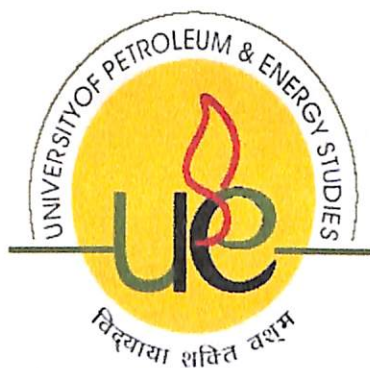


MODELING AND SIMULATION OF R-PLUG FLOW FOR AROMATIC SATURATION

By

MUNAGALA VENKATA SUNIL



College of Engineering

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Dehradun

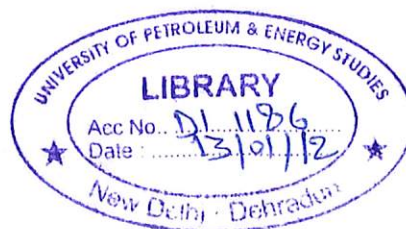
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MODELING AND SIMULATION OF R-PLUG FLOW FOR AROMATIC SATURATION

A thesis submitted in partial fulfilment of the requirements for the Degree of
Master of Technology
(Process Design Engineering)

By

MUNAGALA VENKATA SUNIL

Under the guidance of

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May, 2011

CERTIFICATE

This is to certify that the work contained in this thesis titled "**MODELING AND SIMULATION OF R-PLUG FLOW FOR AROMATIC SATURATION**" has been carried out by **Munagala Venkata Sunil** under my/our supervision and has not been submitted elsewhere for a degree.



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ABSTRACT

A steady-state model for trickle-bed reactors was developed, primarily concerning hydro processing of light oil feedstock containing volatile compounds. The model, based on the two-film theory, was tested with regard to the hydrodesulphurization of light oil feedstocks in a new high-pressure pilot plant operated under isothermal conditions. The effect of hydrogen treatment on the chemical reaction rates was described by Langmuir - Hinshelwood kinetics. In addition, all necessary thermo-physical properties, such as viscosities, diffusivities and kinematic parameters were continuously calculated as a function of the system pressure and temperature. The order of the reaction was estimated using theoretical and experimental data. A suitable numerical package was developed for this kind of calculations. Mass transfer rates were calculated by effective diffusivity method. This model was validated using a set of experimental data from the operation of a pilot scale hydrodesulphurization plant and were found to be in excellent agreement. A user-friendly interface was developed to facilitate the use of the numerical package.

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1. INTRODUCTION

In recent years, awareness of even common people towards the health risks attached with the aromatic content of fuels, especially gasoline and diesel, has increased appreciably. Technically, the aromatics impart poor ignition quality and low cetane number of diesel and enhance smoke point of jet fuel. For these reasons aromatic saturation has been drawing attention of the researchers the world over. Decreasing the aromatic content increases the cetane number of diesel. An aromatic reduction of 10 wt% cetane number increases by 3 to 3.5. Production of cleaner and environment friendly fuels necessitates various hydrotreatments including desulfurization and hydrodearomatization

Hydrogenation process is normally carried out in a trickle bed reactor at an elevated temperature and hydrogen pressure. The temperature and pressure ranges for the hydrogenation of aromatic hydrocarbons in a liquid phase batch reactor were reported to be 450-700 K and 3.5 -17 Mpa.

Operation of trickle-bed reactors is marked by the simultaneous presence of two phases, a gaseous and a liquid one, flowing over and through a third catalyst solid phase. Modeling of three-phase reactors has shown substantial developments recently, though it is very demanding in combining transport phenomena and heterogeneous reaction processes. In the present paper, a steady-state model of three-phase trickle flow fixed bed reactors is presented, suitable for the case of liquid phases containing volatile compounds.

The motivation for this work comes from certain commercial applications in the oil refineries concerning processing of light oil fractions with hydrogen, like hydrodesulfurization and hydrogenation. A fundamental understanding of the underlying phenomena and, especially, the interaction between mass, momentum and heat transport phenomena and heterogeneous catalysis is warranted.

For simplicity, plug flow conditions and uniform pellet properties were assumed. This means that either internal mass and heat transfer limitations are negligible or the kinetic parameters are determined using industrial scale catalyst particles. Therefore, internal mass and heat transfer rates are included in the kinetic models.

To this end, the detailed mass balances were written and solved for each compound in the liquid and the gas phase. In addition, a suitable MATLAB code was developed for the evaluation of the thermophysical properties of oil compounds and mixtures and for the detailed calculation of interfacial mass transfer rates, using effective diffusivity method and gas-liquid equilibrium at the interface.

Moreover, the flow regime under which the bed was operated, the liquid holdup, the wetting efficiency of the solid particles, the two-phase flow pressure drop and the gas-liquid, liquid-solid and gas-solid interfacial areas were all calculated in the same manner as functions of the system variables along the reactor.

Four general chemical processes were modeled:

Desulfurization (HDS), denitrogenation (HDN), saturation of olefins (HTO), and hydrogenation of mono-, di- and tri-aromatics (HTA). Reaction kinetics of the Langmuir-Hinshelwood type was used, taking into account equilibrium of aromatic hydrogenation and inhibition by hydrogen sulfide, ammonia and aromatics.

Results from the detailed model were compared with experimental data from the operation of a pilot plant unit and remarkable agreement was obtained. In view of these results, a first attempt was made to gain some insight of the complex phenomena of such processes. The agreement between theoretical and experimental data led to the development of a user-friendly interface to facilitate the use of the numerical package.

2. LITERATURE SURVEY

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 in other applications. 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 feedstock. Any advancement in TBR technology will thus represent substantial savings and this stimulates the continued research efforts aimed at improving TBR operation and performance.

The critical analysis of literature reported by various author shows the following improvement on trickle bed reactor units over last four decades.

At first, three-phase reactor was reported as pseudo homogeneous plug flow model. These three-phase reactor models were developed based on two film theory and modeled only for hydrotreating reactions. These three-phase reactor models were further developed for hydrodesulphurization and hydrodearomatisation reactions. Later the models were developed for hydrodesulphurization, hydrodearomatisation, and olefins saturation reactions also. Now efforts are being made to develop non-isothermal reactor models. Researchers are going in the area of two phase reactor model development, for analyzing the diesel oil quality obtained from different types of crude oil.

In 1950's the field of hydroprocessing started and in 1960's the study of trickle bed reactors got importance. In 1969, Hochman and Effron 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. Later a brief study on the downward flow was developed. In 1974, Puranik and Vogelpohl teamed up to study the effect of interfacial areas in irrigated

columns. In 1975, Goto and Smith studies the mass transfer in packed bed for two phase flow. They gave the correlations for the mass transfer coefficients for two phase flow. This led to further development in the wetting characteristics when catalysts were used in packed bed reactor. In 1976, the partial wettings of catalysts were studied by Midoux and Charpentier and it was reported in Chemical Engineering Progress. In 1984, Tousan studied the non-foaming systems for cocurrent downward flow in a packed bed which resulted in the development of pressure drop correlations based on Erguns two phase equation.

In 1994, Forment etal gave a kinetic modeling for HDS of oil fractions. This model is still being used as the base for all trickle bed modeling studies. In 1996, Anthari described the kinetics involved in the HDA process in detail. He performed lab scale experiments on various oil fractions and came up with a detailed report on the kinetics for aromatics compounds in gas oil streams. In the same year Kostern and Hoffmann developed a three-phase reactor model for hydrotreating which explained not only the HDA but also other reactions in the hydrotreating process. This model gave a detailed analysis of product sulphur variation with the process variables.

With the turn of the millennium the models became more rigorous and descriptive which had the kinetics, the mass transfer and the hydrodynamics incorporated in them. In 2002, Chowdhry etal 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 studied the catalytic activity of various catalysts and put forth the intrinsic kinetic model for thiophenes over NiMo/Sio₂ catalyst. The kinetics with respect to thiophenes was discussed in detail and the parameters were estimated.

With the advancement made in the field transient modeling, Lappalainen gave the transient modeling of trickle bed reactor to predict the flow. 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 advancement in the year 2004 with the EURO regulations emphasizing on the stringent environmental regulations.

With advancements being made globally, India also joined the race with the research carried out by Bhaskar and his team on the three phase modeling 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. In 2004, Forment and his team made further progress with the study of active catalyst sites on Co-Mo/Al catalyst. The recent study in this field is by Farahani and Shahhosseini. They simulated the general model for trickle bed reactors which can be used to carry out any three phase reactions. The three phase model was developed and simulated in HYSIS Simulation Package. This would serve to be the stable reactor model for further studies to be carried out.

3. THEORETICAL DEVELOPMENT

3.1 AROMATIC COMPOUNDS IN PETROLEUM DISTILLATE

The aromatics found in petroleum and the middle distillates are divided into four groups: 1. Monoaromatics, 2. Diaromatics; 3. Triaromatics; 4. Polycyclic aromatics

Fused multiring aromatics compounds are hydrogenated more easily to the corresponding monoaromatics under mild hydrotreating conditions. The amount and type of aromatics in middle distillates show large variations depending on the origin of the feed.

3.2 REACTIVITY OF AROMATIC COMPOUNDS IN HYDROGENATION REACTION

On all catalysts, the rate of hydrodearomatization generally increases with the number of aromatic rings present, i.e. a low rate of hydrogenation was observed for mono aromatic ring such as benzene. The greater reactivity for hydrodearomatization with highest fused ring systems such as naphthalene and anthracene, is due to the fact that the resonance energy of the second ring of these multiple compounds is less than that for benzene. The reactions of hydrogenation are favored by highly electron donating substituents. Hydrogenation is easier when the ring to be hydrogenated is less aromatic. The partial resonance in fused multiring aromatic systems may be different. In multiring aromatic species, the ring with the lowest aromaticity is hydrogenated first. The following order of

Anthracene > Naphthalene > Phenanthrene > Benzene.

Effects of various factors influencing the hydrogenation reactivity of aromatics and hydrocarbons have been reported.

3.3 THERMODYNAMICS

The hydrodearomatization reaction was reversible and at normal hydrotreating conditions, the complete conversion was not possible because of equilibrium limitations.

The hydrogenation of an aromatic species, A is given by,



where AH is the hydrogenated product.

The equilibrium concentration of an aromatic compound is given by,

$$\frac{Y_A}{Y_A + Y_{AH}} = \frac{1}{1 + K_a \cdot (P_{H_2})^n}$$

Where, Y_A = Mole fractions of the aromatic;

Y_{AH} = Mole fractions of the hydrogenated aromatic (i.e., naphthene);

K_a = Equilibrium constant;

P_{H_2} = Partial pressure of hydrogen;

n = Number of moles of hydrogen required for saturation.

Above equation indicates that high pressures favor low equilibrium concentration of aromatics. Aromatic hydrogenation reactions are exothermic with heats of reaction between 63 and 71 kJ/mol H_2 . K_a decreases and equilibrium aromatics concentration increases with temperature. In benzene homologous hydrogenation, the value of the equilibrium constant decreases with and increases in both the number of side chains and the number of carbon atoms in each side chain. For more than one ring, hydrogenation proceeds via successive steps, each of which is reversible. The equilibrium constant is generally higher for the hydrogenation of the first ring, but more moles of hydrogen were involved in the final ring hydrogenation reaction. Usually hydrogenation of the first ring is thermodynamically less favored than that of the final ring at typical hydrotreating conditions.

3.4 KINETICS

The aromatic content of the product decreases upto certain temperature and then increases, i.e., the aromatic content passes through a minimum. Thus, at lower temperatures, the reaction is kinetically controlled, while at higher temperatures, equilibrium controlled. The kinetic data showed that all reactions were first order in hydrogen and zero order in aromatic compound concentration, indicating a near saturation coverage of the active sites by aromatic species. A use of highly acidic oxide supports (e.g., SiO₂-Al₂O₃, TiO₂) was found to markedly enhance the hydrogenation rate.

3.5 CATALYSTS

Aromatic hydrogenation in industrial feed stocks may be carried out over supported metal or metal sulfide catalysts depending on the sulfur and nitrogen levels in the feedstock. The choice of catalyst varies with applications, nature of the feedstocks and desired activity/selectivity of the reactions.

This is briefly described below.

(1) Metal sulfides: Among the conventional catalysts, CoMo, NiMo or NiW on alumina were used for aromatic saturation. Maximum hydrogenation activity has been obtained with Ni-based catalysts with high metal loading, where the pore size distribution is selected to give maximum activity and stability.

(2) Noble metals: Supported noble metal catalysts are well known for their high hydrogenation activity at low reaction temperatures and moderate hydrogen pressures for deep hydrodearomatization and also for their low resistance to sulfur poisoning.

In this category, three sub-types have been studied.

- (A) Mono-metallic catalyst can be used only in the absence of sulfur in the feed stocks;
- (B) Bimetallic catalysts, a combination of Pt, Pd, Rh, Ir or Re have been shown to exhibit a better resistance to sulfur;
- (C) A combination of the conventional hydrotreating catalysts promoted by a noble metal may contain three metal.

The catalyst activity for the hydrogenation of benzene was reported to be in order
 $Rh > Ru \gg Pt \gg Pd \gg Ni > Co$

3.6 PROCESS FLOW SHEET

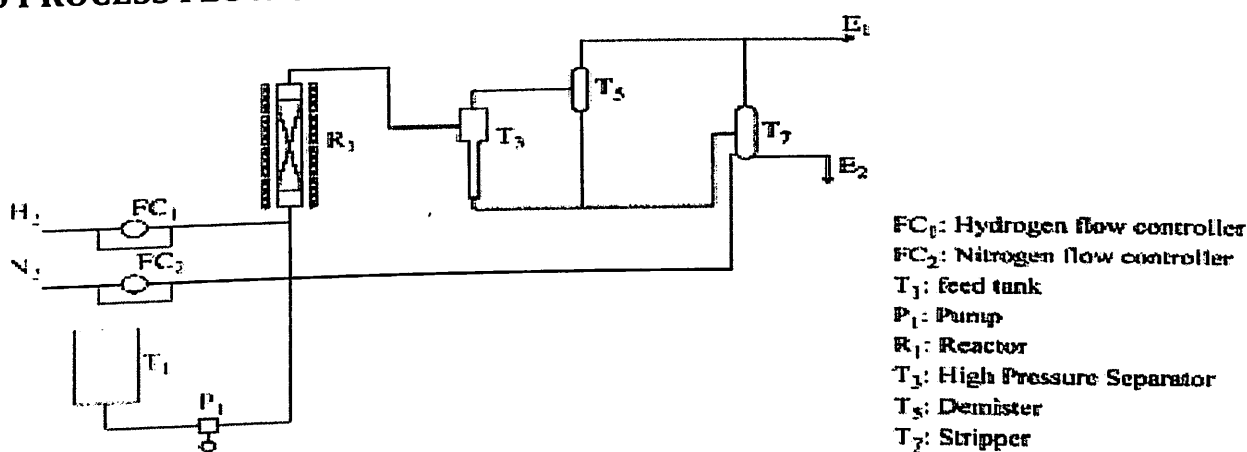


Fig. 2. Schematic diagram of the pilot unit.

The Schematic process flow sheet of the pilot unit was represented in Fig. 2. The light oil feed stock from the stirred and blanketed tank T_1 and a pure hydrogen stream was fed to the reactor R_1 (125cm long, 3cm ID) in co-current up-flow mode, ensuring a good wetting of the catalyst particles. In order to minimize heat losses, to provide an uniform distribution of the gas and liquid flows, and to facilitate the hydrogen saturation of the feed, the catalyst bed was put in the middle part of the reactor and the space above and below filled with inert particles (CSi 1.1 mm). The reaction section was loaded with hydroprocessing commercial catalysts (NiMo/Al₂O₃ or CoMo/Al₂O₃, trilobe shape, equivalent diameter= 1.72 mm) diluted with small inert particles (1:1 (v/v) CSi 0.1 mm), to avoid channeling. The reactor temperature profile, controlled by four independently

heated furnaces, was monitored with a set of four sensors placed in a thermowell located along the center of the catalytic bed and another set of skin thermocouples.

The hydrogenated product exiting the top of the reactor was sent to the high-pressure separator T3 to remove the bulk of the gas from the liquid and then to a nitrogen stripper T5 to release the residual gas trapped into the liquid phase. All process parameters (flow rates, pressure and temperature) were continuously monitored and controlled using a dedicated system, allowing unattended operations.

3.7 REACTOR MODELING

A one-dimensional plug-flow heterogeneous model was established to simulate the concentration profiles of the reactants and products in the gas, liquid and solid phases. Under concurrent flow condition, the following assumptions were made to establish the equations.

3.7.1 ASSUMPTIONS

The following assumptions were made in order to simplify the model so that it can be conveniently suited to the system.

1. The liquid and the gas superficial velocities are same
2. The gas to liquid mass transfer is negligible.
3. Complete catalyst wetting.
4. Isothermal pellets.
5. No axial dispersion.
6. No vaporization and condensation of the feed.
7. No catalyst deactivation.
8. Non foaming system.
9. Pseudo order kinetics.

10. Intra particle mass transfer within the pores of the catalyst may be described by the catalyst effectiveness factor.

Apart for these assumptions for the reactor to perform to the design it always has to be operated in the trickle flow regime. This can be ensured based on the flow rates of the gas and the liquid phase.

3.7.2 MASS BALANCE EQUATIONS

Mass balance equations for the gaseous compound

$$\frac{U_G}{R \cdot T} \cdot \frac{dP^G}{dz} + K^L \cdot a_L \cdot \left(\frac{P^G}{H} - C^L \right) = 0$$

Mass balance equations for the gaseous compounds in the liquid- solid phase

$$U_L \cdot \frac{dc^L}{dz} - K^L \cdot a_L \cdot \left(\frac{P^G}{H} - C^L \right) + K^S \cdot a_S (C^L - C^S) = 0$$

Mass balance equations for the liquid compound

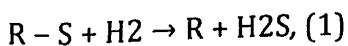
$$U_L \cdot \frac{dc^L}{dz} + K^S \cdot a_S (C^L - C^S) = 0$$

Mass balance equations for the liquid components between the liquid phase and the surface of the catalyst

$$K^S \cdot a_S (C^L - C^S) = -v \cdot r = -v \cdot \rho \cdot \eta \cdot \zeta \cdot r_c$$

3.8 REACTION KINETICS OF HDS

Petroleum feedstock includes a large number of sulfur bearing compounds, and the overall HDS reaction is usually expressed as



where R represents the hydrocarbon molecule which is combined with sulfur.

The HDS reaction rate equation which includes the inhibiting effect of H₂S is usually written in the Langmuir–Hinshelwood form

$$r_{HDS} = \frac{k_{HDS} \cdot C_{H_2}^n \cdot C_S^m}{1 + K_{H_2S} \cdot C_{H_2S}}$$

Where

$$k_{HDS} = k_{HDS}^0 \cdot \exp\left(-\frac{E_{HDS}}{RT}\right) \quad (2)$$

By assuming the validity of the Eq. (2), the range of reaction orders n and m are within a certain range according to the following consideration:

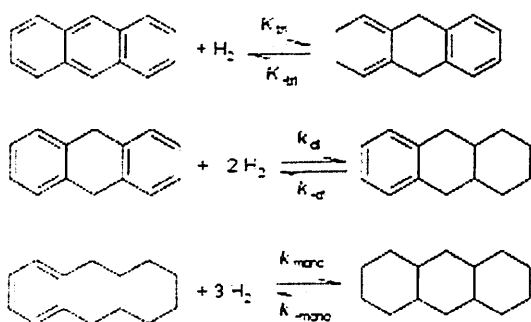
(1) **The order on sulfur:** The reaction rate of an individual sulfur compound is normally represented by a first-order kinetics, however, n th order kinetics with respect to the total sulfur concentration is required to describe the global desulfurization rate.

From an analysis, the reaction order was found only varies between 1.94 and 2.18, regardless of the concentrations of sulfur in the feed.

(2) **The order on H₂:** The theoretical reaction order on hydrogen should be 0.5 in view of the chemical dissociation of hydrogen molecule on the catalyst surface. However, if the mass transfer rate of hydrogen is the limiting step, the order should be 1.0. Thus in the real situation, the value n should be in the range of 0.5–1.0.

3.9 REACTION KINETICS OF HAD

To simplify the modeling work, the total aromatics is conventionally classified into three groups: the mono-, the di-, and the tri-aromatics, where the polyaromatics are lumped into triaromatics. The aromatics hydrogenation removal reactions (HDA) network can be expressed as follows:



The three reactions are exothermic and reversible, and their equilibrium constants were regressed through the present work as

$$\lg K_{\text{mono}} = 17.6 - 0.023T,$$

$$\lg K_{\text{di}} = 11.5 - 0.017T,$$

$$\lg K_{\text{tri}} = 5.5 - 0.007T,$$

where $K_{\text{mono}} = k_{\text{mono}}/k_{\text{-mono}}$, $K_{\text{di}} = k_{\text{di}}/k_{\text{-di}}$, and $K_{\text{tri}} = k_{\text{tri}}/k_{\text{-tri}}$.

The HDA reaction rates are expressed as

$$r_{\text{tri}} = (-k_{\text{tri}}C_{\text{tri}} + k_{\text{-tri}}C_{\text{di}}),$$

$$r_{\text{di}} = (k_{\text{tri}}C_{\text{tri}} - k_{\text{-tri}}C_{\text{di}} - k_{\text{di}}C_{\text{di}} + k_{\text{-di}}C_{\text{mono}}),$$

$$r_{\text{mono}} = (k_{\text{di}}C_{\text{di}} - k_{\text{mono}}C_{\text{mono}} - k_{\text{-di}}C_{\text{mono}} + k_{\text{-mono}}C_{\text{naph}}),$$

$$r_{\text{naph}} = (k_{\text{mono}}C_{\text{mono}} - k_{\text{-mono}}C_{\text{naph}}).$$

4. RESULTS AND DISCUSSIONS

4.1 ESTIMATION OF PARAMETRIC VALUES

4.1.1 EXTERNAL MASS TRANSFER

The gas-liquid mass-transfer coefficient is a function of the liquid superficial mass-flow velocity G_L . For its determination we use the correlation published by Goto and Smith.

$$\frac{k_i^L \cdot a_L}{D_i^L} = \alpha_1 \cdot \left(\frac{G_L}{\mu_L}\right)^{\alpha_2} \cdot \left(\frac{\mu_L}{\rho_L \cdot D_i^L}\right)^{\frac{1}{2}}$$

Where $k_i^L \cdot a_L$, represents the mass transfer, and ρ_L is the density of the liquid. The coefficients α_1 and α_2 are a function of the particle diameter. For the pellets used in this article, $d_p = 1.72$ mm, we get $\alpha_2 = 0.4$ and $\alpha_1 = 7 \text{ (cm)}^{-1.6}$.

The liquid-solid mass transfer in the low interaction regime can be estimated by the van Krevelen-Krekels equation.

$$\frac{k_i^s}{D_i^L \cdot a_s} = 1.8 \cdot \left(\frac{G_L}{\mu_L \cdot a_s}\right)^{\frac{1}{2}} \cdot \left(\frac{\mu_L}{\rho_L \cdot D_i^L}\right)^{\frac{1}{3}}$$

Where a_s is the specific surface area of the packing:

$$a_s = \frac{6}{d_p} \cdot (1 - \epsilon)$$

Where d_p , is the equivalent particle diameter and ϵ is the void fraction of the catalyst bed.

4.1.2 DIFFUSIVITY

The molecular diffusivity D_L of solute i in the liquid was used in external mass transfer and to determine the Gas-liquid mass-transfer coefficients. Assuming infinite dilution, the diffusivity can be estimated by a Tyn-Calus correlation.

$$D_i^L = 8.93 * 10^{-8} \cdot \frac{v_L^{0.267}}{v_i^{0.433}} \cdot \frac{T}{\mu_L}$$

Where T is the temperature in K and μ_L represents the viscosity of the solvent in mPa.s. By using above equation we obtain the diffusivity in cm^2/s .

4.1.3 MOLAR VOLUME OF SOLUTE

The molar volume of solute, v_i or liquid solvent, v_L , at its normal boiling temperature can be estimated by Perry's and Greens correlation.

$$v = 0.285 \cdot v_c^{1.048}$$

The measurement unit of the molar volume is cm^3/mol . The liquid components this characteristic can be obtained by using the Riazi-Daubert correlation.

$$v_c^m = 7.5214 * 10^{-3} \cdot T_{MeABP}^{0.2896} \cdot d_{15.6}^{-0.766}$$

Where v_c^m is the critical specific volume in ft^3/lb . T_{MeABP} represents the mean average boiling point in $^{\circ}\text{R}$ and $d_{15.6}$ is the specific gravity at 15.6°C . The transformation of v_c^m to v_c can be carried out by multiplication with the molecular weight M .

Because of the complex composition of hydrocarbon mixtures, some assumptions are necessary before using diffusivity equation. We consider the organic sulfur compound to have the same density, average boiling point, and molecular weight as the whole liquid sample. In this case the molar volume of the medium sulfur compound is equal to that of the liquid solvent, $v_i=v_L$. The diffusivity decreases because the viscosity rises with increasing pressure.

4.1.4 VISCOSITY

The dependence of dynamic liquid viscosity μ_L on temperature may be described by the Vogel equation. The disadvantage of using this correlation is that it cannot be applied to a hydrocarbon mixture of unknown composition until three parameters have been determined experimentally. Using the density of the oil as a parameter, Glaso's correlation, In terms of API gravity this equation gives the viscosity in mPa-s

$$\mu = 3.141 \cdot 10^{10} \cdot (T - 460)^{-3.44} \cdot [\log (API)]^a$$

Where $a = 10.313 - [1 \log (T - 460)] - 36$. We can take into account the small dependence of liquid viscosity on pressure within the range of interest by using the procedure.

The estimated parametric values are as in the following tables.

Table 1: INPUT PARAMETERS

CHARACTERISTIC	DIMENSION
Temperature, C	400
Pressure, atm	100
Superficial velocity of gas, cm/s	0.1606
Superficial velocity of liquid, cm/s	0.07522
Density of the liquid, g/cm ³	0.8945
Equivalent diameter of packed material, cm	0.172
Average boiling point of feed, C	451
WSHV, 1/h	0.8
\emptyset , NI H ₂ / kg feed	1100

Table 2: ESTIMATED PARAMETRIC VALUES

CHARACTERISTIC	DIMENSION
Diffusivities,cm²/s	
Hydrogen sulfide	5.0611e-007
Hydrogen	6.1615e-007
External mass transfer Gas - Liquid,1/s	
Hydrogen sulfide	0.0033
Hydrogen	0.0037
External mass transfer Liquid - Solid,1/s	
Hydrogen sulfide	1.2710e-009
Hydrogen	1.6523e-009
Sulphur	3.2685e-007
Henry Constant, Mpa*cm³/gmol	
Hydrogen sulfide	438.6440
Hydrogen	223.8858
Solubility in oil	
Hydrogen sulfide	0.9792
Hydrogen	1.9185
Viscosity, g/cm.s	19.1418
Density of oil, g/cm ³	0.7497

4.2 ESTIMATION OF ORDER OF THE REACTION

The rate of chemical reaction can be described by power law or Langmuir- Hinshelwood formulation but Langmuir- Hinshelwood formulation is describes the kinetics of the hydrotreating reactions most appropriately.

The properties of gases and liquids, solubilities, diffusivities, and mass-transfer coefficients, can be calculated by using the correlations given earlier. The rate constant, order of reaction, and adsorption equilibrium constant are arrived from the experimental data.

An objective function was developed to estimate the order of the reaction using the following data.'C' language was used for programming this.

Table 3: INDUSTRIAL DATA OF HYDRODESULPHURIZATION PLANT

Reactor length (cm)	Moles of H ₂ , C _{sh2} (mol/cm ³)	Moles of H ₂ S C _{sh2s} (mol/cm ³)	Moles of sulphur C _{ss} (mol/cm ³)	Experimental rate of reaction R _c
0	0.000604	0	0.000036	1.5380e-006
10	0.000591	0.000012	0.0000245	3.0582e-007
20	0.000593	0.000011	0.0000155	2.0944e-007
30	0.000595	0.000008	0.0000095	1.6553e-007
40	0.000597	0.000007	0.0000055	1.0522e-007
50	0.000599	0.000005	0.0000027	6.4198e-008
60	0.0006	0.000004	0.0000012	3.1187e-008
70	0.000601	0.000003	0.0000005	1.4554e-008

OBJECTIVE FUNCTION

$$F(x) = \sum_i R_c(i) - k_{app} * [\sum_i ((C_{ss}(i)^{m1}) * (C_{sh2}(i)^{m2}) / (1 + 70000 * C_{sh2s}(i))^2)] = 0$$

Where m_1 and m_2 were represent the reaction order concerning the sulfur compound and hydrogen respectively. The Orders of reaction were estimated as $m_1 = 1$ and $m_2 = 0.45$. The value of m_2 appears to be due to a dissociation of H, at the catalyst sites, where the theoretical value would be $m_2 = 0.5$. The adsorption-equilibrium constant of hydrogen sulfide at the catalyst, $K = 70,000 \text{ cm}^3/\text{mol}$, can be obtained by using univariable method.

Using an empirical correlation, as recommended by Satterfield, the measured values of the apparent rate constant as a function of the superficial mass-flow velocity G , in $\text{kg}/(\text{m}^2 \cdot \text{s})$ can be described very well, with the intrinsic rate constant $k_{in} = 0.67 \text{ (cm}^3/(\text{g} * \text{s})) \cdot (\text{cm}^3/\text{mol})^{0.45}$ and the constants $A = 0.21$ and $B = 1.40$

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

The effect of temperature on the rate constant and on the adsorption equilibrium constant of hydrogen sulfide at the catalyst has to be experimentally estimated.

The influence of temperature on the adsorption-equilibrium constant can be described by the Van't Hoff equation.

$$K(T) = K_0 \cdot \exp\left(\frac{\Delta H_{\text{ads}}}{R \cdot T}\right)$$

The enthalpy of adsorption of hydrogen sulfide on an alumina-supported CoMo catalyst has been estimated to be $\Delta H_{\text{ads}} = 2,761 \text{ J/mol}$ in a temperature range of $T = 533\text{-}644 \text{ K}$. If the temperature rises from 370 to 390°C, the adsorption equilibrium constant decreases by

1.6%. In comparison with the effect of temperature on the rate constant, the temperature dependence of the equilibrium constant can be neglected.

Using the Arrhenius equation, the activation energy could be estimated to be $E_A = 72.5 \text{ kJ/mol}$, and the frequency factor is $k_0 = 0.545 \cdot 10^6 \text{ (cm}^3/\text{(g.s)).cm}^3/\text{mol)}^{0.45}$.

$$k = k_0 \cdot \exp\left(-\frac{E_A}{R \cdot T}\right)$$

4.3 COMPONENTS PROFILE

The suggested reactor model was solved using MATLAB code to observe the dynamic behavior of the reactor for individual component throughout the length of reactor.

The H₂ partial pressure decreases down through the reactor because H₂ transfers from gas phase to liquid phase

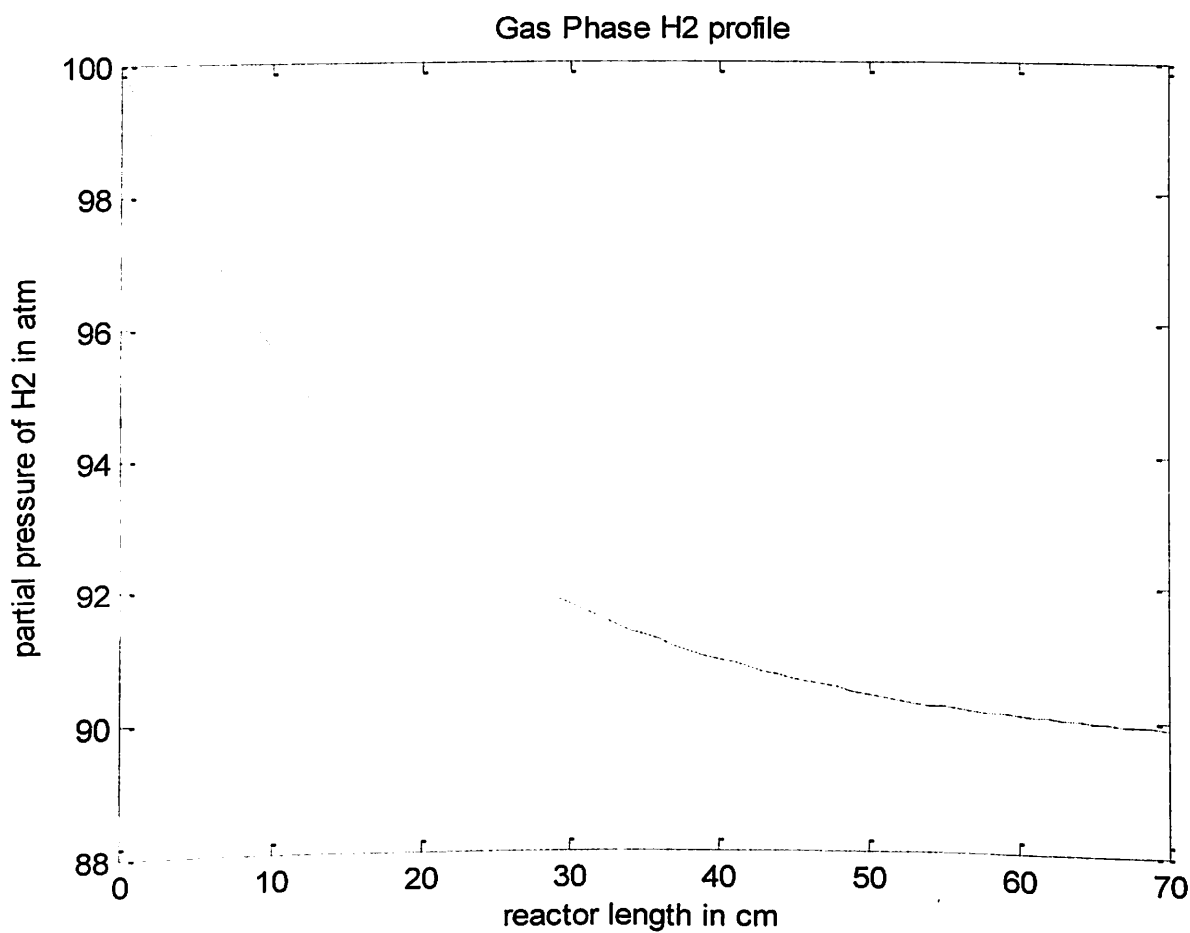


Figure 1: Gas phase H₂ profile

Similarly the H₂ concentration increases down through the reactor because H₂ transfers from gas phase to liquid phase

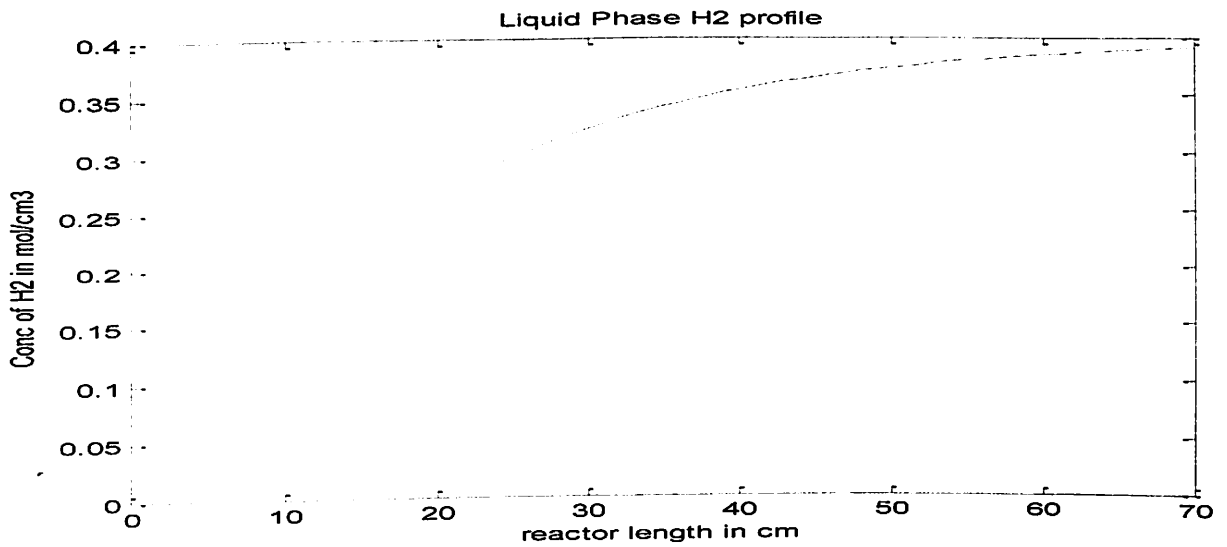


Figure 2: Liquid Phase H₂ profile

It is seen from the figure that a small of H₂S produced and it is rising up along the reactor length.

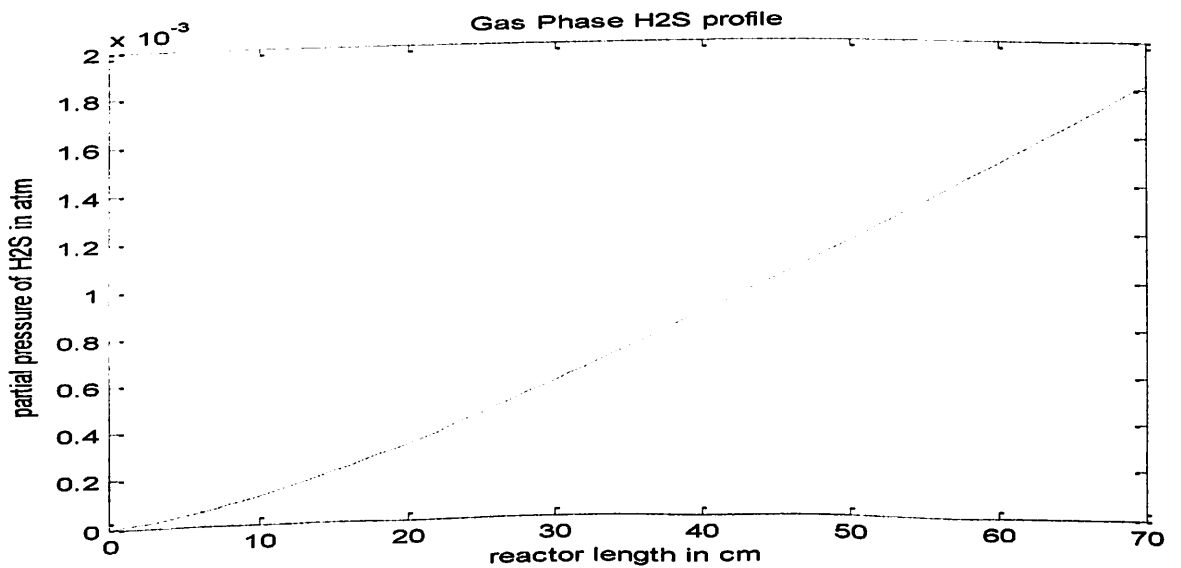


Figure 3: Gas Phase H₂S profile

The profile of H₂S in liquid phase passes through the maximum along the length of reactor as rate of H₂S formation on the catalyst surface is more rapid than its mass rate from liquid to gas phase.

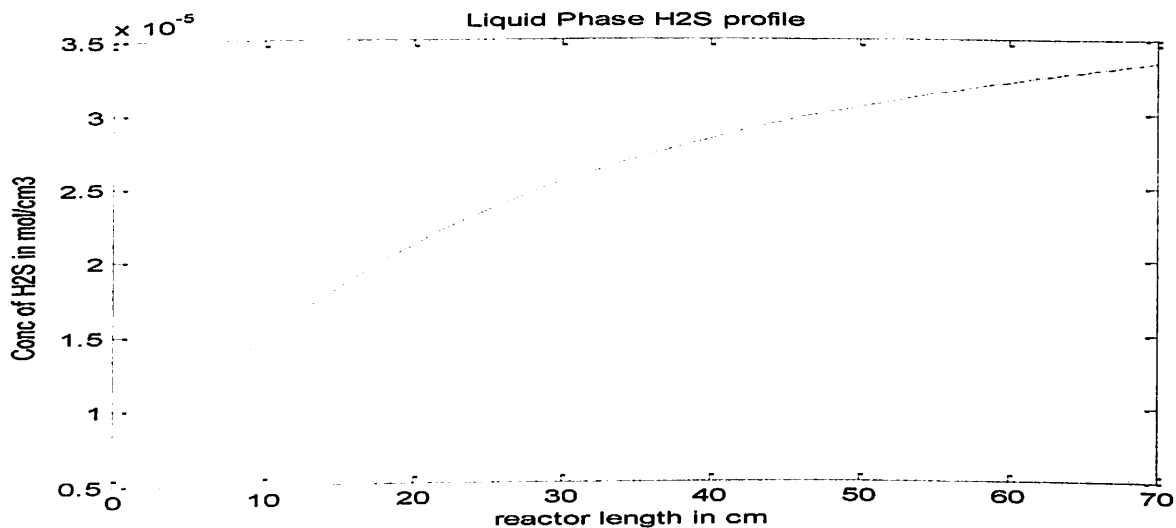


Figure 4: Liquid Phase H₂S profile

The sulphur concentration rapidly decrease through the reactor of the length

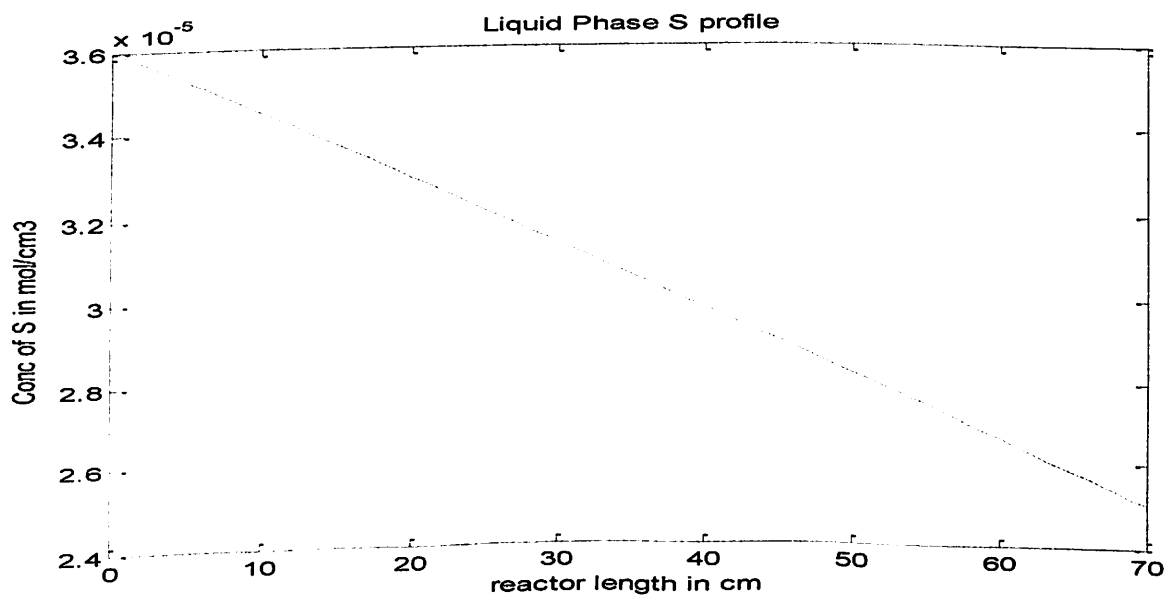


Figure 5: Liquid Phase Sulphur profile

Similarly, the aromatics concentration rapidly decrease through the reactor of the length

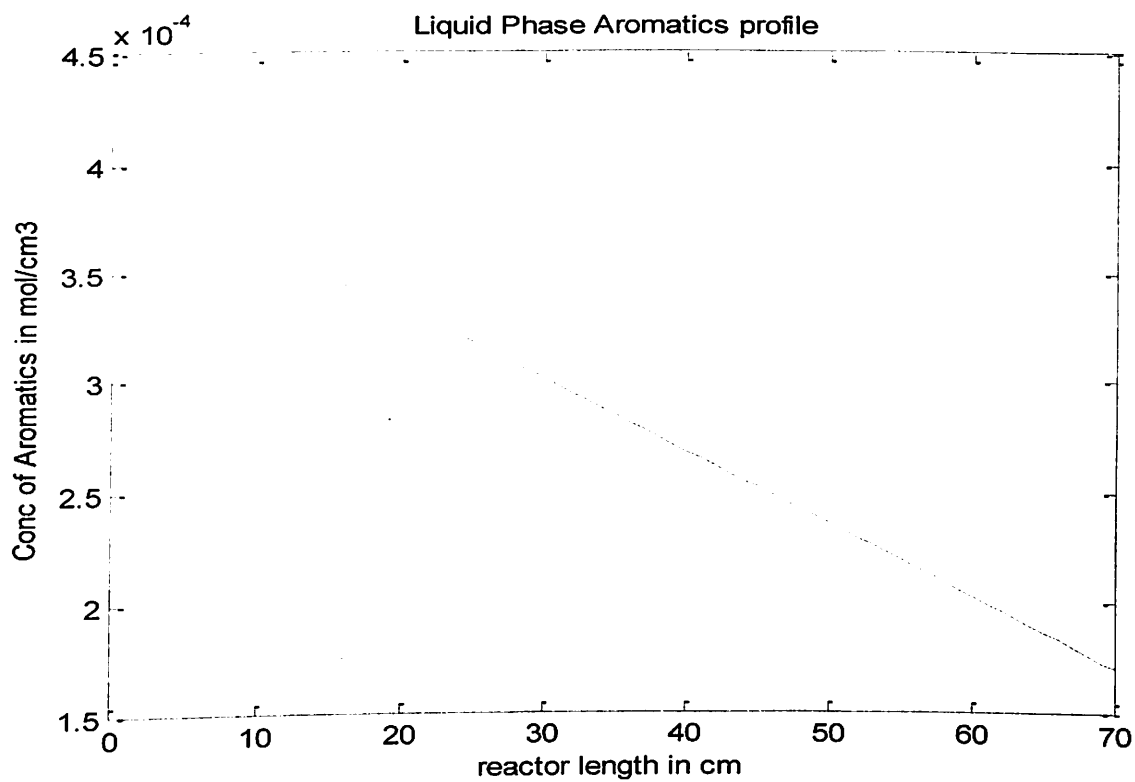


Figure 6: Liquid Phase Aromatics profile

4.4 PARAMERTIC ANALYSIS

The sulphur and H₂S concentration profiles down through the reactor for different temperature. It is seen that the sulphur conversion can be decreased and H₂S increased by increasing the temperature.

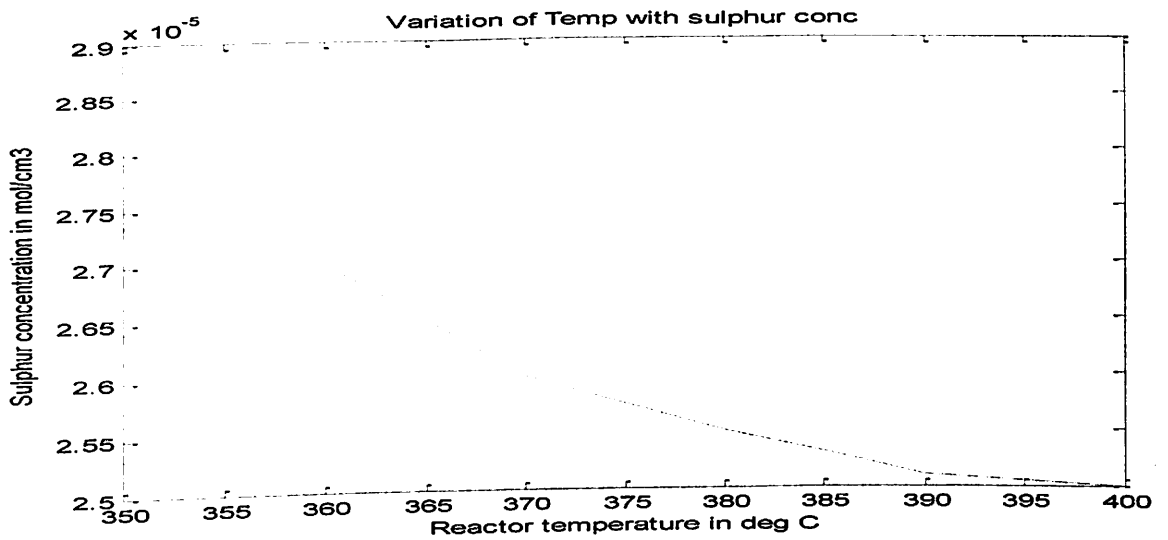


FIGURE 6: VARIATION OF SULPHUR CONCENTRATION WITH TEMPERATURE

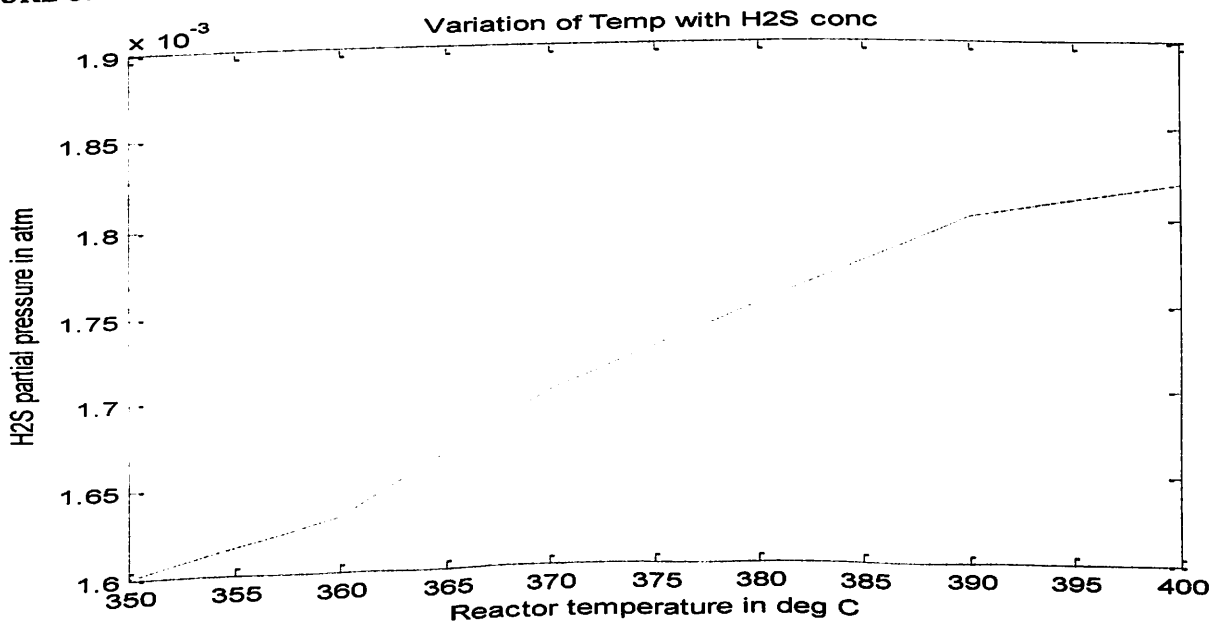


FIGURE 7: VARIATION OF H₂S CONCENTRATION WITH TEMPERATURE

5. CONCLUSION

A steady-state model for trickle-bed reactors was developed to model hydroprocessing of light oil feedstock that contain considerable amounts of volatile compounds. The main conclusions are:

- Hydroprocessing of oil feedstocks in catalytic fixed bed reactors under trickling conditions can be modeled effectively using fundamental principles of reaction engineering, transport phenomena, thermodynamics and by suitable calculation of the thermophysical properties of mixtures of oil compounds that form the flowing liquid and gas phases.
- Since hydrodesulphurization is strongly limited by hydrogen sulfide, the chemical reaction rate is expressed by a Langmuir- Hinshelwood formulation in terms of catalyst surface concentrations.
- As the inlet temperature increases removal of sulfur compounds from the oil feedstock increases, with all other operational parameters kept constant.
- Nevertheless, the mathematical simulation shows reasonably good agreement with the experimental results

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