Design and Modelling of Trickle Bed Reactor for Diesel Hydrodesulphurisation Process

By

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Dehradun
April, 2011.

Design and Modelling of Trickle Bed Reactor for Diesel Hydrodesulphurisation Process

A thesis submitted in partial fulfilment of the requirements for the Degree of

Master of Technology

(Process Design Engineering)

By

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CERTIFICATE

This is to certify that Mr. Sanjay Santhanam student of University of Petroleum Energy Studies, Dehradun has undergone industrial training for his project from 15th January 2011 to 2nd March 2011 at Essar Oil Limited, Vadinar, Jamnagar, Gujarat.

He has successfully completed his project.

He was found to be sincere and hardworking.

We wish him all the success.

For Essar Oil Limited

2nd March 2011

Milind Hiwale
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Abstract

A two phase trickle bed reactor model has been developed in this work to simulate the performance of an industrial reactor for diesel hydrodesulphurisation. The reaction was described by a power law model. The order of reaction and the kinetic properties were obtained from the plant operating data of an industrial reactor at Essar Oils Ltd, Jamnagar. A semi-empirical approach of design based on both correlation and modelling has been attempted successfully in this work. This design apart from considering the reaction kinetics also accounts for the mass transfer between the multiple phases in the reactor. A mechanistic isothermal model was developed and solved using MATLAB. Product sulphur variation with process variables such as temperature, liquid hourly space velocity are also obtained and matched the plant data. The product conversion at a bed depth of 25 m(active catalyst length) in a 6500 mm internal diameter reactor was determined to be 99.35% through the correlation based approach. The simulated result for the above specified reactor was 99.75%. The conversion as per the plant data was 99.82%. Thus it can be observed that both the design procedures matched the plant data with less variation. These variations were due to the approximation of the model by power law and because of neglecting the axial dispersion effects. This work can be used to further enhance the model to match the industrial reactor so that it can be used in design of trickle bed reactors.

Acknowledgements

I would like to thank all people who have helped and inspired me during my masters study.

I especially want to thank my project advisor, Prof. G. Sanjay Kumar, for his guidance during my research and study at UPES. His perpetual energy and enthusiasm in research had motivated all his advisees, including me. In addition, he was always accessible and willing to help his students with their research.

I was delighted to interact with Mr.Ramamurthy Palepu, Head of the Dept., Technical Services, Essar Oils Limited and also to seek his guidance on my work.

Mr.Chandrasekhar Varanasi, Jt. General Manager,EOL deserves a special thanks as my advisor at EOL. In particular, I would like to thank Mr. Chittibabu Sivalingam and Mr.Miland Hiwalae for hiring me as an intern at Essar. The associated experience broadened my perspective on the practical aspects in the industry. A special thanks to Mr.Swaminathan for assisting me in all activities at EOL and helping me out with needed data and design details.

I would like to thank Ajith, Vasanth, Praneeta, Anne and Rajat for their friendship and help in the past six months. They were very vital at all times in assisting me to complete my work both technically and cheering me mentally. Thank you guys.

My deepest gratitude goes to my family for their unflagging love and support throughout my life; this dissertation is simply impossible without them.

Dedicated to

Singaravelu Santhanam

&

Jayanthi Santhanam

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Nomenclature

English

a	gas-liquid interfacial area, m^2/m^3
a_s	bed-specific surface area, m^2/m^3
C	concentration of sulphur, mol/m^3
D	molecular diffusivity, m^2/s
d_p	catalyst particle diameter, mm
g	gravitational acceleration, m/s^2
G	gas mass flux, kg/m^2 s
H	Henrys constant
h	liquid hold up, m
k	intrinsic kinetic constant
k_La	volumetric liquid-side mass-transfer coefficient, s^{-1}
L	liquid mass flux, kg/m2s
M	molecular weight
P	pressure, MPa
p	partial pressure,Mpa
pe	peclet number
Q	volumetric flow rate, m^3/s
Re	Reynolds number, DVρ/μ
R	gas constant
rc	rate constant
T	temperature, ^{o}C
t	time, s
u	superficial velocity, m/s
Z	bed length, m

Greek

$\Delta P/Z$	pressure drop
ϵ	bed porosity
δ	single phase energy loss
λ	solubility coefficient
η	wetting coefficient
μ	dynamic viscosity, Pa s
ρ	density, kg/m^3
σ	surface tension, N/m
Φ_s	sphericity of the catalyst particle

Subscripts

L	liquid phase
G	gas phase
d	dynamic holdup
s	static holdup
in	at the inlet
out	at the outlet
app	apparent
in	intrinsic

Superscripts

S	solid phase
L	liquid phase

Acronyms

DBT	dibenzothiophene
TBR	trickle-bed reactor
HDS	hydrodesulphurisation
HC	hydrocarbons
DHDS	diesel hydrodesulphurisation
PFD	process flow diagram
ULSD	ultra low sulphur diesel
EOL	Essar oils limited
GO	gas oil
NHDS	non hydrodesulphurisation
DNHDS	diesel non hydrodesulphurisation
LHSV	liquid hourly space velocity, hr^{-1}
WHSV	weight hourly space velocity, hr^{-1}

Chapter 1

INTRODUCTION

1.1 Sulphur Removal

The process of removal of sulphur from fuels was known as late as the 1950s but only in recent years has environmental regulation brought the necessity of sulphur removal in to the lime light. Sulfur is present in many forms in petroleum fractions: mercaptans (R-SH), sulfides (R-S-R'), Disulfides (RSSR'), Thiophene, Benzothiphene (BT), Dibenzothiophene (DBT) and their alkyl derivatives. Hydrodesulphurization (HDS) is a catalytic chemical process widely used to remove sulfur (S) from refined petroleum products such as gasoline, jet fuel, kerosene, diesel fuel and fuel oils. The purpose of removing the sulfur is to reduce the sulfur dioxide (SO_2) emissions that result from using these fuels in automotive vehicles.

Catalytic hydrodesulphurisation(HDS) has been extensively used to meet this regulation for environmental protection [15]. However, due to changes in feed stock, catalyst and operating conditions and need to achieve this ultra low sulfur diesel content, existing plants have started revamping.

These changes are necessary because it has been found that the use of conventional catalyst for deep hydrodesulphurisation in traditional diesel oil hydrotreaters would require severe operating conditions such as high temperature, low space velocity and high hydrogen partial pressure. Such severe processing conditions generally lead to rapid catalyst deactivation and shorter cycle lengths.

The feasibility of revamping an existing unit will depend on the original design and operating conditions. For a designed HDS process, it is necessary to analyze the effect of various operating conditions such as temperature, pressure, space velocity and gas to oil ratio on product quality. It needs well developed model incorporating mass transfer, kinetics and hydrodynamics.

In the s-brane process removal of sulphur is carried out in a double stage removal process where the initial feed is sweetened using a pervaporisation membrane (S-Brane) to give out two product streams. One (70% feed volume) which contains 30 ppm of sulphur and the other (30 % feed volume) containing 20000 ppm of sulphur .The second stream is thensweetened by conventional HDS process.

1.2 Process of Sulphur Removal

sulphur compounds are some of the most problematic impurities present in various petroleum fractions. When present in fuels they cause environmental pollution as SO_2. When present in the refining and petrochemical processes they poison catalysts. Sulphur in oils and lubricants can cause corrosion of equipment parts and poisonous emissions such as SO_2 and H_2S when the fuel is burned. Several processes have been proposed to remove these compounds.

Hydrodesulphurization is very effective in sulfur removal from all fractions. The molecules that contain sulfur lose these atoms by hydrogenation reactions. The sulfur containing components are converted to H_2S and hydrocarbons on solid catalyst in presence of hydrogen. Hydrodesulphurization is usually carried out in trickle bed reactors. Langmuir - Hinshelwood kinetics for rate equations gives a good approximation to the reaction mechanisms.[18].

1.2.1 S-Brane Process

S-brane process is a membrane separation process used as a complementary process to achieve low sulphur concentration complying with environmental regulations. The S-brane process can be used to treat hydrotreated diesel. The membrane is capable of treating a feed of 10000 ppm (as an example) and produce two streams. A clean diesel, (less than 30 ppm sulphur) which is called retentate, comprises 70 vol% of the feed and is sent to the diesel pool.

The other diesel stream concentrated with sulphur compounds is called permeate and comprises 30 vol% of the feed. This stream has around 20000 ppm of sulphur. The permeate stream is sent to a conventional hydrodesulphurization unit. The hydrotreated diesel is then sent to the diesel pool. The details of S-brane process is briefly explained [15]. A schematic diagram of the process is shown in figure 1.1

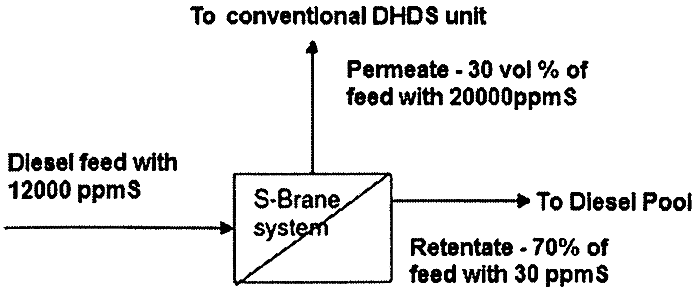
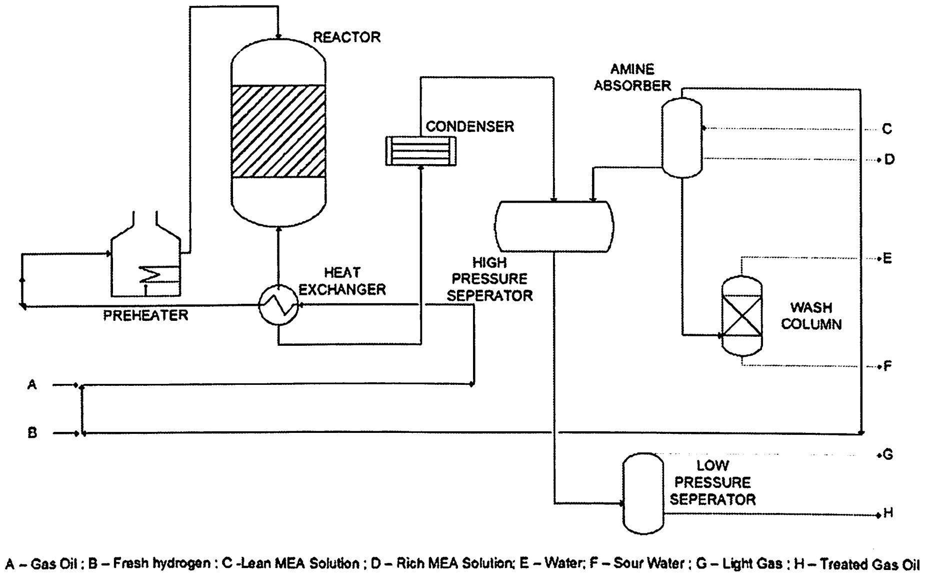


Figure 1.1: S Brane Process

The S-brane is operated as pervaporation mode membrane. A vacuum of about 0.5 to 0.1 bar (0.75- 1.5 psia) is applied on the permeate side. Sulphur compounds flow through membrane to the permeate side while clean diesel flow in the retentate side and then to the diesel pool.

1.2.2 Conventional HDS Process

The second stage of the double stage sulphur removal is the conventional HDS unit where the sour diesel containing 2000 ppm of sulphur is treated to obtain a product with 50 ppm sulphur. The PFD for the same is as shown in the figure 1.2.



A – Gas Oil ; B – Fresh hydrogen ; C -Lean MEA Solution ; D – Rich MEA Solution; E – Water; F – Sour Water ; G – Light Gas ; H – Treated Gas Oil

Figure 1.2: HDS Process Flowsheet

Feed stock and hydrogen (makeup and recycle hydrogen) are heated in a preheater and fed into the reactors. Sometimes more than one reactor is arranged in parallel to increases the capacity of plant. The outlet streams are admitted into a high-pressure separator, where H_2S, NH_3, etc. along with unreacted hydrogen are seperated from the treated product.

The product stream from high- pressure separator goes to a low-pressure separator, where gases are separated and the bottom product is sent to further processing. Hydrogen from high-pressure separator is associated with impurities formed in hydro treatment. So, treating with amine solution purifies the gas. Treated hydrogen is recycled to the reactor. The reactor used for hydrodesulphurization is a concurrent down flow trickle bed reactor.

1.2.3 Process Variables

Important process variables are

1. Reactor temperature
2. Reactor pressure
3. Reactor pressure
4. Space velocity
5. Gas to hydro carbon ratio

HDS process is used to desulphurise diesel as it is necessary to reduce the total sulphur down to the parts per million range or lower in order to meet environmental regulations. When the process is used for desulphurising diesel oils, the latest environmental regulations in the United States and Europe, require what is referred to as ultra-low sulfur diesel (ULSD), which in turn requires that deep hydrodesulphurization is used.

In the early 2000s, the governmental regulatory limits for highway vehicle diesel was within the range of 300 to 500 ppm by weight of total sulfur. As of 2006, the total sulfur limit for highway diesel is in the range of 15 to 30 ppm by weight [5]

1.2.4 State of Sulphur in Diesel

Sulphur that is present in diesel may be categorized in the following groups:

1. Free Elemental sulphur
2. Mercaptans & Thiols (R-SH)
3. Hydrogen Sulfide
4. Sulfides
5. Disulfides (R-S-S-R')
6. Poly Sulfides (R-Sn-R')
7. Thiophenes and their derivatives such as BenzoThiophenes(BT) & DiBenzoThiophenes (DBT)

As the complexity of the structure increases, so does the difficulty of removal of sulphur from the compound. Thus DBT's which have a hindered suplhur are more difficult to treat than the rest of the groups. The change in ease of removal is given by [1] and as shown in figure 1.3.

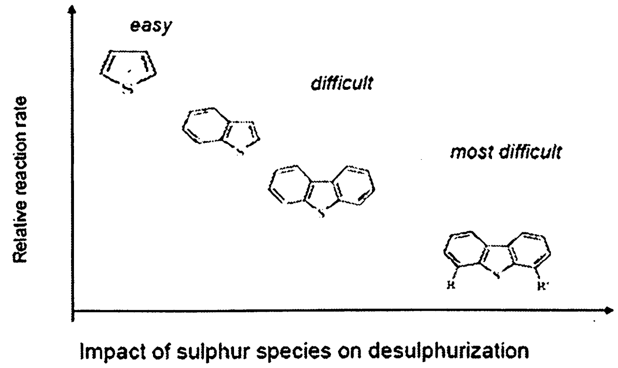


Figure 1.3: Effect of sulphur type on removal

1.3 Trickle Bed Reactor

Among the three-phase gas-liquid-solid reaction systems encountered in industrial practice, trickle-bed reactors (TBRs) are the most widely used. They are employed in petroleum, petrochemical, and chemical industries, in waste treatment, and in biochemical and electrochemical processing, as well as other applications. The economic impact of how well these reactors operate is considerable, since in the petroleum sector alone the TBR annual processing capacity for various hydrotreatments (e.g., hydrodesulphurisation, hydrocracking, hydrorefining, hydrodemetallization, hydrodenitrogenation,etc.) is estimated at 1.6 billion metric tons (Trambouze,[21]). With the current market evolution toward increasing demand for light oil products, such as middle distillates, and the decreasing needs for heavy cuts, the refiners will have to keep improving their processing units for upgrading heavy oil and residual feedstocks. Any advance in TBR technology will thus represent substantial savings, and this stimulates the continued research efforts aimed at improving TBR operation and performance. A trickle-bed reactor (TBR) consists of a fixed bed of catalyst particles contacted by a cocurrent downward gas-liquid flow carrying both reactants and products. When the gas and liquid are fed cocurrently upward through the catalyst bed, the system is called a floodedbed reactor (FBR) or upflow reactor. The upflow configuration is used sparingly in industrial practice where TBRs prevail. Owing to a motionless catalyst bed, nearly plug flow is achieved in TBRs, and in that respect they are superior to other three-phase reactors where the catalyst is either slurried or fluidized. For instance, TBRs high catalyst loading per unit volume of the liquid and low energy dissipation rate make them preferable to slurry reactors. However, the disadvantages of TBRs are their impracticality for reactions with rapidly deactivating catalysts, such as in heavy oil hydrotreating processes, and the possibility of liquid maldistribution,which may give rise to hot spots and reactor runaway. The layout of a TBR is as shown in the Figure 1.4

Most commercial TBRs normally operate adiabatically at high temperatures and high pressures and generally involve hydrogen and nonwaterlike liquids with superficial gas and liquid velocities up to 30 and 1 cm/s, respectively. Kinetics of reactions conducted in TBRs usually require high temperatures, which in turn increases gas expansion and impede the gaseous reactant from dissolving sufficiently into the liquid. Therefore, elevated pressures (up to 60 MPa) are necessary to improve the gas solubility,to improve the mass and heat transfer rates, to handle large gas volumes at less capital expense, and to slow down the catalyst deactivation which may be triggered by hydrogen starvation of the catalyst. Due to complexities associated with transport-kinetics coupling in TBRs, general scale-up and scale-down rules for the quantitative description of transport phenomena in TBRs working under realistic conditions remain elusive. This is especially true since the majority of the literature is concerned exclusively with nearly atmospheric conditions.

In view of the rapid advances that are being realized in the area of high-pressure TBRs, it is useful to build a model which would clearly reflect the operation of such complicated reactors.

1.4 Objectives of Project

The present work's objective is to design a trickle bed reactor for HDS for the second stream of S-brane to produce ULSD in a double stage sulphur removal process. A further objective is to develop a two-phase reactor model for trickle bed reactor. The design also includes basic engineering and detailed engineering of the reactor and the reactor internals,if time permits.

The project was carried out at Essar Oils Limited - Jamnagar and UPES - Dehradun. On completion of the work, a detailed design of HDS reactor will be the primary outcome. A good design will result in efficient removal of Sulphur to meet the current and future environmental norms.

This chapter deals about process of sulphur removal and important process variables.A discussion on literature related to present work is given in chapter 2. Details of theoretical development has been presented in chapter 3. Computation and validation of empirical correlations are presented in chapter 4. Chapter 5 deals with model formulation methodology & correlations used for estimating properties of material under process condition and other transport properties of material involved. Chapter 6 gives a brief methodology on the reactor design. Finally the results obtained from model validation are discussed in chapter 7.

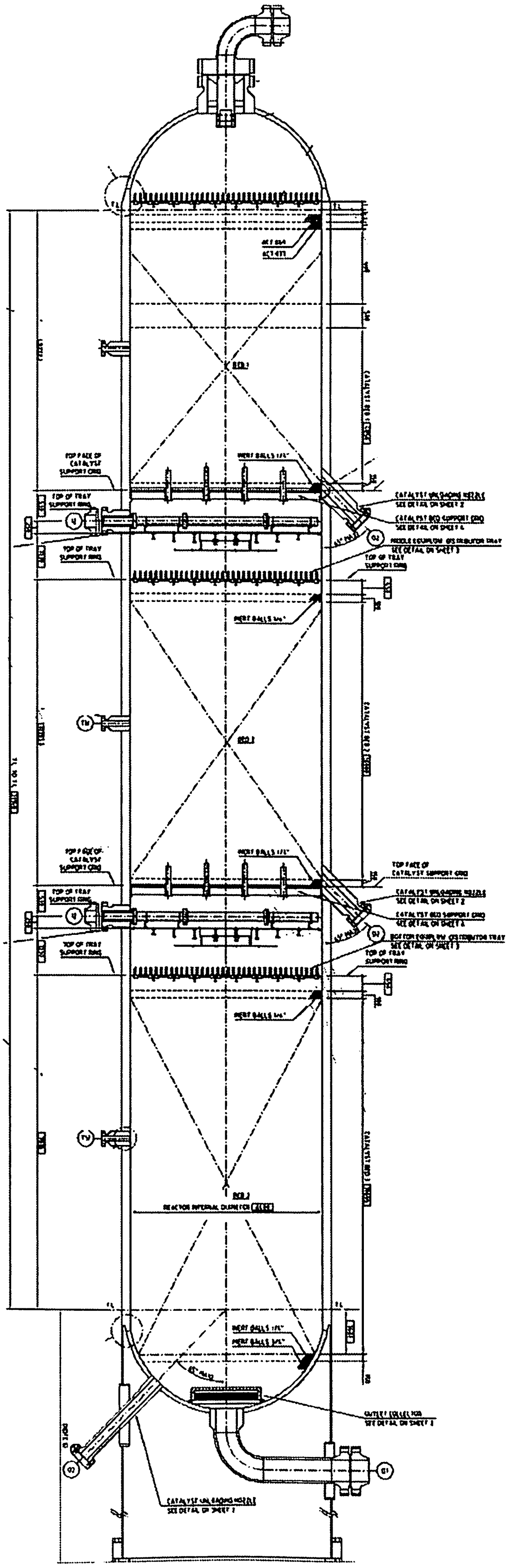


Figure 1.4: Trickle Bed Reactor Source:EOL DHDS Process Book

Chapter 2

LITERATURE REVIEW

An analysis of literature shows the following improvement on hydrodesulphurization unit over last four decades,

- In the earliest stages, the three-phase reactor was modelled as pseudo homogeneous plug flow model.
- Three-phase reactor models were then developed based on two-film theory and only hydrodesulphurisation reaction was modeled.
- Later three-phase reactor models were developed for hydrodesulphurisation as well as hydrodearomatisation reactions.
- Three-phase reactor models were developed which considered hydrodesulphurisation, hydrodearomatisation, and olefins saturation reactions. An effort was made to develop non-isothermal reactor model.
- Three phase reactor model was simplified to two phase model.

Research is going in the area of two phase reactor model development, for analyzing the diesel oil quality obtained from different types of crude oil. In this present work a two phase non isothermal model for trickle bed reactor was developed. This model was used to calculate exact conversion of sulphur in the non isothermal industrial reactor.

The field of hydroprocessing dates back to early 1950's [19]. The study of trickle bed reactors started from late 1960's [15]. In 1969, Hochman and Effron [10] were the first to study the two phase flow in cocurrent packed bed reactors. The flow was initially upward which had a high retention time [4]. Later a brief study on the downward flow was developed by the authors. In 1974, Puranik and Vogelpohl [16] teamed up to study the effect of interfacial areas in irrigated columns. They proposed that the interfacial area directly affects the extent of reaction. In 1975, Goto and Smith [9] studied the mass transfer in packed bed for two phase flow. They gave the correlations for the mass transfer coefficients for two phase flow. Based on this work the resistance caused due to incomplete gas-liquid-solid phases came into light. This led to further development in the improvement of wetting characteristics when catalysts were used in packed bed reactor. In 1976, the partial wetting of catalysts were studied by Midoux and Charpentier [14] and they gave the relation between the partial wetting of the catalyst and the extent of desulphurisation. In 1984, Tousan [20] studied the non-foaming systems for cocurrent downward flow in a packed bed which resulted in the development of pressure drop corelations based on Erguns two phase equation.

The whole field of research changed in the early 1990's. In 1994, Forment *et al* [7] gave a kinetic modelling for HDS of oil fractions. This model is still being used as the base for most trickle bed modelling studies. In 1996, Anthari {Anthari1996 described the kinetics involved in the HDS process in detail. He performed lab scale experiments on various oil fractions and presented a detailed report on the kinetics for sulphur compounds in gas oil streams. In the same year Kostern and Hoffmann [11] developed a three-phase reactor model for hydrotreating which explained not only the HDS but also other reactions in the hydrotreating process. This model gave a detailed analysis of product sulphur variation with the process variables.

The models have become more rigorous and descriptive with the kinetics, the mass transfer and the hydrodynamics were incorporated in them. In 2002, Chowdhry *et al* [17] described a two phase model of trickle bed reactor for hydrotreating process with all major reactions considered in it. In the year 2003, Borgna and Niemantsverdriet [1] studied the catalytic activity of various catalysts and put forth the intrinsic kinetic model for thiophenes over NiMo/SiO_2 catalyst. The kinetics with respect to thiophenes was discussed in detail and the parameters were estimated. With the advancement made in the field of transient modelling, Lappalainen gave the transient modelling of trickle bed reactor to predict the flow regime. This model is the base to determine the nature of the flow in a reactor based on the superficial velocities.

The field of hydroprocessing experienced a drastic challenge in the year 2004 with the EURO regulations on environment becoming more strigent all over the globe. In India Bhaskar developed a three phase model of trickle bed reactor. The model simulated the performance of a pilot plant and compared it to an industrial reactor. The reactions which involved saturation of olefins were also considered.

A recent study of TBR is by Farahani and Shahhosseini [6]. They simulated the a general model for trickle bed reactors which can be used to carry out any three phase reaction. The three phase model was developed and simulated in HYSYS Simulation Package. This serves as the stable reactor model for further studies.

2.1 Desulphurisation Technologies

Apart from the conventional technologies there are several other ways of removing sulphur in the gas oil stream. The Non-Hydrodesulphurization(NHDS) methods involve the selective adsorption of sulphur compounds by selective interaction in the presence of aromatic hydrocarbons under ambient or mild conditions without hydrogen. NHDS may include oxidizing sulphur compounds by liquid-phase oxidation reactions, followed by the separation of the oxidized sulphur compounds. Bio-desulphurization can also be used to attack sulphur atoms by using bacteria via microbial desulphurisation. More methods for desulphurisation are either by extraction with new ionic liquids or by membrane separation technology that is integrated into a clean fuel strategy at low capital cost relative to hydrotreating.

2.1.1 Selective Adsorption for Sulphur Removal

Selective adsorption for sulphur removal (SASR) is a new approach for DNHDS. The idea is still being studied in laboratories, but the results of the experiments show the approach that could replace the current HDS units in the next few years. The main idea of this approach is to selectively separate the sulphur compounds (Thiophens, benzothiophens, and di-benzothiophens) from the fuel using an appropriate adsorbent agent. As a result of this separation, only 1% by mass of the fuel is adsorbed by the adsorbent agent.

2.1.2 Oxidation and Extraction for Desulphurisation

Oxidation of a sulphur atom in liquid phase with hydrogen peroxide followed by extraction of a oxidized species can lead to the desulphurisation of diesel fuels. The oxidizing agents that can be used include t-butyl, peroxy organic acids, inorgani peroxy acids, and peroxy salts. Hydrogen peroxide in the presence or absence of catalysts under ambient conditions has been used [3].The resultant sulphur is extracted by suitable solvent such as N-methyl pyrrilidone (NMP).

2.1.3 Bio-desulphurisation

Bio-desulphurisation is a process that removes sulphur from fossil fuels using a series of enzyme-catalyzed reactions. Biocatalytic sulphur removal from fuels has applicability for producing low sulphur gasoline and diesel fuels. Certain microbial biocatalysts have been identified that can bio-transform sulphur compounds found in fuels, including ones that selectively remove sulphur from dibenzothiophene. The distillate stream is first mixed with an aqueous media containing the bacteria, caustic soda and nutrients for the bacteria. Enzymes in the bacteria first oxidize the sulphur atoms and then cleave some of the sulphurcarbon bonds. The sulphur leaves the process in the form of hydroxyphenyl benzene sulphonate which can be used commercially as a feedstock to produce surfactants.

2.1.4 Extraction with Ionic Solvent

Ionic solvent can be used instead of organic solvent to extract sulphur compounds. The ionic solvent is prepared using a mixture of CuCl-based ionic liquid exhibits remarkable desulphurisation ability in the desulphurisation of gasoline when used as an extraction absorbent. The effectiveness of sulphur removal may be attributed to the complexation of a Cu ion with thiophene.

2.2 Environmental Regulations

As per current regulations a diesel must contain only 50 ppm of sulphur to qualify under the Euro-V norms. In double stage sulphur removal the proposed sulphur content of 30 ppm would meet not only the present requirements but also of the future. The detailed standards are shown in the Table 2.1.

	Current Indian standards	Euro-III	Euro-IV
Gasoline			
Benzene(%)	5	1	none
Aromatics(%)	none	42	35
Sulphur (ppm)	500	150	50
Diesel			
Cetane min	49	51	none
PAH (%)	none	11	none
Sulphur (ppm)	500	350	50

Table 2.1: Euro-Standards Currently in Use

2.3 Present Indian Scenario

The sulphur content of diesel products from Indian refineries is listed below in Table 2.2

Refinery	Group	Year	Specifications	S Content
Jamnagar Refinery*	EOL	2006	BS IV	50
Mathura Refinery	IOCL	1999	BS II	2500
Digboi Refinery	IOCL	1999	BS III	500
Panipat Refinery	IOCL	1999	BS III	500
Haldia Refinery	IOCL	1999	BS II	2500
Manali refinery	CPCL	1999	BSIII	500
Mumbai Refinery	BPCL	1999	BS III	500
Bharat Oman Refineries Limited	BPCL	1999	BS III/IV	500/50
Jamnagar Refinery*	Reliance	1999	EURO V	50

Table 2.2: The sulphur content of diesel products from Indian refineries

The two private refineries, EOL and RIL which supply their products to the international market meet the required specifications. But none of our state run refineries currently meet the norms. Hence the proposed project would be of great help for the state run refineries to switch over to environmental friendly fuel production.

Chapter 3

THEORETICAL DEVELOPMENT

The research done so far in the field of design of trickle bed reactors has lead to various developments. These results were instrumental in deriving numerous correlations based on which the design of trickle bed reactor can be done. In this chapter a brief these empirical correlations are summarized.

3.1 Empirical correlations

There are various empirical correlations which describe the trickle bed reactor's operation. These correlations were developed for various systems as discussed by Shah [22]. The correlations used in this design are based on those derived specifically for hydrogen and hydrocarbon(HC) systems. The feed of hydrodesulphurisation consists mainly of gas oil fractions which are either straight run or from cracking units, apart from gas oil they also consists of light and heavy kero fractions in them. These streams are blended together which form the product diesel.

3.1.1 Liquid Holdup

The liquid holdup in a downflow reactor is less when compared to the cocurrent upflow reactor. The effective catalyst wetting, as well as the thickness of the liquid film surrounding the catalyst particles depends strongly on the liquid holdup. The effect of liquid holdup on the performance of a trickle-bed reactor depends upon the nature of the reaction. For hydro treating operations of residual gas oils sufficiently high liquid holdup is required so that all the catalyst surfaces are effectively wetted. In a dynamic situation, the total liquid holdup is the sum of the operating holdup and static holdup. Static holdup is the amount of liquid in the bed after the liquid inlet is shut off and the column is allowed to drain. Operating holdup, which largely represents the liquid external to the catalyst particle, depends upon the liquid and gas flow rates, the liquid and gas properties such as viscosity, density and surface tension, the reactor dimensions, and the liquid and gas distributor design. When the reaction occurs only in the liquid phase, only dynamic or operating holdup is important for kinetic data evaluation.

In DHDS process the reaction is assumed to take place on the surface of the catalyst only. Hence the operating holdup is only to be considered.

$$\begin{aligned}\text{Operating holdup} &= \text{f}(\text{G}_L, G_G, \mu_L, \mu_G, \rho_L, \rho_G, \sigma_L, \sigma_G) \\ &\quad + \text{f(Reactor dimensions)} \\ &\quad + \text{f(Gas and liquid distributor design)}\end{aligned}$$

For a hydrogen-HC system the operating liquid holdup is given by Midoux et al [14]

$$h_L = (0.664(X'^{0.81}))/(1 + 0.66(X'^{0.81})) \tag{3.1}$$

Here $0.1 \leq X' \leq 80$

$$X' = \sqrt{\zeta_L/\zeta_G} \tag{3.2}$$

$$\zeta_L = \frac{G_L}{\epsilon}\left[\frac{1}{\rho_L}\left(\frac{\Delta H}{\Delta Z}\right)_L + \frac{1}{\rho_m}\right] \tag{3.3}$$

$$\zeta_G = \frac{G_G}{\epsilon}\left[\frac{1}{\rho_G}\left(\frac{\Delta H}{\Delta Z}\right)_G + \frac{1}{\rho_m}\right] \tag{3.4}$$

$$\Delta H = \left(\frac{\Delta P}{\rho_m g}\right) \tag{3.5}$$

$$\rho_m = [h_L\rho_L + (1 - h_L)\rho_G] \tag{3.6}$$

3.1.2 Pressure Drop

The pressure drop for concurrent downflow of gas and liquid in a packed bed can be predicted using correlations of the Lockhart and Martinelli [12]. The pressure drop for each phase flowing separately through the bed is calculated using the Ergun equation and these values are defined by a parameter χ.

$$\phi_L = 1 + \frac{1}{\chi} + \frac{1.424}{\chi^{0.576}} \tag{3.7}$$

$$\phi_L = \sqrt{\frac{(\Delta P/\Delta Z)_{GL}}{(\Delta P/\Delta Z)_L}} \tag{3.8}$$

$$\chi = \sqrt{\frac{(\Delta P/\Delta Z)_L}{(\Delta P/\Delta Z)_G}} \tag{3.9}$$

By erguns equation:

$$\frac{\Delta P}{\Delta Z} = \left[\frac{150\mu u_0}{(\Phi_s d_P)^2}\right]\frac{(1-\epsilon)^2}{\epsilon^3} + \left[\frac{1.75\rho\mu^2}{\Phi_s d_P}\right]\frac{(1-\epsilon)}{\epsilon} \tag{3.10}$$

These equations based are widely used for trickle bed reactors for the process of hydrodesulphurization. This resultd from minor changes made to the Ergun's equation to account for the energy losses in the combined gas and liquid phase.

Abbott [2] suggested the following equations for a hydrogen-HC system based on the combined energy losses. According to this correlation, the overall two phase energy loss for the gas and liquid passing through the reactor is related to the two individual single-phase energy losses as given by

$$log_{10}\left(\frac{\delta_{LG}}{\delta_L + \delta_G}\right) = \frac{K_1}{(log_{10}X)^2 + K_2} \tag{3.11}$$

where

$$\left(\frac{\Delta P}{\Delta Z}\right) = (\delta_{LG} - \rho_m) \tag{3.12}$$

$$\delta_L = \left(\frac{\Delta P}{\Delta Z}\right)_L \tag{3.13}$$

$$\delta_G = \left(\frac{\Delta P}{\Delta Z}\right)_G \tag{3.14}$$

$$X = \left(\frac{\delta_L}{\delta_G}\right)^{0.5} \tag{3.15}$$

$$\rho_m = [h_L\rho_L + (1 - h_L)\rho_G] \tag{3.16}$$

In the above equation the liquid hold up is given by Bischoff [8] as below

$$log_{10}(h_L) = (-0.44) + (0.4log_{10}(X)) - (0.12(log_{10}X)^2) \tag{3.17}$$

The values of constants as given by Midoux and Charpentier [14] are
$K_1 = 0.620$ and $K_2 = 0.830$

It is also to be noted that the above correlation holds good only if the operating pressure is 38.5 to 62.5 bar and the catalyst size must be less than 0.16 cm. The reactor at EOL is operated at 58.3 bar and the catalyst used is 0.15 cm in size. Hence these correlations are well suited for the system.

3.1.3 Axial Dispersion

There are a large number of models proposed to evaluate macro mixing in a trickle-bed reactors [22]. The axial dispersion coefficient for the liquid phase is dependent upon the liquid flow rate, liquid properties, and the nature and size of the packings, but it is essentially independent of the gas flow rate. The correlations for axial dispersions are as given by Hochman and Effron [10]. The trickle flow can be approximated to a single phase flow if the

$$h_{dL}/h_{sL} > 8 \tag{3.18}$$

For such a system the correlations based on Hochman and Effron predict the actual dispersion based on the Peclet number model.

For a liquid phase dispersion

$$N_{pe} = \left[\frac{D_p * G}{D_v}\right] \tag{3.19}$$

For a hydrocarbon system

$$N_{peL} = (0.042)Re_L^{0.5} \tag{3.20}$$

where

$$Re_L = \frac{\rho_L.G.D_p}{\mu_l(1-\epsilon)} \tag{3.21}$$

For a gas phase dispersion

$$N_{peG} = (1.8)Re_G^{-0.7}(10^{-0.005Re_L}) \tag{3.22}$$

Where

$$Re_G = \frac{\rho_G.G.D_p}{\mu_l(1-\epsilon)} \tag{3.23}$$

The gas phase dispersion can be neglected as there is no much consideration given to liquid to gas mass transfer.

3.1.4 Gas-Liquid Mass Transfer

The gas-liquid mass-transfer coefficient is a function of the liquid superficial mass-flow velocity. For its determination the correlation given by Goto and Smith [9] is used. The correlation gives the gas liquid mass transfer coefficients as a function of liquid superficial mass velocity and diffusivity of the species diffusing in the liquid phase. The constants in the correlation are specific to a particular catalyst size. For the catalyst of the size between 1.5 - 2.5 mm the specified values of the constants are given by Korsten and Hoffmann [11].

The correlation given by Goto and Smith [9] is as follows:

$$\frac{k_i^L.a_L}{D_i^L} = \alpha_1.\left(\frac{G_L}{\mu_L}\right)^{\alpha_2}.\left(\frac{\mu_L}{\rho_L.D_i^L}\right)^{0.5} \tag{3.24}$$

where

$\alpha_1 = 0.4$ and $\alpha_2 = 7(cm)^{-1.6}$

$$D_i^L = 8.93 \times 10^{-8} \frac{v_c^{0.267}}{v_i^{0.433}} \frac{T}{\mu_L} \tag{3.25}$$

Because of the complex composition of hydrocarbon mixtures, some assumptions are necessary before using the above correlations. Here the organic sulphur compound has been considered to have the same density, average boiling point, and molecular weight as gas oil. In this case the molar volume of the medium sulphur compound is equal to that of the liquid solvent. The diffusivity decreases because the viscosity rises with increasing pressure.

3.1.5 Liquid-Solid Mass Transfer

The liquid-solid mass transfer in the low interaction regime can be estimated by the van Krevelen-Krekels equation as given by Froment and Bischoff [8]. The equation is very similar to that for the gas-liquid coefficients except that the specific surface area of the catalyst particle is also considered.

$$\frac{k_i^S}{D_i^L a_s} = 1.8 \left(\frac{G_L}{\mu_L a_s}\right)^{1/2} \left(\frac{\mu_L}{\rho_L D_i^L}\right)^{1/3} \tag{3.26}$$

Where

$$a_s = \frac{6}{d_P}(1 - \epsilon) \tag{3.27}$$

3.1.6 Overall Kinetics

The DHDS process was taken to be a pseudo-first order reaction. The sulphur containing compounds are combined to a lump which on the whole gives the net sulphur in the gas oil. Puranik and Vogelpohl [16] gave the following relation which suggests a fit between the first order kinetics and the Liquid Hourly Space Velocity

(LHSV). This equation accounts for both the intrinsic kinetics and the mass transfer effects. The conversion is also proportional to the length of the reactor bed. Taking the catalyst wetting to be complete and neglecting the changes in the surface tension the conversion is given by

$$log_{10}\frac{C_{in}}{C_{out}} \approx Z^{(0.32)}LHSV^{-0.68}D_p^{0.18}\left(\frac{\mu_L}{\rho_L}\right)^{(-0.05)} \tag{3.28}$$

The above relation is valid for

$$(\rho_L.V/\Omega) < 54\ kg/m^2s. \tag{3.29}$$

Chapter 4

COMPUTATION AND VALIDATION

4.1 Design of Trickle Bed Reactor

The proposed design is to be carried in three parts. The first part is based on the empirical correlations that are available in literature. The second part is to determine the system parameters such as diffusivity, mass transfer coefficients for various phases and most importantly to arrive at the kinetics of the process of hydrodesulphurizaton by making use of the empirical correlations and the available plant data from Essar Oil Limited(EOL). The final phase of design is to model the trickle bed reactors in a one dimensional system from fundamental principles. A detailed engineering consisting of all reactor internals will also be done in the design, if time permits.

4.1.1 Assumptions

The following assumptions were made in order to simplify the model

1. Quasi homogeneous system (The liquid and the gas superficial velocities are same)
2. Liquid is well saturated by the gas at the reactor inlet.
3. Complete catalyst wetting.
4. Isothermal pellets.

5. No axial dispersion.
6. No vaporization of the feed (gas oil).
7. No catalyst deactivation.
8. Non foaming system.
9. Pseudo first order kinetics.
10. No hydrogenation and denitrogenation

Apart for these assumptions for the reactor to perform as designed it always has to be operated in the trickle flow regime. This is ensured by the flow rates of the gas and the liquid phase.

4.2 Verification of empirical correlations

Among the above empirical correlations those which explain the overall kinetics were validated. Correlations for the axial dispersion, liquid holdup and pressure drop were also verified.

4.2.1 Flow regime

In the trickle-flow regime, the liquid trickles over the packing in the discontinuous shape of films, rivulets, and drops near a stagnant continuous gas phase as illustrated in Figure 4.1.

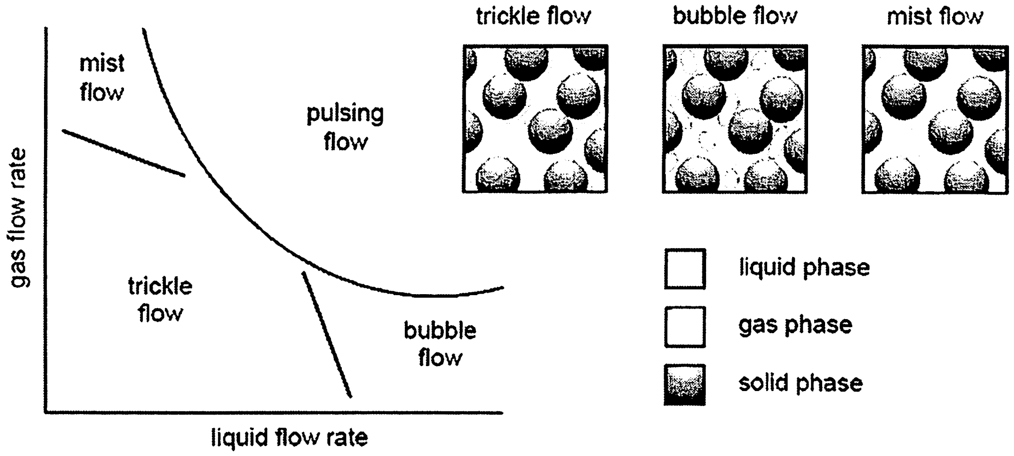


Figure 4.1: Various Flow Regimes

The gas-continuous region of flow includes laminar liquid- laminar gas flow as well as laminar liquid-turbulent gas flow. Hence it is mandatory to determine the kind of flow which is associated with the system. At EOL the liquid and gas flow rates were 407,488 kg/hr and 89,575 kg/hr respectively.

For the purpose of validation of the flow regime the combined velocity of gas and liquid phase are neglected for the time being and the superficial velocities are considered. The superficial velocities of liquid and gas phases are 0.00533 m/s and 0.05098 m/s. When these data ares plotted in the transition curve as given by Tosun [20] it falls well in the trickle flow regime as shown in Figure 4.2.

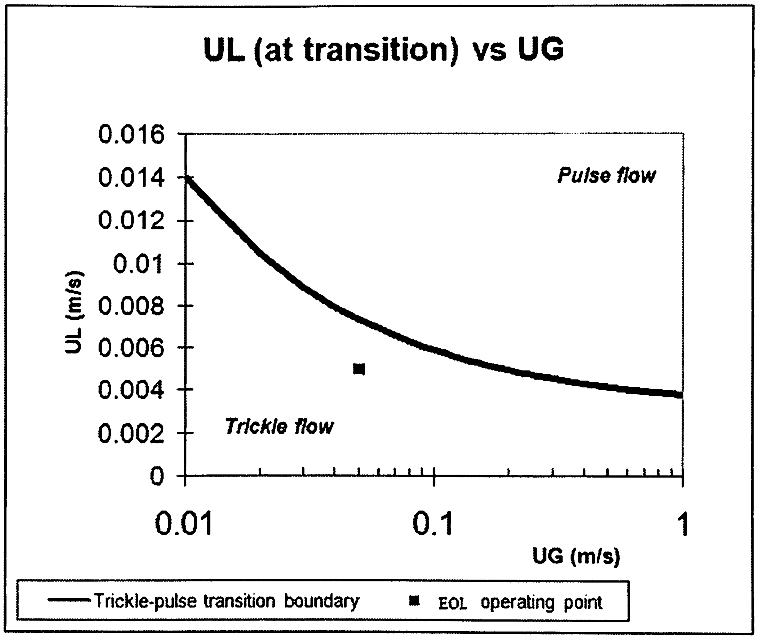
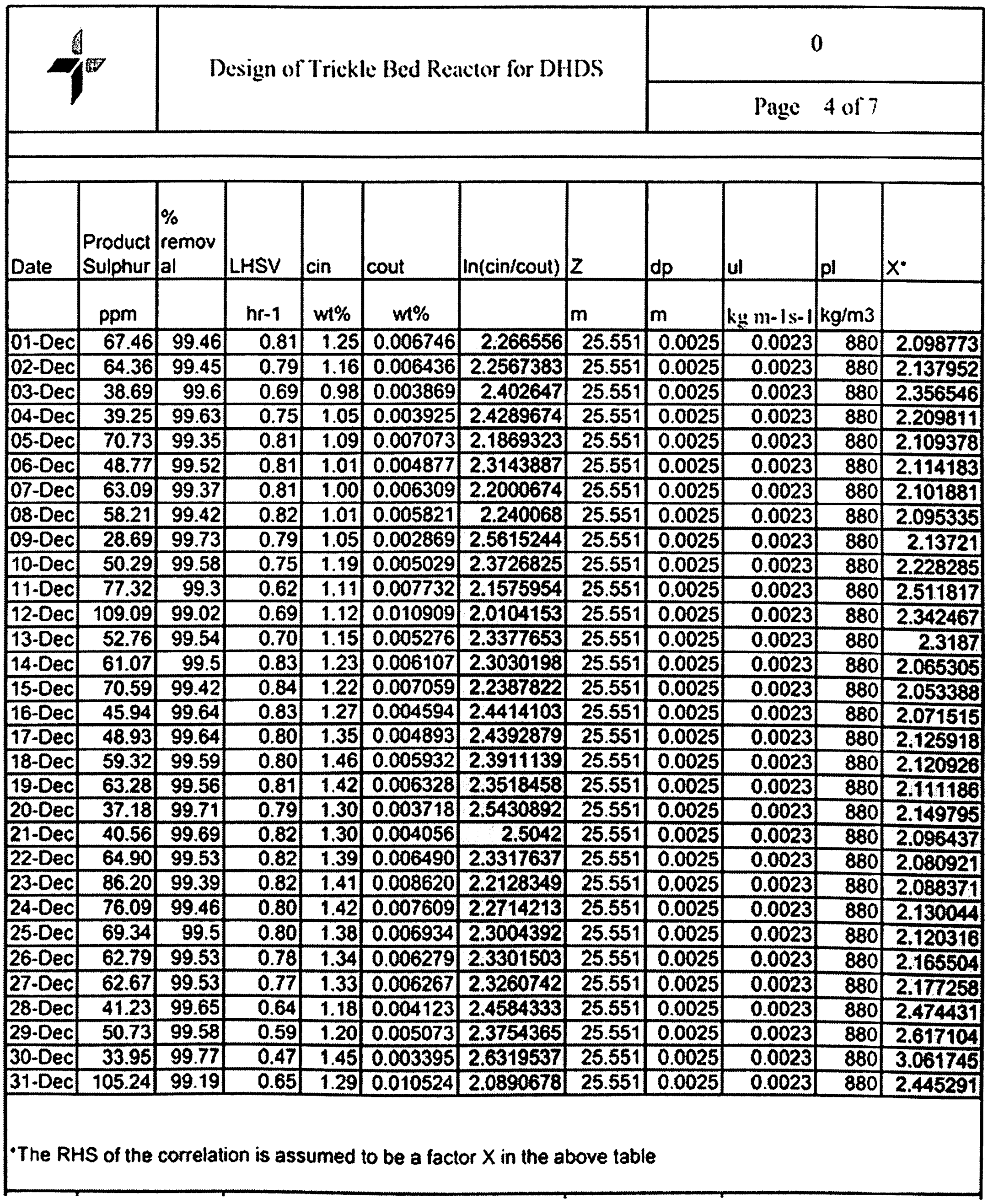


Figure 4.2: Flow regime for EOL data

4.2.2 Validation of Overall kinetics

A high degree of consistency was seen in the fit between plant data with the empirical correlations for the overall kinetics. The fit of the data with the correlation shows the process can be considered pseudofirst order in nature. The values obtained from the plant for the month of December 2010 was used to validate the kinetics. As mentioned before the validation is possible only if the catalyst wetting is taken to be complete. In the case of an industrial scale reactor due to the high liquid and gas flow rates the catalyst wetting is taken to be complete. The results obtained by the fit are given in the Figure 4.3.

Based on the overall kinetics a concentration profile was calculated to determine the length of the reactor at which the outlet sulphur is at the desired level. The



	Design of Trickle Bed Reactor for DHDS	0
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Date	Product Sulphur	% removal	LHSV	cin	cout	ln(cin/cout)	Z	dp	ul	pl	X*
	ppm		hr-1	wt%	wt%		m	m	kg m-1s-1	kg/m3	
01-Dec	67.46	99.46	0.81	1.25	0.006746	2.266556	25.551	0.0025	0.0023	880	2.098773
02-Dec	64.36	99.45	0.79	1.16	0.006436	2.2567383	25.551	0.0025	0.0023	880	2.137952
03-Dec	38.69	99.6	0.69	0.98	0.003869	2.402647	25.551	0.0025	0.0023	880	2.356546
04-Dec	39.25	99.63	0.75	1.05	0.003925	2.4289674	25.551	0.0025	0.0023	880	2.209811
05-Dec	70.73	99.35	0.81	1.09	0.007073	2.1869323	25.551	0.0025	0.0023	880	2.109378
06-Dec	48.77	99.52	0.81	1.01	0.004877	2.3143887	25.551	0.0025	0.0023	880	2.114183
07-Dec	63.09	99.37	0.81	1.00	0.006309	2.2000674	25.551	0.0025	0.0023	880	2.101881
08-Dec	58.21	99.42	0.82	1.01	0.005821	2.240068	25.551	0.0025	0.0023	880	2.095335
09-Dec	28.69	99.73	0.79	1.05	0.002869	2.5615244	25.551	0.0025	0.0023	880	2.13721
10-Dec	50.29	99.58	0.75	1.19	0.005029	2.3726825	25.551	0.0025	0.0023	880	2.228285
11-Dec	77.32	99.3	0.62	1.11	0.007732	2.1575954	25.551	0.0025	0.0023	880	2.511817
12-Dec	109.09	99.02	0.69	1.12	0.010909	2.0104153	25.551	0.0025	0.0023	880	2.342467
13-Dec	52.76	99.54	0.70	1.15	0.005276	2.3377653	25.551	0.0025	0.0023	880	2.3187
14-Dec	61.07	99.5	0.83	1.23	0.006107	2.3030198	25.551	0.0025	0.0023	880	2.065305
15-Dec	70.59	99.42	0.84	1.22	0.007059	2.2387822	25.551	0.0025	0.0023	880	2.053388
16-Dec	45.94	99.64	0.83	1.27	0.004594	2.4414103	25.551	0.0025	0.0023	880	2.071515
17-Dec	48.93	99.64	0.80	1.35	0.004893	2.4392879	25.551	0.0025	0.0023	880	2.125918
18-Dec	59.32	99.59	0.80	1.46	0.005932	2.3911139	25.551	0.0025	0.0023	880	2.120926
19-Dec	63.28	99.56	0.81	1.42	0.006328	2.3518458	25.551	0.0025	0.0023	880	2.111186
20-Dec	37.18	99.71	0.79	1.30	0.003718	2.5430892	25.551	0.0025	0.0023	880	2.149795
21-Dec	40.56	99.69	0.82	1.30	0.004056	2.5042	25.551	0.0025	0.0023	880	2.096437
22-Dec	64.90	99.53	0.82	1.39	0.006490	2.3317637	25.551	0.0025	0.0023	880	2.080921
23-Dec	86.20	99.39	0.82	1.41	0.008620	2.2128349	25.551	0.0025	0.0023	880	2.088371
24-Dec	76.09	99.46	0.80	1.42	0.007609	2.2714213	25.551	0.0025	0.0023	880	2.130044
25-Dec	69.34	99.5	0.80	1.38	0.006934	2.3004392	25.551	0.0025	0.0023	880	2.120316
26-Dec	62.79	99.53	0.78	1.34	0.006279	2.3301503	25.551	0.0025	0.0023	880	2.165504
27-Dec	62.67	99.53	0.77	1.33	0.006267	2.3260742	25.551	0.0025	0.0023	880	2.177258
28-Dec	41.23	99.65	0.64	1.18	0.004123	2.4584333	25.551	0.0025	0.0023	880	2.474431
29-Dec	50.73	99.58	0.59	1.20	0.005073	2.3754365	25.551	0.0025	0.0023	880	2.617104
30-Dec	33.95	99.77	0.47	1.45	0.003395	2.6319537	25.551	0.0025	0.0023	880	3.061745
31-Dec	105.24	99.19	0.65	1.29	0.010524	2.0890678	25.551	0.0025	0.0023	880	2.445291

*The RHS of the correlation is assumed to be a factor X in the above table

Figure 4.3: Validation results of process kinetics

concentration profile is as shown in the figure 4.4

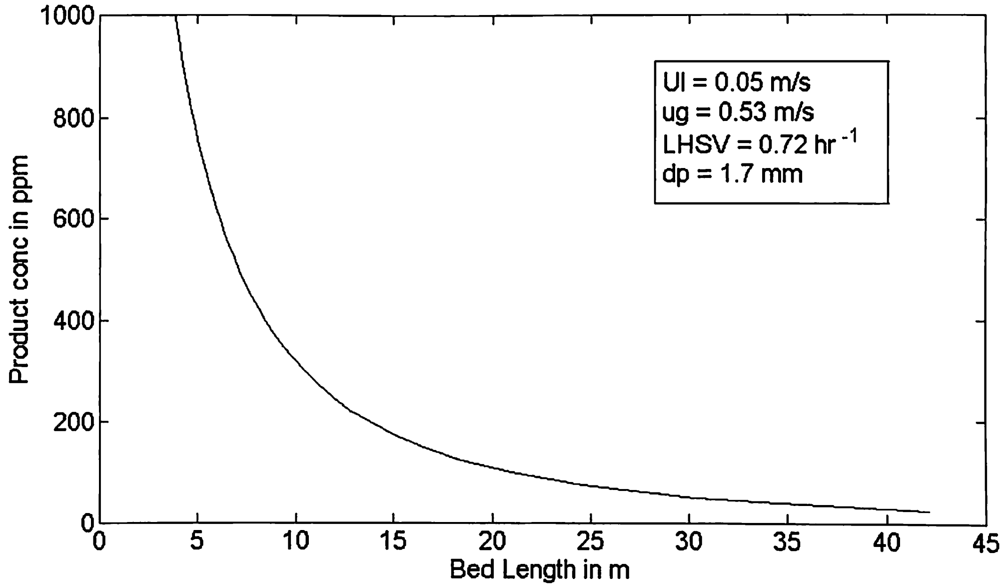


Figure 4.4: Concentration profile

The profile generated shows the concentration of sulphur at the outlet reduces to 30ppm for a bed length of 25 metres. This is the effective the bed length if the catalyst particles which the reaction occurs are only considered.

4.2.3 Effect of Temperature on Kinetics

The temperature effects on the kinetics of DHDS is as given by the Shell's Book of Hydrotreating [19]. The book gives a correlation based on which the maximum conversion for a given temperature can be obtained.According to the equation

$$\frac{C_{in}}{C_{out}} - 1 = \frac{F \times M \times P}{WHSV} \times K_2.exp\left(\frac{-E_a}{RT}\right). \tag{4.1}$$

This equation was validated for the plant data and the conversion levels were cross referenced with the bed WABT of the reactor. The match of the data were found to be good. The above correlation can be used to determine the conversion possible at a given feed conditions and WHSV. The activation energy reported by Korsten [11] as 23814 KJ/K.mol was used. The results obtained by this fit are summarized for different WHSV in the Figure 4.5.

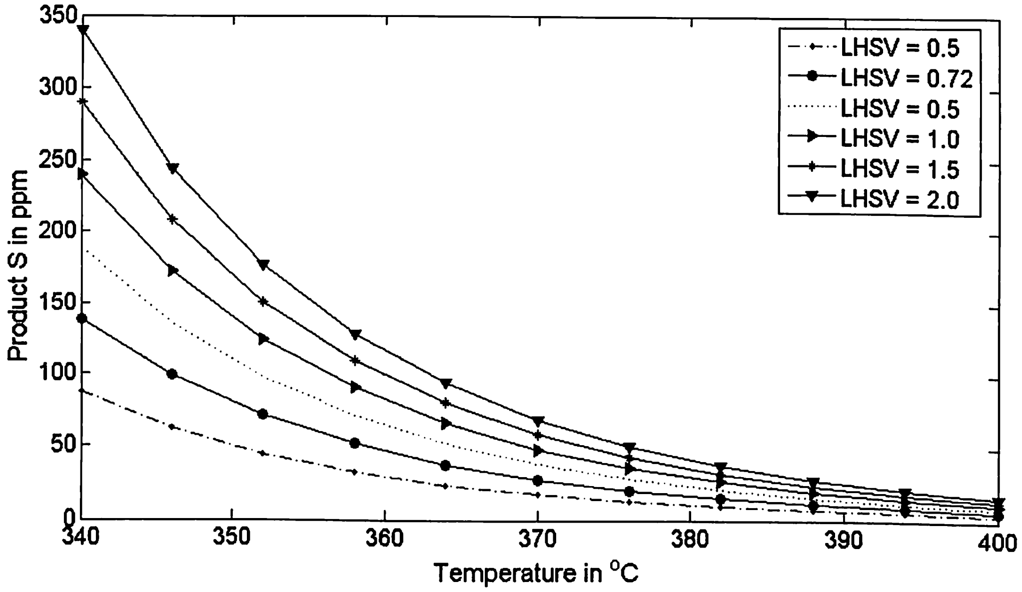


Figure 4.5: Temperature dependence of final sulphur concentration for different LHSV values

It can be seen that for a temperature of 360 °C the final concentration reduces to 30 ppm at a LHSV of 0.72.The WABT for a conversion of 99.75 percentage is 358

^{o}C from the plant operating data. Hence the above correlation is also found to be a good fit to plant data.

4.2.4 Validation of Kinetics Based on Reactor Volume

The reactor volume can be determined by the use of a general nth order kinetic equation.

$$kt = \frac{1}{n-1}\left(\frac{1}{C_{out}^{n-1}} - \frac{1}{C_{in}^{n-1}}\right) \tag{4.2}$$

The kinetic constant is given by the Arrhenius equation as given by Korsten [11]

$$k = 9.5 \times 10^{15} exp\left(\frac{-21384}{T}\right) \tag{4.3}$$

From the above equation the value of time taken can be determined if given the values of C$_{in}$ and C$_{out}$. This time is inversely proportional to the liquid hourly space velocity (LHSV). Thus

$$LHSV = \frac{1}{t} = \frac{volumetric\, feed\, rate}{volume\, of\, catalyst} \tag{4.4}$$

The value of order of the reaction is taken to be 1.75 for a blend of gas oil and vacuum gas oil [15].This gives a volume needed to treat 407488 kg/h of feed is 873 m^3. The actual catalytic volume in the reactor from design data is found to be 871 m^3. The volume calclated from the correlation matched the design data.

4.2.5 Validation of Pressure Drop Correlation

The pressure drop correlation data as discussed in 3.1.2 was also validated with the plant operating data. The pressure drop for individual beds were calculated using the two phase pressure drop equation as given by Abbott *et.al.* [2]. The calculated pressure drop for individual bed showed about ± 10 % error. The overall pressure drop matched the plant operating data with a deviation of $\leq$ 2 % error. Thus the correlations for pressure drop seem to be holding good in determination of the reactor operation. This can be used to design the reactor. The results obtained with reference to the plant operating data are shown in the Table 4.1

	$\Delta PBed - 1$	$\Delta PBed - 1$	$\Delta PBed - 1$	Total ΔP
Instrumentation Tag	40-DPI-025	40-DPI-026	40-DPI-147	
Unit	kg/cm^2	kg/cm^2	kg/cm^2	kg/cm^2
Plant Data	0.64	1.23	2.19	4.06
Computed Data	0.71	1.46	1.96	4.02
% Deviation	-11	-8	9	1

Table 4.1: Validation of Pressure Drop

Chapter 5

MODELLING

A mathematical model is a system of equations, which describes the relationship among the physical and chemical variables governing the behavior of a process. In heterogeneous catalytic reactor applications these equations are the energy, mole and momentum balances, rate equations and physical property relationships.

In this present work only mole balance equations are taken in to account as reactor was considered isothermal. In the following section the development of model equations, the simplifying assumptions incorporated and the simulation algorithms used in obtaining solutions. As explained in earlier section 1.3, the reactor used for HDS is co-current down flow trickle bed reactor. Industrial reactors are operated at trickle flow regime. Hence the HDS reactor models are developed for trickle flow regime. Applying mass conservation law over an elemental reactor volume we develop the model equations. The elemental reactor volume consists of gas, liquid and solid phases.

In trickle flow regime, it is clear that there is no direct contact between gas and solid surface. Liquid flows over the catalyst as revolute, which in turn depends on liquid and gas velocity. The feed gas flows over the liquid flowing film coated solid catalyst. In view of this the model equations are developed separately for gas phase and liquid phases.

The concentration model developed is based on the three-film theory with hydrogen, hydrocarbon and catalyst as the three distinct phases. As per the assumptions the reactions of HDS occur only in the liquid phase and not in the gas or solid phase. The following model equations give the concentration profile of four species namely hydrogen, hydrogen sulphide, hydrocarbon and organic sulphur. The constants involved in the model an be evaluated by the correlations proposed by Farahani and Shahhosseini [6]

5.1 Mole Balances

5.1.1 In Gas Phase

A steady state plug flow mole balance gives the needed model equations to describe the system. The mass transfer in the gas phase is as give in the Figure 5.1.
For the Component A

$$[Moles\,of\,A\,in] - [Moles\,of\,A\,out] - [Moles\,of\,A\,reacted]$$
$$- [Moles\,of\,A\,transfered\,to\,liquid\,phase] = 0$$

5.1.2 In Liquid Phase

A steady state plug flow mole balance gives the needed model equations to describe the system. The mass transfer in the liquid phase is as give in the Figure 5.1.
For the Component A

$$[Moles\,of\,A\,in] - [Moles\,of\,A\,out] - [Moles\,of\,A\,reacted]$$

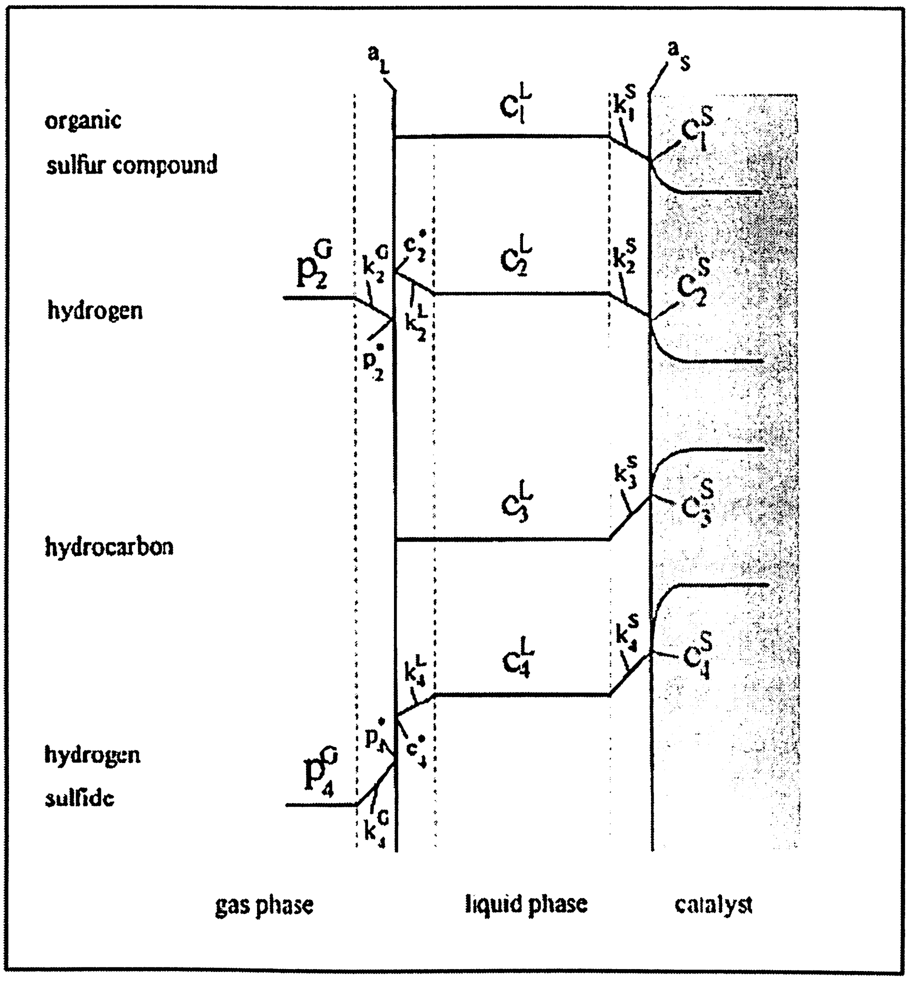


Figure 5.1: Three-film theory profile - Korsten [11]

$- [Moles\ of\ A\ transfered\ from\ liquid\ phase\ to\ gas\ phase] = 0$

As the volume element AΔZ becomes small it approaches the differential volume element and the final mole balance is as given below.

5.2 Hydrogen Balance

The hydrogen phase is the reactor's gaseous phase which is in equilibrium with the hydrocarbons in the reactor. As per the assumptions made in section 4.1.1, the liquid phase is assumed to be saturated with hydrogen the concentration profile along the length of the reactor is going to be unaffected. But to understand the nature of the variation of this phase the profile has been developed.

5.2.1 In Gas phase

$$\left(\frac{U_G}{R.T}\right)\left(\frac{dp^G_{H_2}}{dZ}\right) + K^L_{H_2}.a_L\left(\frac{p^G_{H_2}}{H_{H_2}} - C^L_{H_2}\right) = 0 \tag{5.1}$$

5.2.2 In Liquid phase

$$U_L\left(\frac{dC^L_{H_2}}{dZ}\right) - K^L_{H_2}.a_L.\left(\frac{p^G_{H_2}}{H_{H_2}} - C^L_{H_2}\right) - K^S_{H_2}.a_S\left(C^L_{H_2} - C^S_{H_2}\right) = 0 \tag{5.2}$$

5.2.3 On solid surface

$$K^S_{H_2}.a_S\left(C^L_{H_2} - C^S_{H_2}\right) = \Pi_{H_2}.r_c \tag{5.3}$$

5.3 Hydrogen Sulphide Balance

The initial concentration of hydrogen sulphide is known from the composition of the recycle gas stream. The hydrogen sulphide produced in the reactor gets added up to this stream and a profile is obtained. The model is as below.

5.3.1 In Gas phase

$$\left(\frac{U_G}{R.T}\right)\left(\frac{dp^G_{H_2S}}{dZ}\right)+K^L_{H_2S}.a_L\left(\frac{p^G_{H_2S}}{H_{H_2S}}-C^L_{H_2S}\right)=0 \tag{5.4}$$

5.3.2 In Liquid phase

$$U_L\left(\frac{dC^L_{H_2S}}{dZ}\right)-K^L_{H_2S}.a_L.\left(\frac{p^G_{H_2S}}{H_{H_2S}}-C^L_{H_2S}\right)-K^S_{H_2S}.a_S\left(C^L_{H_2S}-C^S_{H_2S}\right)=0 \tag{5.5}$$

5.3.3 On solid surface

$$K^S_{H_2S}.a_S\left(C^L_{H_2S}-C^S_{H_2S}\right)=\Pi_{H_2S}.r_c \tag{5.6}$$

5.4 Hydrocarbons Balance

The hydrocarbon phase constitutes the majority of the liquid phase. This phase is assumed to remain unaltered along the length of the reactor as there is no considerable change in its concentration. The desulphurised hydrocarbon added to this stream in negligible when compared to the feed stream concentration. Hence it also is expected to maintain a flat profile like that of hydrogen. The model equations are as given below.

5.4.1 In Liquid phase

$$U_L\left(\frac{dC^L_{HC}}{dZ}\right)+K^S_{HC}.a_S\left(C^L_{HC}-C^S_{HC}\right)=0 \tag{5.7}$$

5.4.2 On solid surface

$$K^S_{HC}.a_S\left(C^L_{HC}-C^S_{HC}\right)=\Pi_{HC}.r_c \tag{5.8}$$

5.5 Organic Sulphur Balance

The organic sulphur stream consists of the net sulphur in the gas oil. This stream is a combined notation given to the various sulphur compounds present in the gas oil fraction. The inlet concentration of S is known. This serves as one of the boundary condition to solve the system of equations. The sulphur profile is given by the model equations as below.

5.5.1 In Liquid phase

$$U_L\left(\frac{dC_s^L}{dZ}\right)+K_s^S.a_S\left(C_s^L-C_s^S\right)=0 \tag{5.9}$$

5.5.2 On solid surface

$$K_s^S.a_S\left(C_s^L-C_s^S\right)=\Pi_s.r_c \tag{5.10}$$

5.6 The Rate of Desulphurisation

The term r_c which occurs in the above equations is based on a power law model. Since HDS being considered as an irreversible equation.

$$r_c=k_{app}\times[C_S]^n \tag{5.11}$$

Here the rate of reaction per unit mass of the catalyst is correlated with the concentrations of sulphur. The rate constant k_{app} is given as the apparent rate constant which includes both the mass transfer and the diffusional effects in it. The equation for the apparent rate constant is given by Korsten [11] as

$$\frac{1}{k_{app}} - \frac{1}{k_{in}} = \frac{A}{G_L^B} \tag{5.12}$$

The constants A= 0.21 and B= 1.40.

5.7 Boundary Conditions

The above mentioned ODE are to be solved with the help of the following boundary conditions. At the inlet of the reactor the concentration of sulphur, hydrogen, H_2S are known. They are as follows

$$p_{H_2}^G = p_{H_20}^G \tag{5.13}$$

$$C_S^L = C_{S0}^L \tag{5.14}$$

$$p_{H_2S}^G = p_{H_2S0}^G \tag{5.15}$$

$$C_{HC}^L = C_{HC0}^L \tag{5.16}$$

$$C_{H_2S}^L = 0 \tag{5.17}$$

5.8 Simulation Algorithm

We must know the values of interface mass transfer coefficients, Henry's coefficient, kinetic parameters, physical and chemical properties of components at a given process condition, range of process operating conditions, initial value of the dependent variables and numerical method which is appropriate for the problem.

5.9 Parameter Estimation

5.9.1 Gas-Liquid Mass Transfer

The gas-liquid mass transfer coefficient can be determined by the correlation published by goto and smith [9].

$$\frac{k_i^L.a_L}{D_i^L} = \alpha_1.\left(\frac{G_L}{\mu_L}\right)^{\alpha_2}.\left(\frac{\mu_L}{\rho_L.D_i^L}\right)^{0.5} \tag{5.18}$$

Where

$\alpha_1 = 0.4$ and $\alpha_2 = 7(cm)^{-1.6}$

$$D_i^L = 8.93 \times 10^{-8}\frac{v_c^{0.267}}{v_i^{0.433}}\frac{T}{\mu_L} \tag{5.19}$$

5.9.2 Density Variation

The density of the oil at process conditions can be determined by the standingkatz correlation

$$\rho\,(P,T) = \rho_0 + \Delta\rho_P - \Delta\rho_T \tag{5.20}$$

Pressure Correction

$$\Delta\rho_P = \left[0.167 + 16.181 \times 10^{-0.0425}.\rho_0\right]\left[\frac{P}{1000}\right] - 0.01\left[0.299 + 263 \times 10^{-0.0603}.\rho_0\right]\left[\frac{P}{1000}\right]^2. \tag{5.21}$$

Temperature Correction

$$\Delta\rho_P = \left[0.0133 + 152.4\,(X)^{-2.45}\right]T - \left[8.1 \times 10^{-6} - 0.062 \times 10^{-(0.764(X))}\right]T^2 \tag{5.22}$$

where

$$X = \rho_0 + \Delta\rho_P \tag{5.23}$$

$$T = T(^oR) - 520 \tag{5.24}$$

5.9.3 Viscosity

The dependence of liquid viscosity on temperature may be described by the Glasco's correlation. In terms of API gravity this equation gives the viscosity as,

$$\mu_L = 3.141 \times 10^{10} - (T(^oR) - 46O)^{-3.444} \left[log_{10}\left(API\right)\right] \tag{5.25}$$

$$a = 10.313 \left[log_{10}\left(T(^oR) - 460\right)\right] - 36.447 \tag{5.26}$$

5.9.4 Specific volume

The molar volume of solute at its boiling temperature can be estimated by following relation

$$v = 0.285.v_c^{1.048} \tag{5.27}$$

The critical specific volume for the liquid component can be obtained by using the Riazi-Daubert correlation.

$$v_c = v_c^m \times M \tag{5.28}$$

$$v_c^m = 7.5214 \times 10^{-3} T_{MeABP}^{0.2896} (sg_{15.6})^{-0.7666} \tag{5.29}$$

Molar critical specific volume can be obtained by multiplying with the molecular weight.

5.9.5 Henry coefficient

The Henry coefficient can be determined from solubility coefficients

$$H_i = \frac{v_N}{\lambda_i . \rho_L} \tag{5.30}$$

Solubility of hydrogen and hydrogen sulphide in hydrocarbon mixtures can be determined from the following correlation

For hydrogen and hydrogen sulphide,

$$\lambda_{H_2} = a_0 + a_1 \times T + a_2 \times \frac{T}{\rho_{H_{20}}} + a_3 \times T^2 + a_4 \times \frac{T}{\rho_{H_{20}^2}} \tag{5.31}$$

$$\lambda_{H_2S} = exp\,(3.3670 - 0.008470 \times T) \tag{5.32}$$

The various parameters such as gas-liquid mass transfer coefficients, liquid to solid mass transfer coefficients, henry's constants, density, viscosity of gas oil at reactor conditions, solubility of hydrogen and hydrogen sulphide in the gas oil at reactor conditions were estimated prior to their use in the model. A MATLAB(R2008a) code was compiled and these data were calculated. The code is as given in the appendix.

5.9.6 Solution to Model Equations

The equations shown above are simultaneous first order differential equations. The equations from 1 through 16 are to be solved simultaneously for which a code in MATLAB(R2008a) using the inbuilt ode45 algorithm is compiled and the results are validated with the industrial data. Though the model needs further fine tuning the developed model satisfactorily fits the industrial reactor and the simulation is complete. The results obtained are discussed later in the thesis.

Chapter 6

DESIGN OF REACTOR

A reactor to treat the concentrated stream from the s-brane process has been designed in this chapter. The initial feed properties are set and are as given in the Table 6.1 and 6.2

Property	Test Method	Value
Quantity, MT/SD		3733
Density at 15°C, gm/cc	D4052	0.8490
Viscosity at 40°C,cP	D445	2.3
Sulphur,wt%	D2622	2.50
Total Nitrogen,ppm wt	D4629	249
Cetane index (calculated)	D4737	45.0
Flash point CC, Pensky-Martens, °C	D93	51.0
Total Aromatics FIA, vol%	D1319	39.0

Table 6.1: Properties of Diesel Oil Feed Stock

ASTM D-86 Distillation	
IBP,°C	131
5 vol.%, °C	230
10 vol.%, °C	258
20 vol.%, °C	293
30 vol.%, °C	311
50 vol.%, °C	331
70 vol.%, °C	358
80 vol.%, °C	374
90 vol.%, °C	402
FBP, °C	425

Table 6.2: ASTM D-86

6.1 Methodology for Design

Based on plant data, certain process parameters such as

1. Feed Flow rate.
2. Feed conditions.
3. Initial Sulphur content.
4. Desired removal of sulphur.
5. Catalyst used and the kinetics.

were frozen and then the design based on the developed models was done. Models which have been previously developed were thoroughly analyzed and the design equations were developed. [13].

6.2 Information Flow Sequence for Design

The information flow sequence illustrated in the Figure 6.1 shows the complete iterative design of a TBR.

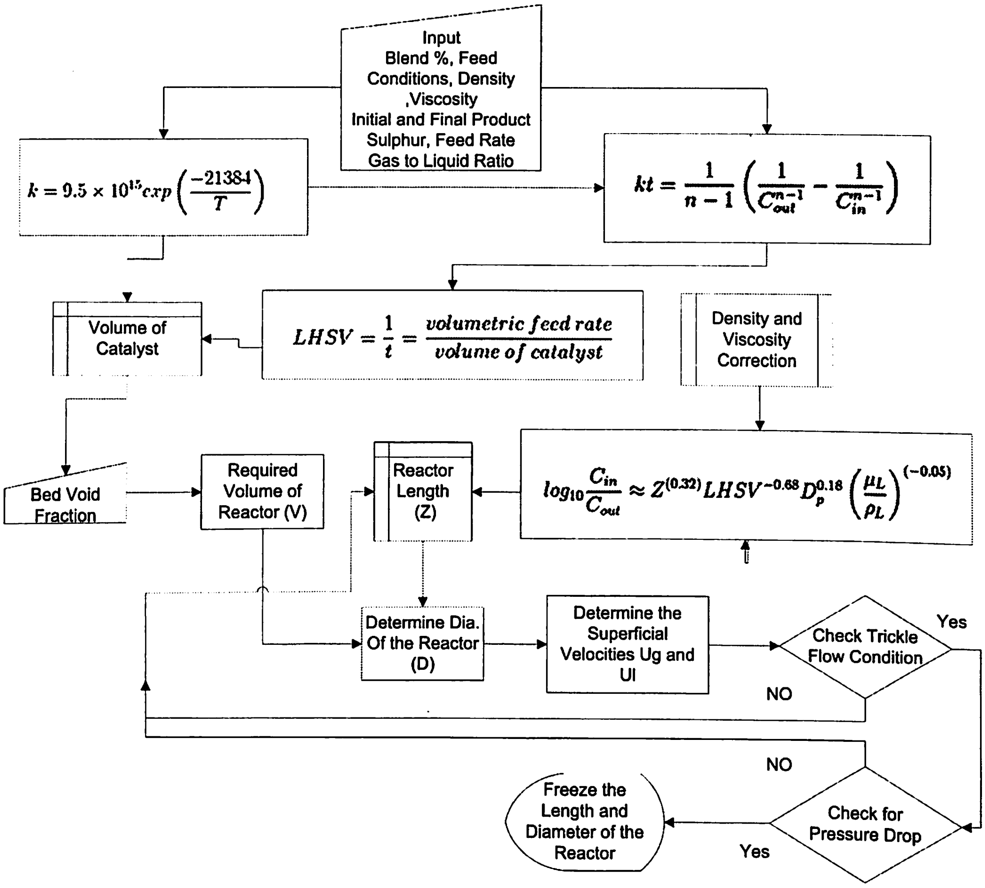


Figure 6.1: Information Flow Diagram

Chapter 7

RESULTS AND DISCUSSION

7.1 Simulation Results

7.1.1 Concentration Profiles

The concentration profiles along the length of the bed are as shown in the following figures. These illustrate the various profiles of H_2, H_2S,and Sulphur in the gas and the liquid phases.

Initially the consumption of hydrogen is less. Hence, the partial pressure of hydrogen in gas decreases slightly along the length of catalyst bed. This trend is due to the contact of H_2 with H_2 saturated fresh feed. But along the length , hydrogen is the liquid phase gets consumed and hence the hydrogen from gas phase is transfered to the liquid phase. Model reveals this behavior exactly as shown in Figure 7.1.

The concentration profile of hydrogen along the length of reactor. The trend is due to the concentration difference of hydrogen between gas-liquid interface and bulk liquid phase. initially it was high and then it decreases as shown in Figure 7.2.

Figure7.3 gives the concentration profile of H_2S in gas phase. H_2S produced by reaction was initially high and then decreases rapidly. Hence the partial pressure of H_2S was high and then remains constant.

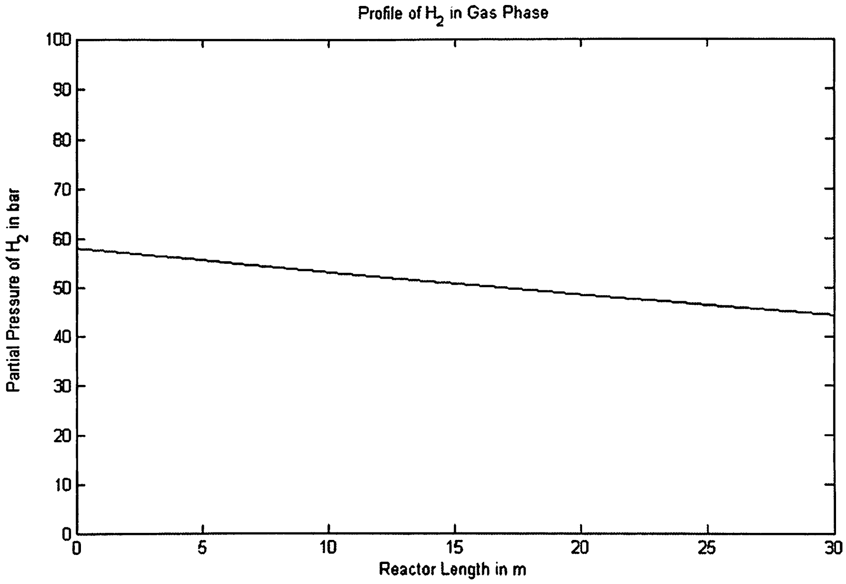


Figure 7.1: Partial Pressure of Hydrogen in Gas Phase

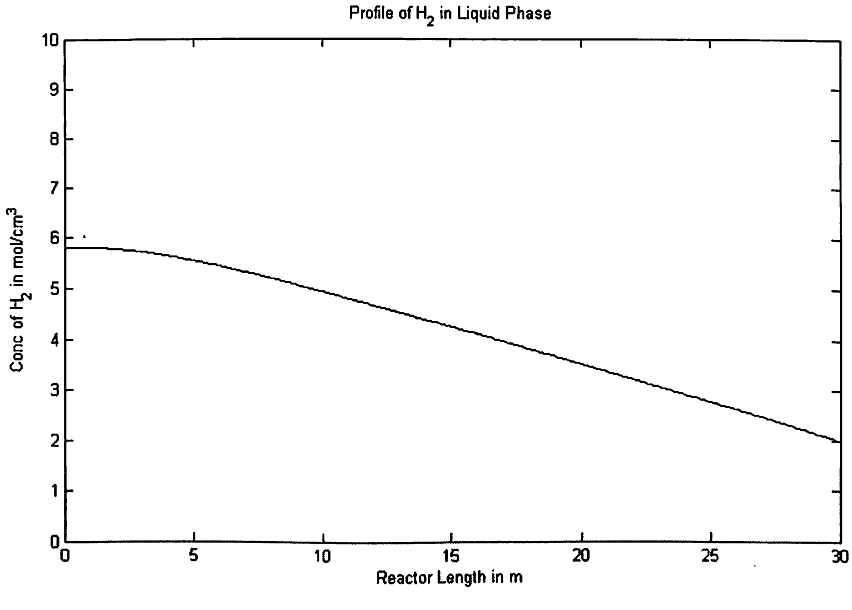


Figure 7.2: Concentration profile of Hydrogen in Liquid Phase

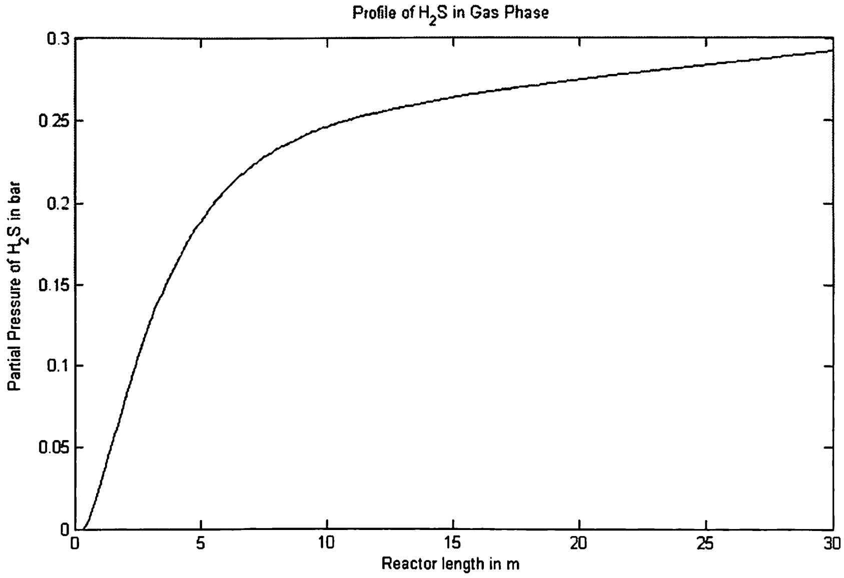


Figure 7.3: Partial Pressure of H_2S in Gas Phase

The concentration profile of H_2S in liquid phase is as given in Figure 7.4. Initially the concentration is the liquid phase was high because of HDS reaction and then decreases rapidly.

The profile of sulphur concentration along the reactor is as given in Figure 7.5. Here the initial sulphur content is high which rapidly decreases along the reactor as the HDS reaction proceeds. It decreases in an exponential manner which clearly resembles the way the overall kinetics described it. Hence it can be noted that the model as well as the correlation based approach holds good.

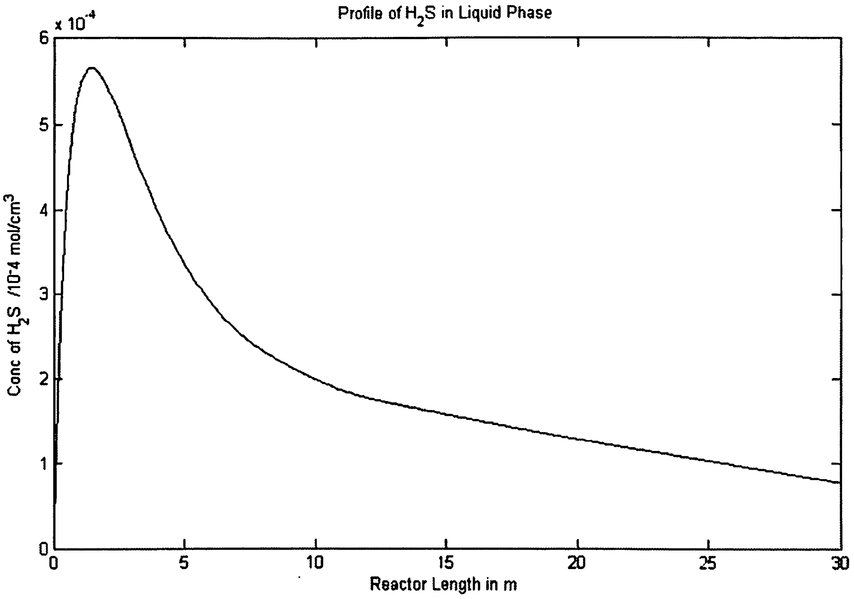


Figure 7.4: Concentration profile of H_2S in Liquid Phase

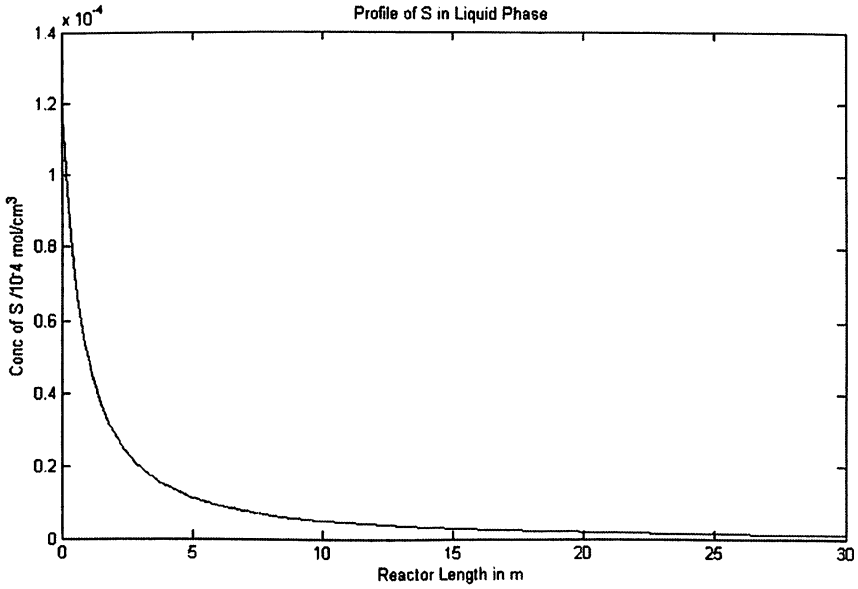


Figure 7.5: Concentration Profile of S

7.2 Effect of Process Variables

Effect of process variables of hydrodesulphurisation are temperature, pressure, space velocity and gas to hydro carbon ratio. Mostly industrial reactors are .operated at constant pressure and gas to oil ratio. The concentration of various reactants at reactor outlet can be changed by adjusting the two process variables reactor temperature and liquid hourly.Since these two variable are those that can be easily manipulated the are used widely to control the performance of the reactor.

7.2.1 Effect of LHSV

It should be noted that the conversion in trickle bed reactors strongly depends on gas-liquid and liquid-solid interfacial area. In this present work all the three phases are taken into account to study the performance of the reactor. At elevated liquid velocity, the mass transfer is high hence the conversion is also high for the given LHSV. But it is also observed that beyond a particular temperature the conversion is not much influenced by the space velocity. Hence it is better to operate the reactor at a lower LHSV at a optimum temperature where the conversion is maximum in order to process more feed. Operating the reactor at a lower LHSV would effect in increased profits to the refinery.

As per the data given by Shell's book on hydrotreating [19] a plot on the the effect of LHSV on product conversion at various temperature is given in Figure 7.6

This result of LHSV was compared to that derived from the basic kinetic equation. The variation of product sulphur composition with respect to the liquid hourly space velocity was analysed for various temperatures. The curve obtained is as given as

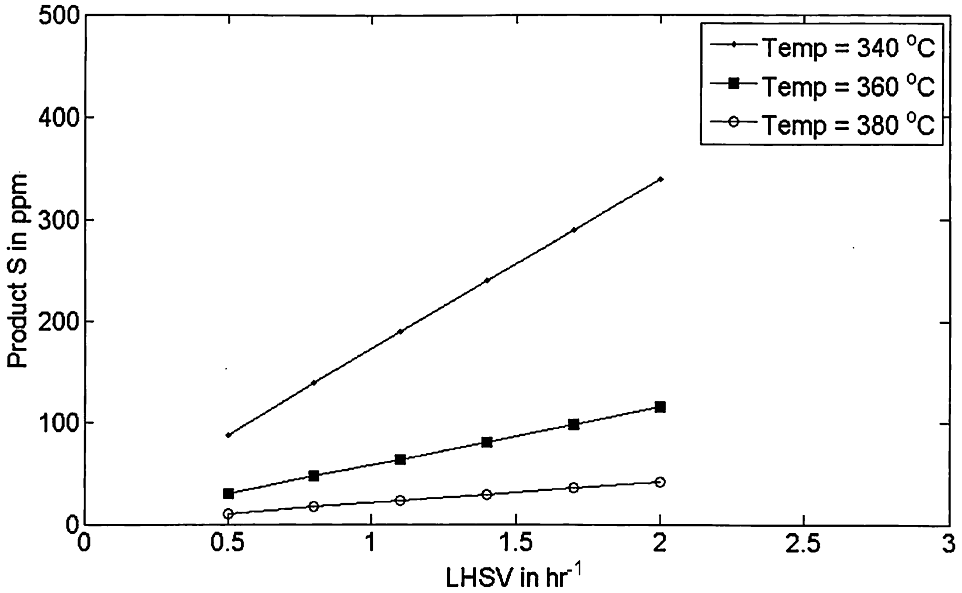


Figure 7.6: Product Sulphur variation with LHSV by shell's correlation

in Figure 7.7. This result from the basic nth order kinetics was compared to the results obtained from the shell's correlation for variation of product sulphur with LHSV. Thought the curves showed a similar pattern there was a wide variation in the product sulphur as the former was developed for an nth order rate and the later assumes a pseudokinetics of the hydrodesulhurisation process. The comparison is as given in the Figure 7.8.

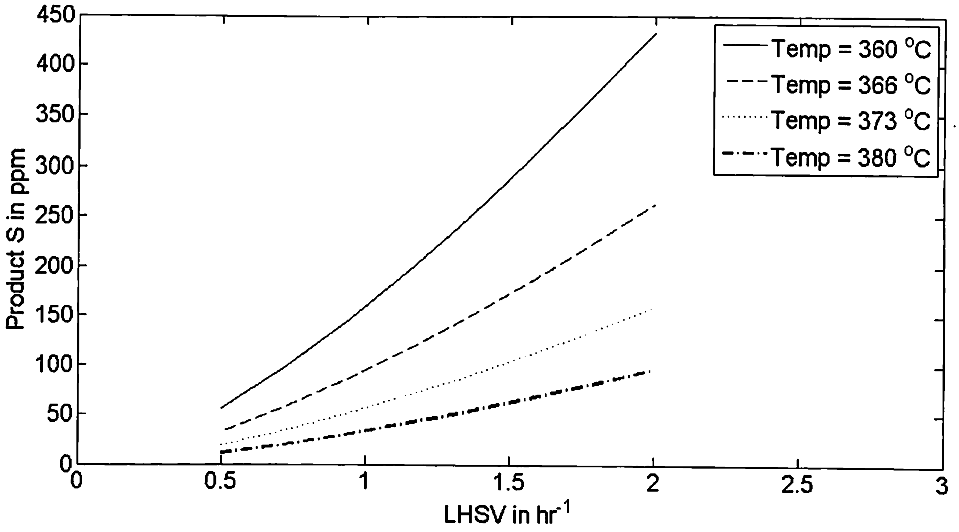


Figure 7.7: Product Sulphur variation with LHSV by nth order kinetic data

7.2.2 Effect of Temperature

The conversion of sulphur increases with increasing temperature. The reason is rate constant of rate expression has direct proportion with temperature and at a constant LHSV. Mass transfer parameters and Henry's coefficient increases with increasing temperature. These two valid reasons have strong influence on product sulphur content. In addition to this, increase in temperature has increased mild hydro cracking reaction. Hence it is necessary to operate at an optimum temperature at which the cracking reactions are minimized and HDS reactions are favored.The final sulphur concentration variation with temperature at different LHSW is given in the Figure 7.9

The product sulphur variation with the reactor temperature was studied from the nth order kinetic data also. The results obtained from this method is as given in the Figure 7.10. This clearly shows the same patter of behaviour of the system.

of LHSV2.jpg

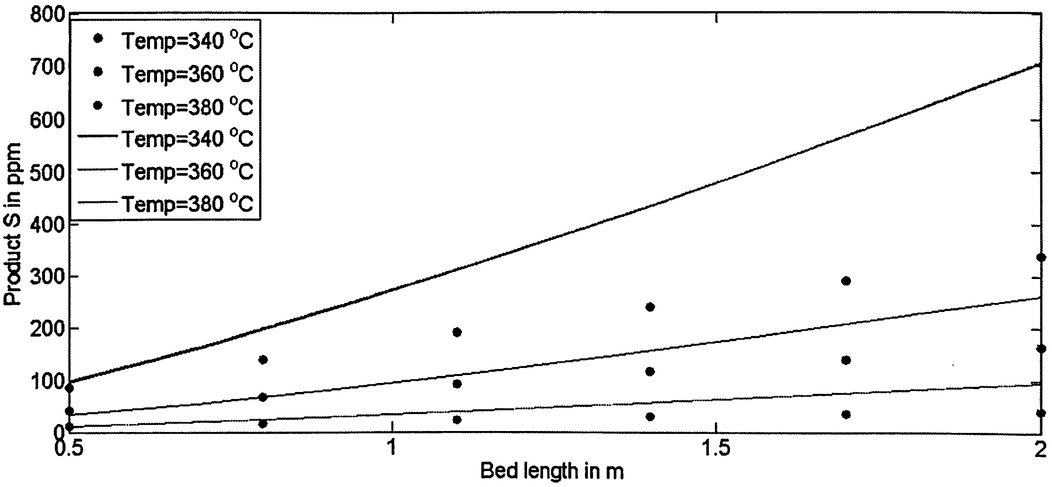


Figure 7.8: Comparison of effect of LHSV

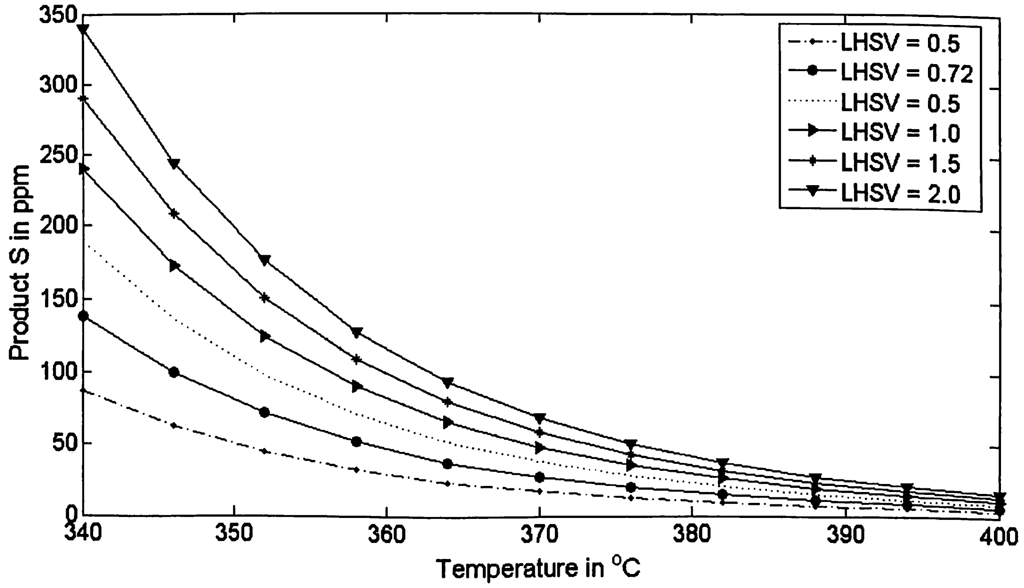


Figure 7.9: Product Sulphur variation with Temperature by shell's correlation

When the temperature is increased the product sulphur concentration is seen to decrease drastically to a certain extent and the it saturates. Lower the LHSV for better the conversion. Hence at a optimal LHSV the temperature of the reactor so as to achieve the required conversion. The feed vaporisation at that temperature must also be considered so that accordingly the pressure of the reactor is fixed. The combined curve which illustrates the results from the two approaches, viz. shell's hydrotreating correlation approach and nth order kinetic equation based approach is as given in the Figure 7.11

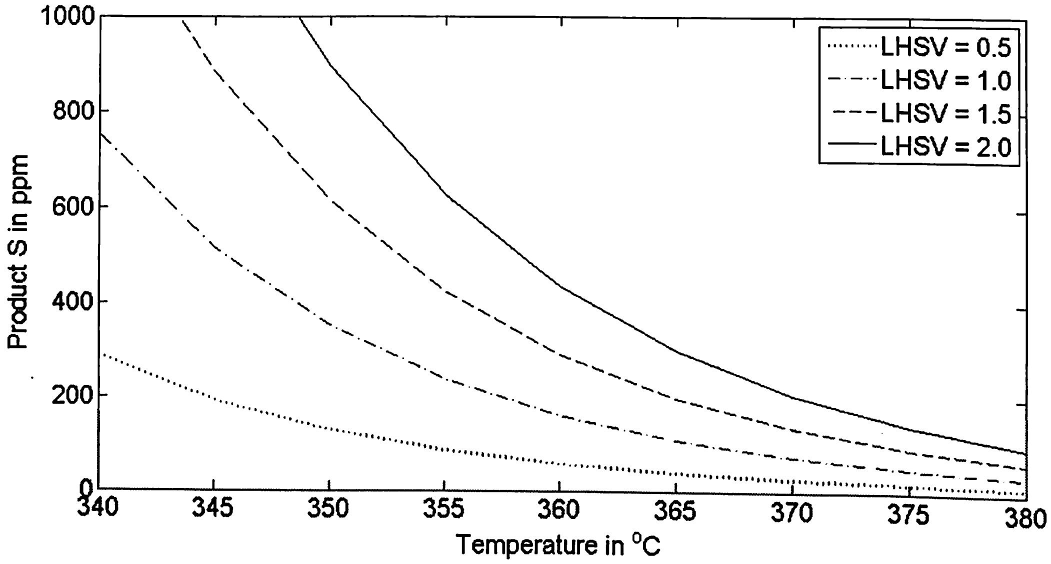


Figure 7.10: Product Sulphur variation with Temperature by nth order kinetic data

of Temp.jpg

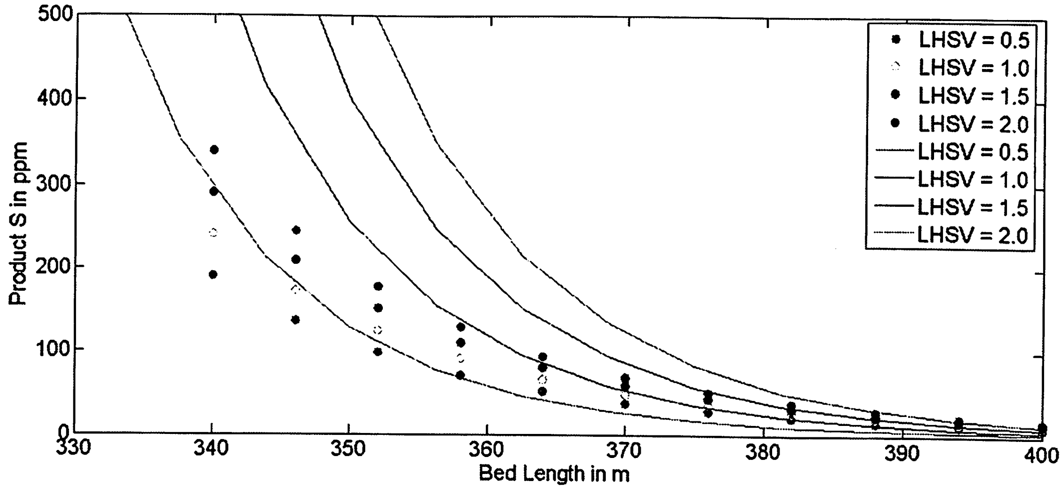


Figure 7.11: comparison of effect of temperature

7.3 Discussion

A combined curve of the concentration profile predicted by the correlations and that predicted by the model are shown in the Figure 7.12. The curve gives a plot between the reactor length and the percentage conversion.

These results were obtained for the following conditions

Reaction Temperature = 375 ^oC

Reactor Pressure = 58 bar

Catalyst particle diameter = 1.2 mm

Liquid hourly space velocity = 0.72

Initial S concentration = 1.4 wt%

Density at 15 ^oC = 849.1 kg/m^3

Viscosity at 15 ^oC = 0.15 cP

It can be seen from the Figure 7.12 that the product conversion at a bed depth of 25 m is 99.35% for the profile given by the model equations and it is 99.75 % for the profile got from the design correlation. The actual plant conversion is about 99.80%. Thus it can be seen that both the models predict the final concentration in a very close manner. The deviation in the conversion are due to various reasons they are

1. Variation due to approximation of reaction kinetics by power law.
2. Variation due to neglecting the axial dispersion.

Among the design procedure the correlation based approach gives a better fit to the plant data as these correlations were developed as a result of studies conducted on various operating reactors. The second best match which is based on the model equations can be further fine tuned by incorporating the axial dispersion, catalyst deactivation and the hydrodynamic effects in the reactor.

Figure 7.13 gives an idea about the way the sulphur from the gas phase reacts with the hydrogen in the reactor to for hydrogen sulphide. At a bed length of 11 m the conversion is almost 75 % complete. But inorder to achieve $\geq$ 99 % it is necessary to provide the excess bedlength of about 15 m. This ensures that the product sulphur concentration is well below the established regulatory standards.

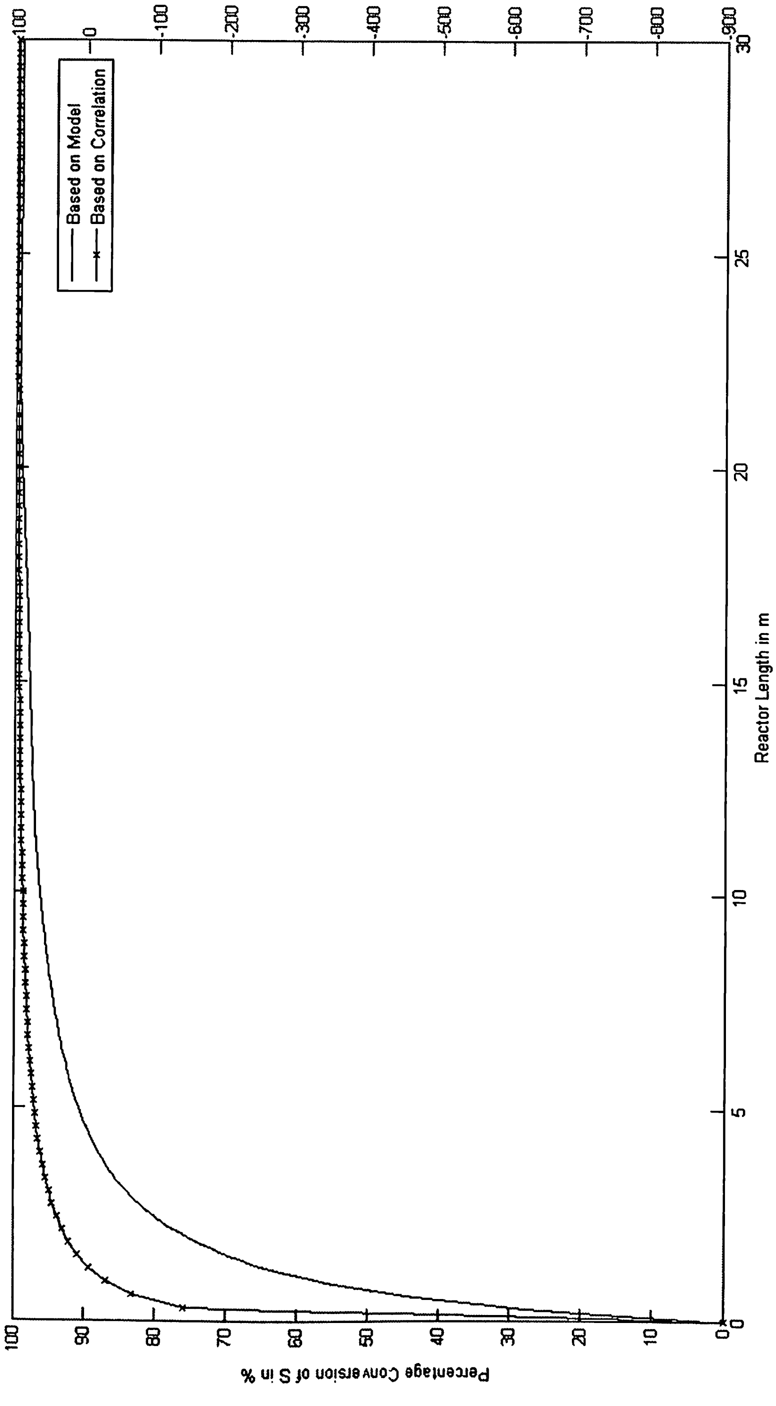
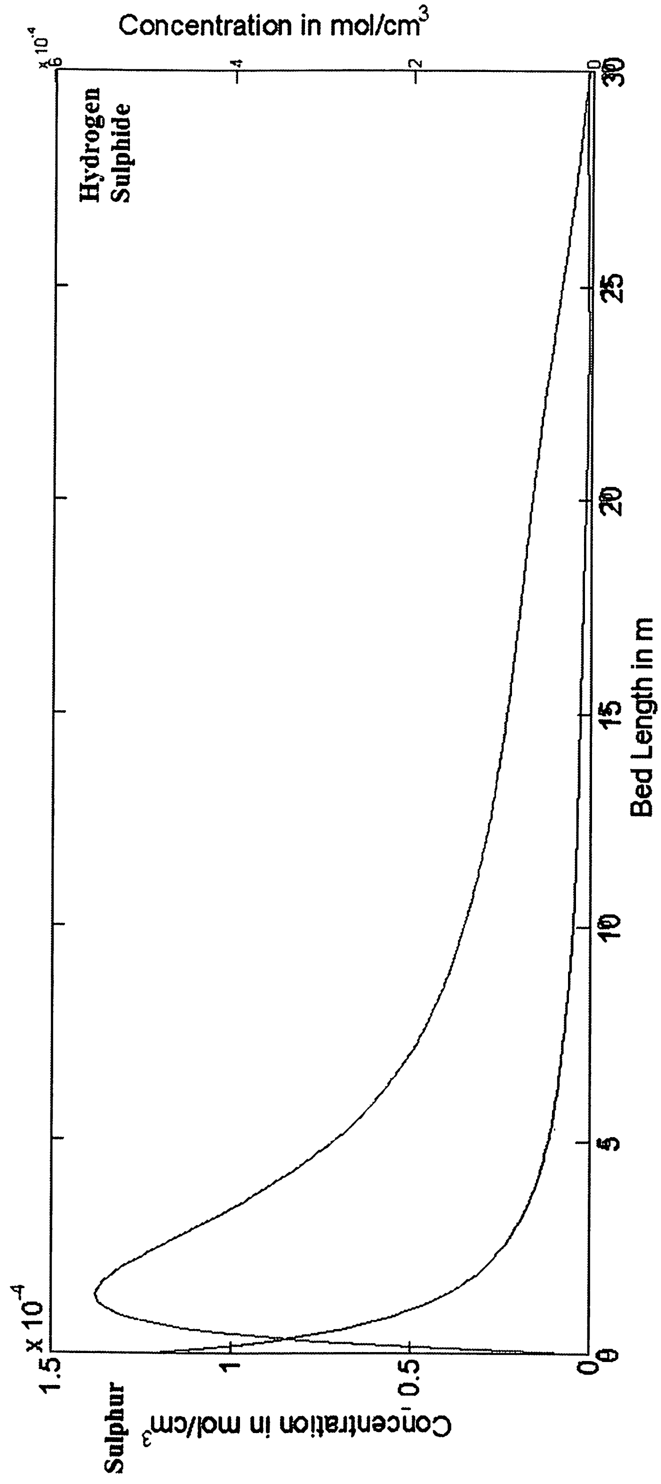


Figure 7.12: Percentage conversion of S with Reactor Length


Concentration in mol/cm^3
x 10^{-4}
6
4
2
0
Hydrogen Sulphide
Bed Length in m
0
5
10
15
20
25
30
1.5 x 10^{-4}
1
0.5
0
Sulphur
Concentration in mol/cm^3

Chapter 8

CONCLUSION

8.1 Conclusions of Present Work

1. A two phase reactor model was developed to analyze the performance of Trickle Bed reactor.
2. A semi-empirical approach of design based on both correlation and modelling was used to design the reactor.
3. Plant data collected were used to estimate kinetic parameters. A correction was made on kinetic parameter so that it can be used for feeds which consists blends.
4. The model developed was used to predict concentration change of each species along the length of the reactor.
5. The model was validated using the plant data and also with the correlation results.
6. Product sulphur variation with process variables such as temperature, liquid hourly space velocity are also obtained and matched to plant data.

8.2 Application

1. Model can be used to analyze the effect of important process variables on product quality over a wide range of operating conditions.
2. Model can be used to evaluate the performance of various catalysts on product quality.
3. Kinetic parameter estimated from pilot plant can be used for effective hydrotreater design.
4. Optimum operating condition required for ultra low sulfur diesel production can be analyzed using the developed model.

8.3 Ultra low sulfur diesel oil production

As discussed earlier the main operating condition of HDS process is temperature, pressure, weight hourly space velocity of liquid and gas to oil ratio. To get ultra low sulfur the operating condition used to simulate the model was as shown below, temperature 350C, LHSV 0.72 hr^{-1}, Pressure 5.8 Mpa and gas to oil ratio 200 Nm^3/m^3. The reason for above condition selection was due to the following reason.

8.3.1 Temperature

The temperature of the reactor affects catalyst stability and feed oil vaporization inside the reactor. Hence temperature selection for the process is much important. Much of industrial operations are carried out at an average temperature of 350 C. Hence this condition was used for ULSD oil production analysis.

8.3.2 Weight hourly space velocity

LHSV has direct relation with through put of the reactor. The demand of petroleum product in the market is very high. So the reactor must be operated at high through put rate. But increasing through put rate decreases the product quality. Hence the LHSV must be maintained at optimum. So the LHSV selected for ULSD oil production was 0.72 hr.

8.3.3 Pressure

Kinetics of reactions occurring in the reactor require high temperatures, which in return increase gas expansion and impede the gaseous reactant from dissolving sufficiently into the liquid. Therefore, elevated pressures (up to 60 MPa) are necessary to improve the gas solubility and the mass and heat transfer rates, to handle large gas volumes at less capital expense, and to slow down the catalyst deactivation which may be triggered by hydrogen starvation of the catalyst. Hence an optimum pressure of 5.5 Mpa is suggested for operation.

Thus by adjourning to all the above said process conditions the production of ULSD can be ensured.

8.4 Recommendations for future work

The following are the recommended work to be carried out in the future

1. Analysis of catalyst deactivation with time.
2. Variation of rate of deactivation with temperature.
3. Accounting for the axial dispersion.
4. Development of non-isothermal model.

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Appendix A

Code for Reactor Validation

A.1 File - tbr.m

```
 % Data Input
clear;
clc;
%input feed blend percentage
vgo=20;
srgo=80;
%input feed rate in kg/h
w_feed = 140000;
%feed sulphur in ppm
cin = 25000;
%needed product spec in ppm
cout= 30;
%process temperatre in celcius
tc = 375;
%oil density at 15 deg C kg/m3
density=849.1;
%diameter of catayst particle in m
dp=0.0017;
```

```
%viscosity of oil in kg/m.s
visoil=0.15;
%input operating LHSV
LHSV = 0.72;
%unit change of temp
tk = tc+273; %process temperatre in kelvin
tr = 1.8*tk; %process temperatre in rankine
r=8.314; % gas constant
%density correction
row=density/1000; % as sp. gr
rowlb=62.43*row; %density in lb
pma=5.8; % pressure in MPa
psi=14.7*(1/1.01325e5)*pma*1e6; %pressure in psi
% effect of P on oil density
denp=0.167+16.181*(10^(-0.0425*rowlb))*(psi/1000)-
0.01*(0.299+263*(10^(-0.0603*row)))*((psi/1000)^2);
% effect of T on oil density
dent=(0.0133+152.4*((rowlb+denp)^-2.45))*(tr-520)-
(8.1*(10^-6)-0.06222*(10^-(0.764*(rowlb+denp))))*((tr-520)^2);
den= rowlb+denp-dent; %corrected density in lb/ft3
denc=den*0.01602; % density in kg/m3
%Concentration Profile
percon = linspace(1,100,1000);
cprod = ((100-percon)*cin/100);
```

```
a=log10(cin./cprod);
x=LHSV^(-0.68)*dp^(0.17)*((visoil/1000)/(denc*1000))^(-0.05);
bedlen=(a/x).^3.125;
subplot(2,1,1)
plot(bedlen,cprod)
%(1) Basic Kinetics to calculate the voume of catalyst needed
%estimation of reaction order
n=1.54*srgo/100+2*vgo/100
v_feed = w_feed/denc/1000; %feed rate in m3/h
%kinetic data
ko = 9.5e15;
E_A = 21384;
%Based on nth order kinetics
kin=ko*exp(-E_A/tk);
time=(1/kin)*(1/(n-1)*(((cout/10000)^(n-1)))^(-1)
-((cin/10000)^(n-1))^(-1));
lhsvin = time^-1;
catvol = v_feed/lhsvin
%Sp variation with Temperature
F = 1.7; % Feed Factor depends on the blend of GO
M = 1; % Boiling Range factor to be set from the crude assay
ptot =54; %total pressure of the reactor
xH2 = 0.86; %purity of the inlet H_2 phase
P = sqrt(ptot * xH2); %factor for H2 partial pressure
```

```
% LHSV Range
LHSV = linspace(0.5, 2, 6);
rhocat = 0.88; %bulk catalyst density
Sf = 12000; %feed sulphur in ppm
%kinetic data
ko = 9.5e15;
E_A = 21384;
%calculation
TC = linspace(340,400, 11);
TK = TC + 273;
for i=1:length(LHSV)
    k=ko*exp(-E_A./TK);
    AAA = F * M * P * k ./ LHSV(i)*rhocat;
    Sp(i,:)=Sf./(1 + AAA);

end
[TC' Sp']
subplot(2,1,2)
plot(TC, Sp)
```

A.2 File - TBR2

```
 %Sp variation with LHSV
clear
clc
F = 1.7; % Feed Factor depends on the blend of GO
M = 1; % Boiling Range factor to be set from the crude assay
ptot =54; %total pressure of the reactor
xH2 = 0.86; %purity of the inlet H_2 phase
P = sqrt(ptot * xH2); %factor for H2 partial pressure
    % LHSV Range
    LHSV = linspace(0.5, 2, 6);
    rhocat = 0.88; %bulk catalyst density
    Sf = 12000; %feed sulphur in ppm
    %kinetic data
    ko = 9.5e15;
    E_A = 21384;
    %calculation
    TC = linspace(340,380,4);
    TK = TC + 273;
    for i=1:length(LHSV)
        k=ko*exp(-E_A./TK);
        AAA = F * M * P * k ./ LHSV(i)*rhocat;
        Sp(i,:)=Sf./(1 + AAA);
```

```
    end
    plot(LHSV, Sp)
    save lhsvvar LHSV Sp
```

A.3 File - combined.m

```
clear;
clc;
%enter the inlet sulphur conc in ppm
insulp = 12300;
%enter the desired length for calculation
    len=30;
    ZSPAN=[0:.1:len];
    d = insulp*10^-8;
    YSPAN = [58 0 4 0 d];
    [T,Y] = ode15s(@rigid,ZSPAN,YSPAN);
    %subplot(2,3,1)
    %plot(T,Y(:,1))
    %subplot(2,3,2)
    %plot(T,Y(:,2))
    %subplot(2,3,3)
    %plot(T,Y(:,3))
```

```
%subplot(2,3,4)
%plot(T,Y(:,4))
%subplot(2,3,5)
%plot(T,Y(:,5))
T;
Y(:,5);
sulpout=Y(:,5);
sulpout;
percona=100*(((1.23e-5)-(sulpout))/(1.23e-5));
A=(100-percona)/10;
% Data Input
%input feed blend percentage
vgo=20;
srgo=80;
%input feed rate in kg/h
w_feed = 140000;
%feed sulphur in ppm
cin = 12300;
%needed product spec in ppm
cout= 30;
%process temperatre in celcius
tc = 375;
%oil density at 15 deg C kg/m3
density=849.1;
```

```
%diameter of catayst particle in m
dp=0.0017;
%viscosity of oil in kg/m.s
visoil=0.15;
%input operating LHSV
LHSV = 0.72;
%unit change of temp
tk = tc+273; %process temperatre in kelvin
tr = 1.8*tk; %process temperatre in rankine
r=8.314; % gas constant
%density correction
row=density/1000; % as sp. gr
rowlb=62.43*row; %density in lb
pma=5.8; % pressure in MPa
psi=14.7*(1/1.01325e5)*pma*1e6; %pressure in psi
% effect of P on oil density
denp=0.167+16.181*(10^(-0.0425*rowlb))*(psi/1000)-0.01*(0.299+263*(10^(-0.0603*row)))*((psi/1000)^2);
% effect of T on oil density
dent=(0.0133+152.4*((rowlb+denp)^-2.45))*(tr-520)-(8.1*(10^-6)-0.06222*(10^-(0.764*(rowlb+denp))))*((tr-520)^2);
den= rowlb+denp-dent; %corrected density in lb/ft3
denc=den*0.01602; % density in kg/m3
%Concentration Profile
```

```
bedlen = linspace(0,30,100);
%cprod = ((100-percon)*cin/100);
y=LHSV^(-0.68)*dp^(0.17)*((visoil/1000)/(denc*1000))^(-0.05);
x=bedlen.^(0.32)*LHSV^(-0.68)*dp^(0.17)*((visoil/1000)/(denc*1000))^(-0.05);
cprod=cin./(10.^x);
percon=100-(cprod/cin)*100;
B=100-percon;
%subplot(2,1,1)
plotyy(bedlen,percon,T,percona)
square plot
bedlen';
cprod';
```

A.4 File - lhsvvar.m

```
clear;
clc;
cin = 1.23;
n=1.632;
ko = 9.5e15;
E_A = 21384;
LHSV = linspace(0.5, 2, 8);
for i=1:length(LHSV)
```

```
    tk=linspace(340+273,380+273,4);
    kin=ko*exp(-E_A./tk);
    t(i,:)=1/LHSV(i);
    cout = (cin^(1-n)+kin*t(i)*(n-1)).^(1/(1-n));
    s(i,:)=cout*10000
end
a=tk-273
s
plot(LHSV,s)
lhsva=LHSV;
sa=s;
save lhsvsim lhsva sa
```

A.5 File - lhsvcompare.m

```
clear;
clc;
load lhsvvar
load lhsvsim
plot(LHSV,Sp,red'o',lhsva,sa)
```

A.6 File - tempvar.m

```
clear;
clc;
cin = 1.23;
n=1.632;
ko = 9.5e15;
E_A = 21384;
LHSV = linspace(0.5, 2, 6);
for i=1:length(LHSV)
    tk=linspace(300+273,400+273,17);
    kin=ko*exp(-E_A./tk);
    t(i,:)=1/LHSV(i);
    cout = (cin^(1-n)+kin*t(i)*(n-1)).^(1/(1-n));
    s(i,:)=cout*10000
end
a=tk-273
s
plot(a,s)
save tempsim a s
```

Appendix B

Simulation Code

B.1 Program, File - rigid.m

```
 function dY = rigid(T,Y)
tc = 375; %process temperatre in celcius
tk = tc+273; %process temperatre in kelvin
tr = 1.8*tk; %process temperatre in rankine
r=8.314; % gas constant
density=849.1; % kg/m3 oil at 5 deg C
row=density/1000; % as sp. gr
rowlb=62.43*row; %density in lb
pma=5.8; % pressure in MPa
psi=14.7*(1/1.01325e5)*pma*1e6; %pressure in psi
% effect of P on oil density
denp=0.167+16.181*(10^(-0.0425*rowlb))*(psi/1000)-0.01*(0.299+263*(10^
(-0.0603*row)))*((psi/1000)^2);
% effect of T on oil density
dent=(0.0133+152.4*((rowlb+denp)^-2.45))*(tr-520)-(8.1*(10^-6)
-0.06222*(10^-(0.764*(rowlb+denp))))*((tr-520)^2);
den= rowlb+denp-dent; %corrected density in lb/ft3
denc=den*0.01602; % density in kg/m3
```

```
%solubility of h2 in oil
solh2=-0.559729-(0.42949*(10^-3)*tc)+(3.07539*(10^-3)*(tc/row))+
(1.94593*(10^-6)*(tc^2))+(0.835783*(1/(row^2)));
%solubility of h2 in oil
solh2s=exp(3.3670-0.008470*tc);
%henry's constant
hh2= (23.693*1000)/(solh2*denc); %henry's constant of hydrogen
hh2s=(23.693*1000)/(solh2s*denc); %henry's constant of H2S
a=10.313*(log10(tr-460))-36.447; %constant used in viscosity correlation
vis=3.141e10*((tr-460)^-3.444)*((log10(43))^a); %viscosity correction
tmean = 282; % Average boiling point of crude(from crude assay)
tmeanr= 1.8*(tmean+273); % tmean in R
vh2s=99;vh2=64;vcm=7.5214*(10^-3)*(tmeanr^0.2896)*(row^-0.7666)*(1/0.016); %crit-
ical molar volume
vc=vcm*204;
v=0.285*(vc^1.408); % molar volume
%diffusivity of H2 and H2S in oil
dih2=(8.93*(10^-8)*((v^0.267)/(vh2^0.433))*(tk/vis));
dih2s=(8.93*(10^-8)*((v^0.267)/(vh2s^0.433))*(tk/vis));
% superficial velocities in cm/s (can be changed)
ul = 0.05010;
ug = 0.5310;
%mass velocity in kg/cm2.s
gl = ul*denc;
```

```
%masstransfer K values
khh2=dih2*7*((gl/vis)^0.4)*((vis/(denc*dih2))^0.5)*(100^-0.1); %(s-1)
khh2s=dih2s*7*((gl*100/vis)^0.4)*((vis/(denc*100*dih2s))^0.5); %(s-1)
%ODE EQNS
ks = 9.5e15*exp(-21384/tk);
PH2 = Y(1);
CH2 = Y(2);
PH2S = Y(3);
CH2S = Y(4);
CS = Y(5);
%RS = 1.1806e-7;
RS = 1*.86*.881*ks*CS^1.7;
dPH2 = (-khh2*r*tc/ug)*((PH2/hh2));
dPH2S = (-khh2s*r*tc/ug)*((PH2S/hh2s)-CH2S);
dCH2 = (khh2/ul)*((PH2/hh2)-CH2)+(15*RS/ul);
dCH2S = (khh2s/ul)*((PH2S/hh2s)-CH2S)+(9*RS/ul);
dCS = (-RS/ul);
%dY = zeros(5,1);  % a column vector
dY = [dPH2 dPH2S dCH2 dCH2S dCS]';
```

Clling function, File - rigidstart.m clear;clc;

```
ZSPAN=[0:.1:30];
YSPAN = [58 0 5.8 0 12e-5];
[T,Y] = ode15s(@rigid,ZSPAN,YSPAN);
subplot(2,3,1)
```

```
plot(T,Y(:,1))
subplot(2,3,2)
plot(T,Y(:,2))
subplot(2,3,3)
plot(T,Y(:,3))
subplot(2,3,4)
plot(T,Y(:,4))
subplot(2,3,5)
plot(T,Y(:,5))
```