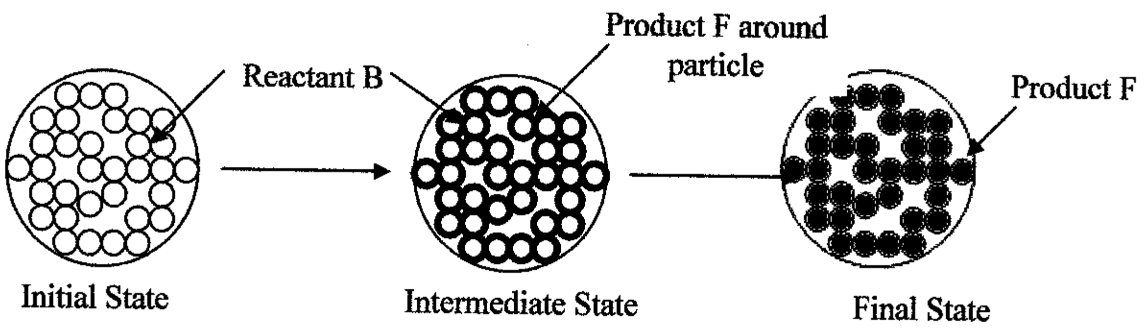
2.2.1 Single Particle Behavior

The sequence steps of a fluid reacting with a solid starts by reaction at an active site on the solid which occurs by adsorption of fluid reactant at the site, followed by surface reaction involving the adsorbed molecule. For the fluid molecule to reach the active site it must first be transported to the outer surface and then diffuse into the particle to an active site. A key parameter in formulating the rate of reaction for a single particle is how the active sites and surface areas for adsorption are distributed. One of the major effects of this parameter is the porosity of the unreacted particle. Consider the general form below to evident the effect of particle porosity in three different cases.

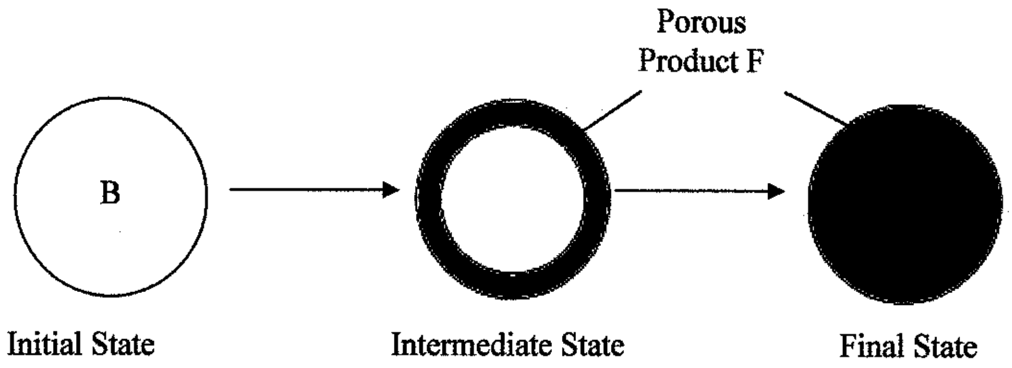
$A\,(g) + bB\,(s) \rightarrow E\,(g) + F\,(s)$



(a) Highly Porous Reactant



(b) Porous Reactant



(c) Shrinking Core Model

Figure 2.2: Models for gas-solid noncatalytic reactions

(i) Highly Porous Reactant

In this case, the solid reactant is considered to be so porous that the fluid reactant can reach all parts of the solid without diffusion resistance and the concentration of reactant in the fluid phase is the same at any location within the particle. The rate per particle varies as the surface of solid reactant changes with time and the layer of solid product accumulates.

(ii) Porous Reactant

This is an intermediate pore-diffusion resistance case for a solid reactant formed by compressing nonporous particles into a porous pellet. The pores surrounding the particles are small enough that the fluid reactant concentration decreases towards the center of the pellet.

(iii) Shrinking Core

In the case whereby the reactant is nonporous, the reaction occurs at its outer surface only. As the time goes by, the surface recedes with reaction. The reaction always occurs at a surface boundary which is the interface between unreacted core and the surrounding product. Product F builds up around the unreacted core of reactant as reaction takes place. A porous particle might also behave in this way if the resistance to reaction is much less than the resistance to diffusion of fluid reactant in the pores of the particle.

2.2.2 Shrinking Core Model (SCM) [7]

The reaction between ZnO and H_2S is a typical non-catalytic gas-solid reaction. Of the various models, two of the most frequently used are the SCM and the grain model. The shrinking core model indicates that the reaction occurs only on the sharp interface between reactant gas and unreacted solid core. The reactant is further converted to another solid material leaving behind the unreacted solid in this case ZnO is converted to ZnS. The unreacted core shrinks as the reaction proceeds, but the overall particle size basically remains constant. It is suitable for the reaction of compact, porous-free solid pellet or the mass transfer controlled by the pore diffusion. Because the sulfidation reaction is mainly controlled by the interior diffusion and the sulfided sorbent has little pore volume and surface area, the SCM is used in the present study. Although the unreacted shrinking core model does not precisely represent the whole mechanism of gas-solid reactions, it is accepted as the best simple model for the majority of reacting gas-solid systems.

2.2.3 Grain Model [6]

The grain model is one of the available models for reactions between porous solids and gas. In this model, the solid pellet is visualized as being composed of a large number of fine grains. Surrounding these grains are macropores through which the gas has to diffuse to reach the various grains. The reaction occurs in each grain according to the unreacted core model. In the overall pellet, however, the reaction occurs in a zone rather than at a sharply defined boundary. The grain model is thought to be particularly attractive because structural parameters of the solid reactants, such as grain size, grain shape, porosity, etc, are included in the model. However, a mathematical representation of this model led to a set of simultaneous differential equations which are very lengthy, unclear and the results deviated from the experimental values.

2.2.4 Shrinking Particle Model [8]

For the shrinking particle model, reactions are confined at the surface of the particle and the size of the particle is reduced by gasification of the products of flaking off the solid products. An important difference between a shrinking particle reacting to form only gaseous product(s) and a constant size particle reacting so that a product layer surrounds a shrinking core is that, in the former case, there is no product or 'ash' layer and hence no ash-layer diffusion resistance for the gaseous species. This model successfully represents the fluorination of uranium dioxide where uranium hexafluoride gas is produced through uranyl fluoride as a solid intermediate. However, this model is not suitable for the reaction between H^2S and ZnO because the ZnO will be converted to ZnS in solid form which is surrounding the core.

CHAPTER 3

METHODOLOGY

After much consideration of the available reaction models suitability and applications, the Shrinking Core Model (SCM) by Smith (1981) is chosen for the designing and sizing of the desulphurization unit. The model promotes the idea on how to link the conversion of single solid sorbents versus time which are developed using Excel. As shrinking core model only provide the solid conversion versus time for a single adsorbent pellet, sizing the adsorption column is applied to calculate the amount of solid sorbents used in a column so that it can be applied in the industry.

3.1 SHRINKING CORE MODEL

The general reaction shown in Eq. (3-1) is used in the development of the SCM. Detailed derivation of the SCM can be found in Smith (1981).

$$A\,(g) + bB\,(s) \rightarrow E\,(g) + F\,(s) \qquad (3\text{-}1)$$

In the establishment of the SCM, the solid reactant B which is initially a sphere of radius r_s is considered to be non-porous and is initially surrounded by a gas film A with concentration C_b through which mass transfer occurs between the solid particle and the bulk of the fluid. Consider the case where the temperature is uniform throughout the heterogeneous region. As the reaction proceeds, an ash/ inert layer F forms around the unreacted core of reactant B. The converted material, which is sometimes called "ash", is regarded as porous and inert substance, so that the gas reactant A can diffuse from the external surface of the particle through the layer of F to react at the interface between F and the unreacted core. Thus, the unreacted core shrinks as the reaction proceeds, but the overall particle size basically remains constant.

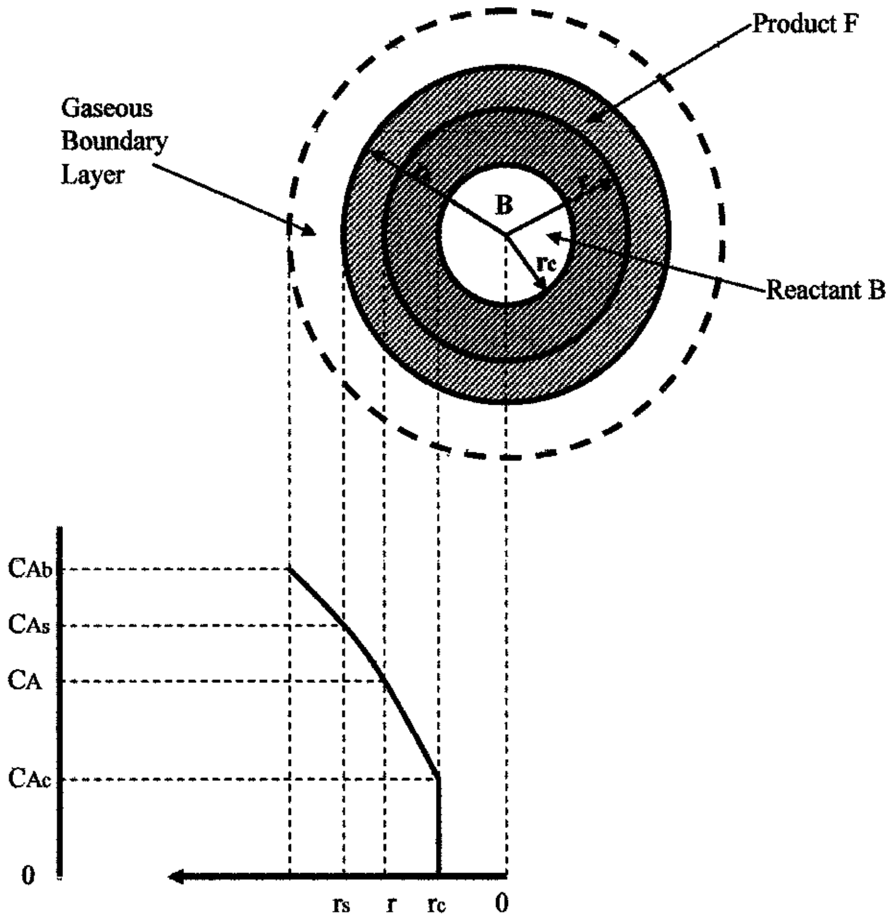


Figure 3.1: Concentration Profile in a Spherical Pellet (SCM)

Figure 3.1 shows the concentration of A labeled at various locations. The shape of the concentration profile from bulk gas to reacting surface is also indicated. It is assumed that the pellet retains its spherical shape during reaction. It is also assumed for convenience, that the densities of the porous product and the reactant B are the same, so that the total radius of the pellet does not change with time and there is no gaseous region between the pellet and the product layer F [7].

Pseudo-steady state approximation (PSSA), that is, the rate of movement of the interface at r_c (dr_c/dt) between the unreacted core and the ash/ inert layer is much slower than the rate of diffusion of A through the product layer is applied on the system before a simple mathematical analysis is feasible. This implies that the interface can be assumed to be stationary at any time and the steady-state diffusion problem can be solved to find concentrations profiles. It was determined that, for the

PSSA to be valid, the ratio of the concentration of the fluid to the molar density of the solid must be less than 10^{-3} [9].

The form of the rate equation is determined by the control regime, or the rate-limiting steps which can be one of the following three:

(i) Diffusion through the liquid film surrounding the solid particle
(ii) Diffusion through the ash/ inert solid layer
(iii) Chemical reaction at the surface of the unreacted core

r_c : radius of unreacted core zinc oxide (cm)
r_s : total radius of reactant, zinc oxide (cm)
$(C_A)_b$: concentration of H_2S (gmol/cm^3)
k : chemical reaction rate constant (cm/min)
k_m : external mass-transfer coefficient (cm/min)
D_e : effective diffusivity of H_2S through the product layer (cm^2/min)
ρ_B : density of solid reactant, zinc oxide (g/cm^3)
M_B : molecular weight of reactant, zinc oxide (g/mol)
t : time (min)
t* : ideal breakthrough time
b : order of the intrinsic reaction rate
x_B : conversion of reactant, zinc oxide

$$-\frac{dr_c}{dt}=\frac{bM_Bk(C_A)_b/\rho_B}{1+(r_c^2/r_s^2)(k/k_m)+(kr_c/D_e)(1-r_c/r_s)} \qquad (3\text{-}2)$$

Eq. (3-2) which is produced from the detail derivation as stated in Smith (1981) provides a differential equation whose solution gives r_c=f(t). This equation can be integrated to give r_c as a function of $(C_A)_b$ and t. However, to be unable to integrate, it is necessary to know how $(C_A)_b$ varies with time which will be determined by the model used to represent the flow of particles and of fluid through the reactor.

3.1.1 Reactor Models

To produce a simpler model, it is assumed that the solid is spherical with constant total radius r_s, irreversible first-order reaction in A and it reacts with the fluid isothermally. Also, the concentration of the reacting fluid $(C_A)_b$ is assumed to be constant or in excess. Firstly, conversion-vs.-time relations for single particles are developed and these relations are used to predict the performance of reactors where $(C_A)_b$ is constant.

Conversion vs. Time for Single Particle (Constant Fluid Concentration)

If $(C_A)_b$ is constant, Eq. (3-2) is easily integrated. Starting with $r_c = r_s$ at $t = 0$.

$$-\frac{bM_B k(C_A)_b}{\rho_B}\int_0^t dt = \int_{r_s}^{r_c}\left[1+\frac{r_c^2 k}{r_c^2 k_m}+\frac{kr_c}{D_e}\left(1-\frac{r_c}{r_s}\right)\right]dr_c \tag{3-3}$$

In terms of dimensionless time:

$$t^* = \frac{bM_B k(C_A)_b}{\rho_B r_s}t \tag{3-4}$$

Two groups relating the diffusion and reaction resistances:

$$Y_1 = \frac{D_e}{k_m r_s} = \frac{\text{external diffusion resistance}}{\text{diffusion resistance in product layer}} \tag{3-5}$$

$$Y_2 = \frac{kr_s}{D_e} = \frac{\text{diffusion resistance in product layer}}{\text{reaction resistance at } r_c} \tag{3-6}$$

In terms of Y_1 and Y_2, Eq. (3-3) can be integrated to give:

$$t^* = \left(1-\frac{r_c}{r_s}\right)\left\{1+\frac{Y_1Y_2}{3}\left[\left(\frac{r_c}{r_s}\right)^2+\frac{r_c}{r_s}+1\right]+\frac{Y_2}{6}\left[\left(\frac{r_c}{r_s}+1\right)-2\left(\frac{r_c}{r_s}\right)^2\right]\right\} \tag{3-7}$$

x_B is related to the radius of the unreacted core by the expression:

$$x_B = \frac{\text{initial mass - mass at t}}{\text{initial mass}} = \frac{\frac{4}{3}\Pi r_s^3\rho_B - \frac{4}{3}\Pi r_c^3\rho_B}{\frac{4}{3}\Pi r_s^3\rho_B} \tag{3-8}$$

or

$$x_B = 1-\left(\frac{r_c}{r_s}\right)^3 \tag{3-9}$$

Eliminating r_c/r_s between Eq. (3-7) and (3-9) gives the desired relationship between conversion and time for a single particle:

$$t^* = \left[1-(1-x_B)^{1/3}\right]\left\{1+\frac{Y_1Y_2}{3}\left[(1-x_B)^{2/3}+(1-x_B)^{1/3}+1\right]+\frac{Y_2}{6}\left[(1-x_B)^{1/3}+1-2(1-x_B)^{2/3}\right]\right\} \tag{3-10}$$

Chemical Reaction Controlling

If the gas-phase velocity relative to that of the solid particle is high, as in a fixed bed reactor, external-diffusion resistance may be negligible. Also, for highly porous product layer and for low conversions, diffusion resistance through the product may be small. Under such conditions the intrinsic reaction step at r_c will determine the rate, and Y_1 and $Y_2 \rightarrow 0$. Therefore Eq. (3-7) reduces to:

$$t^* = 1-\frac{r_c}{r_s} \tag{3-11}$$

or

$$t=\frac{\rho_B r_s}{bM_B k(C_A)_b}\left(1-\frac{r_c}{r_s}\right)=\frac{\rho_B r_s}{bM_B k(C_A)_b}\left[1-(1-x_B)^{1/3}\right] \tag{3-12}$$

Diffusion through Product Controlling

For rapid chemical reaction at the interface and a low D_e, diffusion through the product layer may determine the rate, even at small conversions. If this is the case, $Y_1 = 0$ and Y_2 is large.

$$t^*=\left(1-\frac{r_c}{r_s}\right)\frac{Y_2}{6}\left[\frac{r_c}{r_s}+1-2\left(\frac{r_c}{r_s}\right)^2\right] \tag{3-13}$$

or

$$t=\frac{\rho_B r_s^2}{6D_e bM_B(C_A)_b}\left[1-3\left(\frac{r_c}{r_s}\right)^2+2\left(\frac{r_c}{r_s}\right)^3\right] \tag{3-14}$$

3.2 FRAMEWORK OF THE ADSORPTION COLUMN DESIGN

The framework to facilitate the systematic design of the adsorption column for the process removal of organic sulfur from a natural gas stream is produced referring to the Shrinking Core Model (SCM) theory and mathematical equations as been explained in the section 3.1. Refer to Appendix B for the detail procedures of the developed framework.

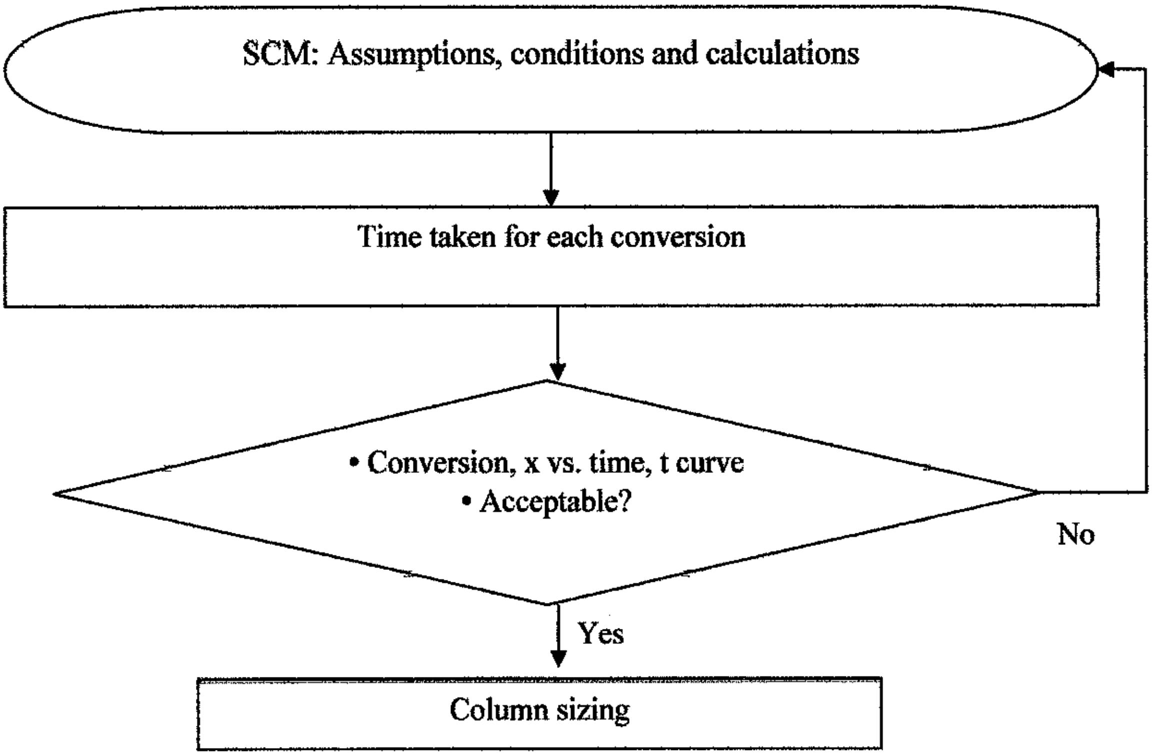


Figure 3.2: Framework of the design of adsorption column

In this modeling project, the main purpose is to remove hydrogen sulfide from the natural gas by the means of adsorption. Hydrogen sulfide as explained earlier gives harmful effect in term catalyst poisoning, lowering conversion and selectivity as well as environmental damaging. In order to remove hydrogen sulfide, sulfidation of zinc oxide was proposed for the desulphurization process. Therefore, this systematic framework which is designed based on the Shrinking Core Model (SCM) is applicable for the desulphurization column which utilizes zinc oxide as the adsorbent bed.

One of the main assumptions made is that the desulphurization reaction on each zinc oxide pellet is based on the SCM theory. At the same time, the zinc oxide pellets are considered to be highly non-porous and is initially surrounded by the natural gas film through which mass transfer occurs between the solid particle and the bulk of the fluid. As the irreversible first-order reaction proceeds in the isothermal condition, it is assumed that the actual interfaces move from the outer shell to the inner core and results in the spherical shape pellet remains unchanged throughout the reaction. It is also assumed for convenience, that the densities of the porous inert layer product (zinc sulfide) and the zinc oxide pellet are the same, so that the total radius of the pellet does not change with time and there is no gaseous region between pellet and the product layer. In the other hand, high flow rate of constant hydrogen sulfide concentration which obeys the ideal gas law is assumed to simplify the model.

One more restriction must be placed on the system before a simple mathematical analysis is feasible. The rate of movements of the reaction interface at r_c (radius of unreacted zinc oxide pellet), that is drc/ dt is small with respect to the velocity of diffusion of hydrogen sulfide through the product (zinc sulfide) layer. The requirement for this pseudo steady state concept has been carefully developed but approximately stated, it is valid if the densities of the gas in the pores of the product layer is small with respect to the density of solid zinc oxide pellet which in this case is applicable.

Due to the assumption that the flow rate of natural gas which contains hydrogen sulfide is high, the external diffusion resistance is assumed to be negligible. Therefore Y_1 will approach zero.

$$Y_1 = \frac{D_e}{k_m r_s} = \frac{\text{external diffusion resistance}}{\text{diffusion resistance in product layer}} \approx 0 \qquad (3\text{-}15)$$

Once the assumptions had been applied on the system to produce a simpler model, the operating conditions of the column are set whereby the temperature is in the range of 370°C to 400°C and the pressure is within 40 barg to 42 barg. The catalyst used in the desulphurization column is entirely zinc oxide with the radius of 2mm. The zinc oxide use has the density of 5.61 g/cm^3 and the molecular weight of 81.41 g/mol. In the other hand, constant hydrogen sulfide concentration (60ppmv) in the natural gas is assumed throughout the process to simplify the calculation.

With the suitable assumptions made and conditions applied, calculations of the Shrinking Core mathematical models can be on practical use for this project. Firstly, calculation of the rate of reaction can be done based on the Arhenius Equation whereby the frequency factor, k_o = 9.81E-02 mol/cm^{2}min, activation energy, E_a = 19.32 kJ/mol and the gaseous constant, R is given as the value 8.314 J/mol.K.

Arhenius Equation to calculate the rate of reaction, k:

$$k = k_o \exp\left(-\frac{E_a}{RT}\right) \qquad (3\text{-}16)$$

$$k = 9.81 \text{ X } 10^{-2} \exp(-19.32/RT) \qquad (3\text{-}17)$$

Further on, diffusion coefficient is also calculated based on the Arhenius Equation using the frequency factor, D_{eo} of the value 6.30E-3 mol/cm.min, diffusion activation energy, E_d value of 31.54 kJ/mol and gaseous constant, R = 8.314 J/mol.K.

Arhenius Equation to calculate the diffusion coefficient, D_e:

$$D_e = D_{eo} \exp\left(-\frac{E_d}{RT}\right) \tag{3-18}$$

$$D_e = 6.30 \text{ X } 10^{-3} \exp(-31.54/RT) \tag{3-19}$$

Before proceeding with the Shrinking Core mathematical model calculation, to make things easier the hydrogen sulfide concentration in ppmv should be converted to mg/m³ using the equation given below. Information needed are molecular weight of hydrogen sulfide, M = 34.082 g/mol and absolute pressure of the system is P = 43 atm.

$$C_{ppm} = 0.08205\left(\frac{T}{PM}\right)\left(\text{mg/m}^3\right) \tag{3-20}$$

For a high velocity of gas-phase relative to that of the solid particle, external diffusion resistance may be negligible. Therefore, Y_1 approaches zero and Y_2 which is referred to diffusion resistance in product layer divided by the reaction resistance at interface, r_c between the inert layer and the core pellet is calculated using the equation given below.

$$Y_2 = \frac{kr_s}{D_e} \tag{3-21}$$

Lastly, all the calculated values are substituted into the final equation to obtain the time taken for a complete conversion for a single zinc oxide pellet. The results are then tabulated and the conversion (x_B) vs. time (t) graph can be constructed from the data available.

$$t^* = \left[1-(1-x_B)^{1/3}\right]\left\{1+\frac{Y_2}{6}\left[(1-x_B)^{1/3}+1-2(1-x_B)^{2/3}\right]\right\} = \frac{bM_B k(C_A)_b}{\rho_B r_s} t \tag{3-22}$$

CHAPTER 4

RESULTS AND DISCUSSION

4.1 GENERATION OF BREAKTHROUGH CURVE

By applying the methodology as in Chapter 3, the results of time taken, t for each conversion (x = 0 until x = 1) obtained are tabulated in Table 4.1.
(Examples of calculation are shown in appendix C)

Table 4.1: Single particle solid reactant conversion vs. time

Conversion, x	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1	1	1
Time, t (min)	0	0.08	0.21	0.40	0.68	1.06	1.56	2.24	3.17	4.58	8.32	10	15

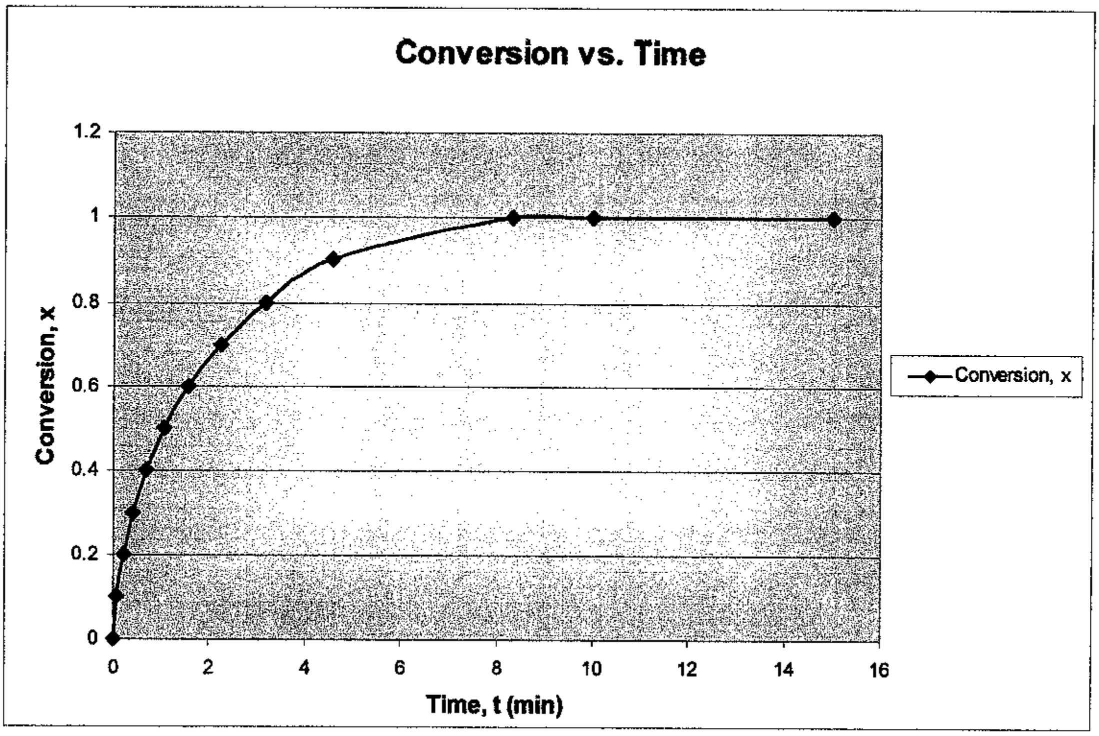


Figure 4.1: Conversion of single particle zinc oxide vs. time (breakthrough curve)

Conversion vs. time curve for a single catalyst pellet (zinc oxide) as shown in Figure 4.2 was constructed from the values obtained by applying the shrinking core model mathematical equations. Based on the graph, by considering 100% adsorption selectivity and efficiency, a single zinc oxide pellet of radius 2mm takes 8.32 min to complete the solid conversion by adsorbing 0.0023 moles of H^2S at a temperature of 400°C (x_B=1 and r_c=0). Therefore, a single zinc oxide pellet is able to handle a basis flowrate of 9.07 g/ hr of natural gas with a maximum H^2S composition of 5% before it reaches its breakthrough limit. The curve shows a continuous and consistent increase of solid reactant conversion as time goes by.

The sulfidation reaction occurs by the means of adsorption. As hydrogen sulfide is being adsorbed on the active site of solid reactant, solid conversion keep increasing with time which indicates the continuous reaction of sulfidation. Increasing on the solid conversion indicates the removal of the hydrogen sulfide from the mixture until no more hydrogen sulfide can be adsorbed when the solid conversion reaches its saturation point (equilibrium). Further on, column sizing needs to be done in order to determine the amount of solid sorbent available in the column, so that the desulphurization process can be prolong and the breakthrough curve for the whole column can be produced.

4.2 CASE STUDY: SIZING OF DESULPHURIZATION COLUMN AT PETRONAS FERTILIZER KEDAH (PFK)

The task of sizing an adsorption column requires several parameters which are known as input data. They can virtually never be predicted, but must be measured and justified. Therefore, a case study was taken from Petronas Fertilizer Kedah Ammonia Plant whereby the operating and mechanical data are as stated below:

Table 4.2: Sulfur Absorber Operating Data [10]

Fluid: Natural Gas	**Values**	**Units**
Gas: Quantity	26,404	kg/ h
Molecular weight	16.3	g/ mol
Density	12.5	kg/ m^3
Operating temperature	400	°C
Operating pressure	42	barg
Design temperature	425	°C
Design pressure	49.1	barg
Shell id	2300	mm
Catalyst bed height	6740	mm
Corrosion allowance	1.5	mm
Shell material	1¼ Cr ½ Mo	
Catalyst: Type	Topsøe HTZ-3	
Size	4	mm
Volume (each vessel)	28.0	m^3
Weight	36,400	kg
Weight of ceramic	4500	kg
Design pressure drop	0.7	barg

According to the information obtained from PFK, there are 100 mm of ½" ceramic balls placed above the catalyst to protect the catalyst from being damaged. It has also been found that the reactor will be able to operate at conditions which will be corresponding to 110% production capacity of the plant. Each desulphurization column has a service life of 6 months which is able to handle a maximum sulfur concentration of 60ppm throughout the time. At the same time, it is predicted that the maximum sulfur adsorption is comparable to 100 kg of zinc oxide adsorbent is able to adsorb 39 kg of sulfur before it reaches its saturation limit.

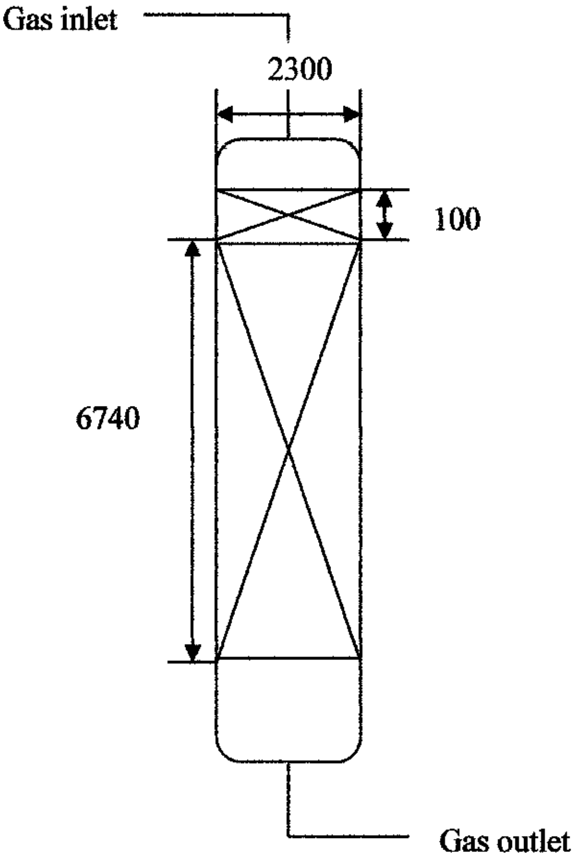


Figure 4.2: Sulfur Absorber with its Dimensions

For a single adsorbent pellet (ZnO):

- radius, r = 2mm
- volume, V = 0.0335cm³
- molecular weight, MW = 81.41 g/mol
- weight, W = 0.188 g
- no. of moles, n = 0.0023 moles
- breakthrough time, t = 8.3151 mim

$ZnO\ (s) + H_2S\ (g) \rightarrow H_20\ (g) + ZnS\ (s)$

1 mol 1 mol 1 mol 1 mol

1 ZnO: 0.0023 moles ➔ 8.3151 min

X moles ➔ 60 min

➔ X = 0.0166 moles/hr

Therefore, H_2S adsorbed = 0.00166 moles/hr

Natural gas (NG): 26,404 kg/hr

H_2S (0.1% of NG) = (26,404 g/hr) / (34.08 g/mol)

= 774.7653 mol/hr

0.188 g ZnO ➔ 0.0166 mol/hr

Y g ZnO ➔ 774.7653 mol/hr

➔ Y = 8.7745 kg ZnO (per hour)

Therefore, amount of ZnO needed per hour is 8.7745 kg and for a service lifetime of 6 months, 34,746.82 kg of ZnO is estimated.

Table 4.3: Results of Column Sizing Calculation

Parameters	Model	Actual (PFK)	Deviation (%)
Column: Diameter (mm)	2300	2300	0.00
Catalyst: Bed height (mm)	6430	6740	4.60
Volume (m^3)	26.73	28.00	4.54
Weight (kg)	34,746.82	36,400	4.54

Maximum Sulfur Adsorption:

39 kg S ➔ 100 kg ZnO

Z kg S ➔ 34,746.82 kg ZnO

➔ Z = 13,551.26 kg S / 6 months (breakthrough limit)

Once the breakthrough time for a single solid sorbent has been achieved, a simple sizing column need to be develop in order to determine the amount of solid sorbent required in the sulfur removal process to remove the amount of hydrogen sulfide specified. The Shrinking Core Model that is being used in the modeling only refers to a single particle behavior. In order to observe the breakthrough curve for the whole sulfur removal unit, sizing column is the best option.

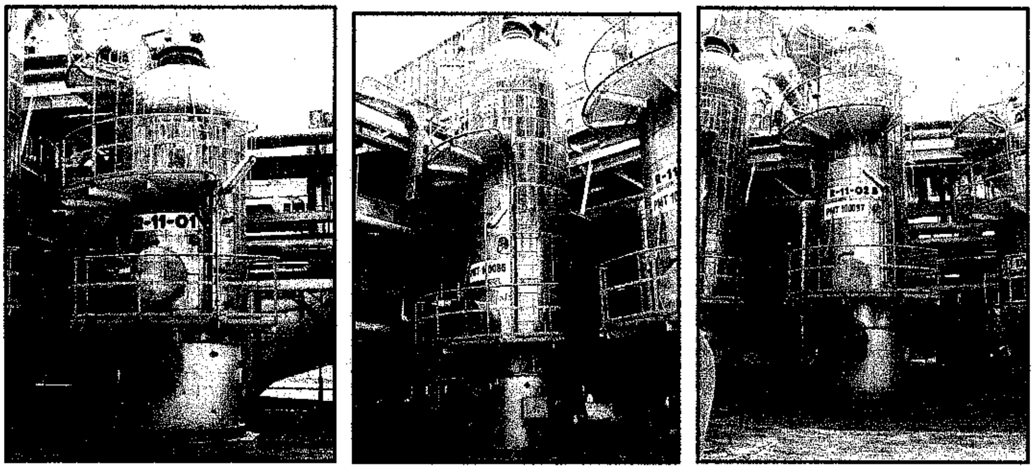
For a single adsorbent zinc oxide pellet of radius 2mm, it has a volume of 3.35E-02 cm^3. Other figures required for sizing the column are the zinc oxide molecular weight, MW = 81.41 g/mol. From there we can predict the weight and number of moles of each pellet which results in W = 0.188 g and n = 0.0023 moles. From the graph produced earlier, is has been found that the breakthrough time for a single zinc oxide pellet is 8.32 min.

$ZnO\ (s) + H_2S\ (g) \rightarrow H_20\ (g) + ZnS\ (s)$

The equation stated above shows that one mole of zinc oxide solid reacts with one mole of hydrogen sulfide gas to produce one mole of water in gaseous form and one mole of porous zinc sulfide solid. Therefore, this means that for a single zinc oxide pellet of 0.0023 moles are able to adsorb 0.0023 moles of hydrogen sulfide from the feed stream in 8.32 min before it saturates. Hence, 0.0166 moles of hydrogen sulfide are able to be removed from the natural gas in an hour.

A case study is undertaken, whereby the natural gas feed flow rate is 26,404 kg/hr and it contains 0.1% of hydrogen sulfide. This implies than 774.77 moles of hydrogen sulfide flows into the desulphurization column every hour. As mentioned earlier, a single zinc oxide pellet of 0.188g is able to adsorb 0.0166 moles per hour of hydrogen sulfide. Consequently, to remove 774.77 moles of hydrogen sulfide per hour, this requires 8.77 kg of zinc oxide catalyst.

From the calculations done, it has been found that the estimated amount of ZnO adsorbent needed for a service life of 6 months is 34,747 kg which slightly deviates from the actual amount applied in the industrial. A single ZnO pellet is able to adsorb 1.66E-03 moles of H_2S per hour before it reaches its saturation limit and within the service life of 6 months, 13,551 kg sulfur can be adsorb on the adsorbent bed. The dimensions of the desulphurization column obtained from the model calculation are then compared to the actual ones utilized in PFK Ammonia Plant. Acceptable results with a small deviation of less than 5% have been recorded as tabulated in Table 4.3. As a result of the case study done, the Shrinking Core mathematical model and systematic procedures are applicable for industrial use.



(a) (b) (c)

Figure 4.3:

Pictures of (a) R-11-01 Hydrogenator, (b) R-11-02A Desulfurizer and (c) R-11-02B Desulfurizer taken from PFK Ammonia Plant

4.3 SUSTAINABILITY

4.3.1 Safety

In ammonia, methanol, hydrogen and other plants having a steam reforming unit, it is imperative to remove sulfur efficiently from the hydrocarbon feed in order to prevent poisoning of the nickel catalyst in the reformer. At the same time, sulfur from the ammonia plant PFK will be supplied to the urea plant nearby with the maximum allowable level of 1ppm. Therefore, it is essential that the sulfur compound be removed as effectively as possible with the application of proper design procedures for natural gas desulphurization.

4.3.2 Economic

By saving the catalyst employed in reactions from being poisoned, this can help to reduce cost of replacing the catalyst before it reaches its lifetime limit. In the other hand, a suitable model for example the shrinking core model able to calculate the optimum amount of adsorbent needed for a particular breakthrough time. This helps to size the column effectively and avoid any unwanted costs.

4.3.3 People and Environment

Many industrially important feed stocks are contaminated with sulfur compounds, ultimately released into the atmosphere as sulfur oxides. The sulfur oxides are converted to acid rain, which damages the whole ecosystem, attacking vegetation and stonework and acidifying lakes and rivers with detrimental effects on aquatic life. Clearly, sulfur-containing pollutants are a major threat to the environment. Although measures are now underway to control sulfur compound emissions, the large increase in instances of childhood asthma and the continuing detrimental effects of acid rain on the environment indicate that the effects of sulfur on the environment will continue to be a problem for years to come. With that, systematic procedures of sulfur removal are highly necessary to avoid or minimize the unwanted effects to people and the environment.

CHAPTER 5
CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

Several theoretical models have been proposed for the reaction of solids with gases. The two most common models are the shrinking core model and the grain model. Through literature review, it has been found that shrinking core model is more applicable and suitable for the desulphurization of natural gas. The shrinking core model assumes that H_2S diffuses through a gas film which surrounds a spherical particle of sorbent to the oxide surface where it reacts. The oxide 'core' then shrinks as the reaction proceeds. The H_2S must continually diffuse through the sulfided sorbent to unreacted oxide. The rate-controlling step could be the diffusion of H_2S through the gas film, the diffusion of H_2S through the sulfided sorbent or the reaction of H_2S with the oxide at the sulfide/ oxide interface, but it is generally found that the gas film does not offer much resistance to mass transfer and so one of the latter two steps are rate limiting.

Based on the shrinking core model with applicable assumptions, the conversion vs. time curve for a single solid sorbent particle of zinc oxide has been produced whereby the breakthrough time is 8.32 min. From the results obtained, it shows that the conversion of solid sorbent increases continuously with time which indicates the removal of H_2S from the natural gas feed. This reflects part of the objectives of this research as been stated in section 1.3.

The shrinking core model that is being applied in the modeling only refers to one single particle behavior. Therefore in order to observe the breakthrough curve for the whole sulfur removal unit, sizing column is the best option. As a result, for a service life of 6 months, 34,747 kg of ZnO catalyst is needed in the sulfur removal process to remove the amount of hydrogen sulfide specified. From the comparison of column dimensions calculated with the industrial equipment data available from

PFK, it has been found that the deviation is less than 5% therefore the model and procedures used are applicable to facilitate the systematic design of the desulphurization column.

It is clear that an appropriate choice of model and procedures can help to simplify or optimize certain processes whereby in this case the shrinking core model have successfully been applied for natural gas desulphurization problem. This is of great interest in process engineering because sulfur removal is consistently important and utilized in various field, therefore the framework or systematic design procedures can be applied.

5.2 RECOMMENDATIONS

To improve the outcome of the research project, several recommendations have been identified and should be looked into for future project work.

(i) In this research so far, the diffusion of hydrogen sulfide into the active site of solid sorbent zinc oxide is assumed to be perfect (100% efficiency) without any interference from other compound molecules exist in the natural gas mixture. To improve this research, consideration about the effect of other compound molecules diffuse into the active site and taking over the available space for desulphurization of hydrogen sulfide has to be taken into account.

(ii) A more detail research on the effect of zinc oxide as the adsorbent on other compounds in the natural gas feed has to be done. This is to avoid contamination of desulphurized gas after the process.

(iii) All the constants and values used in the shrinking core modeling need to be identified to avoid making errors and large deviation in the results of the model equation.

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APPENDICES

APPENDIX A: Project's Time Frame

No	Details / Weeks	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
1	Briefing & updates	■																			
2	Project work commences		■	■	■	■	■	■	■	■	■										
3	Submission of Progress Report 1				•																
4	Submission of Progress Report 2 (Draft of Final Report)										•										
5	Poster Exhibition / Pre-EDX/ Progress Reporting											■									
6	EDX												■								
7	Submission of Final Report (CD Softcopy & Softbound)														•						
8	Final Oral Presentation																		■	■	
9	Submission of hardbound copies																				•

APPENDIX B:

Detail Framework of the Adsorption Column

Below are the step-by-step approaches to produce the final result of breakthrough curve by applying the SCM mathematical equations based on the following reaction equation:

H^2S (g) + ZnO (s) → H^2O (g) + ZnS (s)

Apply these assumptions:

(i) Desulphurization reaction on each zinc oxide pellet is based on shrinking core model.
(ii) Highly nonporous solid reactants.
(iii) The actual interfaces move from outer shell to inner core.
(iv) Spherical shape pellet and remains unchanged throughout reaction.
(v) Constant total radius of zinc oxide pellet.
(vi) H_2S obeys ideal gas's law.
(vii) High flow rate of constant H_2S concentration.
(viii) Irreversible first-order reaction (b = 1) in isothermal condition.

The external diffusion resistance is assumed to be negligible due to high gas flow rate. Therefore Y_1 will approach zero.

$$Y_1 = \frac{D_e}{k_m r_s} = \frac{\text{external diffusion resistance}}{\text{diffusion resistance in product layer}}$$

Conditions applied:

- (i) Operating temperature, T: 400°C/ 673K [10]
- (ii) Operating pressure, P: 42barg/ 42atm [10]
- (iii) Catalyst type: zinc oxide [10]
- (iv) Total radius of catalyst pellet, r_s: 2mm [10]
- (v) H_2S concentration, $(C_A)_b$: 60ppmv (max) [10]
- (vi) Density of solid reactant (zinc oxide), ρ_B: 5.61g/cm^3 [11]
- (vii) Molecular weight of solid reactant (zinc oxide), M_B: 81.41 g/mol [11]

Rate of reaction, k is calculated based on Arhenius Equation:

$$k = k_o \exp\left(-\frac{E_a}{RT}\right)$$

- Frequency factor, k_o: 9.81 X 10^{-2} mol/cm^{2}min [6]
- Activation energy, E_a: 19.32 kJ/mol [6]
- Gaseous constant, R: 8.314 J/ mol.K

⇒ $k = 9.81 \text{ X } 10^{-2} \exp(-19.32/ RT)$

Diffusion coefficient, D_e is calculated based on Arhenius Equation:

$$D_e = D_{eo} \exp\left(-\frac{E_d}{RT} \right)$$

- Frequency factor, D_{eo}: 6.30 X 10^{-3} mol/cm min [6]
- Diffusion activation energy, E_d: 31.54 kJ/mol [6]
- Gaseous constant, R: 8.314 J/ mol.K

⇨ $D_e = 6.30 \text{ X } 10^{-3} \exp(-31.54/ RT)$

H_2S concentration, $(C_A)_b$ in ppmv is converted to mg/m^3 using the equation:

$$C_{ppm} = 0.08205 \left(\frac{T}{PM} \right) \left(\text{mg/m}^3 \right)$$

- Molecular weight of H_2S, M: 34.082 g/mol [11]
- Absolute pressure, P: 43atm

Y_2 is calculated based on the following equation: $Y_2 = \frac{kr_s}{D_e}$

All the calculated values are substituted into the following equation to obtain the time, t. Conversion (x_B) vs. time (t) curve were constructed from the data obtained

$$t^{*} = \left[1-(1-x_B)^{1/3}\right]\left\{1+\frac{Y_2}{6}\left[(1-x_B)^{1/3}+1-2(1-x_B)^{2/3}\right]\right\} = \frac{bM_B k(C_A)_b}{\rho_B r_s}t$$

APPENDIX C:

Example of calculations by applying the Shrinking Core Model equations

Assumptions made:

(i) Desulphurization reaction on each zinc oxide pellet is based on shrinking core model.
(ii) Highly nonporous solid reactants.
(iii) The actual interfaces move from outer shell to inner core.
(iv) Spherical shape pellet and remains unchanged throughout reaction.
(v) Constant total radius of zinc oxide pellet.
(vi) H_2S obeys ideal gas's law.
(vii) High flow rate of constant H_2S concentration.
(viii) Irreversible first-order reaction (b = 1) in isothermal condition.

Conditions applied:

(i) Operating temperature, T: 400°C/ 673K [10]
(ii) Operating pressure, P: 42barg/ 42atm [10]
(iii) Catalyst type: zinc oxide [10]
(iv) Total radius of catalyst pellet, r_s: 2mm [10]
(v) H_2S concentration, $(C_A)_b$: 20ppmv (max) [10]
(vi) Density of solid reactant (zinc oxide), ρ_B: 5.61g/cm^3 [11]
(vii) Molecular weight of solid reactant (zinc oxide), M_B: 81.41 g/mol [11]

Step 1: Original equation based on Shrinking Core Model

$$t^* = \left[1-(1-x_B)^{1/3}\right]\left\{1+\frac{Y_1Y_2}{3}\left[(1-x_B)^{2/3}+(1-x_B)^{1/3}+1\right]+\frac{Y_2}{6}\left[(1-x_B)^{1/3}+1-2(1-x_B)^{2/3}\right]\right\}$$

Based on assumptions, reduces to:

$$t^* = \left[1-(1-x_B)^{1/3}\right]\left\{1+\frac{Y_2}{6}\left[(1-x_B)^{1/3}+1-2(1-x_B)^{2/3}\right]\right\} = \frac{bM_Bk(C_A)_b}{\rho_B r_s}t$$

Step 2: Calculate the rate of reaction, k

$$k = k_o \exp\left(-\frac{E_a}{RT}\right)$$

- Frequency factor, k_o: 9.81 X 10^{-2} mol/cm^{2}min [7]
- Activation energy, E_a: 19.32 kJ/mol [7]

- Gaseous constant, R: 8.314 J/ mol.K

$$k = 9.81 \times 10^{-2} \exp(-19.32/RT)$$
$$k = 9.81 \times 10^{-2} \exp(-19.32 \times 10^{3}/ 8.314 \times 673)$$
$$k = 3.11 \times 10^{-3} \text{ mol/ cm}^{2}\text{.min}$$
$$k = 1.99 \times 10^{5} \text{ cm/ min}$$

Step 3: Calculate the diffusion coefficient, De

$$D_e = D_{eo} \exp\left(-\frac{E_d}{RT}\right)$$

- Frequency factor, D_{eo}: 6.30 X 10^{-3} mol/cm min [7]
- Diffusion activation energy, E_d: 31.54 kJ/mol [7]
- Gaseous constant, R: 8.314 J/ mol.K

$$D_e = 6.30 \times 10^{-3} \exp(-31.54/RT)$$
$$D_e = 6.30 \times 10^{-3} \exp(-31.54 \times 10^{3}/ 8.314 \times 673)$$
$$D_e = 2.25 \times 10^{-5} \text{ mol/ cm.min}$$

Step 4: Converting H_2S concentration

$$C_{ppm} = 0.08205\left(\frac{T}{PM}\right)\left(\text{mg/m}^3\right)$$

$$C_{ppm} = 0.08205\left(\frac{673}{(43)(34.082)}\right)\left(\text{mg/m}^3\right)$$

$$C_{H_2S} = 1592.3962 \text{ mg/ m}^3$$
$$= 4.6725 \times 10^{-8} \text{ mol/ cm}^3$$

Step 5: Calculate Y_2

$$Y_2 = \frac{kr_s}{D_e}$$

$$Y_2 = \frac{(3.11x10^{-3})(0.2)}{2.25x10^{-5}} = 27.64$$

Step 6: Calculate time, t

$$t^* = \left[1-(1-x_B)^{1/3}\right]\left\{1+\frac{Y_2}{6}\left[(1-x_B)^{1/3}+1-2(1-x_B)^{2/3}\right]\right\} = \frac{bM_Bk(C_A)_b}{\rho_B r_s}t$$

$$t^* = \left[1-(1-x_B)^{1/3}\right]\left\{1+\frac{27.64}{6}\left[(1-x_B)^{1/3}+1-2(1-x_B)^{2/3}\right]\right\} = \frac{bM_Bk(C_A)_b}{\rho_B r_s}$$

$$t = \frac{t^*\rho_B r_s}{bM_Bk(C_A)_b} = \frac{t^*(5.61)(0.2)}{1(81.41)(1.99x10^5)(4.67x10^{-8})}$$

When x = 0.1

$$t^* = \left[1-(1-0.1)^{1/3}\right]\left\{1+\frac{27.64}{6}\left[(1-0.1)^{1/3}+1-2(1-0.1)^{2/3}\right]\right\} = 0.051$$

$$t = \frac{(0.051)(5.61)(0.2)}{1(81.41)(1.99x10^5)(4.67x10^{-8})} = 0.075\,\text{min}$$

When x = 0.5

$$t^* = \left[1-(1-0.5)^{1/3}\right]\left\{1+\frac{27.64}{6}\left[(1-0.5)^{1/3}+1-2(1-0.5)^{2/3}\right]\right\} = 0.714$$

$$t = \frac{(0.714)(5.61)(0.2)}{1(81.41)(1.99x10^5)(4.67x10^{-8})} = 1.06\,\text{min}$$

Conversion, x_B	**Dimensionless time, t***	**Time taken, t (min)**
0	0	0
0.1	0.050602483	0.075004
0.2	0.139347571	0.206544
0.3	0.272885617	0.404477
0.4	0.460191673	0.682105
0.5	0.713930732	1.058203
0.6	1.053091726	1.560914
0.7	1.508750208	2.2363
0.8	2.139353115	3.170992
0.9	3.088184118	4.577369
1.0	5.609866667	8.315057

APPENDIX D:

Desulphurization Process Flow Diagram

● FCS1-04 SS-COM ERR

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Desulphurization