4.1 TRICKLE BED REACTOR MODEL

Trickle flow regime occurs in cocurrent down flow two-phase reactors under lower superficial velocities of gas and liquid. In this regime, the liquid forms a fine film over the surface of the catalyst and trickles downward in the reactor. The gaseous components occupy remaining void spaces between catalyst particles and form a continuous phase. It can be assumed that the entire void space in the reactor is filled by liquid and gaseous components. The schematic diagram of trickle bed reactor is shown in Figure 4.1.

It can be visualized that each catalyst particle is covered with two thin films of liquid and gaseous components. The fraction of catalyst particle wetted by liquid reactant depends on the operating conditions of the reactor apart from physical properties of liquid and gaseous components and surface characteristics of catalyst particles. For a given catalyst and feed system, the wetting efficiency was found to increase with liquid velocity. If we assume that the reaction occurs only on the surface of the catalyst particle and not in liquid and gas phases, the reactants are required to transfer from bulk gas phase to liquid and then to catalyst surface. The reaction products are required to be transported from catalyst surface to liquid phase and then to gas phase. At steady state, the mass transfer rate across gas-liquid becomes equal to the mass transfer rate across liquid-solid interface. The mass transfer across interfaces is equal to the rate of disappearance/formation of various species due to chemical reactions taking place on the catalyst surface. The model based on two-film theory
The hydrodesulfurization catalyst has two active sites, namely the sulfided Co-Mo and Al₂O₃ acid sites. The sulfided Co-Mo sites help to accomplish the hydrodesulfurization of organic sulfur compounds while the acid sites promote hydrocracking of hydrocarbons. The hydrogen sulfide formed on the solid surface due to hydrodesulfurization reactions gets transported to liquid phase and then subsequently to gas phase. The hydrogen sulfide present in the liquid phase gets adsorbed on the sulfided Co-Mo sites and thus inhibits hydrodesulfurization reactions (Papayannakos and Marangozis, 1984). Thus the distribution and mass transfer rate of hydrogen sulfide in the different phases is very important in modelling hydrotreating reactions. These effects are neglected in pseudo homogeneous plug flow model. The catalyst also promotes other reactions such as hydrodenitrogenation, dearomatization,
saturation of olefins and mild hydrocracking simultaneously. Three phase heterogeneous model based on two-film theory can effectively describe the distribution and transfer of various reactants and products in different phases.

4.2 ASSUMPTIONS

The three phase model takes into account the mass transfer of reactants and products in all the phases. The model equations are based on the transport coefficients of the system at gas-liquid and liquid-solid interfaces and include the mass transfer rates and distribution of reactants and products in different phases.

The mass balance equations for a differential element of the reactor are written based on the following assumptions.

1. The reactor operates under isothermal, isobaric and steady state conditions. This assumption is valid for the pilot plant reactor as it is normally operated with external electric furnace maintained at a constant temperature and generally the pressure drop observed are negligible. Adequate stabilization time was allowed before collecting experimental data to ensure steady state conditions of the reactor.

2. The reactor behaves like plug flow reactor (Levenspiel, 1982) as the dispersion group determined for the reactor is 0.00036.

3. Axial dispersion or backmixing effects are neglected in the present work. Korsten and Hoffmann (1996) have studied residence time distribution of pilot scale reactor, similar to the one used in the present work, and neglected axial dispersion effects. Application of the Mears (1971) criterion resulted in a $L_d/d_p$ ratio of around 250 indicating significant axial dispersion effects. The minimum $L_d/d_p$ ratio was reported to vary in the range of 450 – 3,850 with different correlations used to estimate Peclet number.
4. Evaporation of diesel feedstock occurs instantaneously only at the entrance of the reactor. The evaporation of reacting components can be neglected due to their high molecular weight (Chowdhury et al., 2002).

5. Condensation of gaseous reactants can be neglected in the range of operating conditions employed in the reactor.

6. The velocities of gaseous and liquid streams do not change along the length of the reactor due to negligible evaporation and condensation of reacting components and very little cracking of liquid components.

7. There are no radial concentration gradients within the reactor.

8. Mass-transfer resistance lies at gas-liquid and liquid-solid interfaces. The mass transfer resistance to pore diffusion can be neglected (Valerius et al., 1996).

9. The gas and liquid phases are in equilibrium at their interface.

10. The catalyst activity does not change with time due to reasonably longer cycle lengths of hydrotreating catalysts.

11. The chemical reactions take place only on the catalyst surface and not in the gas or the liquid phase.

12. The adsorption coefficient of hydrogen sulfide, $k_{ad}$, does not change with temperature (Korsten and Hoffman, 1996 and Chowdhury et al., 2002).

13. Hydrodesulfurization reactions are assumed to be inhibited only by hydrogen sulfide and not by other reactants and products.
14. The reactions studied in the present work are assumed to be non-competitive independent reactions.

15. Dearomatization reactions are assumed to be reversible. The forward reactions are assumed to follow pseudo first order kinetics with respect to aromatics as hydrogen is used as excess reactant while the backward reactions are assumed to follow pseudo first order kinetics with respect to the products (Girgis and Gates, 1991; Wilson and Kriz, 1984).

16. Other reactions studied in the present work are assumed to be irreversible.

17. Arrhenius equation was used to account for temperature dependency of rate constants for all the reactions in the range of operating conditions studied.

18. Heat of reaction for dearomatization reactions is assumed to be 67 kJ/mol of hydrogen reacted (Stanislaus and Cooper, 1994; Chowdhury et al., 2002). Von’t Hoff correlation is used to estimate equilibrium rate constants for dearomatization reactions at varied reactor temperatures.

4.3 REACTIONS MODELED

Under normal operating conditions, hydrotreating catalysts promote several reactions simultaneously. Some of these reactions are desirable while others are not. Hydrodesulfurization, hydrogenation, saturation of olefins and hydrodearomatization reactions are the important desirable reactions where as hydrocracking and coking are undesirable reactions. Desirable reactions reduce heteroatomic impurities such as sulfur, nitrogen and saturate olefinic compounds.
Hydrocracking reactions promoted by acidic sites of catalyst support result in cracking of diesel to lighter hydrocarbons and reduces the yield of diesel. Polymerisation of olefinic compounds to form large hydrogen-deficient molecules, known as coke, is a major undesirable reaction. The activity of the catalyst reduces due to coke deposition on active sites over a period of time. The loss in activity due to coke deposition is a slow, gradual and reversible process under normal operating conditions. The coking reactions can be neglected if we assume that activity of catalyst do not change with time.

The following reactions were modelled in the present work. These reactions essentially account for all the major reactions taking place in a hydrodesulfurization unit and assume paramount importance in the design, operation and optimization of industrial reactors.

4.3.1 Hydrodesulfurization

Sulfur generally forms single largest heteroatomic impurity in any petroleum fraction. The amount of sulfur in a typical straight run diesel can vary between 0.1 – 2.5 wt.%. In the context of growing concern for cleaner environment, removal of sulfur in petroleum products is becoming increasingly important.

The most important reaction that takes place in hydrodesulfurization is the removal of sulfur atom from hydrocarbon molecule. This reaction is known as hydrodesulfurization since hydrogen is used to remove sulfur as hydrogen sulfide by reacting it with hydrogen. Hydrodesulfurization is carried out at elevated temperature and pressure conditions and catalyzed by Co-Mo or Ni-Mo sulfides supported on alumina.
In petroleum fractions, sulfur can be present in different structures combined with hydrocarbon molecule. The common types of sulfur compounds present in petroleum fractions are shown in Figure 4.2. Sulfur compounds such as thiophenes, benzothiophenes, alkyl substituted benzothiophenes are the most common structures of sulfur compounds present in diesel fractions. Sulfur compounds like mercaptans, sulfides and disulfides can also be present in diesel fraction according to their boiling point. The number of sulfur compounds present in diesel fraction can be as high as 70 (Ma et al., 1995). Identification and measurement of individual sulfur compounds is very cumbersome and time consuming. Analytical methods using P.F.P.D. (Pulsed Flame Photometric Detector) and S.C.D. (sulfur-sensitive chemiluminescence detector) are generally used for the quantitative measurement of sulfur compounds in petroleum fractions.

Individual sulfur compounds might follow different reaction paths and thus can have different rates of reaction during hydrodesulfurization. Due to the large number of sulfur compounds and problems in their identification and measurement, it is very difficult to model all the reactions individually. All the sulfur compounds are generally grouped as single lump and considered as single reaction to study the kinetics of desulfurization reactions (Korsten and Hoffmann, 1996; Bhaskar et al., 2002; Chowdhury et al., 2002).

In the present work total sulfur content in the diesel fraction was treated as a single lump. The average molecular weight of the sulfur compound was assumed to be that of diesel feedstock.

The hydrodesulfurization reactions are exothermic and irreversible under the reaction conditions employed industrially. (Gates et al., 1979; Speight, 1981; Vrinat, 1983).
Figure 4.2 Common Types of Sulphur Compounds

R - SH  Mercaptans
R - SR'  Sulphides

Cyclic Sulphides

Thiophene

Benzothiophene

Dibenzothiophene

Methyl Dibenzothiophene

4,6 Di-methyl Dibenzothiophene

Naphthobenzothiophene
The following generalised desulfurization reaction was assumed in the present work:

\[ R-S + \frac{1}{2} H_2 \xrightarrow{k_s} R-H + H_2S \]  

... (4.1)

Where \( R-S \) is the hydrocarbon structure containing sulfur, \( H_2 \) is the hydrogen, \( R-H \) is the sulfur-free hydrocarbon and \( H_2S \) is the hydrogen sulfide. The reaction was assumed to be elementary with the stoichiometric coefficients as shown in equation (4.1).

### 4.3.2 Hydrodenitrogenation

Nitrogen is present in the form of indoles, pyridines, quinolines and amines. The amount of nitrogen in the diesel fraction is usually less than 200 ppmw. But in diesel fractions derived from high nitrogenous crudes, the nitrogen content can be as high as 2000 ppmw. The common types of nitrogen compounds that can be present in petroleum fractions are shown in Figure 4.3. Nitrogen can cause problems in processing and storage of the petroleum products. Basic nitrogen, which can be characterized by its titrability with perchloric acid, poisons acid catalyst and reduces conversion in refining processes such as Fluidized Catalytic Cracking and hydrocracking. Nitrogen imparts colour and deteriorates the stability of petroleum products.

The other important reaction that takes place in hydrotreating of diesel fraction is the removal of nitrogen from the feed. This reaction is known as hydrodenitrogenation since hydrogen is used to remove nitrogen as ammonia by reacting it with hydrogen. This is a parallel reaction to hydrodesulfurization and catalysed by Co-Mo or Ni-Mo sulfides supported on alumina. The rate of
Figure 4.3 Common Types of Nitrogen Compounds
hydrodenitrogenation is lower compared to hydrodesulfurization under normal operating conditions.

As in the case of desulfurization, all the nitrogen compounds present in the feed oil are grouped together as a single lump and the following rate of reaction is used for nitrogen removal reactions.

\[ R - N + 2H_2 \xrightarrow{k_N} R - H + NH_3 \quad \ldots \text{(4.2)} \]

Where \( R-N \) is the hydrocarbon structure containing nitrogen, \( H_2 \) is the hydrogen, \( R-H \) is the sulfur-free hydrocarbon and \( NH_3 \) is the ammonia. The reaction is assumed to be elementary with the stoichiometric coefficients shown in equation (4.2).

4.3.3 Hydrodearomatization

The aromatic compounds present in the feed oil are grouped into poly-, di- and monoaromatics. The hydrocarbon molecules that contain one aromatic ring in their structure are grouped as monoaromatics. The hydrocarbons with two-ring aromatic structures as part of their molecule are grouped as diaromatics. The polyaromatics are defined to contain three or more number of ring-structures.

These aromatic hydrocarbons are hydrogenated to produce naphthenic or lower aromatic hydrocarbons. Each of the aromatic groups undergoes different hydrogenation reactions. These reactions are reversible and thermodynamically limited. Hydrogenation of polyaromatics produces diaromatics. Similarly hydrogenation of diaromatics and monoaromatics result in monoaromatics and naphthenes. The relative rates of these reactions are different and limited thermodynamic equilibrium constants. These reactions can be modeled as series reactions.
The following rate equations represent the hydrodearomatization reactions.

\[
\begin{align*}
\text{Polyaromatics} + H_2 & \xrightleftharpoons[k_{\text{poly}}]{k_{\text{poly}^-}} \text{Diaromatics} \quad \cdots (4.3) \\
\text{Diaromatics} + 2H_2 & \xrightleftharpoons[k_{\text{Di}}]{k_{\text{Di}^-}} \text{Monoaromatics} \quad \cdots (4.4) \\
\text{Monoaromatics} + 3H_2 & \xrightleftharpoons[k_{\text{mono}}]{k_{\text{mono}^-}} \text{Naphthenes} \quad \cdots (4.5)
\end{align*}
\]

The dearomatization reactions are treated as pseudo first order reactions with respect to the concentration of poly-, di- and monoaromatics as the hydrogen is used in excess as suggested by Girgis and Gates (1991) and Wilson and Kriz (1984).

4.3.4 Saturation of Olefins

The olefinic compounds present in the feed oil react with hydrogen and form saturated hydrocarbons. As the feed normally contains cracked streams containing unsaturated hydrocarbons, the hydrogenation of olefins becomes an important reaction. The following rate equation is assumed to represent olefin saturation.

\[
R - CH = CH_2 + H_2 \overset{k_{\text{H2S}}}{\longrightarrow} R - CH_2 - CH_3 \quad \cdots (4.6)
\]
4.3.5 Hydrocracking

Acid sites on Al₂O₃ support promote mild hydrocracking reactions and produce lighter hydrocarbons in gas and liquid products. The cracking reactions are treated using three lumps of diesel, wild naphtha and light hydrocarbons as given below.

![Diagram of hydrocracking reactions](attachment:diagram.png)

4.4 MODEL FORMULATION

4.4.1 Model Description

The schematic representation of the trickle bed reactor model based on two-film theory for the reactions treated in the present work is shown in Figure 4.4. At steady state, the mass transfer rate of any component across gas-liquid becomes equal to the mass transfer rate across liquid-solid interface. Further, the interfacial mass transfer rates are equal to the rates of disappearance/formation of various components due to chemical reactions taking place on the catalyst surface. Hence model equations can be formulated for all the reactions based on differential mass balance across gas-liquid and liquid-solid interfaces.

In the present system of reactions, hydrogen forms the bulk of gas phase. For the reactions to occur, the hydrogen is to be transferred from gas phase to liquid phase and then adsorbed on the catalyst surface to react with other reactants, namely...
Figure 4.4 Schematic Diagram of Trickle Bed Reactor Model
sulfur, nitrogen, aromatics, olefins and hydrocarbons. The reaction products such as hydrogen sulfide, ammonia, water and light hydrocarbons will be transported to gas phase as determined by the phase equilibrium at the operating conditions of the reactor. The other reaction products, namely diesel oil with reduced sulfur, nitrogen, olefins, aromatics etc., will be transported to bulk liquid phase. As the vaporization of diesel oil is assumed to be negligible under these conditions, the mass transfer of these components to gas phase can also be neglected.

4.4.2 Mass Balance

Since no reaction occurs in the gas phase, the differential mass balance equation for hydrogen can be written by equating mass transfer rate of hydrogen to its pressure gradient in the gas phase as follows:

$$\frac{u_G}{R.T} \frac{dP_{H_2}}{dz} = -k_{H_2}^l a_p \left( \frac{P_{H_2}}{H_{H_2}} - C_{H_2}^l \right)$$

where $u_G$ is the superficial velocity of the gas, $R$ is the gas constant; $T$ represents the reaction temperature; $P_{H_2}$ is the partial pressure of hydrogen; $C_{H_2}^l$ is the concentration of hydrogen in liquid phase; $k_{H_2}^l a_p$ describes the mass transfer between the gas and liquid phase.

It is assumed that the gas-liquid equilibrium can be described by Henry’s law and the liquid phase concentration of hydrogen in equilibrium with bulk partial pressure is represented by the term $\frac{P_{H_2}}{H_{H_2}}$, where $H_{H_2}$ is the Henry’s coefficient for hydrogen.
On rearranging equation (4.7), we get

\[
\frac{dP_{H_2}}{dz} = \frac{RT}{u_g} k'_{H_2} a_p \left( \frac{P_{H_2}}{H_{H_2}} - C^l_{H_2} \right)
\]  \hspace{1cm} \ldots (4.8)

Equation (4.8) presents a relationship between change in partial pressure of hydrogen in the gas phase and its rate of mass transfer across gas-liquid interface.

Similarly, we can write following equations for other gas phase components of the present system of reactions as follows:

\[
\frac{dP_{H_2S}}{dz} = \frac{RT}{u_g} k'_{H_2S} a_p \left( \frac{P_{H_2S}}{H_{H_2S}} - C^l_{H_2S} \right)
\]  \hspace{1cm} \ldots (4.9)

\[
\frac{dP_{NH_3}}{dz} = \frac{RT}{u_g} k'_{NH_3} a_p \left( \frac{P_{NH_3}}{H_{NH_3}} - C^l_{NH_3} \right)
\]  \hspace{1cm} \ldots (4.10)

\[
\frac{dP_{HC}}{dz} = \frac{RT}{u_g} k'_{HC} a_p \left( \frac{P_{HC}}{H_{HC}} - C^l_{HC} \right)
\]  \hspace{1cm} \ldots (4.11)

Where \( P_{H_2S}, P_{NH_3}, \) and \( P_{HC} \) are the partial pressures; \( k'_{H_2S}, k'_{NH_3}, \) and \( k'_{HC} \) are mass transfer coefficients; \( C^l_{H_2S}, C^l_{NH_3}, \) and \( C^l_{HC} \) are the liquid phase concentrations of hydrogen sulfide, ammonia and light hydrocarbons respectively.

Equations (4.8) through (4.11) represent a system differential equations that relate partial pressures of hydrogen, hydrogen sulfide, ammonia and light hydrocarbons with the mass transfer of the compounds across gas-liquid interface.

These can be solved to get partial pressure profiles of gaseous compounds along the length of catalyst bed if their liquid phase concentrations are known.
The differential mass-balance equation for the liquid phase concentration of hydrogen in non-reactive zone can be written by equating concentration gradient to mass transfer of hydrogen across gas-liquid phase as follows:

\[
\frac{dC_{H_2}^l}{dz} = k'_{H_2}a_p \left( \frac{P_{H_2}}{H_{H_2}} - C_{H_2}^l \right)
\] ... (4.12)

Similarly, we can write mass balance equations for other gaseous compounds, namely hydrogen sulfide, ammonia, water vapour and light hydrocarbons as:

\[
\frac{dC_{H_2S}^l}{dz} = k'_{H_2S}a_p \left( \frac{P_{H_2S}}{H_{H_2S}} - C_{H_2S}^l \right)
\] ... (4.13)

\[
\frac{dC_{NH_3}^l}{dz} = k'_{NH_3}a_p \left( \frac{P_{NH_3}}{H_{NH_3}} - C_{NH_3}^l \right)
\] ... (4.14)

\[
\frac{dC_{HC}^l}{dz} = k'_{HC}a_p \left( \frac{P_{HC}}{H_{HC}} - C_{HC}^l \right)
\] ... (4.15)

The mass transfer across liquid-solid interface is zero in non-reactive zone of the reactor, such as preheating and disengaging sections of pilot plant reactor. The equations (4.8) through (4.15) can be solved simultaneously to obtain partial pressure and liquid phase concentration profiles of gaseous compounds in non-reactive zone.

In reactive zone, the mass transfer across liquid-solid interface must be taken into consideration while writing mass balance equations for liquid phase concentrations of gaseous compounds.
The mass balance equation for hydrogen can be written as:

\[
\frac{dC_{H_2}^l}{dz} = \frac{1}{u_L} \left( k_{H_2}^l a_p \left( \frac{P_{H_2}}{H_{H_2}} - C_{H_2}^l \right) + k_{H_2}^l a_s \left( C_{H_2}^l - C_{H_2} \right) \right)
\]  

... (4.16)

Where \( u_L \) is the superficial velocity of the liquid; \( k_{H_2}^l a_s \) describes the mass transfer across liquid-solid interface and \( C_{H_2} \) is the concentration of hydrogen on catalyst surface.

Similarly, the mass balance equations for other gaseous compounds can be written as follows:

\[
\frac{dC_{H_2S}^l}{dz} = \frac{1}{u_L} \left( k_{H_2S}^l a_p \left( \frac{P_{H_2S}}{H_{H_2S}} - C_{H_2S}^l \right) + k_{H_2S}^l a_s \left( C_{H_2S}^l - C_{H_2S} \right) \right)
\]  

... (4.17)

\[
\frac{dC_{NH_3}^l}{dz} = \frac{1}{u_L} \left( k_{NH_3}^l a_p \left( \frac{P_{NH_3}}{H_{NH_3}} - C_{NH_3}^l \right) - k_{NH_3}^l a_s \left( C_{NH_3}^l - C_{NH_3} \right) \right)
\]  

... (4.18)

\[
\frac{dC_{HC}^l}{dz} = \frac{1}{u_L} \left( k_{HC}^l a_p \left( \frac{P_{HC}}{H_{HC}} - C_{HC}^l \right) - k_{HC}^l a_s \left( C_{HC}^l - C_{HC} \right) \right)
\]  

... (4.19)

Where \( k_{H_2S}^l a_s \), \( k_{NH_3}^l a_s \) and \( k_{HC}^l a_s \) describe the mass transfer across liquid-solid interface and \( C_{H_2S}^l, C_{NH_3}^l \) and \( C_{HC}^l \) are the surface concentrations of hydrogen sulfide, ammonia and light hydrocarbons respectively.

As the vapourisation of diesel oil is negligible under hydrosulfurization conditions, the organic sulfur, nitrogen, olefins and poly-, di- and monoaromatics can be assumed to be non-volatile. The mass balance equations for these components can be written by equating their liquid phase concentration gradients to mass transfer
between liquid phase and catalyst surface. The mass balance equation for the concentration of organic sulfur in liquid phase can be written as:

\[
\frac{dC^t_S}{dz} = -\frac{1}{u_L} k^t_S a^i_s \left( C^t_S - C^t_S' \right) \quad \ldots (4.20)
\]

Where \( C^t_S \) and \( C^t_S' \) are the concentrations of sulfur compounds in liquid phase and catalyst surface respectively; \( k^t_S a^i_s \) describes the mass transfer of sulfur compound across liquid-solid interface.

The mass-balance equations for the concentration of other components in the liquid phase can be written as:

\[
\frac{dC^t_N}{dz} = -\frac{1}{u_L} k^t_N \left( C^t_N - C^t_N' \right) \quad \ldots (4.21)
\]

\[
\frac{dC^t_O}{dz} = -\frac{1}{u_L} k^t_O a^i_s \left( C^t_O - C^t_O' \right) \quad \ldots (4.22)
\]

\[
\frac{dC^t_{GO}}{dz} = -\frac{1}{u_L} k^t_{GO} \left( C^t_{GO} - C^t_{GO}' \right) \quad \ldots (4.23)
\]

\[
\frac{dC^t_{WN}}{dz} = -\frac{1}{u_L} k^t_{WN} \left( C^t_{WN} - C^t_{WN}' \right) \quad \ldots (4.24)
\]

\[
\frac{dC^t_{HC}}{dz} = -\frac{1}{u_L} k^t_{HC} \left( C^t_{HC} - C^t_{HC}' \right) \quad \ldots (4.25)
\]

\[
\frac{dC^t_{Poly}}{dz} = -\frac{1}{u_L} k^t_{Poly} \left( C^t_{Poly} - C^t_{Poly}' \right) \quad \ldots (4.26)
\]

\[
\frac{dC^t_{Di}}{dz} = -\frac{1}{u_L} k^t_{Di} \left( C^t_{Di} - C^t_{Di}' \right) \quad \ldots (4.27)
\]
Where \( C_{LN} \), \( C_{SN} \) are the concentrations of nitrogen in liquid phase and catalyst surface; \( C_{GO}^{l}, C_{GO}^{s} \) represents the concentrations of olefinic hydrocarbons in liquid phase and catalyst surface. As discussed earlier, three-lump kinetic scheme was assumed to represent hydrocracking of diesel oil, \( GO \), into wild naphtha, \( WN \), and light hydrocarbons, \( HC \). \( C_{GO}^{l}, C_{GO}^{s}, C_{WN}^{l}, C_{WN}^{s}, C_{HC}^{l}, C_{HC}^{s} \) represent the concentrations of diesel oil and wild naphtha and light hydrocarbons in liquid phase and catalyst surface. \( C_{Poly}^{l}, C_{Poly}^{s}, C_{Di}^{l}, C_{Di}^{s}, C_{Mono}^{l}, C_{Mono}^{s}, C_{Naph}^{l}, C_{Naph}^{s} \) are the concentrations of poly-, di-, monoaromatic and naphthenes in liquid phase and on catalyst surface. The \( k_{Poly}^{s} a_j, k_{Di}^{s} a_j, k_{WN}^{s} a_j, k_{HC}^{s} a_j, k_{Poly}^{l} a_j, k_{Di}^{l} a_j, k_{Mono}^{l} a_j \) and \( k_{Naph}^{s} a_j \) describes the mass transfer of nitrogen, olefins, diesel oil, wild naphtha, light hydrocarbons, poly-, di-, monoaromatics and naphthenes across liquid-solid interface respectively.

The equations (4.20) through (4.29) can be integrated along the length of the catalyst bed to get concentration profiles of sulfur, nitrogen, olefins, diesel, wild naphtha, light hydrocarbons, poly-, di-, monoaromatic and naphthenes in the reactor provided their concentrations on the catalyst surface are known. The concentrations of these components on the catalyst surface change as the reactions proceed along the length of the catalyst bed.
The compounds transferred across liquid-solid interface are consumed or produced due to chemical reactions. By equating liquid-solid interfacial mass transfer of these compounds with their reaction rates, we get following equations.

\[ k_{H_2} a_s (C^l_{H_2} - C^t_{H_2}) = \rho_b \xi \eta \left( r_S + \frac{3}{2} r_N + r_{poly} + 2 r_{Di} + 3 r_{Mono} + r_{GO} + r_{WN} + r_{HC} + r_D \right) \]  

\[ k_S a_s (C^l_S - C^t_S) = \rho_b \xi \eta r_S \]  

\[ k_{H_2S} a_s (C^l_{H_2S} - C^t_{H_2S}) = -\rho_b \xi \eta r_S \]  

\[ k_N a_s (C^l_N - C^t_N) = \rho_b \xi \eta r_N \]  

\[ k_{NH_3} a_s (C^l_{NH_3} - C^t_{NH_3}) = -\frac{1}{2} \rho_b \xi \eta r_N \]  

\[ k_O a_s (C^l_O - C^t_O) = \rho_b \xi \eta r_O \]  

\[ k_{H_2O} a_s (C^l_{H_2O} - C^t_{H_2O}) = (-\rho_b \xi \eta r_O \]  

\[ k_{GO} a_s (C^l_{GO} - C^t_{GO}) = \rho_b \xi \eta r_{GO} \]  

\[ k_{WN} a_s (C^l_{WN} - C^t_{WN}) = -\rho_b \xi \eta r_{WN} \]  

\[ k_{HC} a_s (C^l_{HC} - C^t_{HC}) = -\rho_b \xi \eta r_{HC} \]  

\[ k_{Poly} a_s (C^l_{Poly} - C^t_{Poly}) = \rho_b \xi \eta r_{Poly} \]  

\[ k_{Di} a_s (C^l_{Di} - C^t_{Di}) = \rho_b \xi \eta r_{Di} \]  

\[ k_{Mono} a_s (C^l_{Mono} - C^t_{Mono}) = \rho_b \xi \eta r_{Mono} \]  

\[ k_{Naph} a_s (C^l_{Naph} - C^t_{Naph}) = \rho_b \xi \eta r_{Naph} \]  

Where \( \rho_b \) is the bulk density of the catalyst pellets in the bed; \( \eta \) represents the catalyst effectiveness factor; and \( r_S, r_N, r_O, r_{GO}, r_{WN}, r_{HC}, r_{Poly}, r_{Di}, r_{Mono} \) and \( r_{Naph} \) represent intrinsic rates of reactions per unit mass of the catalyst of sulfur, nitrogen, olefins, diesel oil, wild naphtha, light hydrocarbons, poly-, di-,
monoaromatics and naphthenes respectively. The $\xi$ represents the fraction of catalyst bed diluted by inerts, defined as:

$$\xi = \frac{V_c}{V_c + V_i}$$

... (4.44)

Where $V_c$ is the volume of active catalyst and $V_i$ the volume of inert particles. The $\xi$ has significance for pilot plant reactors when the catalyst is diluted with inert particles to improve catalyst wetting. In the case of industrial reactors, catalyst bed is generally not diluted with inerts.

Equations (4.20) through (4.29) are the first order differential equations representing the concentration profiles of various reactants and products in the liquid phase. Equations (4.30) through (4.43) are the algebraic equations relating mass transfer across liquid-solid interface and reaction rates of various compounds. Equations (4.20) through (4.43) along with Equations (4.8) through (4.11) form isothermal three phase heterogenous model describing the performance of pilot plant trickle bed reactor.

4.4.3 Heat Balance

The hydrotreating reactions are exothermic. Since the industrial reactor is operated under non-isothermal conditions, the reactor temperature increases along the length of the reactor. We can write a differential heat balance equation for the industrial reactor to account for non-isothermal behaviour as follows by neglecting the heat transfer resistance between liquid and catalyst surface.

$$u_L \rho C_p \frac{dT_z}{dz} = r_s \xi \eta(-\Delta H_s) + r_n \xi \eta(-\Delta H_n) + r_o \xi \eta(-\Delta H_o) + r_{go} \xi \eta(-\Delta H_{go}) + r_{poly} \xi \eta(-\Delta H_{poly}) + r_{di} \xi \eta(-\Delta H_{di}) + r_{mono} \xi \eta(-\Delta H_{mono}) ...(4.45)$$
Where \( C_p \) is the specific heat of the feed and \( T_R \) is the reactor temperature; 
\(- \Delta H_s, - \Delta H_N, - \Delta H_O, - \Delta H_{\text{GO}}, - \Delta H_{\text{Poly}}, - \Delta H_{\text{Di}} \) and \(- \Delta H_{\text{Mono}} \) are the heats of reactions of hydrosulfurization, hydrogenation, olefin saturation, mild hydrocracking of diesel oil and hydrogenation of poly-, di- and monoaromatics respectively. The equation (4.48) can be integrated along the length of the catalyst bed to obtain temperature profiles in the reactor if the heats of reactions are known or can be determined experimentally. It can be assumed that the heats of reactions do not change with temperature.

The pilot plant experiments were carried out at constant reactor temperature where the reactor is heated by an electric furnace. It is difficult to determine the heats of reactions from pilot plant experiments as many reactions take place simultaneously and smaller volumes of catalyst bed compared to industrial reactors. The rise in the catalyst bed temperature is hardly observed in pilot plant experiments.

Of the reactions considered in the present work, the heat of reaction of hydrosulfurization is predominant when compared to other reactions. The heat of reaction of dearomatization also assumes significance. The heat of reaction of other reactions can be neglected considering their concentration in the feed and negligible heat of reaction values. Then the equation (4.48) can be written as:

\[
\frac{dT_R}{dz} = - \frac{1}{u_L \rho C_p} \left[ r_\text{SS} \xi \eta (- \Delta H_s) + r_\text{Poly} \xi \eta (- \Delta H_{\text{Poly}}) + r_\text{Di} \xi \eta (- \Delta H_{\text{Di}}) + r_\text{Mono} \xi \eta (- \Delta H_{\text{Mono}}) \right]
\]

... (4.46)

The simultaneous solution of equation (4.46) along with equations (4.8) through (4.11), equations (4.20) through (4.29) and equations (4.30) through (4.43) yields temperature profile along the length of the catalyst bed if the heats of reaction for hydrosulfurization and aromatics hydrogenation are known. In the present work,
the heat of reaction of aromatics hydrogenation is assumed as 67 KJ/mol of hydrogen reacted as reported by Stanislaus and Cooper, 1994. The same data was used by earlier investigators for estimating equilibrium constants for hydrodearomatization reactions (Chowdhury et al., 2002).

The heat of reaction for HDS reaction is estimated from the data collected from industrial reactor. The value of $-\Delta H_s$ representing the temperature rise in the industrial reactor was assumed as the heat of reaction for hydrodesulfurization. Once the $-\Delta H_s$ is estimated using test run data, the same value can be used to simulate the performance of industrial reactor with any other catalyst system.

Equations (4.8) through (4.11), equations (4.20) through (4.29), equations (4.30) through (4.43) and equation (4.46) form non-isothermal three phase heterogenous model describing the performance of industrial reactor. The solution of equations (4.30) through (4.43) require intrinsic rates of reactions per unit mass of the catalyst. The intrinsic rates of various reactions can be estimated as discussed below.

4.4.4 REACTION KINETICS

As discussed in Section 4.3, hydrodesulfurization, hydrodenitrogenation, olefin saturation, hydrogenation of aromatics and mild hydrocracking reactions are modelled in the present work. The model equations derived in sections 4.4.2 and 4.4.3 can be integrated along the length of the catalyst if reaction rates are known. The rate equations can be written in terms of surface concentrations as discussed below.

Hydrodesulfurization reactions are known to be irreversible under normal operating conditions (Girgis and Gates, 1991). Further, it is also assumed that the concentration of sulfur and hydrogen has positive effect on rate of reaction while hydrogen sulfide adsorbed on the catalyst surface will inhibit the rate of reaction. The
following Langmuir-Hinshelwood type rate equation is used to describe hydrodesulfurization reactions.

\[ r_s = k_{app, s} \left( \frac{C_s^*}{C_{sH}} \right)^{m_1} \left( \frac{C_{H_2}}{1 + k_{ad} C_{H_2S}} \right)^{m_2} \] \hspace{1cm} ... (4.47)

Where \( r_s \) is the rate of reaction per unit mass of the catalyst; \( C_s^* \), \( C_{H_2}^* \) and \( C_{H_2S}^* \) are the concentrations of sulfur, hydrogen and hydrogen sulfide on catalyst surface respectively; \( m_1 \) and \( m_2 \) represent the order of reaction for sulfur and hydrogen respectively; \( k_{app, s} \) is the apparent rate constant for hydrodesulfurization reaction; \( k_{ad} \) represent adsorption-equilibrium constant for hydrogen sulfide.

Hydrodenitrogenation reaction is also assumed to be irreversible under normal operating conditions. The concentration of hydrogen on the catalyst surface is much higher compared to the concentration of nitrogen since hydrogen is used as excess reactant. Hence hydrodenitrogenation can be assumed to follow pseudo-first-order kinetics with respect to the concentration of nitrogen as given below.

\[ r_N = k_{app, N} C_N^* \] \hspace{1cm} ... (4.48)

Where \( k_{app, N} \) is the apparent rate constant for hydrodenitrogenation reaction and \( C_N^* \) represent the concentration of nitrogen on catalyst surface.

Similarly, olefin saturation reaction is also assumed to be pseudor-first-order with respect to the concentration of olefins as given by the following rate equation.

\[ r_O = k_{app, O} C_O^* \] \hspace{1cm} ... (4.49)
Where $k_{app,O}$ is the apparent rate constant for olefin saturation reaction and $C'_O$ represent the concentration of olefins on catalyst surface.

As discussed in Section 4.3.4, mild hydrocracking reactions were treated using a three lump model consisting of diesel oil, wild naphtha and light hydrocarbons. The reactions were assumed to follow pseudo-first-order kinetics. Hence the rate equations for mild hydrocracking reactions can be written as:

\[
    r_{GO} = (k_1 + k_2) C'_O 
\]

\[
    r_{WN} = -k_2 C'_O + k_3 C'_WN 
\]

\[
    r_{HC} = -k_1 C'_O - k_3 C'_WN 
\]

Where $k_1$, $k_2$ and $k_3$ are apparent rate constants; $C'_O$ and $C'_WN$ are surface concentrations of diesel oil and wild naphtha respectively.

The following rate equations were used to describe the hydrogenation of aromatics.

\[
    r_{Poly} = k^{*}_{Poly} P_H^n C'_Poly - k_{-Poly} C'_Di 
\]

\[
    r_{Di} = k^{*}_{Di} P_H^n C'_Di - k_{-Di} C'_Mono 
\]

\[
    r_{Mono} = k^{*}_{Mono} P_H^n C'_Mono - k_{-Mono} C'_Naph 
\]

\[
    r_{Naph} = -r_{Mono} = -k^{*}_{Mono} C'_Mono P_H^n + k_{-Mono} C'_Naph 
\]

Where $k^{*}_{Poly}$, $k^{*}_{Di}$, $k^{*}_{Mono}$, $k^{*}_{Naph}$ and $k_{-Poly}$, $k_{-Di}$, $k_{-Mono}$, $k_{-Naph}$ are the forward and backward rate constants; $P_H^n$ is the partial pressure of hydrogen and $n_1$, $n_2$, $n_3$ are the exponents of hydrogen.
As \( P_{H_2}^* \), \( P_{H_2}^{*2} \), and \( P_{H_2}^{*3} \) remain constant when the reaction pressure is held constant, applying assumption 15, equation (4.56) through (4.58) reduce to the following equations.

\[
 r_{Poly} = k_{Poly} C_{Poly}^t - k_{-Poly} C_{Di}^t 
\]

... (4.57)

\[
 r_{Di} = k_{Di} C_{Di}^t - k_{-Di} C_{Mono}^t 
\]

... (4.58)

\[
 r_{Mono} = k_{Mono} C_{Mono}^t - k_{-Mono} C_{Naph}^t 
\]

... (4.59)

Where

\[
 k_{Poly} = k_{Poly}^* P_{H_2}^* 
\]

... (4.60)

\[
 k_{Di} = k_{Di}^* P_{H_2}^{*2} 
\]

... (4.61)

\[
 k_{Mono} = k_{Mono}^* P_{H_2}^{*3} 
\]

... (4.62)

Now \( k_{Poly} \), \( k_{Di} \) and \( k_{Mono} \) are the forward rate constants for hydrogenation of aromatics reactions. To determine the rate constants for the backward reactions, dynamic equilibrium constants were defined as follows:

\[
 K_{Poly} = \frac{k_{poly}}{k_{-Poly}} 
\]

... (4.63)

\[
 K_{Di} = \frac{k_{Di}}{k_{-Di}} 
\]

... (4.64)

\[
 K_{Mono} = \frac{k_{Mono}}{k_{-Mono}} 
\]

... (4.65)
The equilibrium constants at a reference temperature are taken from the data published by Chowdhury et al., 2002. Van't Hoff correlation, as defined below, is used to determine dynamic equilibrium constants at different temperatures.

\[
\frac{d(\ln K_{\text{Poly}/\text{Di}/\text{Mono}})}{dT} = \frac{\Delta H_{\text{Poly}/\text{Di}/\text{Mono}}}{RT^2}
\]  (4.66)

Where \( \Delta H_{\text{Poly}/\text{Di}/\text{Mono}} \) are the heats of reactions as discussed in assumption 18; \( R \) is a gas constant and \( T \) is the temperature in °K.

### 4.4.5 CONVERSIONS

The conversion of various compounds was calculated using their concentrations in the feed and product using the following equations.

\[
X_s = \frac{C_{i,0}^l - C_s^l}{C_{i,0}^l}
\]  (4.67)

\[
X_N = \frac{C_{i,0}^l - C_N^l}{C_{i,0}^l}
\]  (4.68)

\[
X_O = \frac{C_{i,0}^l - C_O^l}{C_{i,0}^l}
\]  (4.69)

\[
X_{GO} = \frac{C_{i,0}^l - C_{GO}^l}{C_{i,0}^l}
\]  (4.70)

\[
X_{\text{Poly}} = \frac{C_{i,0}^l - C_{\text{Poly}}^l}{C_{i,0}^l}
\]  (4.71)

\[
X_{\text{Di}} = \frac{C_{i,0}^l - C_{\text{Di}}^l}{C_{i,0}^l}
\]  (4.72)
\[ X_{\text{Mono}} = \frac{C_{\text{Mono},0} - C_{\text{Mono}}'}{C_{\text{Mono},0}} \quad \ldots \ (4.73) \]
\[ X_{\text{Tot}} = \frac{C_{\text{Tot},0}' - (C_{\text{Poly}}' + C_{\text{Di}}' + C_{\text{Mono}}')}{C_{\text{Tot},0}} \quad \ldots \ (4.74) \]

Where \( X_S, X_N, X_{\text{Olefin}}, X_{\text{Poly}}, X_{\text{Di}}, X_{\text{Mono}}, X_{\text{Tot}} \) are the conversions of sulfur, nitrogen, olefins, poly-, di-, monoaromatics and total aromatics and \( C_{S,0}', C_{N,0}', C_{O,0}', C_{\text{Di},0}', C_{\text{Mono},0}', C_{\text{Tot},0}' \) are their concentrations in the feed respectively.

We can derive equations to determine equilibrium conversions of aromatic compounds. At equilibrium,

\[ r_{\text{Poly}} = r_{\text{Di}} = r_{\text{Mono}} = 0. \quad \ldots \ (4.75) \]

Therefore, using Equations (4.57) through (4.65),

\[ C_{\text{Poly},e} = \frac{1}{K_{\text{Poly}}} C_{\text{Di},e} \quad \ldots \ (4.76) \]
\[ C_{\text{Di},e} = \frac{1}{K_{\text{Di}}} C_{\text{Mono},e} \quad \ldots \ (4.77) \]
\[ C_{\text{Mono},e} = \frac{1}{K_{\text{Mono}}} C_{\text{Naph},e} \quad \ldots \ (4.78) \]

On rearrangement equation (4.78) we get

\[ C_{\text{Naph},e} = K_{\text{Mono}} C_{\text{Mono},e} \quad \ldots \ (4.79) \]

From Equations (4.76) and (4.77), we can get

\[ C_{\text{Poly},e} = \frac{1}{K_{\text{Di}} K_{\text{Poly}}} C_{\text{Mono},e} \quad \ldots \ (4.80) \]
By making total mole balance of aromatics and naphthenes, we get

\[ C_{\text{Tot},0} + C_{\text{Naph},0} = C_{\text{Poly},e} + C_{\text{Di},e} + C_{\text{Mono},e} + C_{\text{Naph},e} \]  \hspace{1cm} (4.81)

Where

\[ C_{\text{Tot},e} = C_{\text{Poly},e} + C_{\text{Di},e} + C_{\text{Mono},e} \]  \hspace{1cm} (4.82)

Substituting the expression for \( C_{\text{Naph,e}} \), \( C_{\text{Poly,e}} \) and \( C_{\text{Di,e}} \) from equations (4.79), (4.80) and (4.77) and simplifying for \( C_{\text{ Mono,e}} \), we can get

\[ C_{\text{ Mono,e}} = \frac{C_{\text{Tot,0}} + C_{\text{Naph,0}}}{1 + K_{\text{Mono}} + \frac{1}{K_{\text{Di}}} + \frac{1}{K_{\text{Di}}K_{\text{Poly}}}} \]  \hspace{1cm} (4.83)

We can calculate \( C_{\text{ Mono,e}} \) using equation (4.86) using \( C_{\text{Tot,0}}, C_{\text{Naph,0}} \) and equilibrium constants \( K_{\text{Mono}}, K_{\text{Di}} \) and \( K_{\text{Poly}} \). Then equilibrium concentrations naphthenes, poly- and diaromatics can be calculated using equations (4.79), (4.80) and (4.77).

The following equations can be used to estimate equilibrium conversion of various aromatic compounds:

\[ X_{\text{Poly,e}} = \frac{C_{\text{Poly,e}} - C_{\text{Poly,0}}}{C_{\text{Poly,0}}} \]  \hspace{1cm} (4.84)

\[ X_{\text{Di,e}} = \frac{C_{\text{Di,e}} - C_{\text{Di,0}}}{C_{\text{Di,0}}} \]  \hspace{1cm} (4.85)

\[ X_{\text{Mono,e}} = \frac{C_{\text{Mono,e}} - C_{\text{Mono,0}}}{C_{\text{Mono,0}}} \]  \hspace{1cm} (4.86)
4.5 CORRELATIONS USED

4.5.1 Liquid phase concentrations

The concentration of sulfur compound in the liquid can be estimated by assuming that the molecular weight of sulfur compound has the same molecular weight as that of feed. The feed molecular weight was estimated from specific gravity and average boiling point (Nelson, 1987).

\[
C_s^l = \frac{\rho_L \cdot w_s}{M_s} \quad \ldots (4.89)
\]

Where \(C_s^l\) is the concentration of sulfur compound in the liquid; \(\rho_L\) is the density of feed oil at process conditions; \(M_s\) is the molecular weight of sulfur compound; and \(w_s\) is the weight fraction of sulfur compound.

Similarly the concentration of nitrogen, olefin, poly-, di-, monoaormaïtcs and naphthenes in the liquid phase were estimated using the following equations.

The molecular weight of nitrogen and olefinic hydrocarbon was assumed to have same molecular weight as that of feed while the molecular weight of poly-, di-, monoaaromatics and naphthenes was computed from their molecular formula without any alkyl substituents.
Where $C'_{N}$, $C'_{O}$, $C'_{Poly}$, $C'_{Di}$, $C'_{Mono}$ and $C'_{Naph}$ are the concentrations of nitrogen, olefins, poly-, di-, monoaroatics and naphthenes; $M_{N}$, $M_{O}$, $M_{Poly}$, $M_{Di}$, $M_{Mono}$, $M_{Naph}$ are the molecular weights of nitrogen, olefins, poly-, di-, monoaroatics and naphthenes; and $w_{N}$, $w_{O}$, $w_{Poly}$, $w_{Di}$, $w_{Mono}$ and $w_{Naph}$ are the weight fractions of nitrogen, olefins, poly-, di-, monoaroatics and naphthenes.

The density $\rho_{L}$ of the diesel at process conditions can be determined by Standing-Katz correlation. Korsten and Hoffmann, 1996 also used the same correlation.

$$\rho(p, T) = \rho_{o} + \Delta \rho_{p} - \Delta \rho_{T}$$  \hspace{1cm} (4.96)

Where $\rho_{o}$ represents the density at standard conditions (15.6°C and 101.3 kPa) in lb/ft$^3$; $\Delta \rho_{p}$ and $\Delta \rho_{T}$ account for pressure and temperature dependence of density and can be estimated as follows:
\[
\Delta \rho_p = \left[0.167 + 16.181 \times 10^{-0.0425 \eta_p} \right] \left[ \frac{p}{1000} \right]
- 0.01 \left[0.299 + 263.10^{-0.0603 \eta_p} \right] \left[ \frac{p}{1000} \right]^2
\]
\[
\Delta \rho_T = \left[0.0133 + 152.4 \left( \rho_p + \Delta \rho_p \right)^{2.45} \right] \left[ T - 520 \right]
- \left[8.1 \times 10^{-6} - 0.0622 \times 10^{-0.764 \left( \rho_p + \Delta \rho_p \right)} \right] \left[ T - 520 \right]^2
\]

Where \( p \) is the pressure in psia and \( T \) is the temperature in °R.

4.5.2 Gas-Liquid Equilibrium

As it is assumed that the gas-liquid equilibrium can be described by Henry's law, the Henry's coefficient are required to be estimated for all the components that can be present in the gas phase. The Henry's coefficients can be estimated from solubility coefficients \( \lambda_i \) using the following equation:

\[
H_i = \frac{\nu_i}{\lambda_i \rho_L}
\]

(4.98)

Where \( H_i \) is the Henry's coefficient of compound \( i \); \( \nu_i \) is the molar gas volume at standard conditions and \( \rho_L \) represents the density of liquid at under process conditions. For hydrogen and hydrogen sulfide, the correlations proposed by Korsten and Hoffmann, 1996 based on published data is used in the present work.

For hydrogen:

\[
\dot{\rho}_2 = a_0 + a_1 T + a_2 \frac{T}{\rho_{20}} + a_3 T^2 + a_4 \frac{1}{\rho_{20}^2}
\]

(4.99)
with the following constants:

\[
\begin{align*}
a_0 &= -0.559729 \\
a_1 &= -0.42947 \times 10^{-3} \\
a_2 &= 3.07539 \times 10^{-3} \\
a_3 &= 1.94593 \times 10^{6} \\
a_4 &= 0.835783
\end{align*}
\]

Where \( T \) is the temperature in °C; \( \rho_{20} \) is the density at 20°C in g/cm³; and the hydrogen solubility is given in \((\text{M} H_2)/(\text{kg. oil})(\text{MPa})\).

For hydrogen sulfide:

\[
\lambda_s = \exp(3.670 - 0.008470 \cdot T)
\]

\[\text{... (4.100)}\]

For other gaseous components, solubility coefficients were estimated from Aspen Plus process flow sheet simulator.

### 4.5.3 External Mass Transfer

The gas-liquid mass transfer coefficient is a function of the liquid superficial mass flow velocity \( G_L \). The gas-liquid mass transfer coefficient was estimated by using correlation proposed by Goto and Smith, 1975.

\[
\frac{k^l_i \cdot \rho_{p}}{D^l_i} = \alpha_i \left( \frac{G_L}{\mu_L} \right)^{\alpha_2} \left( \frac{\mu_L}{\rho_L \cdot D^l_i} \right)^{\frac{1}{2}}
\]

\[\text{... (4.101)}\]

Where \( k^l_i \cdot \rho_p \) describes the mass transfer of compound \( i \); \( \rho_L \) is the feed density at process conditions as determined by equation (4.99). The coefficients \( \alpha_i \),
and \( \alpha \), depend on particle diameter and are to be determined experimentally. The values reported by Korsten and Hoffmann, 1996 for similar particle diameter were used in the present work. \( G_L \) represents the mass liquid velocity and can be determined by liquid hourly space velocity and reactor diameter. The \( \mu_L \) is the viscosity of liquid at process conditions. The \( D'_L \) represents the molecular diffusivity of compound in liquid.

In order to use equation (4.105) to determine gas-liquid coefficients, we need to estimate the viscosity, \( \mu_L \) and diffusivity, \( D'_L \) of the compound at process conditions. The dependence of liquid viscosity \( \mu_L \) on temperature can be described by Vogel equation, as published by Reid et al., 1987 as:

\[
\mu_L = 3.141 \times 10^{10} (T - 460)^{3.44} \left[ \log_{10}(AP) \right]^a
\]

(4.102)

Where

\[
a = 10.313 \left[ \log_{10}(T - 460) \right] - 36.447
\]

(4.103)

Where the temperature is in °R. The dependence of liquid viscosity on pressure is very small in the operating range of pressure and hence can be neglected.

The following equation proposed by Tyn-Calus and published in Reid et al., 1987 was used to estimate diffusivities, \( D'_L \).

\[
D'_L = 8.93 \times 10^{-8} \frac{V_L^{0.267} T}{V_i^{0.435} \mu_L}
\]

(4.104)
Equation (4.108) gives the $D_j'$ in cm$^2$/s. The temperature is in °K and $\mu_L$ represents the viscosity in mPa.s. The $v_i$ and $v_L$ are the molar volumes of solute and liquid, cm$^3$/mol.

The molar volume, $v_i$, for the gaseous compound can be estimated from the following equation as published in Perry and Green, 1984.

$$v_i = 0.285\cdot v_{i,0.548} \quad \ldots \ (4.105)$$

The critical volume, $v_c$, of the gases can be obtained from Reid et al., 1987. For liquid components, the following equation can be used to estimate molar volume (Korsten and Hoffmann, 1996).

$$v_L = 7.5214 \times 10^{-3} T_{BP}^{0.2896} d_{15.6}^{-0.7666} \cdot M \quad \ldots \ (4.106)$$

Where $T_{BP}$ is the mean average boiling point in °R; $d_{15.6}$ is the specific gravity at $15.6^\circ$C and $M$ is the molecular weight of the liquid.

Korsten and Hoffmann, 1996 has used Krevelen-Krekels equation for estimating liquid-solid mass transfer coefficients. This equation describes mass transfer in low interaction regime. The same equation is used to estimate liquid-solid mass transfer in the present work.

$$\frac{k_i^{s}}{D_i^{l}a_{s}} = 1.8 \left( \frac{G_{L}}{a_{s} \cdot \mu_L} \left( \frac{\mu_L}{\rho_{L}D_i^{l}} \right)^{\frac{1}{3}} \right) \quad \ldots \ (4.107)$$
4.6 CONCLUSIONS

The model formulated and developed in this chapter is based on two-film theory and takes into account mass transfer resistances across gas-liquid and liquid-solid interfaces. The model also presents rate equations for all the major reactions taking place in a hydrotreating unit. The inhibiting effect of hydrogen sulfide on hydrodesulfurization reaction was effectively described using Langmuir-Hinshelwood reaction kinetics.

The model equations can be integrated along the catalyst bed length to determine exit concentrations and conversions of respective reactants. The model becomes a boundary value problem with a set of differential and algebraic equations when used to estimate kinetic parameters from pilot plant experiments. While it becomes an initial value problem when applied to simulate the performance of pilot plant and industrial trickle bed reactor with known kinetic parameters.

The model equations along with initial and boundary values are presented in Appendix 1.