Study on Hydrodesulphurization Reactor

By

Suziati Binti Sulaiman

Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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Approved by.

(Prof. Dr. Duvurri Subbarao)
Main Supervisor

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.

Suziati Binti Sulaiman

ABSTRACT

Crude naphtha consists of variable hydrocarbons and undesirable compound such as sulphur which must be removed to prevent corrosion and environmental problems. Existence of sulphur compound also results in deactivating the catalysts, disrupting the catalysts performance, lowering the conversion and selectivity and increasing the temperature that need to be applied for a particular amount of conversion. Therefore this research is done to develop a modelling for a trickle bed reactor of the process of removal the organic sulphur from a crude naphtha. Deep desulfurization is necessary because sulphur content in crude oil is getting higher and higher while the regulated sulphur limits are becoming lower and lower. The essentials of the chemistry and catalysis are well established. There is a great need for reactor development to improve efficiency and economics. Modelling can be great help in this direction. A dynamic plug flow heterogeneous one dimensional (1D) model was developed to simulate the temperature, concentration profile change along the reactor and change a few parameters such as LHSV and H2/CH ratio to observe the effect on decreasing the sulphur content. The modelling is based on the mass and enthalpy balance of the reactions.

ACKNOWLEDGEMENT

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ABBREVIATIONS AND NOMENCLATURES

a_s	Liquid- solid interfacial area per unit volume of the reactor
a_L	Gas – liquid interfacial area per unit volume of the reactor
u_g	Superficial velocity of gas phase
u_L	Superficial velocity of liquid
${C_{ai}}^L$	Molar concentration of hydrogen in liquid
${C_{bi}}^L$	Molar concentration of component sulfur in liquid
${C_{ai}}^S$	Molar concentration of hydrogen inside the solid
${C_{bi}}^S$	Molar concentration of component sulfur inside the solid
R	Gas constant
T	Temperature
H	Henry constant
P	Pressure
LHSV	Liquid hourly space velocity
K_{LG}	Gas-liquid mass transfer
K_{LS}	Liquid-solid mass transfer
ρ_L	Density of liquid
C_{P_L}	Heat capacity of liquid
ΔH_j	Heat of reaction
ρ_B	Catalyst bulk density
K_r	Reaction rate constant
r_j	Rate of reaction
h_L	Heat transfer coefficient
η	Effectiveness factor
f_s	Liquid holdup
N	Naphtha

CHAPTER 1
INTRODUCTION

1.1 Background of Study

Hydrodesulphurization (HDS), a fundamental step in the production of petroleum fuels, is of particular important for the improvement of both feed and process products properties. This result from the basic role of hydrodesulphurization, the process aimed at removal sulfur, nitrogen, aromatics and other undesired compounds from oil fractions. Apart from protecting the catalyst in the processes where sulfur and nitrogen compounds act as a catalytic poisons, HDS is performed to improved products quality in terms of their chemical stability, color, odor and cetane number.[6,16]

Hydrodesulphurization of petroleum fractions has gained considerable importance in the international refining industries in order to meet the stringent environmental regulations. Hydrodesulphurization of products e.g. naphtha, kerosene/ATF, diesel and cracked gas oils are carried out to upgrade the products quality and render them environmentally friendly. Apart from the above, HDS is also used to pretreat the feed stocks for secondary processing e.g. FCC, hydrocracking, delayed coking and etc [1].

The hydrodesulphurization process involves removal of sulfur from the complex petroleum mixture through hydrogenation. The organo sulfur compound loose sulfur on hydrogenation. Sulfur is released in the form of hydrogen sulphide. The reaction is carried out under moderate pressure in a trickle bed reactor.

Generally speaking, petroleum crudes are complex mixtures of various organic compounds, and the major components are hydrocarbons. Large amount of heteroatoms are also included and their concentrations change depending on their origin. While sulfur is generally the most abundant heteroatoms , the concentration of sulfur is specifically higher in crudes from the middle east where 50% of world petroleum deposits exist [2].The compound with these heteroataoms are distributed aver the entire boiling range, and the concentration of heteroatoms

increases with increases the boiling point. In lighter fractions, sulfur is present in the forms of thiols, sulfides, disulfides, mercaptans and and thiophenes, while various alkylbenzothiophenes and alkyldibenzothiophenes are included in the heavier gas oil fraction. [1, 2].
Mathematical modeling of any reaction system is very important because it is a powerful tool in their design, optimization and operation/control. Models are also useful in evaluation of catalyst and feed stocks. As proper design, optimization of process parameters and selection of suitable catalyst are absolutely necessary for profitable HDS operation, it is necessary to have a reliable and fairly accurate model for the purpose.

However, the main goal is to show how the parameters involved can be utilized for real predictions of the process conditions in industrial plant. In here, the author tried to illustrate how the severe process conditions (e.g. increasing pressure, temperature and ratio H_2/CH) influence on decreasing of sulfur content in products.

On the basis of proposed and verified reactor and kinetic model, study was performed to see how the changes in the process variables change the sulfur content in the product.

1.1 Problem Statement

The problems of excessive sulphur in motor fuels is basically related to catalytic cracking, bringing total sulphur content in motor fuels to up to 95%. In other words, quality parameters of petroleum fuels are directly associated with the process in question [1]. Because of this, hydrodesulphurization is a very important process, as these oils are used as feedstocks in catalytic cracking.

Since various years ago refiners have been subjected to continuous pressure to produce the so-called low sulphur diesel or other products. This pressure will continue in the near future due to new and more severe specifications in sulphur content (15wppm since 2006 in the US and 10wppm around 2008 in the EU) [1]. Catalytic hydrodesulphurization (HDS), a mature technology with proven commercial experience, has been extensively used to achieved the current fuels quality, however, in order to fulfil the even more stringent environmental requirements it is necessary to have a deep understanding on the behaviour of the HDS process from different points of view: catalyst formulation, process configurations, reactor design, feed selection, reactor internal, effect of operating condition.

It has been recognized that the achievement of almost zero values of sulphur in fuels has to be done through a combination of more than one of these approaches. The study of some of them depends totally or partially on experimental work, e.g. catalyst formulation and feed selection.

However, others (operating condition, reactor design and etc) can be undertaken theoretically via process modelling and simulation [2].

1.3 Objectives and Scope of Study

1.3.1 Objectives

The main objective of the present study is to develop three phase mathematical model of trickle bed reactor for simulating the performance of hydrodesulphurization unit. Kinetic parameters from literature are used for simulating the hydrodesulphurization reactor performance by 1D tank in series material and energy balances and considering TBR hydrodynamics.

1.3.2 Scope of Study

This research is an attempt to study the kinetic modeling and effect of operating condition and catalyst behavior towards reactor performance. In this work, the modeling is focused in three aspects:

1) To obtain a reactor model by mass and heat balances.
2) To find the expression for physicochemical properties
3) Investigate the influence of severe process condition (Temperature, LHSV, H_2/CH ratio) on decreasing sulfur content in products.

CHAPTER 2
LITERATURE REVIEW

Hydrodesulphurization (HDS), is a key process in every major refinery, it occurs in a hydrotreating reactor in which not only the elimination of sulfur is obtained, but the cracking of large organic molecules, and the hydrogenation of olefins and aromatics as well. Compounds with a low boiling point, are easier to desulfurize than compounds with higher boiling points. Generally, it is easy to remove sulfur from paraffins and more difficult to remove sulfur from naphthenes followed by aromatics [1].

In the petroleum refining industry, hydrodesulphurization process is commonly accomplished in trickle bed reactor. In this mode, gas and liquid flow concurrently downward through packed beds to undergo chemical reactions [2-4]. Concurrent downward operation mode is the most used in practice because it has less severe limitations in throughput than concurrent up-flow and countercurrent operations [5]. The reactions occur between the dissolved gas reactant and the liquid phase reactant at the surface of the catalyst. Some of sulfur atoms attached to the hydrocarbon molecules react with hydrogen on the surface of catalyst to form hydrogen sulfide (H_2S). The catalyst used is normally mixed metal sulfides of molybdenum promoted by cobalt or nickel supported on a high surface area γ-alumina [6]. The operating conditions of treatment are a function of type of feed and desulfurization levels desired in treated product. All hydrodesulphurization reactions are irreversible and exothermic in nature [7, 8]. The reactions can be representing as:

$$N.S + H_2 = N + H_2S$$

It has been recognized that achievement of reduced sulfur in fuels has be done through understanding on behavior on HDS process such as catalyst formulation, reactor design, feed selection effect of operating condition, etc. In recent years, many works devoted to the numerous aspects of behaviour in trickle bed reactors, such as hydrodynamics, chemical kinetics, mass and heat transfer have been published. Macias and Ancheyta [9] have developed an isothermal reactor model of straight-run gas oil. The process is considered isothermal due to less sulfur content in lighter gas oils consequent little in temperature changes. Simulation results shown feed properties and process conditions are the most relevant parameters that play an important role in determining the performance of reactor. Murali et al. [10] have developed trickle bed reactor model for hydrodesulphurization reactions by taken diesel as a case study. Feed vaporization is taken into account to simulate catalyst bed temperature accurately. Going through the catalyst bed, the temperature of the reaction mixture rises due to exothermic reaction of hydrodesulphurization processes. Besides that, the simulation results highlighted the effect of process variables on the sulfur removal. Simulation result shown the percentages of feeds get vaporized was higher as the ratio of hydrogen gas to oil increased. Moreover, Jimenez et al. [11] developed a model for hydrodesulphurization of the vacuum gas oil in a trickle bed reactor, accounting inhibition effects. The sulfur and nitrogen conversion are improved at high temperature and pressure while lower LHSV.

Particle size plays an important role in HDS reaction. Extrudate particles are the preferred catalyst shape for HDS process. Small catalyst particles ranging in 1.3-3.0 mm diameter have demonstrated that pore diffusion limitation plays an important role in commercial application. However, the use of smaller particles is impracticable because of the strong increase of the pressure drop in the catalyst bed. With non-cylindrical extrudate particles relatively low pressure drop might be achieved since they have a high external area to volume ratio. Moreover, they exhibit better diffusion performance. On the other hand, large particles often have low activity and cause low pressure drop. Therefore, a good selection of particle size and shape has to be made depending on the type of feedstock and operating conditions in order to optimize catalyst behavior [9, 12]. Various experimental and theoretical studies of the effect of shape, size and loading on catalyst behavior have been reported in the literature. Pressure drop limitation, catalyst pore size and catalyst loading all affect the selection of catalyst shape used in HDS reactor.

There are many papers focused on the hydrodesulphurization technology, catalysts and reactor performance. A few mathematical models to describe the performance of hydrodesulphurization reactors are available. The available information on reactor models is reviewed and an attempt is made to develop a simple model to describe the hydrodesulphurization process in a trickle bed reactor which can be useful for optimizing the process conditions and decision making. The main objective of the present study is to develop a plug flow heterogeneous 1D model of trickle bed reactor for simulating the performance of hydrodesulphurization unit. 1D model is applied in the reaction system to predict the temperature profiles and the change of species concentration along the reactor axis. Kinetic parameters from literature are used for simulating the hydrodesulphurization reactor performance by material and energy balances and considering TBR hydrodynamics.

2.1 Naphtha and its Composition

Naptha has its origins in decayed living matter, most likely as the result of the action of bacteria upon dead animal and plant material. Naptha, like petroleum, is a mixture of many organic substances. The most common substances are summarized in the Table 2.1.

The table just below lists some fairly typical virgin heavy naphthas, available for catalytic reforming, derived from various crude oils. It can be seen that they differ significantly in their content of paraffins, naphthenes and aromatics:

Typical Heavy Naphthas				
Crude oil name ⇒ **Location ⇒**	**Barrow Island** **Australia**	**Mutineer-Exeter** **Australia**	**CPC Blend** **Kazakhstan**	**Draugen** **North Sea**
Initial boiling point, °C	149	140	149	150
Final boiling point, °C	204	190	204	180
Paraffins, liquid volume %	46	62	57	38
Naphthenes, liquid volume %	42	32	27	45
Aromatics, liquid volume %	12	6	16	17

Table 2.1: Typical Heavy Naphthas

Taken from: http://en.citizendium.org/wiki/Naphtha

2.2 Hydrotreating of Hydrogen Sulfide (H_2S)

.Hydrotreating is a process in petroleum refining used to remove about 90% sulfur from liquid petroleum fractions. These contaminants, if not removed from the petroleum fractions as they travel through the refinery processing units, can have detrimental effects on the equipment, the catalysts, and the quality of the finished product.

The HDT process involves removal sulfur from the complex petroleum mixture through hydrogenation. The organo-sulfur compounds loose sulfur on hydrogenation. Sulphur is released in the form of hydrogen sulfide. The reaction is carried out under the moderate pressure in a trickle bed reactor.

Being the three phase catalytic reactor the heart of an HDT unit, this equipment is then the target for modeling purposes. In HDT reactors gas and liquid phases (hydrogen and hydrocarbon) are contacted with a solid phase (catalyst). The reaction occurs between the dissolved gas reactant and the liquid phase reactant at the surface of the catalyst.

Depending on whether the main mass transfer resistance is located, three phase catalytic are operated either with the continuous gas and distributed liquid phase (trickle operation), or with distributed gas and a continuous liquid phase (bubble operation). Commercial HDT processes usually operate in a trickle bed regime, with concurrent downward flow of gas and liquid over a randomly fixed bed of catalyst particles while reactions take place [8].

2.3 Description of three phase reactors

Multiphase catalytic packed-bed reactor (PBR) are operated either with continuous gas and a distributed liquid phase (trickle operation), when the main mass transfer resistance is located in the gas phase or with a distributed gas and a continuous liquid phase (bubble operation) [14], when the main mass transfer resistance is located in the liquid phase, the modes of operation generally used in three phase are: trickle or packed bed reactor (Figure 2.3.1).

According to the reactor design, gas and liquid move cocurrently downflow or gas is fed countercurrently upflow. In the most applied commercial reactor configuration cocurrent downflow, the liquid phase flow mainly through the catalyst particles in the form of films, rivulets and droplets as shown schematically in figure 2.3.2 [15].

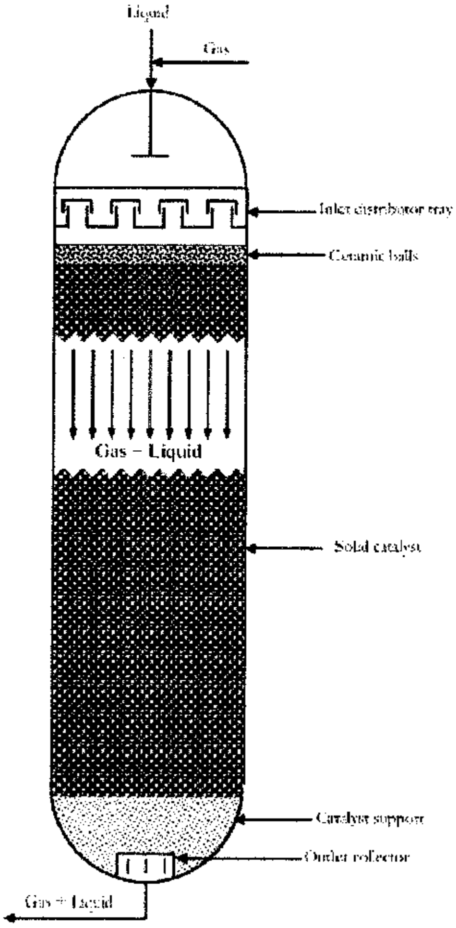


Figure 2.3.1: Trickle bed reactor

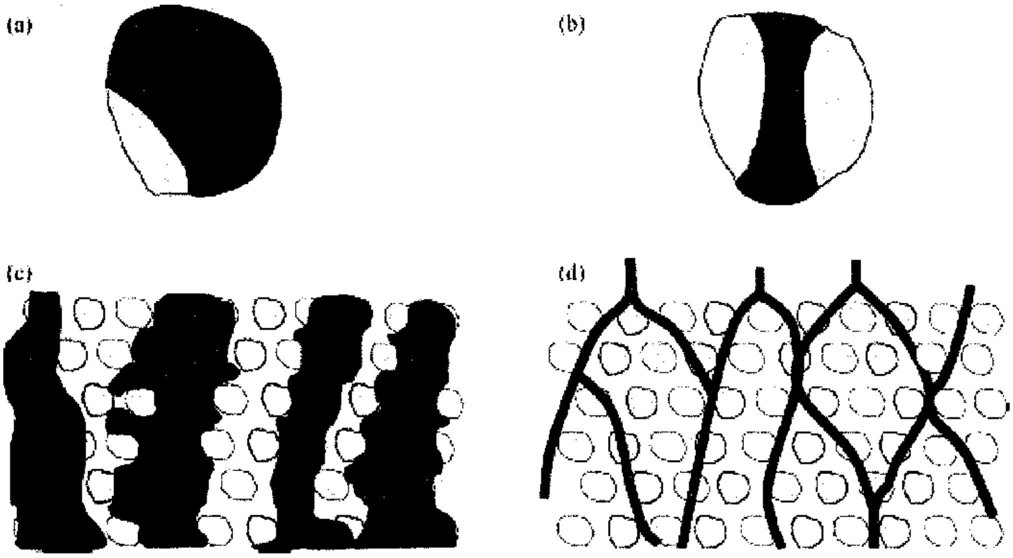


Figure 2.3.2: Schematic representation of liquid flow textures encountered during trickle flow regime in TBR: (a) particle scale film flow, (b) particle scale rivulet flow, (c) bed scale film flow, (d) bed scale rivulet flow.

In the case of catalytic packed beds with two phase flow; for straight run naptha hydrodesulphurization (HDS), from a reaction engineering perspective, large catalyst to liquid volume ratio and plug flow of both phases are preferred, and catalyst deactivation is very slow or negligible, which facilitate reactor modeling.

2.4 Conventional trickle bed reactors with cocurrent gas-liquid downflow

In a TBR, the catalyst bed is fixed (figure 1), the flow pattern is much closer to plug flow, and the ratio of liquid to solid catalyst is small. A TBR consists of a column that may be very high (above 10-30m), that is equipped with one or several fixed beds of solid catalyst, throughout which gas and liquid move cocurrent downflow.

Figure 2.4.1 shows the typical film flow texture found during trickle flow regime in TBR [15]. In this mode, gas is the continuous phase and liquid holdup is lower. This operation is the most often used in practice, since there are less severe limitations in throughput than in countercurrent operation [14].

For gas limited reactions (high liquid reactant flux to the catalyst particle, low gas reactant flux to the particles), especially at partially wetted conditions. Thus, a downflow reactor is preferred as it facilitates the transport of the gaseous reactant to the catalyst [12].

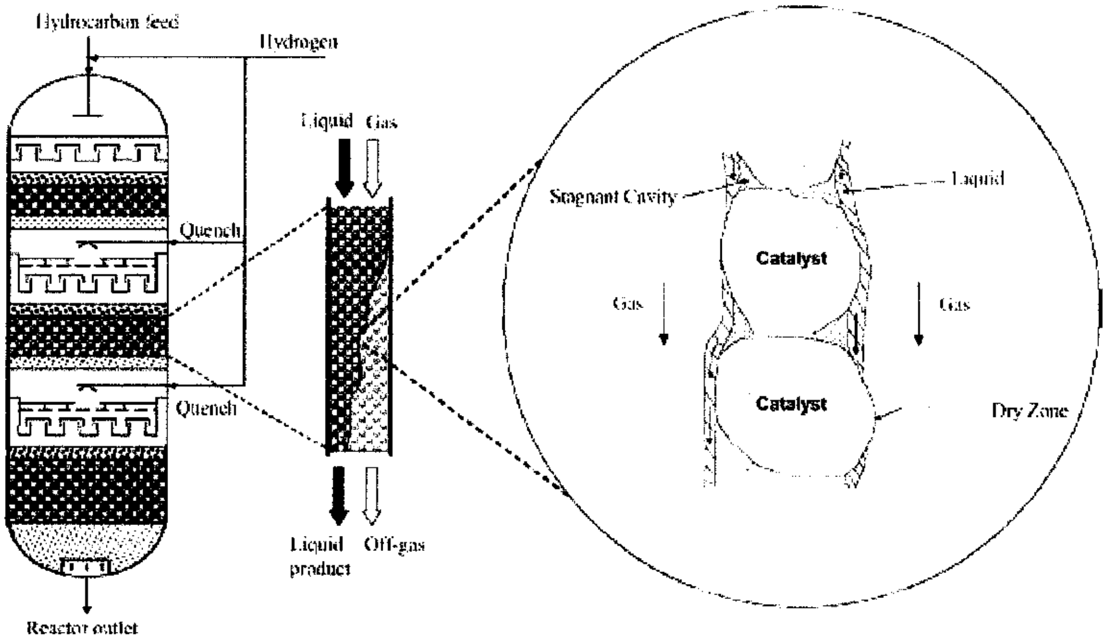


Figure 2.4.1: Typical trickle flow regime (film flow texture)

2.5 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. A simple way of visualizing adsorption is in terms of additional valence bonds at the surface, which are available for bonding. 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.

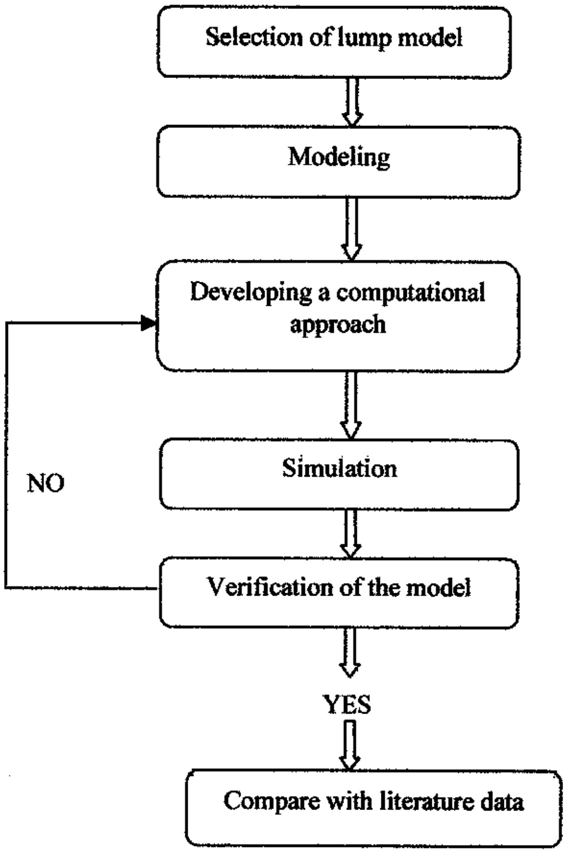
Adsorption is to be distinguished from absorption, a process in which atoms or molecules move into the bulk of a porous material, such as the absorption of water by a sponge. Sorption is more general term that includes both adsorption and absorption. Desorption refers to the reverse of adsorption and 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.

CHAPTER 3

METHODOLOGY

The aims of this work to study and make the modeling of an industrial reactor for hydrodesulphurization process. General methodology adopted in this research is divided in two stages:

1) Develop new mathematical modeling of hydrodesulphurization reactor
    - Selection of appropriate lumping model
    - Use reaction kinetic equation
    - Specious mass conservative
    - Energy equations
    - Data collection
2) Simulation of model equation using Excel programming
    - Apply the plant data into this model and compare the result achieve with the plant result



3.1 Construction of mass balance & enthalpy equations

Reactor model is one dimensional heterogeneous which included gas, liquid and solid phase. The reactions occurred in the liquid phase in contact with the catalyst surface, this means that the reaction occurred between dissolved hydrogen in the liquid phase and the other reactants in the feed. Below is the cross section of the reactor taken; simplified to compartment in order to obtain proper reactor model and balance equation. The model (especially for mass transfer) follows the scheme presented in figure 3. Other than that, the assumptions and model simplifications were made:

1. The reactor operates isothermally; it means that catalyst, liquid and gas are at the same temperature.
2. The liquid volume in the reactor remains constant.
3. The velocity of the liquid and gas remains constant.
4. External mass transfer is negligible.
5. Uniform pellet properties; catalyst wetting is complete and there is no catalyst deactivation.
6. There is no evaporation of the liquid.

The cross sections of the reactor are narrowed to compartment view. In here, the compartments are separated into three phases which is liquid, gas and solid. The solid phases represent the catalyst inside the reactor. The arrows show how the reaction occurs and move to the other phase. The reaction occurs are:

1. Diffusion from gas to liquid phase due to the high solubility and concentration.
2. Diffusion from liquid to solid phase
3. Reaction occurred at the surface of the catalyst
4. Diffusion from solid to liquid phase
5. Diffusion from liquid to gas phase

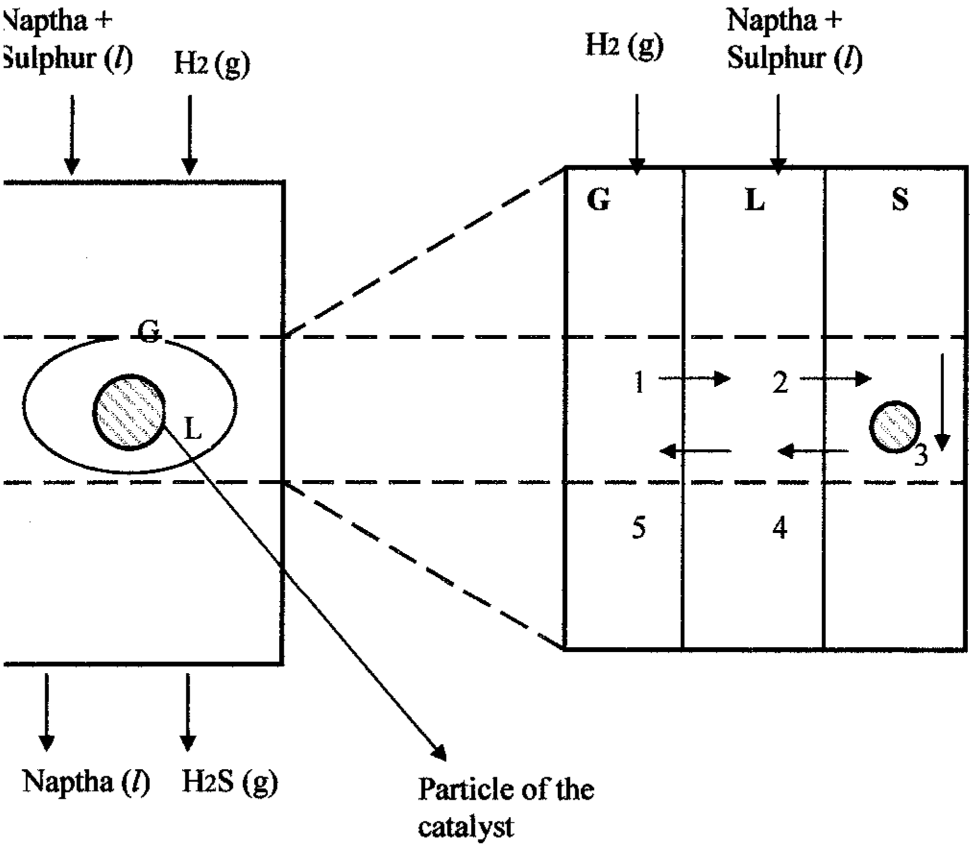


Figure 3.1: cross section of the reactor to compartment view

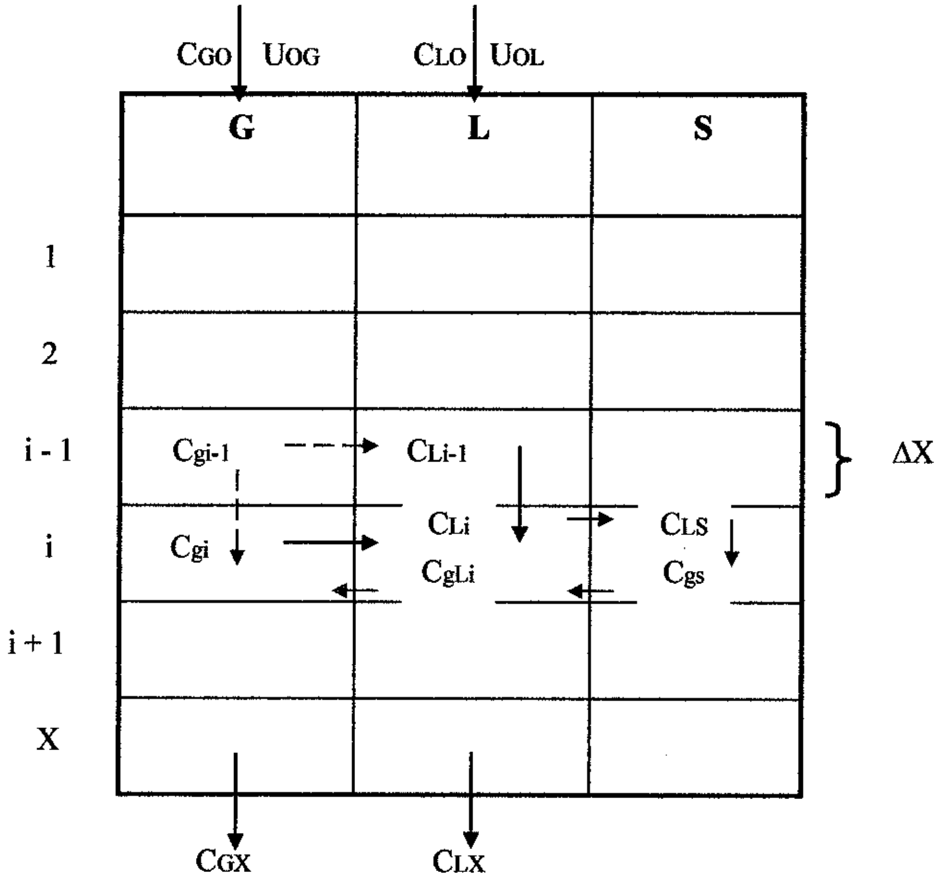


Figure 3.2: Reactor-compartment view

The main balance equations of the model are briefly presented:

H2 (g) + N.S (*l*) → N (*l*) + H2S (g)

3.2 Mass Balance Equations

Gaseous phase

$$\frac{u_g P_{i-1}{}^G}{RT} = \frac{U_g P_i{}^G}{RT} + K_{LG} a_L \left(\frac{P_i{}^G}{H_i} - C_{gi}{}^L\right)\Delta z$$

Liquid phase

$$Naptha: u_L {C_{ai-1}}^L = u_L {C_{ai}}^L + K_{LS_i} a_s ({C_{ai}}^L - {C_{ai}}^S)\Delta z$$

$$Sulfur\ compounds: u_L {C_{bi-1}}^L = u_L {C_{bi}}^L + K_{LS_i} a_s ({C_{bi}}^L - {C_{bi}}^S)\Delta z$$

Solid Catalyst

$$K_{LS_a} a_s ({C_{ai}}^L - {C_{ai}}^S) + K_{LS_b} a_s ({C_{bi}}^L - {C_{bi}}^S) = \rho_B K_r {C_{ai}}^S {C_{bi}}^S \eta f_s$$

3.2 Heats Balance Equations

Liquid phase: $u_L \rho_L C_{P_L} T_{Li-1} = u_L \rho_L C_{P_L} T_{Li} + h_L a_s (T_{Li} - T_{si})\Delta z$

Solid Catalyst: $h_L a_s (T_{Li} - T_{si}) = \rho_B \sum \eta_j r_j (-\Delta H_j)$

$$-\frac{dC_A}{d(1/LHSV)} = k_{ap} C_A^n$$

$$= 6.213 \times 10^{15} e^{-33940/RT} C_A^{2.4}$$

3.4 Characteristic of the catalyst bed

The void fraction can be calculated in the following way. This equation was developed for packed bed of spheres.

$$\varepsilon_B = 0.38 + 0.073 \left[1 + \frac{(D_R/d_{peq} - 2)^2}{(D_R/d_{peq})^2}\right] \qquad \text{------------------------------3.4.1}$$

The bed density can be evaluated from the equation

$$\rho_B = \rho_p (1 - \varepsilon_B) \qquad \text{------------------------------3.4.2}$$

The surface area of the particles per unit volume of the bed was determined with

$$a_t = \frac{6(1-\varepsilon_B)}{d_{peq}} \qquad \text{--3.4.3}$$

Liquid and gas pressure drops can be calculated with Ergun equation

$$\frac{\Delta P_i}{L_B} = \frac{150(1-\varepsilon_B)^2}{\varepsilon_B{}^3}\frac{u_i\mu_i}{d_{peq}{}^2} + \frac{1.75(1-\varepsilon_B)}{\varepsilon_B{}^3}\frac{u_i{}^2\rho_i}{d_{peq}} \qquad \text{--3.4.4}$$

Both liquid and gas phase pressure drops can be correlated in terms of χ parameter. For 0.05< χ<30 values, the following equations are employed to calculate the two phase pressure drop in the reactor.

$$\chi = \left(\frac{\Delta P_L}{\Delta P_G}\right)^{0.5}$$

$$log\frac{\Delta P_{GL}}{\Delta P_G+\Delta P_L} = \frac{0.416}{0.666+(\log\chi)^2} \qquad \text{--3.4.5}$$

For calculating $k_{GL}$and k_{LS} the following generalized correlation was used

$$\frac{K_{GL}a_L}{D_A} = 7\left(\frac{G_L}{\mu_L}\right)^{0.4}\left(\frac{\mu_L}{\rho_L D_A}\right)^{0.5} \qquad \text{--3.4.6}$$

$$\frac{k_{LS}d_{peq}}{D_A} = 0.8\frac{Re_L^{0.5}}{\varepsilon_L}\left(\frac{\mu_L}{\rho_L D_A}\right)^{0.333} \qquad \text{==3.4.7}$$

The liquid holdup (ε_L) was determined with the following equation

$$\varepsilon_L = 0.185\varepsilon_B a_t{}^{0.333}\chi^{0.22} \qquad \text{--3.4.8}$$

Liquid Reynolds number was evaluated with

$$Re_L = \frac{d_{peq}G_L}{\mu_L} \qquad \text{--3.4.9}$$

The molecular diffusivity of solute A in the liquid is

$D_A = 8.93 \times 10^{-8} \frac{v_L^{0.267} T}{v_A^{0.433} \mu_L}$ --3.4.10

Where v_L and $v_A$are molar volumes of solute and liquid solvent respectively.

The effectiveness factor (η)in commercial hydrodesulfurization catalysts has been reported to be in the range of 0.4-0.6.These low η values give ϕ>1 which may be considered to be within strong internal diffusional limitations. This assumption will be demonstrated with further calculations of Thiele modulus. In such a case η becomes proportional to $1/\emptyset$.

Density of oil

$\rho_L(P,T) = \rho_0 + \Delta\rho_p - \Delta\rho_T$

$$\Delta\rho_p = [0.167 + 16.181 \times 10^{-0.0425\rho_0}]\left[\frac{P}{1000}\right] - 0.01[0.299 + 263 \times 10^{-0.0603\rho_0}] \times \left[\frac{P}{1000}\right]^2$$

$$\Delta\rho_T = \left[0.0133 + 154.2\left(\rho_0 + \Delta\rho_p\right)^{-2.45}\right][T - 520] - \left[8.1 \times 10^{-6} - 0.0622 \times 10^{-0.764(\rho_0 + \Delta\rho_p)}\right][T - 520]^2$$

(18)

Dynamic liquid viscosity

$\mu_L = 3.141 \times 10^{10}(T - 460)^{-3.444}[log_{10}(API)]^a$

$a = 10.313[log_{10}(T - 460)] - 36.447$

Gas properties: $\mu_g = 26.693 \times 10^{-6} \frac{(PM\,T)^{0.5}}{\sigma}$

CHAPTER 4

RESULTS AND DISCUSSION

4.1Hydrodesulfurization basis parameter

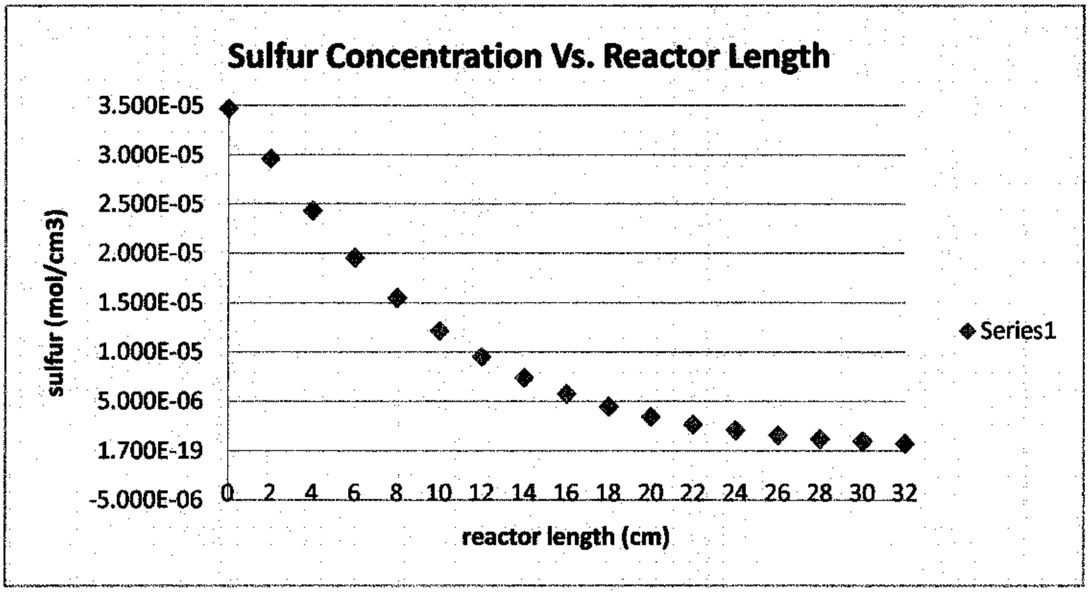


Figure 4.1.1: Sulfur concentration versus reactor length

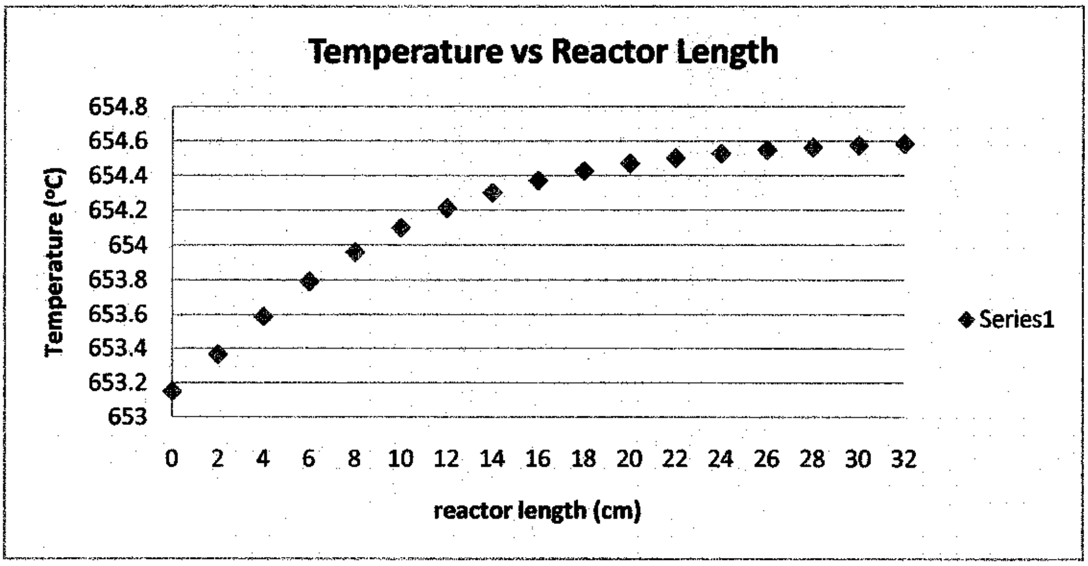


Figure 4.1.2: Temperature profile versus reactor length

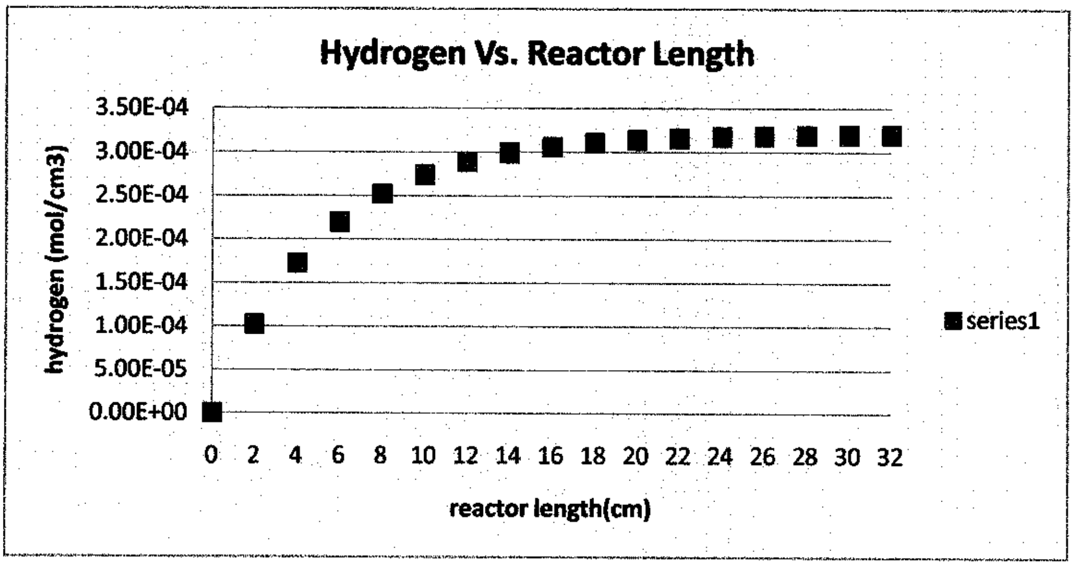


Figure 4.1.3: Hydrogen concentration versus reactor length

The discussion will cover on the very basis part where all the main parameters such as temperature, concentration of hydrogen and sulfur were investigated, in order to prove that the modeling is really works. After that, it will cover where this modeling can be optimize using others parameter in section 4.2.

Figure 4.1.1 presents the steady state liquid molar concentration profiles of sulfur along the catalytic bed with concurrent downward flow of gas and liquid. Due to high reaction rate in the initial part of the catalyst bed, sulfur concentration decreased rapidly.

Figure 4.1.2 shows the dynamic temperature profiles at the exit of the reactor. Since the cocurrent operation gave the highest sulfur conversion as was described previously. Therefore, the highest liquid temperature at the exit of reactor would be also expected. This is because the reaction involves is a exothermic reaction.

Figure 4.1.3 shows that for cocurrent operation, the concentration of hydrogen in the liquid phase slightly decreases at the beginning of the reactor until certain point because of the high reaction rates in this zone, and then it starts to increase by the large mass transfer of hydrogen to the liquid phase.

4.2 Hydrodesulphurization optimize parameter

Mathematical models for trickle bed catalytic reactor can be very complex due to many micro and macro effects occurring inside the reactor: flow patterns of both phases, size and shape of a catalyst particle, wetting of the pores of a catalyst with the liquid phase, pressure drop and of course kinetic effect on the catalyst surface.

A series of simulation was carried out under different space velocity (1.0, 4.0, 6.0 $m^3m^{-3}h^{-1}$), H_2/CH ratio (0.118, 0.354, 0.590 Nm^3/kg), pressure (40bar), and temperature of 300^{O}C [13]. Each different condition was analyzed for sulfur content and discussed how it will effect to reduce it more.

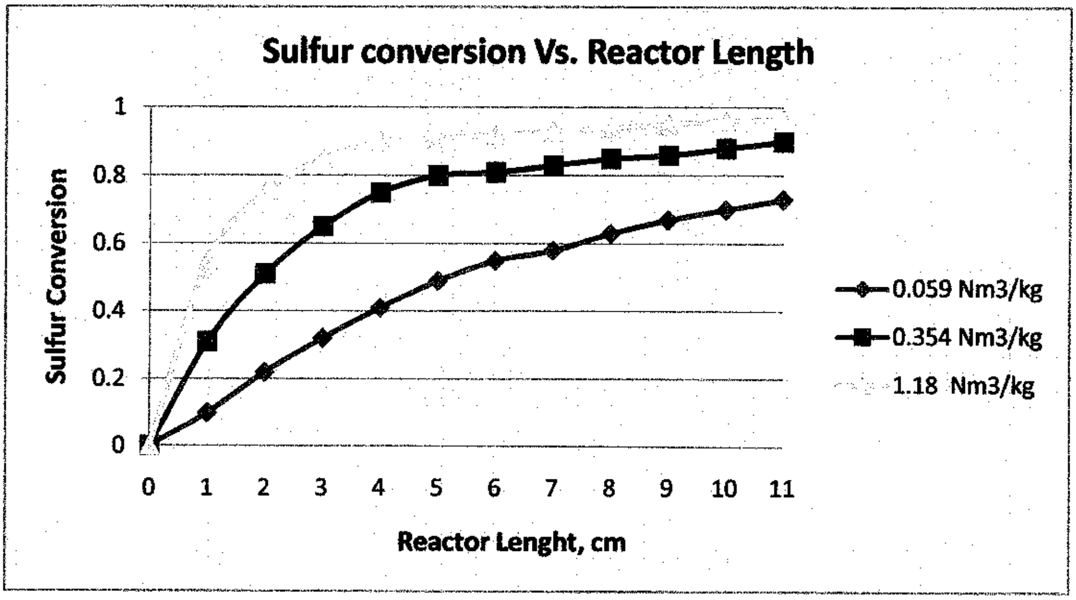


Figure 4.2.1: Simulation of the reactor by changing H2/CH ratio. Conversion against the reactor length (LHSV=1 $m^3m^{-3}h^{-1}$, T=300 ^{O}C, P=40 bar)

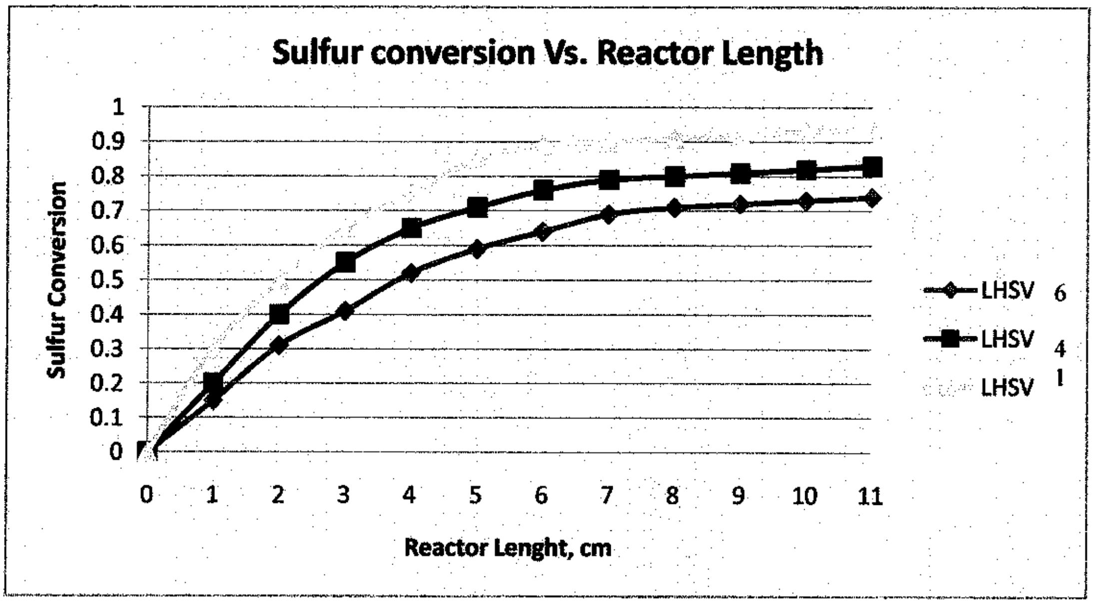


Figure 4.2.1: Simulation of the reactor by changing LHSV. Conversion against the reactor length (H_2/CH ratio= 0.118 Nm^3/kg, T=300 ^OC, P=40 bar)

Simulation was performed by changing process parameters (the ratio H2/CH and LHSV) and keeping other parameters constant. The influence of these parameters on decrease of sulfur content was investigated.

Figure 4.2.1, the result obtained by changing the ratio of H_2/CH, which are (0.118, 0.354 and 0.590 Nm^3/kg). The value for CH is constant and the only value that varies in this simulation is the hydrogen amount. By increasing the hydrogen amount, the rate of reaction will increase rapidly due to mass transfer since more hydrogen will dissolved to the liquid phase (naptha) and thus promotes the reaction at the surface of the catalyst. In here, more hydrogen sulfide produced and as expected slightly smaller sulfur content was recorded in the exit stream of the reactor as the H_2/CH increased.

Figure 4.2.2, the result obtained by changing the LHSV were in agreement with the role of the pronounce residence time in the reactor. The smaller the LHSV, the greater contact time both of the naptha and hydrogen can dissolve and react at the surface of the catalyst to form hydrogen sulfide while at the same time produced treated naphta.

However the residence time tells us how long the gas-fluid elements have been in the reactor, but it does not tell anything about the exchange of matter between the fluid elements. Still, through the observation made; the smaller LHSV the better desulfurization.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

For this project, technical details of the existing researches project on hydrodesulphurization were collected by carrying out an intensive web search, reports and journal reference. As to date, the modelling equation is found to be successful apart of some difficulties on understand and find the right parameter.

A steady state model for a trickle bed catalytic reactor was developed to model hydrodesulphurization of crude naptha containing considerable amount of sulphur compounds. The kinetic parameters were estimated on the basis of journal pilot plant and from here; the simulation revealed that increase of H_2/CH as well as decrease of LHSV had positive effect on the removal of sulphur compound from the crude naphta.

From the literature, the expected results shown in the following:

1. Bed temperature rises as reactant going downward along the reactor due to exothermic reaction of hydrodesulphurization.
2. As the reactor length was increased, the concentration of sulphur decreased.
3. The concentration of hydrogen decreased due to the mass transfer occurs; gas phase of hydrogen dissolved to the liquid phase of naphta before it reacts at the catalytic surface.
4. High H2/CH ratio, while low LHSV improve the sulphur conversion.

CHAPTER 6

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APPENDIXES

$$\frac{2.54)^{2}}{4} \quad = 5.067\ cm^{2}$$

$$= 5.067 \times 10^{-4}\ m^{2}$$

umetric flowrate

$lo_{L} = 1.75 \times 10^{-2}\ cm/s$

$$1.75 \times 10^{-2}\ \frac{cm}{s} \times 5.067\ cm^{2}$$

$$= 0.08867\ \frac{cm^{3}}{s}$$

$$= 8.86725 \times 10^{-8}\ \frac{m^{3}}{s}$$

nsity of oil : 22 API

$$S_g = \frac{141.5}{131.5 + API} = \frac{141.5}{131.5 + 22}$$

$$= 0.922$$

$$\therefore\ \rho_o = 922\ kg/m^{3}$$

$$= \frac{922\ kg}{m^{3}} \left| \frac{1\ lb_m}{0.45359\ kg} \right| \frac{0.028317\ m^{3}}{1\ ft^{3}} = 57.559\ \frac{lb_m}{ft^{3}}$$

$$P = \frac{5.3\ mPa}{} \left| \frac{14.696\ psia}{1.01325 \times 10^{5}\ Pa} \right. = 768.703\ psia$$

$T_L = 380°C$

$$({}^{\circ}R) = (380 \times 1.8) + 32 + 459.67 = 1175.67\ {}^{\circ}R.$$

$$: \left[0.167 + (16.181 \times 10^{-0.0425\rho_o})\right]\left(\frac{P}{1000}\right) - 0.01\left[0.299 + (263 \times 10^{-0.0603\rho_o})\right]\left(\frac{P}{1000}\right)^{2}$$

$$0.167 + (16.181 \times 10^{-0.0425(57.559)})\Big]\left(\frac{768.703}{1000}\right) - 0.01\left[0.299 + (263 \times 10^{-0.0603(57.559)}\right]\left(\frac{768.70}{1000}\right.$$

$$0.1729 - 2.292 \times 10^{-3}$$

$$0.1706\ lb/ft^{3}$$

$0.0133 + 152.4(\rho_0 + \Delta\rho_p)^{-}](T_L - 520) - [8.1\times10^{-6} - 0.0622\times10^{-0.764(\rho_0+\Delta\rho_p)}](T_L - 520)^2$

$133 + 152.4(57.559 + 0.1706)^{-2.45}](1175.67 - 520) - [8.1\times10^{-6} - 0.0622\times10^{-0.764(57.559+0.1706)}](117$

$3.5537 - 3.4822$

$0.0715\ lb/ft^3$

$+ \Delta\rho_p - \Delta\rho_T$

$7.559 + 0.1706 - 10.0715$

$7.6581\ lb/ft^3$

$\frac{7.6581\ lb}{ft^3} \Big| \frac{0.45359\ kg}{lb} \Big| \frac{ft^3}{0.028317\ m^3} = 763.401\ kg/m^3$

lass flowrate

$86725\times10^{-8}\ \frac{m^3}{s} \times 763.401\ \frac{kg}{m^3} = 6.769\times10^{-5}\ kg/s$

for sulfur

$\frac{109}{\;0} \times 6.769\times10^{-5}\ \frac{kg}{s} = 1.3599\times10^{-6}\ \frac{kg}{s}$

$= 1.3599\times10^{-3}\ g/s$

ntration of $S = \frac{1.3599\times10^{-3}\ g}{s} \Big| \frac{mol}{441.9\ g} \Big| \frac{s}{0.08867\ cm^3}$

$= 3.471\times10^{-5}\ \frac{mol}{cm^3}$

$= 34.71\ \frac{mol}{m^3}$

[illegible] $T(^\circ C)$, $\rho_{20}\,(g/cm^3)$

$= \frac{9226}{m^3} = 0.922\,\frac{g}{cm^3}$

380°C

$559729 - 0.42947\times10^{-3}T_L + 3.07539\times10^{-3}\left(\frac{T_L}{\rho_{20}}\right) + 1.94593\times10^{-6}T_L^2 + \frac{0.835783}{\rho_{20}^2}$

$559729 - 0.42947\times10^{-3}(380) + 3.07539\times10^{-3}\left(\frac{380}{0.922}\right) + 1.94593\times10^{-6}(380)^2 + \frac{0.83578}{0.922^2}$

088 Nl H_2/MPa kg oil

$$= \frac{22.4L}{mol}\left|\frac{MPa\,kg}{1.8088\,L}\right|\frac{m^3}{763.401\,kg} = 1.622\times10^4\,Pa\,m^3/mol$$

$$= 1.622\times10^{10}\,Pa\,cm^3/mol$$

$3.141\times10^{10}(T-460)^{-3.444}(\log API)^{a}$, $T = {}^\circ R$

$= 10.313\log(T-460) - 36.447$

$= 10.313\log(1175.67-460) - 36.447$

$= 7.006$

$3.141\times10^{10}(1175.67-460)^{-3.444}(\log 22)^{-7.006}$

$\boxed{0.55809\,mPa\,s}$

ity

$7.5214\times10^{-3}\,T_{meABP}^{0.2896}\,d_{15.6}^{-0.7666}$

$.5214\times10^{-3}(1548.47)^{0.2896}(0.922)^{-0.7666}$

$0.06453\,ft^3/lb_m$

$$\frac{0.06453\,ft^3}{lb_m}\left|\frac{441.9\,g}{mol}\right|\frac{1\,lb_m}{453.59\,g}\left|\frac{45968.5\,cm^3}{1\,ft^3}\right. = 2889.74\,\frac{cm^3}{mol}$$

$85(2889.74)^{1.048}$

[illegible]

ity of H_2 Nl H_2 / MPa kg oil [illegible]

$= 922 \frac{kg}{m^3} = 0.922 \frac{g}{cm^3}$

<u>380°C</u>

$559729 - 0.42947 \times 10^{-3} T_L + 3.07539 \times 10^{-3} \left(\frac{T_L}{\rho_{20}}\right) + 1.94593 \times 10^{-6} T_L^2 + \frac{0.835783}{\rho_{20}^2}$

$559729 - 0.42947 \times 10^{-3}(380) + 3.07539 \times 10^{-3} \left(\frac{380}{0.922}\right) + 1.94593 \times 10^{-6}(380)^2 + \frac{0.83578}{0.922^2}$

088 Nl H_2 / MPa kg oil

$= \frac{22.4L}{mol} \left| \frac{MPa\ kg}{1.8088\ L} \right| \frac{m^3}{763.401\ kg} = 1.622 \times 10^4\ Pa\,m^3/mol$

$= 1.622 \times 10^{10}\ Pa\,cm^3/mol$

$3.141 \times 10^{10} (T - 460)^{-3.444} (\log API)^{a}$, T = °R

$= 10.313 \log(T - 460) - 36.447$

$= 10.313 \log(1175.67 - 460) - 36.447$

-7.006

$3.141 \times 10^{10} (1175.67 - 460)^{-3.444} (\log 22)^{-7.006}$

$\boxed{0.55809\ mPa\,s}$

<u>ity</u>

$7.5214 \times 10^{-3}\ T_{meABP}^{0.2896}\ d_{15.6}^{-0.7666}$

$7.5214 \times 10^{-3} (1348.47)^{0.2896} (0.922)^{-0.7666}$

$0.06453\ ft^3/lb_m$

$\frac{0.06453\ ft^3}{lb_m} \left| \frac{441.9\ g}{mol} \right| \frac{1\ lb_m}{453.59\ g} \left| \frac{45968.5\ cm^3}{1\ ft^3} \right. = 2889.74 \frac{cm^3}{mol}$

$85(2889.74)^{1.048}$

[illegible] cm^3/mol

$\text{₂)} = -252.87°C = 36.504°R$

$\text{1atm)} = 0.08988\ g/L$

$\text{°C, atm)} = 0.08988 \times 273.15 \div 288.75 = 0.085024\ g/L$

$5214 \times 10^{-3} (36.504)^{0.2896} (8.5024 \times 10^{-5})^{-0.7666}$

$8.1298\ ft^3/lb_m$

$$\frac{8.1298\ ft^3}{lb_m} \left| \frac{2\ g}{mol} \right| \frac{1\ lb_m}{453.59\ g} \left| \frac{45968.5\ cm^3}{1\ ft^3} \right. = 5701.56\ cm^3/mol$$

$285 (5701.56)^{1.048}$

$61.08\ cm^3/mol$

for H_2 D_i

$$8.93 \times 10^{-8} \left(\frac{v_L^{0.267}}{v_i^{0.433}} \right) \left(\frac{T_L}{\mu_L} \right)$$

$$8.93 \times 10^{-8} \left(\frac{1507.327^{0.267}}{2461.08^{0.433}} \right) \left(\frac{653.15}{0.58809} \right)$$

$2434 \times 10^{-5}\ cm^2/s$

$2434 \times 10^{-9}\ m^2/s$

Schmidt num

$$\frac{k_L}{} = 7 \left(\frac{G_L}{\mu_L} \right)^{0.4} \left(\frac{\mu_L}{\rho_L D_i^{L}} \right)^{0.5}$$

$$= 7 \left[\frac{0.7634\ g/cm^3 \times 1.75 \times 10^{-2}\ cm/s}{0.58809 \times 10^{-2}\ g/cm.s} \right]^{0.4} \left[\frac{0.58809 \times 10^{-2}\ g/cm.s}{0.7634\ g/cm^3 \times 2.2434 \times 10^{-5}\ cm^2/s} \right] \times 2.2434 \times 10^{-5}\ cm^2/s$$

$$= 7 (1.3885)(18.531)(2.2434 \times 10^{-5})$$

$$= 4.0406 \times 10^{-3}\ \frac{cm}{s}$$

Balance

K_{LG} [illegible]

$$= \frac{U_G P_i^G}{RT} + K_{LG} a_L \left(\frac{P_i^G}{H_i} - C_{gi}^L \right) \Delta z$$

$$= P_i^G \left[\frac{U_G}{RT} + \frac{K_{LG} a_L \Delta z}{H_i} \right] - K_{LG} a_L C_{gi}^L \Delta z$$

$$= \frac{\frac{U_G P_{i-1}^G}{RT} + K_{LG} a_L C_{gi}^L \Delta z}{\frac{U_G}{RT} + \frac{K_{LG} a_L \Delta z}{H_i}}$$

$$\frac{\frac{0.28\ \text{cm/s} \times 5.3\times10^6\ \text{Pa}}{8.314\times10^6\ \frac{\text{Pa cm}^3}{\text{mol.K}} \times 653.15\ \text{K}} + 4.0406\times10^{-3}\ \text{s}^{-1}\left(1.0256\times10^{-4}\ \frac{\text{mol}}{\text{cm}^3}\right) 2\ \text{cm}}{\frac{0.28\ \frac{\text{cm}}{\text{s}}}{8.314\times10^6\ \frac{\text{Pa cm}^3}{\text{mol.K}} \times 653.15\text{K}} + \frac{4.0406\times10^{-3}\ \text{s}^{-1}\ (2\text{cm})}{1.622\times10^{10}\ \text{Pa cm}^3/\text{mol}}}$$

$$= 5.265 \times 10^6\ \text{Pa}$$

$$0.38 + 0.073 \left[1 + \frac{(D_R/d_{peq} - 2)^2}{(D_R/d_{peq})^2} \right]$$

$$.38 + 0.073 \left[1 + \frac{\left(\frac{0.0254}{0.00254} - 2 \right)^2}{\left(\frac{0.0254}{0.00254} \right)^2} \right]$$

$$38 + 0.073 \left[1 + \frac{64}{100} \right]$$

49972

$$= \frac{6(1-\varepsilon_B)}{d_{peq}}$$

$$= \frac{6(1-0.49972)}{0.00254}$$

$$= 1181.764\ m^2/m^3$$

Balance for liquid phase

$$C_{ai-1}^{L} = U_L C_{ai}^{L} - K_{LG} a_L \left(\frac{P_i}{H_i} - C_{ai}^{L} \right) \Delta z + K_{LS} a_S \left(C_{ai}^{L} - C_{ai}^{S} \right) \Delta z$$

Concentration in liq phase (C_{ai}^{L}) and at the solid surface (C_{ai}^{S}) are close

$$U_L C_{ai-1}^{L} = U_L C_{ai}^{L} - K_{LG} a_L \left(\frac{P_i}{H_i} - C_{ai}^{L} \right) \Delta z$$

$$= C_{ai}^{L} \left[U_L + K_{LG} a_L \Delta z \right] - K_{LG} a_L \frac{P_i}{H_i} \Delta z$$

$$C_{ai}^{L} = \frac{U_L C_{ai-1}^{L} + K_{LG} a_L \frac{P_i}{H_i} \Delta z}{U_L + K_{LG} a_L \Delta z}$$

$$\frac{1.75 \times 10^{-2} \frac{cm}{s} \times 0 + 6.97 \times 10^{-3} \frac{(5.251 \times 10^{6}\ Pa)}{1.622 \times 10^{10}\ Pa \frac{cm^3}{mol}} \times 2\ cm}{1.75 \times 10^{-2} \frac{cm}{s} + 6.97 \times 10^{-3} s^{-1} (2\ cm)}$$

$$= 1.021 \times 10^{-4} \frac{mol}{cm^3}$$

$$^{L} = \frac{U_L C_{ai-1}^{-} + K_{LG} a_L \frac{P_i^{-}}{H_i} \Delta z}{U_L + K_{LG} a_L \Delta z}$$

$$= \frac{U_L C_{ai-1}^{L} + \frac{K_{LG} a_L \Delta z}{H_i} \left[\frac{\frac{U_G P_{i-1}^{G}}{RT} + K_{LG} a_L C_{ai}^{L} \Delta z}{\frac{U_G}{RT} + \frac{K_{LG} a_L \Delta z}{H_i}} \right]}{U_L + K_{LG} a_L \Delta z}$$

$$= \frac{U_L C_{ai-1}^{L} + \frac{K_{LG} a_L \Delta z}{H_i} \left[\frac{\frac{U_G P_{i-1}^{G} + K_{LG} a_L C_{ai}^{L} \Delta z RT}{RT}}{\frac{U_G H_i + K_{LG} a_L \Delta z RT}{RT H_i}} \right]}{U_L + K_{LG} a_L \Delta z}$$

$$\frac{C_{ai-1}^{L} + \frac{K_{LG} a_L \Delta z}{\cancel{H_i}} \left[\frac{U_G P_{i-1}^{G} + K_{LG} a_L C_{ai}^{L} \Delta z RT}{\cancel{RT}} \times \frac{\cancel{RT} \cancel{H_i}}{U_G H_i + K_{LG} a_L \Delta z RT} \right]}{U_L + K_{LG} a_L \Delta z}$$

$$\frac{C_{ai-1}^{L} + \frac{K_{LG} a_L \Delta z U_G P_{i-1}^{G} + (K_{LG} a_L \Delta z)^2 C_{ai}^{L} RT}{U_G H_i + K_{LG} a_L \Delta z RT}}{U_L + K_{LG} a_L \Delta z}$$

$$U_L + K_{LG} a_L \Delta z) - \frac{(K_{LG} a_L \Delta z)^2 C_{ai} RT}{U_G H_i + K_{LG} a_L \Delta z \cancel{RT}} = U_L C_{ai-1}^{L} + \frac{K_{LG} a_L \Delta z U_G P_{i-1}^{G}}{U_G H_i + K_{LG} a_L \Delta z RT}$$

$$\left. K_{LG} a_L \Delta z - \frac{(K_{LG} a_L \Delta z)^2 RT}{U_G H_i + K_{LG} a_L \Delta z RT} \right] = U_L C_{ai-1} + \frac{K_{LG} a_L \Delta z U_G P_{i-1}^{G}}{U_G H_i + K_{LG} a_L \Delta z RT}$$

$$\frac{U_L C_{Ai-1} + \dfrac{K_{LG}\, a_L\, \Delta z\, U_G\, P_{i-1}^{G}}{U_G H_i + K_{LG}\, a_L\, \Delta z\, RT}}{U_L + K_{LG}\, a_L\, \Delta z - \dfrac{(K_{LG}\, a_L\, \Delta z)^2 RT}{U_G H_i + K_{LG}\, a_L\, \Delta z\, RT}}$$

$$\frac{5\times10^{-2}\,\frac{cm}{s}\times 0 + \dfrac{4.0406\times10^{-3}\,s^{-1}(2cm)(0.28\,\frac{cm}{s})(5.3\times10^{6}\,Pa)}{0.28\frac{cm}{s}\times 1.622\times10^{10}\,\frac{Pa\,cm^3}{mol} + 4.0406\times10^{-3}\,s^{-1}(2cm)(8.314\times10^{6}\,\frac{Pa\,cm^3}{mol.K}\times 653}}{\times10^{-2} + 4.0406\times10^{-3}\,s^{-1}(2\,cm) - \left[\dfrac{(4.0406\times10^{-3}\times 2)^2\times 8.314\times10^{6}\,\frac{Pa\,cm^3}{mol\,K}\times 653.15K}{0.28\,\frac{cm}{s}\times 1.622\times10^{10}\,\frac{Pa\,cm^3}{mol} + 4.0406\times10^{-3}\,s^{-1}(2\,cm)\,8.314\times10^{6}\times}\right.}$$

$$\frac{0 + \dfrac{11992.5}{4.5855\times10^{9}}}{75\times10^{-2} + 8.0812\times10^{-3} - \left[\dfrac{3.5463\times10^{5}}{4.5855\times10^{9}}\right]}$$

$$\frac{2.61531\times10^{-6}}{0.0255}$$

$$\boxed{1.0256\times10^{-4}\,\frac{mol}{cm^3}}$$

$32.065\ g/mol$ $\rho = 2.067\ g/cm^3$

$444.6°C = 1291.95°R.$

$$7.5214\times10^{-3}(1291.95^{0.2896})(2.067)^{-0.7666}$$

$0.0343\ ft^3/lb$

$0.0343 ft^3$	$32.065 g$	lb_m	$45968.5\ cm^3$
lb	mol	$453.59g$	$1ft^3$

$111.46\ cm^3/mol$

$$0.285(111.46)^{1.048} = 39.831\ mol/cm^3$$

$$8.93\times10^{-8}\left[\frac{1207.327^{0.267}}{39.831^{0.433}}\right]\left(\frac{653.15}{0.58809}\right)$$

$: 1.337\times10^{-4}\ cm^2/s$

$$mPa.s = \frac{kg}{m.s^2}\times s = \frac{1\times10^{-3}\times10^{3}}{10^2}$$

$$= 10^{-2} g/cm.s$$

$$= 1.8\left[\overset{re.num}{\frac{G_L}{a_s\mu_L}}\right]^{0.5}\left[\overset{sc.num}{\frac{\mu_L}{\rho_L D_i^L}}\right]^{1/3}$$

$$= 1.8\left[\frac{0.7634\ g/cm^3\times1.75\times10^{-2}\ cm/s}{11.818\ cm^{-1}\times0.58809\times10^{-2}\ g/cm.s}\right]^{0.5}\left[\frac{0.58809\times10^{-2}\ g/cm.s}{0.7634\ g/cm^3\times1.337\times10^{-4}\ c}\right.$$

$$\times\left[1.337\times10^{-4}\ cm^2/s\times11.818\ cm^{-1}\right]$$

$$= 1.8(0.1922)^{0.5}(57.618)^{1/3}\times1.337\times10^{-4}\times11.818$$

$$= 4.816\times10^{-3}\ cm/s$$

$$= 4.816\times10^{-3}\ cm/s\times11.818\ cm^{-1}$$

Re. num Sc. num

$$\frac{K_{LS}}{D_i^L a_s} = 1.8\left[\frac{G_L}{a_s \mu_L}\right]^{0.5}\left[\frac{\mu_L}{\rho_L D_i^L}\right]^{1/3}$$

$$K_{LS} = 1.8\left[\frac{0.7634\,g/cm^3 \times 1.75\times10^{-2}\,cm/s}{11.818\,cm^{-1} \times 0.58869\,mPa.s \times 10^{-2}}\right]^{0.5}\left[\frac{0.58809\,mPa.s}{0.7634\,g/cm^3 \times 2.6576\times10^{-5}}\right.$$

$$\times 2.6576\times10^{-5}\,\frac{cm^2}{s} \times 11.818\,cm^{-1}$$

$$= 1.8 \times \overset{0.43843}{\cancel{0.043843}} \times \overset{6.618\;\cancel{46.623}}{30.71855} \times 2.6576\times10^{-5} \times 11.818$$

$$= 7.6139\times10^{-4}\,\frac{cm}{s} \qquad 1.64\times10^{-3}$$

r compound

$${}_{i-1}^{L} = U_L C_{bi}^{L} + K_{LS} a_s \left(C_{bi}^{L} - C_{bi}^{S}\right)\Delta z \qquad — ①$$

$${}_s\left(C_{bi}^{L} - C_{bi}^{S}\right) = \rho_B K_r C_{ai}^{0.45} C_{bi}^{S}$$

$$a_s C_{bi}^{L} = C_{bi}^{S}\left[K_r C_{ai}^{0.45}\rho_B + K_{LS} a_s\right]$$

$${}^{S} = \frac{K_{LS} a_s C_{bi}^{L}}{K_r C_{ai}^{0.45}\rho_B + K_{LS} a_s} \qquad — ②$$

$$= K_0 e^{-E/RT}$$

$4.266 \times 10^{9}\ cm^3 g^{-1} s^{-1}$

$131\,993\ J/mol$

$-251\,000\ J/mol$

$4.266\times10^{9}\, e^{-(131993/8.314(653.15))}$

$1.185 \times 10^{-1}\ cm^3 g^{-1} s^{-1}$

itute ② into ①

$$ {}_{i-1}^{\;L} = U_L C_{bi}^{L} + K_{LS}\, a_s \left[C_{bi}^{L} - \frac{K_{LS}\, a_s\, C_{bi}^{L}}{K_r C_{ai}^{0.45} \rho_B + K_{LS}\, a_s} \right] \Delta z $$

$$ = U_L C_{bi}^{L} + K_{LS}\, a_s\, C_{bi}^{L} \left[1 - \frac{K_{LS}\, a_s}{K_r C_{ai}^{0.45} \rho_B + K_{LS}\, a_s} \right] \Delta z $$

$$ = C_{bi}^{L} \left[U_L + K_{LS}\, a_s \left(1 - \frac{K_{LS}\, a_s}{K_r C_{ai}^{0.45} \rho_B + K_{LS}\, a_s} \right) \Delta z \right] $$

$$ = \frac{U_L C_{bi-1}^{L}}{U_L + K_{LS}\, a_s \left[1 - \frac{K_{LS}\, a_s}{K_r C_{ai}^{0.45} \rho_B + K_{LS}\, a_s} \right] \Delta z} $$

$$ \frac{1.75 \times 10^{-2}\ \mathrm{cm/s} \times 3.47 \times 10^{-5}\ \mathrm{mol/cm^3}}{5 \times 10^{-2}\ \frac{\mathrm{cm}}{\mathrm{s}} + 0.0569\ \mathrm{s^{-1}} \left[1 - \frac{0.0569\ \mathrm{s^{-1}}}{1.185 \times 10^{-1}\ \frac{\mathrm{cm^3}}{\mathrm{g \cdot s}} \times (1.021 \times 10^{-4})^{0.45}\ \frac{\mathrm{cm^3}}{\mathrm{mol}} \times 0.8163\ \mathrm{g/cm^3} + 0.0569} \right.} $$

$$ \frac{6.07425 \times 10^{-7}}{1.75 \times 10^{-2} + 3.013 \times 10^{-3}} = \frac{6.0725 \times 10^{-7}}{0.0208} $$

$2.961 \times 10^{-5}\ \mathrm{mol/cm^3}$

$$ \frac{2\,\mathrm{g}}{\mathrm{mol}} \left| \frac{\mathrm{mol}}{22.4\,\mathrm{L}} \right. = 0.0893\ \mathrm{kg/m^3} \ @\ (1\,\mathrm{atm}, 273\,\mathrm{K}) $$

$$ \frac{0.0893\,\mathrm{kg}}{\mathrm{m^3}} \left| \frac{5.3 \times 10^{6}\,\mathrm{Pa}}{1.01325 \times 10^{5}\,\mathrm{Pa}} \right| \frac{273.15\,\mathrm{K}}{653.15\,\mathrm{K}} = 1.95\ \mathrm{kg/m^3} $$

$\boxed{Pa}$

Balance Equation

eous phase

$$\rho_G C_{p_G} T_{G_{i-1}} = U_G \rho_G C_{p_G} T_{G_i} + h_G a_L (T_{L_i} - T_{G_i}) \Delta z$$

id phase

$$C_{p_L} T_{L_{i-1}} = U_L \rho_L C_{p_L} T_{L_i} - h_G a_L (T_{L_i} - T_{G_i}) \Delta z + h_L a_s (T_{S_i} - T_{L_i}) \Delta z$$

Catalyst

$$(T_{L_i} - T_{S_i}) = \rho_B \sum n_j r_j (-\Delta H_j)$$

$$_G C_{p_G} + U_L \rho_L C_{p_L}) \frac{dT}{dz} = \rho_B \sum n_j r_j (\Delta H_j)$$

$$\frac{dT}{dz} = \frac{\rho_B k_r C_{a_i}^{0.45} C_{b_i} (\Delta H_j)}{(U_G \rho_G C_{p_G} + U_L \rho_L C_{p_L})}$$

$$= a + bT + cT^2 + dT^3$$

$$= 28.84 \times 10^{-3} + 0.00765 \times 10^{-5} (380) + 0.3288 \times 10^{-8} (380)^2 + (-0.8698 \times 10^{-12})(38$$

$$= 0.0293 \text{ KJ/mol.K}$$

$$\frac{29.3\text{ J}}{\text{mol.K}} \left| \frac{\text{mol}}{2\text{g}} \right. = 14.65 \frac{\text{J}}{\text{g}\cdot\text{K}}$$

$$= \frac{3.3 \times 10^3 \text{ J}}{\text{kg K}} \left| \frac{1\text{kg}}{1000\text{g}} \right. = 3.3 \frac{\text{J}}{\text{g}\cdot\text{K}}$$

$$= \frac{0.8163 \frac{\text{g}}{\text{cm}^3} \times 1.185 \times 10^{-1} \frac{\text{cm}^3}{\text{g}\cdot\text{s}} \times (1.026 \times 10^{-4})^{0.45} (2.96 \times 10^{-5})(251000)}{\left(0.28 \frac{\text{cm}}{\text{s}} \times 1.93 \times 10^{-3} \frac{\text{g}}{\text{cm}^3} \times 14.65 + 1.75 \times 10^{-2} \times 0.7634 \frac{\text{g}}{\text{cm}^3} \times 3.3 \frac{\text{J}}{\text{g}\cdot\text{K}}\right)}$$

$$= 0.222$$

$$V = \frac{nRT}{P} = \frac{0.08206\,\text{L atm}}{\text{mol}\cdot\text{K}} \times \frac{273\,\text{K}}{1\,\text{atm}}$$

$V =$

ak Cbi

$$^{5} = \frac{0.0569\,\text{s}^{-1} \times 2.961\times10^{-5}\,(\text{mol}/\text{cm}^3)}{\left[0.8163\,\text{g}/\text{cm}^3 \times 1.185\times10^{-1}\,\text{cm}^3/\text{g}\cdot\text{s} \times (1-0.256\times10^{-4}) + 0.0569\,\text{s}^{-1}\right]}$$

$$= 2.96\times10^{-5}\,\text{mol}/\text{cm}^3$$