CHAPTER 2

LITERATURE SURVEY

2.1 INTRODUCTION

Though hydrocracking process has greater industrial importance, very little research work was reported in the literature concerning various aspects of hydrocracking process. Most of the literature pertaining to hydrocracking process is based on experiments using pure hydrocarbons. Very limited literature is available with respect to hydrocracking of industrial feedstocks over new generation industrial hydrocracking catalyst system. In this chapter, literature information pertaining to experimental work, kinetics and modeling of hydrocracking reactions is reviewed. The literature pertaining to the applications of hydrocracking process especially with respect to its integration with FCCU and lube base oil manufacturing facility is also reviewed.

2.2 HYDROCRACKING PROCESS
2.2.1 Experimental Work

Hydrocracking of pure hydrocarbon components had been studied by many researchers to investigate the chemistry, reaction mechanism and product yield distribution during hydrocracking. Archibald et al (1960) reported studies on the catalytic hydrocracking of normal paraffins and olefins ranging from C₄ to C₁₆ as well as that of a few branched isomers. They
compared fluid catalytic cracking and hydrocracking processes with respect to reaction mechanisms and selectivity of products.

Coonradt and Garwood (1964) studied hydrocracking of higher molecular paraffinic hydrocarbons on highly active platinum on an amorphous Al₂O₃-SiO₂ catalyst and pointed out the possibility of pure primary cracking and the high degree of isomerisation of the uncracked feed during hydrocracking. Sullivan et al. (1964) used experimental yield distribution data of several model compounds for analyzing the chemistry of hydrocracking.

Langlois and Sullivan (1969) discussed the chemistry of catalytic hydrocracking of hydrocarbons with examples of the hydrocracking of typical pure compounds to illustrate the type of reactions and the principle products during hydrocracking. They also presented reaction mechanisms to account for the observed product distribution in hydrocracking process.

Qader and Hill (1969) extensively reported the results of hydrocracking experiments conducted in a conventional fixed-bed tubular flow reactor over a dual functional hydrocracking catalyst using a gas oil fraction boiling in the range of 300 to 430°C. They reported yield distribution results for single-pass, double-pass and recycle operation at specific operating conditions. They proposed a reaction mechanism involving a combination of simultaneous and consecutive bond breaking reactions followed by isomerisation and hydrogenation of products for hydrocracking of gas oil fraction. They expressed the kinetics of hydrocracking, hydrodesulphurization (HDS) and hydrodenitrogenation (HDN) using simple first-order rate equations and evaluated the rate constants.
Qader and Hill (1969) presented the results of hydrocracking experiments conducted in a tubular reactor using three petroleum fractions and two coal-based oil fractions and compared the behavior of the petroleum and coal-based oils under hydrocracking conditions. They also expressed the kinetics of hydrocracking of gas oil and coal oil fractions using a simple first order rate equation and reported the kinetic constants.

Bennett and Bourne (1972) presented an experimental study of process reactions and corresponding product yields and qualities during hydrocracking of different vacuum gas oil samples for middle distillate production. They conducted pilot plant hydrocracking experiments with four adiabatic reactors in series to get an understanding of the course of hydrocracking reaction and its relation to product yields, compositions and properties build up.

Schulz and Weitkamp (1972) investigated hydrocracking and hydroisomerization of n-Dodecane over three different catalysts based on platinum or palladium on zeolite catalyst. They presented detailed analysis of cracked and isomerized products during hydrocracking of n-Dodecane.

Tom et al (1972) reviewed hydrocracking process with discussions on the production of distillates and those aspects of the hydrocracking chemistry and process considerations that are particularly relevant to making distillates.

Choudhary and Saraf (1975) reviewed the hydrocracking process with special emphasis to hydrocracking catalysts, reactions and reaction mechanism and various commercial hydrocracking processes. Choudhary and Saraf (1978) investigated the hydrocracking of Assam crude residue in a rocking type batch reactor using LaX and NiX catalysts. They studied the
effect of process variables including temperature, hydrogen pressure, charge to catalyst ratio, reaction time, the degree of exchange and the nature of the cation in the catalyst on the conversion of residuum and the distribution of the products.

El-Kady (1979) reported detailed results of hydrocracking of a vacuum distillate fraction in a continuous fixed bed bench scale tubular flow reactor system over a bifunctional Molybdenum-Nickel/Silica-Alumina catalyst. He discussed in detail conversion, product yields and product qualities at different operating temperatures and liquid hourly space velocity. He also presented a reaction mechanism for hydrocracking, hydrodesulphurization and hydrogenation occurring during hydrocracking process similar to the one proposed by Qader and Hill (1969). He also described the overall kinetics of hydrocracking, hydrodesulphurization and hydrogenation reactions considering first order reactions and reported the kinetic parameters for these reactions.

Steijns et al (1981) investigated the hydroisomerization and hydrocracking of n-decane and n-dodecane on an ultrastable zeolite Y, containing 0.5 wt% platinum at temperature of 130-250°C and pressure of 5-100 bar. Steijns and Froment (1981) reported the kinetic analysis of hydroisomerization and hydrocracking data for n-Decane and n-Dodecane. Weitkamp (1982) studied the isomerisation of pure n-alkanes with 6 to 15 carbon atoms on a Pt/CaY zeolite catalyst in the presence of hydrogen. Haizmann et al (1983) presented some aspects on the hydrocracking of relatively heavy feeds to produce high yields of distillate products.

Giannetto et al (1986) studied the transformation of n-heptane at 250°C, 1 atm, and \( p_{\text{H}_2}/p_{\text{heptane}} \) ratio of 9 on a series of Pt-HY catalysts containing from 0.1 to 1.5 wt% platinum and having Si/Al atomic ratios of 3,
9 or 35. They observed that the number of their acid sites and hydrogenating sites governed the activities, stabilities and selectivities of the catalysts. They found that Pt-HY catalysts were ideal hydroisomerization catalysts with less amount of cracking activity up to 50% conversion.

Vazquez et al (1986) conducted hydrocracking experiments of n-heptane in the temperature range 573 to 623 K and at 2.45x 10^6 Pa pressure using NiO-MoO₃ catalyst supported on a HY ultrastable zeolite. They studied two groups of catalysts containing 8 and 12 wt% of MoO₃ and different amounts of NiO. In both series they obtained a maximum in the activity for catalysts with a Ni/Mo atomic ratio of 0.8-1.0. Vazquez et al (1987) studied the hydroisomerization and hydrocracking of n-heptane on a series of Ni-Mo/HY ultra stable zeolite catalysts at 300 - 350°C reaction temperature and 25 kg/cm² total pressure. They discussed the product distribution in the isomerized and the cracked fractions from the point of view of a typical bifunctional mechanism. They found that the Ni/(Ni+Mo) atomic ratio of the catalyst has a strong influence on the activity.

Esener and Maxwell (1989) showed that a stacked bed hydrocracker reactor configuration composed of conventional hydrotreating and zeolite-based catalysts offered marked improvements in performance compared to single bed systems. They also observed significant gains in overall hydrocracking activity together with good catalyst stability for zeolite catalysts. They described the overall hydrocracking and hydrodenitrogenation kinetics using Langmuir-Hinshelwood type kinetics.

Ward (1989) reviewed initial developments of modern hydrocracking process leading to high performance zeolite catalysts. He discussed various process configurations and applications of hydrocracking process.
Korre et al (1997) studied the hydrocracking of model polynuclear aromatic hydrocarbons such as naphthalene and phenanthrene over a presulfided NiW/USY zeolite catalyst in a batch autoclave reactor at a hydrogen partial pressure of 68.1 atm and temperature of 350°C in a cyclohexane solvent. The relationship between molecular structure and reactivity during hydrocracking of model polynuclear aromatic hydrocarbons was examined through detailed kinetic studies based on Langmuir-Hinshelwood-Hougen-Watson type rate equations including product inhibition effects.

Law (2000/01) reviewed process and catalyst characteristics in hydrocracking with emphasis on reaction chemistry, flow schemes, products, reactor internals, utilities, latest innovations etc.

Mindherhoud et al (2001) summarized some of the latest technology and catalyst developments in hydrocracking process. Ali et al (2002) developed five different catalyst formulations for hydrocracking of heavy oils using amorphous silica-alumina (ASA) supports in combination with USY and β-zeolites. They tested the catalyst systems in a fixed-bed flow reaction system for their activity, using desulphurized vacuum gas oil as feedstock. From the catalyst evaluation studies, they showed that β-zeolite alone in combination with the ASA had a potential as a support for developing heavy oil hydrocracking catalysts. Meijburg (2002) presented the importance of the activity of various hydrocracking pretreat catalysts and hydrocracking catalysts for the production of ultra low sulfur diesel product with emphasis to Akzo Nobel hydrocracking catalyst portfolio.

### 2.2.2 Kinetics, Modeling and Simulation of Hydrocracking Process

Researchers investigated the hydrocracking process with different modeling and simulation approaches. Some researchers viewed hydrocracking
chemistry of petroleum fractions with respect to the hydrocracking of a set of model compounds or pseudo compounds. Various experimental yield distribution data on hydrocracking of several model compounds have been generated to be used as guiding factors for analysing the chemistry of hydrocracking (Sullivan et al 1964). Based on the product distribution patterns generated, discrete lumping approach was developed initially to describe the hydrocracking chemistry and kinetics. Later several approaches like sophisticated model compounds and structure-oriented lumping and continuous lumping have been developed over the past few decades.

Stangeland and Kittrell (1972) and Zhorov et al (1971) had developed different hydrocracker models based on discrete lumping approach. All of these researchers developed models based on some form of lumping of the compound types present in the feedstock and products (e.g. lumps of LPG, naphtha, jet fuel, diesel etc) and devised various series and parallel reactions for their hydrocracking reaction scheme. In all the discrete lumping models, the various individual reactions involved had been lumped and viewed as an overall hydrocracking reaction, which results in the distribution of a particular lump of a heavier petroleum fraction into lighter lumps. The accuracy of discrete lumping models lie in the number of kinetic lumps chosen to analyse the reactions.

Zhorov et al (1971) developed a mathematical description of hydrocracking based on two-stage and three-stage chemical reaction scheme. Their system is based on constancy of the mass coefficients for a feedstock of constant quality. They developed their hydrocracking reaction scheme for single-stage hydrocracking of vacuum distillates. They had given detailed mathematical procedure for the estimation of reaction mass coefficients.
Stangeland (1972) and Stangeland (1974) suggested a better and simpler approach for modeling hydrocracking kinetics, which used analogy of cracking with comminution of particles to develop a correlative method for predicting the entire TBP curve of the product for a specified set of operating conditions. Stangeland and Kittrell (1972) studied the jet fuel selectivity in single-stage, extinction recycle hydrocracking of a raw gas oil over supported metal catalyst using a series reaction model.

Koseoglu and Phillips (1988) investigated hydrocracking of Athabasca bitumen in a batch reactor at 620 - 693 K and a hydrogen pressure of 7.2 MPa. They considered a discrete lumped model to describe the hydrocracking reactions. The reactions were assumed to be first order with respect to hydrocarbons and zero order with respect to hydrogen. The kinetic parameters were estimated by considering a minimum number of reactions in the kinetic model.

Krishna and Saxena (1989) suggested a different approach, one that considers hydrocracking analogous to axial dispersion. This is a simplistic model with minimum number of parameters. Mohanty et al (1990) reviewed the hydrocracking process, chemistry, catalysts, kinetics, reactor modeling etc in detail.

Browarzik and Kehlen (1994) formulated a continuous distribution function for the hydrocracking of pure n-alkanes. In this formation, called continuous kinetics, the evolution of the distribution function is described by a continuous partial integro-differential rate equation. Lakshminarasimhan et al (1996) developed a mathematical model to represent hydrocracking process based on continuous lumping approach. They used TBP of the reaction mixture as characterization parameter and reformulated the mass-balance equations in terms of rate constant as a continuous variable.
They used a novel distribution function to determine the fractional yield distribution of species and formulated integrodifferential equations to obtain yields of various fractions as a function of reactor residence time. Model based on continuous lumping requires complex mathematical procedures to solve the resulting integrodifferential equations.

Ayasse et al (1997) investigated hydrocracking of Athabasca bitumen in a continuous flow mixed reactor over a Ni-Mo/γ-alumina catalyst at 430°C and 13.7 MPa. They considered a lumped kinetic model based on a concept of stoichiometric coefficients to represent product selectivities during hydrocracking.

Callejas and Martinez (1999) studied kinetics and product yield distributions for hydrocracking of a Maya residue in a perfectly mixed reactor using a commercial hydrotreating catalyst at various operating conditions. They used a lumping methodology to study the first order kinetics of hydrocracking of residue fraction.

Martens et al (2000) developed a fundamental model for hydrocracking of pure alkanes with carbon number varying from 8 to 12 incorporating carbenium ion chemistry in their kinetic model.

Alhumaizi et al (2001) formulated two kinetic models for hydrocracking of n-heptane on a Ni-Re/ZSM-5 catalyst over a wide range of operating conditions. They considered a reaction mechanism based on Langmuir adsorption isotherm and used a one dimensional pseudo homogeneous model to estimate kinetic parameters.

Martens and Marin (2001) proposed a kinetic model for hydrocracking of VGO based on carbenium ion chemistry. A one-dimensional
heterogeneous model was used to simulate a multiphase adiabatic industrial hydrocracker. They considered the effect of gas-liquid mass transfer in their reactor simulation.

Reinhardt et al (2002) considered a one-dimensional homogenous model for an ideal isothermal plug flow reactor to model the hydrocracking process. They used pseudocomponents based on true boiling point (TBP) of petroleum fractions and the kinetic parameters were estimated for each pseudocomponent.

Balasubramanian et al (2003) used a discrete lumping approach to model the evolution of weight fraction distribution with time using carbon number and true boiling point as characterization factor. They evaluated the kinetic parameters for hydrocracking using a combination of genetic algorithm and sequential quadratic programming.

2.3 INTEGRATION WITH FCC UNIT

Many researchers investigated the mild hydrocracking of heavy distillates for obtaining possible yields of middle distillates and reported their findings in the literature. In the study of Sonneman et al (1984) the overall conversion was ~36% at an operating pressures of below 7 MPa; the middle distillate formed was about 26 vol% of the feed, heavy naphtha 2.3 vol% and lighter products 2 wt%.

Desai et al (1985) performed several pilot plant tests to demonstrate the effect of mild hydrocracking of FCC feedstock on the distillate yields, FCC conversions and product yields etc. Their studies indicated higher selectivity of MHC process for middle distillates production. They tested the MHC unconverted bottoms in a Micro Activity Test (MAT) unit and riser
pilot plant. Their results showed increased conversion and selectivity to gasoline in FCC unit compared to the original untreated vacuum gas oil.

UOP has developed a staged approach to the production of middle distillates from installing a lower cost mild hydrocracker. The mild hydrocracking unit can later be upgraded to full conversion hydrocracking unit. UOP converts the existing VGO hydrotreating units into mild hydrocracking units just by changing the catalyst system in the unit (Basta 1986).

Van Kessel et al (1987) showed the operating flexibility when MHC and FCC units were tailored in a synergic manner. They showed that by increasing the conversion level in MHC, the total gasoline production could be reduced, while the middle distillate production increased.

Gosselink et al (1989) investigated in detail the performance of dedicated multiple catalyst systems with zeolite based bottom cracking catalysts under a wide variety of MHC conditions, simulated in laboratory-scale reactors. They compared the performance differences of these multibed systems based on zeolite as compared with single bed catalysts based on alumina. Their studies showed that multiple bed catalyst systems, consisting of alumina based hydrocracking catalysts on top of zeolite based mild hydrocracking catalysts, exhibit much higher apparent activation energies and much lower apparent reaction orders than single bed alumina based catalysts.

Esener and Maxwell (1989) concluded from their studies on mild hydrocracking that a stacked bed hydrocracker reactor configuration composed of conventional hydrotreating and zeolite based catalysts was shown to offer marked improvements in hydrocracker activity and catalyst
stability compared to single bed systems. Pappal et al (1997) suggested carrying out the high heat release desulphurisation and denitrogenation reactions in the beds that contain only hydrotreating catalyst. The dual catalyst mild hydrocracking provides greater flexibility towards different types of feedstocks and different product requirements (Q Chen Paul et al 1999).

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 at 350-400°C, 7-11 MPa, 0.7-1.5 h⁻¹ LHSV and 600 m³/m³ of H₂/oil ratio. They obtained a conversion of 16-22% under these operating conditions. They described the kinetics of mild hydrocracking reactions based on three pseudo components and three cracking schemes. The degree of conversion was analysed with modified first order kinetics, which incorporates power terms for liquid hourly space velocity and hydrogen partial pressure. Ray Chaudhuri et al (1994) used a large number of boiling fractions to study the mild hydrocracking of crude oil based on series parallel reaction mechanism.

Nat et al (1989) described the effect of increasing pressure on conversion, nitrogen removal and catalyst stability for mild hydrocracking process. They showed that improved nitrogen removal during mild hydrocracking step could lead directly to improved conversion since basic nitrogen is stronger poison for the acidic hydrocracking catalyst.

Desai et al (1992) presented the benefits of FCC feed hydrotreating on the performance of FCC unit in terms of product quality and conversion. The benefits are also applicable when hydrocracking is used for preparation of FCC feedstock.
Dai and Campbell (1994) worked with the mild hydrocracking of heavy feedstock that boils above 538°C. They tried to identify the catalysts with higher conversion of residues and minimum sediment formation. They found that the alumina catalysts containing basic oxides (alkali metal and alkaline earth metal) not only improve heavy oil conversion but also maintain the sediment make at the same level as alumina based catalysts.

Nguyen and Skripek (1994) presented the advantages of FCC feed pretreating. Pitchel and Harkamp (1994) studied the optimization of the mild hydrocracker and fluid catalytic cracker operations using a commercial unit data and a model. They discussed the influence of the mild hydrocracker catalyst and the operating strategy on the combined performance of these two units. They showed that improvement in MHC performance and economics resulted in a more profitable FCC operation within existing constraints.


Pappal et al (1997) described a pilot plant program on the mild hydrocracking of a gas oil fraction at 54 bar hydrogen pressure and 500 normal cubic metres of recycle hydrogen per cubic metre of feed using Akzo Nobel catalyst system. They attained total middle distillate (166-343°C) yields of 31.6 percent 37 percent respectively at 37 and 46 percent net conversion using moderate hydrogen consumptions. They reported high cetane numbers (40-56) and lower sulfur and nitrogen contents in the diesel product. Souza et al (1992) performed mild hydrocracking of an unstable shale oil in a three phase fluidized bed reactor with a commercial sulphided Ni-Mo catalyst.
Soydaner et al (1999) described the strategies to improve the commercial mild hydrocracker performance without additional capital investment by improving operating methods, catalyst management system and maintenance practices.

QChen Paul et al (1999) compared the FCC product yield pattern by using the untreated vacuum gas oil and the unconverted mild hydrocracker bottom as FCC feedstock for the 35% conversion of the vacuum gas oil feed in the mild hydrocracker. Their pilot plant investigation showed a decrease in the gas, coke, light cycle oil and heavy oil yields and increase in the gasoline yields when using mild hydrocracker bottoms as FCC feedstock.

Friedrich Danzinger et al (1999) presented a revamp case study in which they observed a 3 wt% increase in the conversion and good reduction of SO\textsubscript{x} and NO\textsubscript{x} emissions in the flue gas and reduced sulfur levels in all the FCC products while processing hydroprocessed VGO in MHC unit.

Shorey et al (1999) compared the performance characteristics for a conventional mild hydrocracking unit and a once-through hydrocracking unit designed to make diesel with a 50 cetane index. Mild hydrocracking uses a combination of hydrotreating and hydrocracking catalysts at somewhat higher operating temperatures than are used in hydrotreating. Conversion levels of about 25 percent below the feed initial boiling point are possible at heavy gas oil hydrotreating conditions (Law 2000/01). Patrie et al (2001) presented advantages of a new trimetallic catalyst for FCCU feed pretreating.

### 2.4 INTEGRATION WITH LUBE BASE OIL FACILITY

Beuther et al (1964) described a process for converting untreated petroleum fractions to unusually stable, high viscosity index (VI) lube oils which combined hydrogenation with controlled hydrocracking to give high
selectivities to motor oil fractions. They observed that yields of lube oils were greater by 10 to 50% with hydrogenation and hydrocracking route compared to solvent extraction. They reported high yields of lube base oils having viscosity indexes of 120 to 125 obtained from most crudes. They found from hydrotreating experiments that the lube oils produced by hydrogenation and hydrocracking process had very excellent color, low carbon residue and sulfur content, good thermal and oxidation stability and good inhibitor response. Law (1996) discussed the application of hydrocracking process for the manufacture for high quality lube base oils in detail along with the latest changes in lube industry with respect to product quality changes.

2.5 CONCLUSIONS

Literature pertaining to hydrocracking process especially with regard to experimental studies using pure model compounds and industrial hydrocarbon feedstocks was discussed in this chapter. The literature on kinetics, modeling and simulation of hydrocracking process was also summarized. Considerable research work was reported on reaction mechanism, product yield and selectivity during hydrocracking. Literature pertaining to the applications of hydrocracking process such as integration with FCCU and lube base oil manufacturing facility was extensively reviewed. From the literature review on hydrocracking process, it was understood that detailed experimental work on hydrocracking and its associated refinery processes was very scarce. Also, the kinetics of hydrocracking process was not studied in detail and limited only to simple first order kinetics. Simulation of hydrocracker was performed using very complex mathematical models involving cumbersome solution methodology. It has been felt that pilot plant studies on industrial hydrocracking process and its associated applications will help to understand the reactions, reaction mechanism, conversion, product yield, product selectivity, kinetics and its applications.