CHAPTER 2

LITERATURE SURVEY

2.1 INTRODUCTION

Trickle bed reactors can be defined as a fixed bed of catalyst particles contacted by cocurrent downward flow of gas and liquid phases under lower superficial velocities. These reactors assume greater importance among the three-phase gas-liquid-solid reaction systems encountered in industrial practice.

In petroleum refineries, trickle bed reactors are widely employed for hydrotreating of petroleum fractions and hydrocracking of vacuum gas oils. These reactors are often preferred because of their simple and stable mode of operation, ease of control and flexibility of application to a wide range of feedstocks.

In view of their industrial importance, extensive research work was reported in the literature concerning various aspects of trickle bed reactors. Literature pertaining to kinetics and modeling of trickle bed reactors sustaining hydrotreating reactions is reviewed in this chapter.

2.2 KINETICS AND MODELING

Frye and Mosby (1967) obtained the kinetic data on hydrodesulfurization of light cycle oil. They applied the rate equation over a wide range of operating conditions and found to correlate with the experimental data satisfactorily.
Mears (1971) investigated the effects of axial dispersion or backmixing in pilot plant trickle bed reactors. It was reported that at low mass velocities, the axial dispersion adversely affects reactor performance particularly in the case of short pilot plant reactors. He proposed an equation for the minimum bed length of the reactor to neglect axial dispersion effects based on perturbation criterion. The minimum length was reported to depend on conversion and reaction order.

Henry and Gilbert (1973) described the derivation of a model for trickle bed catalytic hydroprocessing reactors. A first order kinetic expression was used to represent desulfurization reactions. Data from a series of pilot plant hydrocracking and aromatics hydrogenation reactions were presented and used to test the model. The implications of the reactor model on the effect of scale up from pilot plant to commercial plant scale on catalyst efficiency were discussed.

Shah and Paraskos (1975a) derived a criterion for significant axial dispersion effects in industrial trickle bed reactors. The criterion reported by them can be used to determine whether axial dispersion can be neglected in high conversion trickle bed reactors. It was reported that the axial dispersion was more significant in adiabatic reactors compared to isothermal reactors.

Shah and Paraskos (1975b) studied the kinetics of hydrodesulfurization and demetallation of 50% reduced Kuwait crude in an isothermal bench scale reactor. Based on the estimated effectiveness factors for these reactions, it was concluded that the optimum reactor performance could be obtained by selecting a catalyst size.

Jaffe (1976) studied the occurrence of steady state hot spots in a commercial hydrogenation reactor extensively and developed a mathematical model taking into account the temperature rise with rapid reaction of fluids as well temperature drop accompanied by the eventual mixing with the cold fluid from the surrounding region.
Yan (1980) proposed a mathematical model to study the dynamic behavior of a trickle bed hydrocracker with and without a quench option. He analyzed the effect of various parameters on transient temperature and hydrocarbon profiles in the reactor.

Shah et al. (1976) studied the exothermic reaction systems and discussed proper quench locations. The dynamics of an adiabatic fixed bed petroleum residue hydrodesulfurization reactor employing a single quench was presented. Mhaskar et al. (1978) extended this model to two gaseous quenches and reported that for the same amount of quench, two quenches gave better reactor cycle life than a single quench.

Crine et al. (1980) presented a phenomenological model accounting for the random and discontinuous nature of the packed bed. They verified the model with the data reported by Paraskos and Frayer (1975) and Montagna and Shah (1975). Two atmospheric residues derived from 53% and 36% Kuwait crude were used. The experimental data was correlated using a single wetting parameter that is independent of the temperature of the bed and the nature of the reactions. The parameter was observed to vary only with the fluid properties and size of the catalyst.

Kilanowski and Gates (1980) studied the kinetics of hydrodesulfurization of benzothiophene (BT) in steady state differential flow microreactor containing particle of Co-Mo/Al₂O₃ catalyst at 252-332 °C. Rate equations of Langmuir-Hinshelwood type were compared with the rate data using a non-linear least squares regression technique. It was reported that benzothiophene and hydrogen sulfide adsorb on one kind of surface and hydrogen on other type supporting hydrogen sulfide inhibition effects. Broderick and Gates (1981) investigated the reaction kinetics of hydrogenolysis and hydrogenation of dibenzothiophene catalyzed by sulfided Co-Mo/Al₂O₃ using dibenzothiophene as the model compound. The relative rates of hydrogenolysis and hydrogenation were compared with the rate of disappearance of dibenzothiophene and kinetic equations based on Langmuir-Hinshelwood kinetics were fitted with experimental data.
Gopal et al. (1981) reported kinetic analysis of hydrodesulfurization (HDS) using dibenzothiophene (DBT) as a model compound. Kinetic data were generated over Co-Mo/Al₂O₃ catalyst at a temperature of 285 to 350°C by varying hydrogen partial pressure, liquid hourly space velocity and DBT feed concentration. Different reaction mechanisms were studied with the help of kinetic models. It was reported that under the conditions studied, the hydrogen sulfide inhibited hydrodesulfurization significantly but did not have any effect on selectivity.

Mohammed and Aboul-Gheit (1981) carried out experimental studies on several catalysts and determined activation energies and entropies of hydrodesulfurization reactions for lubricating base stocks.

Mohammed et al. (1985) extensively studied hydrotreating reactions using Bai-Hasan reduced crude as feedstock over commercial Ni-Mo/Alumina catalyst in a trickle bed reactor. The effect of reactor temperature on the reaction rates was studied. It was reported that nickel was removed more easily than vanadium at lower temperatures where as vanadium removal was found to be more easier at higher reactor temperatures.

Scamangas et al. (1982) reported hydrodesulfurization of atmospheric residues obtained from the Aegean Sea. They showed that residues having high sulfur content follow overall second-order kinetics with respect to sulfur and first order with respect to hydrogen. Takeuchl et al. (1983) studied the asphaltenic bottom cracking process for hydrotreating of heavy residual oils.

Iannibello et al. (1983) measured total liquid holdup and intraparticle apparent diffusivity in a pilot plant trickle bed reactor using a tracer technique. They tested different liquids and catalyst particles and showed that the pore filling of the catalyst
might be considered total even at very low liquid flow rates and relatively high temperatures. The partial catalyst utilization was assumed to be more due to intraparticle diffusivity than partial pore filling.

Mohammed et al. (1988) evaluated the kinetics of hydrodesulfurization of deasphalted oil using second-order rate equation and also using a model comprising two parallel first order reactions. Abbas et al. (1990) carried out hydrotreating experiments using Ni-Mo catalysts in a laboratory trickle bed reactor. They showed that the hydrotreating reactions followed a first order kinetics.

Chu and Wang (1982) studied the kinetics of HDS, HDN and hydrogenation of polynuclear aromatics on a series of model compounds and an actual fuel. Sambi et al. (1982) studied the hydrotreatment of heavy gas oils over a cobalt-molybdenum catalyst in a trickle bed reactor. They also investigated the effect of temperature, pressure and liquid flow rates on the product quality. They obtained lower C/H ratios for products for higher pressures and observed improvements in the Cetane number and diesel index of products with increased temperatures.

Hook (1984) analyzed the above non-isothermal reactor by imposing an empirically fitted temperature profile on the system. Hook and Akgerman (1985) presented a technique to extract the intrinsic kinetics from trickle bed reactor data.

It was reported that in residue catalytic cracking, in the very early stages of cracking had an enormous effect on the behavior of the whole system and the overall coke yield in the residue catalytic cracking is the product of a multiple-time scale process. Ahn and Smith (1984) developed a mathematical model to account for the partial poisoning of the interior pore surface and pre-mouth plugging due to deposition of metals contained in the reactor feed. With the help of this model they predicted the temperature vs. time relationship and discussed this in conjunction with the constant desulfurization activity.
Papayannakos and Marangozis (1984) investigated the kinetics of atmospheric residues in batch recycled reactor using commercial catalyst samples. It was reported that desulfurization rate of polar aromatics was affected by reactor temperature. However, the desulfurization rate of asphaltenic and non asphaltenic aromatics was found to increase with temperature.

Sanford and Yui (1984) carried out pilot scale hydrotreating experiments using three synthetic distillates and three commercial catalysts. They studied the kinetics of HDS, HDN and aromatics hydrogenation and compared the catalyst activities. They also developed a correlation to predict the yield and product properties based on operating conditions. Yui and Sanford (1989) hydrotreated the bitumen derived coker and hydrocracker gas oils in a trickle bed reactor over presulfided commercial Ni-Mo/Al₂O₃ catalysts. They incorporated the power terms for LHSV and hydrogen partial pressures in the kinetic analysis. They also correlated the total liquid product volume yields in the power form of temperature, pressure and LHSV. Yui and Sanford (1991) conducted hydrotreating of five bitumen derived gas oils using pilot scale trickle bed reactor with commercial Ni-Mo/Al₂O₃ catalyst. They developed a power law kinetic model for aromatic hydrogenation assuming a first order reversible reactions. Using this model, they studied the effect of reactor temperature, pressure and LHSV on the hydrogenation levels.

Sutikno and Walas (1984) used the models derived for petroleum oils to test their validity for shale oils. Simulations were made for hydrotreating, hydrocracking and catalytic cracking processes of Paraho shale oils.

Wilson and Kriz (1984) conducted hydrotreating experiments on a middle distillate fraction obtained from a synthetic crude oil of Athabasca bitumen using three different commercial catalysts. The model for hydrogenation kinetics and correlations between aromatic carbon and fuel combustion properties were also reported.
Collins et al. (1985) presented a simple model for an isothermal reactor by assuming the liquid phase in plug flow. The gas and liquid phases are also assumed to be in equilibrium at all the points in the reactor. Akgerman et al. (1985) extended this model incorporating the effect of feed volatility on conversion. Ruecker et al. (1986) included the effect of partial wetting in this simplified model. The effect of different equations of state on predicting performance of the reactor as well as parameter estimation studies were carried out by Akgerman and Netherland (1986).

Iannibello et al. (1985) examined the removal of sulfur and metals from heavy residual oil by hydrotreating in a pilot trickle bed reactor. Catalysts with different active components on two different supports were tested. The results were interpreted via several models that took into account the physical and chemical complexity of the three-phase system. A first order kinetics was found to be valid for bauxite based catalyst with wide pore distribution when the hydrodynamic effects in the reactor had been suitably accounted for by either external liquid holdup or apparent intraparticle diffusivity.

Wilson et al. (1985) used a presulfided Ni-W/γ-Al₂O₃ catalyst to hydrogenate aromatic compounds contained in middle distillate fractions of Alberta synthetic crudes, in a continuous high pressure reactor system. The authors applied low resolution mass spectrometry for the analysis of compound types within the reactant and product hydrocarbon mixtures.

Shmura et al. (1986) measured the diffusivities of standard polystyrenes and asphaltenes in several hydrotreating catalysts having various pore sizes. They used solid-liquid chromatography techniques and investigated the influence of the ratio of diffusing molecular diameter to the pore diameter on effective diffusion coefficient. Kocics and Ho (1986) developed a model to quantify the effects of liquid evaporation-condensation in a trickle bed reactor for dibenzothiophene hydrosulfurization
reaction. They concluded that neglect of evaporation effects can give misleading results on reaction kinetics.

Chao and Chang (1987) simulated an adiabatic hydrodesulfurization reactor undergoing deactivation using one dimensional pseudo homogeneous model. The model incorporates the effects of axial dispersions of both heat and mass transfer. They used the orthogonal collocation method for solving the model equations. They also examined the performance of the reactor during the start up period as well as for longer times of operation. The dynamic behavior of the reactor was studied by giving step changes in feed composition, feed rate and inlet temperature.

Mann et al. (1987) reported the hydrotreatment of heavy gas oils derived from Athabasca bitumen in a trickle bed reactor over Ni-Mo, Ni-W and Co-Mo catalysts. They measured the cetane index, aniline point, diesel index and C/H ratio of products and also compared the activity of catalysts for HDS, HDN reactions. They found that Ni-Mo on alumina is the best for HDN. They analyzed the data using pseudo first-order reaction model.

Lindfors (1988) developed a simulation program to calculate the demetallation and desulfurization conversions of heavy oils in catalytic reactors. The program includes relation between hydrodemetallation and hydrodesulfurization conversion and their dependence on the reaction conditions. Dohler and Rupp (1987) performed the laboratory scale experiments with the same feedstock and catalyst as those being used in an industrial unit. They also obtained the data from a commercial vacuum gas oil hydrotreater. They predicted the adiabatic behavior of the large unit from the simple one dimensional pseudo homogenous model which is based on their laboratory experiments. The model facilitates the determination of the catalyst bed configuration, inlet temperature of feedstock, required quantity of quenching gas and product qualities.
Mann et al. (1988) used Ni-Mo catalyst supported on Zeolite-Alumina-Silica matrix for hydrotreatment of Athabasca bitumen derived heavy gas oils and compared the activity of this catalyst with a Ni-Mo on $\gamma$-Al$_2$O$_3$ catalyst. They used power law model in evaluating kinetic parameters.

Philippoulos and Papayannakos (1988) reported kinetic data for asphaltene cracking and desulfurization of asphaltene and non-asphaltene fractions of Greek atmospheric residues. They used an integral trickle bed reactor and determined the effective diffusivities of the molecules present in residue on different pore structures. Papayannakos and Georgiou (1988) presented a kinetic model for hydrogen consumption rate describing the intrinsic reactions with second-order kinetic equations. They concluded that decrease in desulfurization temperature or catalyst particle size resulted in an increase in the hydrogen consumption.

Skala et al. (1988) performed hydrotreating experiments using a test mixture of quinoline, indole and lauronitrile dissolved in decalin to find out the performance for different types of catalyst loadings (composition of Co-Mo, Ni-Mo, and pure Ni-Mo) in a pilot plant trickle bed reactor. They experimentally measured the hydrogen consumption and found that it is 25% more than that of theoretically calculated one. Tsamatsoulis et al. (1991) observed an improvement in the basic characteristics of heavy residue due to catalytic hydrotreatment. They presented useful correlations concerning hydrodesulfurization (HDS), hydrocracking (HC), asphaltene fraction desulfurization (AFD), non-asphaltene fraction desulfurization (NAFD) and hydrogen consumption (HCON). Nam and Kittrell (1984) derived an empirical model to relate catalyst activity to that catalyst content based on the formation of mono layer and multi layer coke. This model contains ratios of rate constants which can accommodate all the observed temperature dependencies. Finally, they concluded that the model provides the proper functional form to describe typical coke-time data.
Yitzhaki and Aharoni (1988) fractionated the feed and products into narrow boiling ranges. They estimated the desulfurization kinetics for each boiling fraction assuming that no sulfur compounds migrated between fractions. Their results indicate the decrease in HDS reaction rates with increase in average boiling point of fractions.

Trytten et al. (1990) fractionated the Athabasca bitumen into six narrow boiling cuts of nominal 50°C width and catalytically hydروprocessed in CSTR comprising a commercial Ni-Mo catalyst. They observed decrease in rates of reactions (for HDS, HDN and aromatic conversion) with increase in average molecular weight of the feed samples. Gray (1990) studied the lumped reaction kinetics based on structured groups using the data from catalytic and thermal cracking of coker gas oil. They described the feed and product compositions in terms of aliphatic and aromatic carbon groups. They identified the groups that follow pseudo first-order kinetics. They related the reactions of carbon groups (stoichiometrically) to the removal of heteroatoms. They concluded that these stoichiometric ratios can be used to construct the models for hydروprocessing reactions.

Chao et al. (1990) used parameter estimation and identification procedures to develop a ‘grey’ model for an adiabatic deactivating hydrodesulfurization trickle bed reactor. With the help of the grey model they precomputed a set point table, from which an optimal set point for the residue desulfurization reactor unit can be chosen. They selected the inlet feed temperature as the variable and the predetermined outlet sulfur content as the set point criterion. They suggested that the algorithm is applicable for determining the optimal set points for a commercial process. In view of the complex hydrodynamics of the reactor and large scale industrial size units, a suitable mathematical model is necessary for predicting the commercial operation, based on the results derived from bench scale or pilot plant experiments. In order to find out the reason for the rapid deactivation of the catalyst used in the Institut Francais du Petrole (IFP) process of Beograd Refinery, Skala et al (1991) performed the hydروtreatment of the used oil in a pilot plant trickle bed reactor. They presented the results of
hydrogenation kinetics of used oil and developed a mathematical model. Thereby they could determine the sulfur, metal and carbonyl compound conversions for an industrial operation. They used the correlation of Shah et al. (1976) for relating the catalyst activity with the deposits on the catalyst surface. They were able to predict the pressure drop through the catalyst bed using the equation of Charpentier and Favier (1975).

Funk et al. (1990) examined the effects of liquid maldistribution on reaction in a trickle bed reactor. A novel discreet flow distribution model was developed based on a computer-generated, two-dimensional bed packed with equal-sized spherical catalyst pellets. The model was reported to offer advantages over other computational models in terms of overall reaction rate predictions, the ability in the description of irregular morphological features, the absence of the artificial backmixing of materials and others.

Anabtawi and Ali (1991) conducted hydrotreating experiments to evaluate the efficiency of three commercial catalysts using light cycle oil as the feed stock. They observed improvements in the product quality with increase in temperature and pressure and with decrease in space velocities.

Tsai et al. (1991) carried out hydrodesulfurization and hydrometallation of heavy Kuwait atmospheric residues over Co-Mo catalyst supported on Aluminium Borates in a bench scale trickle bed reactor. They showed that Co-Mo/Aluminium Borates are much more active than the conventional Co-Mo/Al₂O₃ catalysts and also formulated a relationship between HDS activity and reducibility of oxidic precursor. They commented that larger surface area and high reducibility of active metal could produce more active sites and result in high HDS activity.
Deep hydrodesulfurization of polyaromatic sulfur-containing compounds in light oil using Co-Mo/Al₂O₃ was reported by Toshiaki et al. (1992). It was reported that alkyl substituted dibenzothiophene among sulfur-containing compounds in light oil were the most difficult to desulfurise. Dialkyl substituted dibenzothiophenes, especially 4,6-dimethyl dibenzothiophene, remained until the final stage of the reactants (390°C) while alkylbenzothiophenes were completely desulfurised at 350°C.

Dente et al. (1992) presented the criterion for the development of complex and irregular kinetic schemes. Chiang and Tiou (1992) used a diffusion model for optimal design of residual oil hydrodematallation in a fixed bed reactor. They also determined the required catalyst pore sizes and their corresponding configuration in the bed based on the total time of activity. They also investigated the influence of Thiele modules on the design of reactor. Hanson and Cooper (1992) presented a model to predict the elemental molar composition, the temperature and the true boiling curve for the resulting product stream. This model requires an input data of hydrogen consumption, gas production in the reactor and the composition of the sulfur and nitrogen in the resulting product.

Shih et al. (1992) studied the hydrodesulfurization of eight individual feedstocks. They developed a correlation relating the temperature requirement for the desulfurization to 0.05 wt.% concentration of 316 °C sulfur and total nitrogen content in the feed. Kabe et al. (1992) carried out the deep hydrodesulfurization of polyaromatics sulfur containing compounds in light oil using Co-Mo/Al₂O₃ catalyst. They found that among sulfur containing compounds, alkyl substituents dibenzothiophenes are difficult to desulfurize. Ishihara and kabe (1993) investigated the effects of solvent in HDS under deep hydrodesulfurization conditions. They reported the inhibiting effects of solvents such as xylene, decalin, tetralin and n-hexadecane on the catalyst activity and the product selectivity in deep HDS of dibenzothiophene catalyzed by Co-Mo/Al₂O₃. They suggested that desulfurization and hydrogenation proceed on different catalytic sites.
Diaz-Real et al. (1993) conducted the hydrotreating experiments using Ni-Mo and in addition, Ni-W and Co-Mo catalysts supported by on Zeolite-Alumina-Silica and found that zeolite supported catalysts more active than that of commercial catalysts. They evaluated kinetic parameters using pseudo first-order reaction model.

Gorra et al (1993) presented the modifications made in an Italian refinery to desulfurize its coker gas oil following reduction in catalytic activity. De Jong (1993) presented a mathematical model to predict the amount of coke deposited on the catalyst during heavy oil conversion in trickle bed reactor. Their model comprises of cracking reactions, coke formation kinetics and vapour-liquid equilibria of the reaction mixture.

Li et al. (1993) prepared a series of Alumina-Alumina Borate (AAB) catalysts using precipitation techniques and carried out hydrodesulfurization of Kuwait atmospheric gas oils in a bench scale trickle bed reactor. They reported that Co-Mo/AAB catalysts are more active than conventional CoO-MoO/Al₂O₃ catalysts also developed a correlation between acidity and hydrodesulfurization activity of the catalysts. They used the pseudo second-order rate equation in representing the kinetics of hydrodesulfurization activity.

Mc Manus et al. (1993) carried out experiments to study the effect of liquid maldistribution on trickle bed reactor performance and tested isothermal trickle bed reactor model proposed by Funk et al. (1990). The experimental study involved measuring the overall reaction rate in packed bed reactor for different inlet configurations over a range of liquid flow rates. The experimental data confirmed the validity of the qualitative predictions of the sphere-pack model proposed by Funk et al. (1990).
Froment et al. (1994) presented an adiabatic multiphase reactor model for diesel hydrodesulfurization using benzothiophene, dibenzothiophene and 4,6 dimethyl dibenzothiophene as model compounds. A structured contribution approach was recommended to reduce the number of parameters to be determined. Inter particle mass transfer, reaction and intraparticle diffusion were considered.

Kwak et al. (1994) analyzed the hydrodesulfurization, hydrodenitrogenation and residue conversion data for the white rocks bitumen and bitumen derived liquid using a modified power rate law model. A power term is included for space velocity to account for deviations from plug flow behaviour. They found that the order of reactions for HDS, HDN ranges from 1 to 2. They also applied a parallel first-order reaction scheme to represent the HDS, HDN reactions.

Ma et al. (1994a) examined the HDS reactivities of various sulfur compounds in the diesel fuel. They used both Co-Mo and Ni-Mo catalysts in one or two stage reactor system. They classified the sulfur compounds present in the diesel fuel into four groups: (i) alkyl benzothiophene (ii) dibenzothiophenes and alkyl dibenzothiophenes without substituents at 4- and 6- positions (iii) alkyl dibenzothiophenes with only of substituents at either the 4- or 6- position (iv) alkyl dibenzothiophenes with two of the alkyl substituents at 4- and 6- positions.

Ma et al. (1994b) investigated the performance of a three stage deep HDS system using a combination Co-Mo and Ni-Mo catalysts at pressures of 2.9 MPa. The Co-Mo catalyst is used in the first stage and the Ni-Mo catalyst used in the second and third stages. The first two stages are carried out at a temperature of 360 °C. Results indicate that first stage effectively removed the benzenothiophenes and the second stage desulfurized most of the dibenzothiophenes including alkyl-substituted derivatives.
Ma et al. (1995) investigated the kinetics of hydrodesulfurization by fractionating gas oil into five fractions at intervals of 20 °C. Each fraction was desulfurized over Ni-Mo and Co-Mo catalysts in an autoclave at 360 °C under a total pressure of 2.9 MPa. The reactivities of the fractions were found to change with their boiling point. The composition analyses of fractions indicated that alkylbenzothiophenes, polyaromatic hydrocarbons and nitrogen compounds in the heavier fractions restricted their reactivities.

Qabazard et al. (1995) compared the performance of a conventional Co-Mo catalyst with high metal loading Co-Mo and Ni-Mo catalysts in deep hydrodesulfurization of Kuwait atmospheric gas oil. They observed that the high molybdenum Co-Mo catalyst is superior to that of conventional Co-Mo catalyst and Ni-Mo catalyst containing a similar high metal loading. They explained the results on the basis of the stacking dispersion of MoS₃ slabs in the catalyst systems.

Korsten and Hoffman (1996) developed and presented a three phase reactor model for hydrotreating in pilot plant trickle bed reactor. The model was based on two-film theory and accounted for hydrogen sulfide inhibiting effect and included correlations required for estimating transport properties. A Langmuir-Hinshelwood kinetic expression was used to represent hydrodesulfurization reactions. The model predictions were validated with experimental data. Lower conversions obtained in pilot plant reactors were attributed to incomplete catalyst wetting produced by low liquid velocities.

Ma et al. (1996) performed the hydrodesulfurization of vacuum gas oil over a commercial Ni-Mo catalyst. They examined the HDS reactivities of sulfur compounds by means of pseudo first-order kinetic approach. Four representative types of aromatic-skeleton sulfur compounds are observed. The authors also presented quantum chemical calculations of representative sulfur compounds and compared the molecular parameters with their different HDS reactivities.
Yuanxin Wu et al. (1996) evaluated trickle bed reactor models for liquid limited reactions. The model suggested by Dudukovik (1977) was evaluated with experimental data. They concluded that both external mass transfer effects and incomplete catalyst wetting need to be considered in improving the model predictions.

Rajasekaram et al. (1998) presented a trickle-bed reactor model for hydrogenation of 2,4 dinitrotoluene and verified with experimental data. The model incorporated the contributions of partial wetting and stagnant liquid holdup effects in addition to external and intraparticle mass transfer resistances for a complex consecutive/parallel reaction scheme under consideration represented by L-H type kinetics. The model also accounted for heat effects since the reactions were exothermic. The model predictions were compared with experimental data and were found to agree well over a wide range of operating conditions.

Ramesh Kumar et al. (2001) discussed axial dispersion and channeling effects in trickle bed reactors and dealt with the problems faced in correlating pilot plant data with that of industrial reactors. They studied the performance of certain commercial catalysts employed in hydrodesulfurization of a diesel oil using a non-linear power law kinetics. The relative volume activity of the catalyst was calculated from the ratio of observed rates of reactions. The axial dispersion and channeling effects were assumed to be negligible based on the criterion suggested by Mears (1971) and radial aspect ratio of the internal diameters of the reactor and catalyst particle.

Bhaskar and Balaraman (2001) applied three phase heterogeneous model suggested by Korsten and Hoffman (1996) to simulate the performance of a pilot plant trickle bed reactor sustaining hydrodesulfurization reactions. Bhaskar et al. (2002) solved three phase heterogeneous model and simulated the performance of pilot plant reactor at varied operating conditions. They produced profiles of concentrations and partial pressures along catalyst bed length. The simulation results were found to agree well with the experimental results.
Chowdhury et al. (2002) 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. The kinetic equations for desulfurization and for the hydrogenation of mono-, di- and polyaromatics were established. Simulated results were found to agree well with the experimental observations.

2.3 CONCLUSIONS

Literature pertaining to kinetics, modeling and simulation of trickle bed employed in hydrotreating of petroleum fractions has been summarized in this chapter. Considerable research work was reported on kinetic modeling of hydrotreating reactions. The trickle bed reactors were modeled as pseudo homogeneous isothermal plug flow reactors using power law kinetics. Reactions such as hydrodesulfurization and hydrocracking were modeled. Though most of these models were successfully applied to simulate the performance of pilot plant reactors, limited efforts were made to scale up to industrial scale. It has been felt that it is necessary to develop a rigorous heterogeneous model to describe the reactor performance with respect to major reactions and validate with the data collected from industrial reactor.