CHAPTER 1

INTRODUCTION

This research work was carried out at the Research and Development Centre of Chennai Petroleum Corporation Limited, Chennai. Chennai Petroleum Corporation Limited, CPCL, is one of the largest refineries in India incorporated in the year 1965. Initially the refinery facilities were designed to process 2.5 million tonnes of crude oil per annum. Subsequent to the implementation of many expansion and modernization projects over the years, the refining capacity was progressively increased to 7.0 million tonnes of crude oil per annum. Another expansion project to increase the refining capacity by 3.0 million tonnes of crude oil per annum is in the advanced stage of implementation. CPCL is one of the most complex refineries in India producing both fuels and lubricating oil base stocks.

To remain at technological forefront in all aspects of refinery operations, CPCL has established its in-house Research and Development Centre in the year 1984. Over the years CPCL R&D centre has developed into a premier research centre in India.

One of the major activities of R&D centre is the evaluation and selection of catalysts used in the hydrotreating units operating at CPCL. As part of this activity, CPCL R&D centre has installed two high pressure trickle bed reactors procured from Vinci Technologies, France and Xytel India Pvt. Ltd., India. These pilot plant units are being used to evaluate different new generation hydrotreating catalysts and
feedstocks for various hydropprocessing applications. But the data generated in pilot plant reactors cannot be correlated with that of industrial reactors due to certain differences in the hydrodynamics and mass transfer characteristics between them. A rigorous mathematical model is necessary to scale up pilot plant data to commercial scale. Thus the present work was initiated with an objective of developing a trickle bed reactor model and validating with industrial data.

The experimental studies reported in the present work were carried out at CPCL R&D Centre. The modeling and simulation work was carried out both at CPCL R&D Centre and A.C. College of Technology, Anna University.

1.1 OUTLINE OF THE THESIS

The thesis has been organized into six chapters and two annexures as outlined below:

Chapter 1 presents the introduction and objectives of the present work. The literature pertaining to kinetics and modeling of trickle bed reactors is reviewed in chapter 2. The details of pilot plant experimental studies and the analysis of feed and product samples are discussed in chapter 3.

The details of model formulation, assumptions, reactions modeled, reaction kinetics and correlations used are presented in Chapter 4. The results of pilot plant experiments and simulation of both pilot plant and industrial reactor are discussed in chapter 5. The major conclusions drawn from this study and suggestions for further work are presented in chapter 6.

The model equations and boundary conditions for the estimation of kinetic parameters and reactor simulation are presented in appendix – 1. The listing of FORTRAN 95 programs used to solve model equations is presented in appendix – 2.
1.2 TRICKLE BED REACTORS

Trickle bed reactors can be defined as fixed beds of catalyst particles contacted by cocurrent downward flow of gas and liquid phases at low superficial velocities. These reactors assume greater importance among the three phase gas-liquid-solid reaction systems encountered in industrial practice. They are widely employed in a petroleum refinery for hydrotreating, hydrofinishing, hydrodesulfurisation and hydrocracking applications.

Trickle bed reactors belong to a special case of fixed bed reactors involving gas and liquid phases and a solid catalyst. Various flow regimes can be encountered in fixed bed reactors depending upon the superficial mass velocities, fluid properties and bed characteristics. Specchia et al. (1977) and Al-Dahhan et al. (1994) have subdivided the flow regimes into low interaction and high interaction regimes based on gas-liquid interactions encountered. Low interaction regime includes trickle flow while high interaction regime includes pulse, wavy, spray and bubble flow patterns.

Flow patterns encountered in two phase reactors, as presented in Ng et al. (1987) is shown in Figure 1.1. In the trickle flow regime, the liquid reactant flowing down through the reactor forms a thin film around the solid catalyst. The gas reactant being the continuous phase fills the remaining void space of the catalyst bed and flows separately.

The trickling flow regime appears at relatively low gas and liquid flow rates and is classified as low-interaction-regime of three-phase reactor systems. Extensive research work was reported in the literature to describe flow patterns and transition of one type of flow to another. The flow regime map presented by Al-Dahhan et al. (1994) is shown in Figure 1.2.
Figure 1.2 Flow Regime Map of Two Phase Reactors
1.3 OBJECTIVES OF THE PRESENT WORK

Prior to industrial applications, the experiments are conducted in pilot plant trickle bed reactors to generate kinetic data, to study the influence of operating conditions and to evaluate new catalysts. As the length of the industrial trickle bed reactor is normally 10-20 times higher than a pilot plant reactor, it is not possible to operate both reactors at the same Liquid Hourly Space Velocity (LHSV) and superficial mass velocity simultaneously.

Generally the experiments are conducted at industrial reactor space velocity, causing the superficial mass velocity in the pilot plant reactor to be 10-20 times lower. The lower superficial mass velocities observed in smaller reactors result in lower levels of conversion. The lower liquid velocities encountered in pilot plant reactors also result in incomplete wetting of catalyst particles. Besides, the axial dispersion or backmixing effects become significant in some pilot plant reactors while they are negligible in the case of industrial reactors. The wall effects and liquid maldistribution are some of the other problems reported to be presented in pilot plant reactors. The difference in the operation of pilot plant and industrial reactors is presented in Table 1.1.

Due to these differences, it becomes difficult to correlate pilot plant data with that of industrial reactor. Generally mathematical models are employed to simulate the performance of pilot plant reactor, scale up to industrial scale and predict its performance from pilot plant experiments.

In the past 40 years, many investigators have attempted different approaches to model trickle bed reactors. A comprehensive review of kinetics and reactor models reported in the literature are discussed in chapter 2. Concisely the reactor models reported in the literature can be broadly categorized into 'kinetic' models and 'hydrodynamic' models.
Table 1.1 Differences between Pilot Plant and Industrial Trickle Bed Reactors

<table>
<thead>
<tr>
<th></th>
<th>Industrial Reactor</th>
<th>Pilot Plant Reactor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length</td>
<td>10 – 25 m</td>
<td>0.5 – 2.0 m</td>
</tr>
<tr>
<td>Diameter</td>
<td>1 – 4 m</td>
<td>0.5 – 4.0 cm</td>
</tr>
<tr>
<td>Gas Velocity</td>
<td>14.8 – 2200 cm/s</td>
<td>1.48 – 220 cm/s</td>
</tr>
<tr>
<td>Liquid Velocity</td>
<td>0.8 – 2.5 cm/s</td>
<td>0.08 – 0.25 cm/s</td>
</tr>
<tr>
<td>Wetting</td>
<td>Complete</td>
<td>Partial</td>
</tr>
<tr>
<td>Flow Regime</td>
<td>Trickle/Slug Flow</td>
<td>Trickle</td>
</tr>
<tr>
<td>Axial Dispersion</td>
<td>Negligible</td>
<td>Significant in some cases</td>
</tr>
<tr>
<td>Catalyst Irrigation</td>
<td>Very Good</td>
<td>Poor</td>
</tr>
<tr>
<td>Mass Transfer</td>
<td>Very Good</td>
<td>Poor</td>
</tr>
<tr>
<td>Channeling and Wall Effects</td>
<td>Negligible</td>
<td>Significant</td>
</tr>
<tr>
<td>Mode of Operation</td>
<td>Non-Isothermal</td>
<td>Isothermal</td>
</tr>
</tbody>
</table>

The kinetic models were generally based on intrinsic rates of reactions and did not account for the influence of hydrodynamics and related phenomena. Currently these models are used for testing and evaluating catalysts in bench scale reactors but cannot be used for scale up purposes as the effects of hydrodynamics are neglected. The hydrodynamic models emphasized the hydrodynamic aspects of the reactor such as external liquid holdup, catalyst wetting, axial dispersion etc. and generally assumed plug flow with first order kinetics. The hydrodynamic models incorporated an apparent rate constant in place of intrinsic rate constant to account for the effects of hydrodynamics.

Henry and Gilbert (1973) have described a pseudo homogeneous plug flow model using a first order kinetics. This model assumes the apparent rate constant as proportional to the external liquid holdup. Iannibello et al. (1985), Tsamatsoulis et al. (1995) and Froment et al. (1994) have attempted to model the performance of trickle
bed reactors by assuming pseudo homogeneous kinetics. These models have limitations in application as they were based on prior assumption of first order kinetics and weak underlying theory.

Korsten and Hoffman (1996) have presented a three phase heterogeneous model for hydrodesulfurisation of vacuum gas oil in a trickle bed reactor. This model was based on two-film theory and incorporated mass-transport phenomena at the gas-liquid and liquid-solid interface. The chemical reaction rates were described by a Langmuir-Hinshelwood mechanism. The simulation procedure had also included the correlations to estimate mass transfer coefficients, gas solubilities and the properties of oils and gases under process conditions. This model was used to analyze the performance of a pilot plant trickle bed reactor and model predictions were found to be in good agreement with experimental results.

Chowdhury et al. (2002) have investigated desulfurization and hydrogenation of aromatics of diesel in an isothermally operated trickle bed reactor using commercial bifunctional Ni-Mo/Al₂O₃ catalysts. A mechanistic mathematical model was developed for a two-phase flow reactor, considering both mass transfer and chemical reaction in the reactor.

Though the models reported in the literature were successfully applied to simulate the performance of pilot plant reactors, limited efforts were made to scale up to industrial scale. The validation data using different reactors and reaction systems is scarce. Moreover, many of the models have not considered all the important reactions taking place in a hydrotreating unit.

In the present work efforts were made to develop a rigorous mathematical model which can account for all the major reactions, include fair amount of complexity and simulate the performance of both pilot and industrial scale trickle bed reactors and correlate pilot plant data with that of industrial reactor.
The objectives of the present research work can be presented as follows:

- Development of a rigorous heterogeneous model to describe the performance of a trickle bed reactor sustaining hydrotreating reactions.

- Application of the model to simulate the performance of pilot plant trickle bed reactor. Estimation of kinetic parameters for hydrotreating reactions from pilot plant experiments.

- Application of the model to correlate the performance of pilot plant reactor with that of industrial reactor and validate the model with the data collected from industrial reactor.

- Application of the model to carry out parameters sensitivity analysis to study the effect of reactor temperature and feed rate on product quality.

- Application of the model to predict the performance of industrial reactor loaded with high activity new generation catalysts from the pilot plant experiments.