CHAPTER 6

CONCLUSIONS

This chapter presents significant conclusions drawn from this work based on the experimental and simulation results discussed in the earlier chapters. The suggestions for further work are also included in this chapter.

6.1 SUMMARY OF THE PRESENT WORK

In the present work, a rigorous heterogeneous model was developed to simulate the performance of pilot plant and industrial trickle bed reactors employed in hydrodesulfurization of diesel fractions. The model is based on two film theory and takes into account the mass transfer resistances at gas-liquid and liquid-solid interfaces. The model equations were formulated by applying differential mass balance across the interfaces along the catalyst bed length at steady state.

Pilot plant experiments were carried to evaluate the performance of four different catalysts using a feed stock collected from industrial diesel hydrodesulfurization unit. The reactor temperature was varied from 320 to 360°C and liquid hourly space velocity from 1.0 h⁻¹ to 2.5 h⁻¹ at a constant operating pressure of 40 kg/cm² and H₂/oil ratio of 200 lit/lit to study the influence of operating conditions on product quality. All the catalysts were evaluated under similar operating conditions using the same feed diesel oil.
The feed and product samples collected from the industrial unit operating at Chennai Petroleum Refineries Limited were characterized for sulfur, nitrogen, olefins, poly-, di- and monoaromatics.

All the major reactions taking place in hydrotreating of diesel fractions were modeled. The hydrodesulfurization reaction rates were described using Langmuir-Hinshelwood mechanism to take into account the inhibiting effects of hydrogen sulfide. The hydrodearomatization reactions were treated as irreversible and pseudo first order reactions with respect to the concentration of aromatics. The hydrodenitrogenation and olefin saturation reactions were assumed to be pseudo first order reactions. The mild hydrocracking reactions were modeled using three lumps of diesel, wild naphtha and light hydrocarbons.

The pilot plant reactor was modeled as isothermal reactor with partial wetting of catalyst particles. The wetting efficiency of the pilot plant reactor was assumed to be a function of liquid mass velocity. The three phase heterogeneous model was solved to estimate kinetic parameters for various hydrotreating reactions using the data generated in pilot plant experiments.

The model comprises of a set of first order differential equations and nonlinear algebraic equations. Runge-Kutta 4th order integration algorithm was used to solve differential equations. The algebraic equations were solved by using Newton-Raphson technique. Linear regression techniques were used to fit the experimental data with model equations. The programs to solve the model equations were coded in FORTRAN.

The model was applied to simulate the performance of pilot plant trickle bed reactor at varied operating conditions and verified with experimental data. The model simulations were found to agree well with experimental data.
The model was also used to simulate the influence of hydrogen sulfide concentration and operating pressure on product quality. The concentration of hydrogen sulfide in the feed gas and operating pressure were found to have significant influence on product quality.

A non-isothermal heterogeneous model was applied to simulate the performance of industrial reactor using the intrinsic rate constants estimated from pilot plant experiments. Temperature profiles in the industrial diesel hydrodesulfurization unit were generated. The model was validated with the data collected from industrial unit.

The industrial reactor model was applied to simulate the performance of industrial reactor at varied operating conditions. The influence of operating conditions such as reactor temperature and feed rate were studied using the model. The model was found to simulate the performance of industrial reactor adequately.

Finally, the model was also applied to predict the performance of industrial reactor loaded with high activity new generation catalysts. The new generation catalysts were found to have higher activity than the present catalyst.

6.2 APPLICATIONS OF THE MODEL

The three phase model developed in the present work can be used to analyze and simulate the performance of pilot plant and industrial trickle bed reactors employed in hydrodesulfurization of diesel fractions.
The model can be used for following applications.

- **Estimation of Kinetic Parameters** – The model can be used to evaluate intrinsic kinetic parameters of different hydrotreating reactions for a given catalyst and feed system from pilot plant evaluations. The kinetic analysis help in catalyst screening and selection based on pilot plant experiments.

- **Simulation of Pilot Plant Reactor** – The isothermal partial wetting model can be used to simulate the performance of pilot plant reactor at varied operating conditions. Kinetic parameters can estimated from limited experimental data and then the model can be used to simulate over wide range of operating conditions to study their influence on product quality. Model can also be used to simulate conditions that are difficult to maintain experimentally. For example, model can be used to simulate varied concentrations of hydrogen sulfide in feed gas.

- The model can be used to simulate the performance of industrial reactor at varied operating conditions. The influence of operating conditions on product quality can be simulated before commercial trials. The model can be used to fix reactor temperature or feed rate with changing quality of feedstock on day to day basis. Thus the model can be used to optimize the operations of industrial reactor.

- The model can be used to correlate pilot plant data with that of industrial reactor. The performance of new catalysts can be evaluated in pilot plant reactor and then scaled up industrial reactor. Thus the model proves to be an effective tool in catalyst selection.
6.3 SUGGESTIONS FOR FURTHER WORK

- In the present work, the activity of the catalyst is assumed to remain constant with time on stream of the catalyst. Further work can be taken up to develop pilot plant test method to compare catalyst deactivation rates and correlations that account for loss in catalyst activity due to coke formation.

- The model can be extended to incorporate hydrodynamic parameters such as pressure drop, liquid holdup and catalyst wetting efficiency etc.

- The heat transfer resistances across gas-liquid and liquid-solid interfaces can be taken up to model the temperature profiles in all the phases and analyze their effects on reactor performance.