CHAPTER 3

EXPERIMENTAL PROCEDURES

3.1 INTRODUCTION

The experimental procedures employed in the present work are oriented towards the evaluation of different hydrotreating catalysts in a pilot plant trickle bed reactor and the estimation of kinetic parameters for the major hydrotreating reactions. The experimental data is also used to validate the three phase heterogeneous model developed in the present work and simulate the performance of pilot plant reactor over a wide range of operating conditions. Further, the kinetic data obtained from pilot plant experiments is used to apply the model to industrial reactor. The details of pilot plant experiments and the analysis of feed and product samples are discussed in this chapter.

3.2 PILOT PLANT EXPERIMENTS

3.2.1 Pilot Plant Reactor

The experiments were conducted in a continuous down flow isothermal trickle bed pilot plant reactor designed to operate at a maximum temperature of 600°C and a pressure of 300 kg/cm². The reactor tube is made of stainless steel-316 with an internal diameter of 2.54 cm and a length of 80 cm. The reactor was operated in isothermal mode by independent temperature control of four zone electric furnace. The electric furnace has four heating zones and each of these zones can be controlled at ± 1°C. The schematic diagram of the unit is shown in Figure 3.1. The photograph of the pilot plant reactor is presented in Figure 3.2.
TIC - Temperature Indication and Control
PIC - Pressure Indication and Control
FIC - Flow Indication and Control
LIC - Level Indication and Control
WI - Weight Indication

Figure 3.1 Schematic Diagram of Pilot Plant Reactor
Figure 3.2 Photograph of the Pilot Plant Reactor
3.2.2 Experimental Details

In the present work, four catalyst samples procured from commercial catalyst suppliers were evaluated using a feed collected from diesel hydrodesulfurization (DHDS) unit operating at Chennai Petroleum Refineries Limited.

Two of these catalyst samples are being used in the first and second reactor of DHDS unit. The other two catalyst samples were procured from different catalyst suppliers. Similar operating conditions were employed to evaluate these catalysts. The physical characteristics of the catalysts are discussed in chapter 5.

3.2.3 Operating Conditions

Operating pressure, $H_2$/oil ratio, liquid hourly space velocity and reactor temperature are the four important parameters which have strong influence on product quality. Of which operating pressure of a hydrotreating unit is not changed and limited by design pressure of the unit. The $H_2$/oil ratio is also kept at an optimum level to achieve desirable cycle length of the catalyst. Normally reactor temperature and liquid hourly space velocity are varied to get desired conversion and product quality from an industrial reactor for a given catalyst and feed system.

In view of this, experiments were carried out at a constant pressure of 40 kg/cm² and a constant $H_2$/oil ratio of 200 lit/lit at varied reactor temperature and liquid hourly space velocity. The reactor temperature was varied from 320°C to 360°C at different liquid hourly space velocities. The liquid hourly space velocity was varied from 1.0 h⁻¹ to 2.5 h⁻¹ at different reactor temperatures. The operating conditions for the present study were chosen considering the feed stock characteristics and typical operating conditions of the industrial reactor. The details of operating conditions employed in experimental studies are presented in chapter 5.
3.2.4 Catalyst Loading Pattern

The hydrotreating experiments were carried out using 200 ml of catalyst in 45 cm bed. The top 30 cm of the reactor was filled with inert \( \text{Al}_2\text{O}_3 \) spheres to ensure homogeneous flow distribution of the feed streams, to heat the reactants to the required temperature and to avoid end effects. The bottom 25 cm of the reactor was filled with inert \( \text{Al}_2\text{O}_3 \) spheres to serve as disengaging section. Figure 3.3 presents schematic diagram of catalyst loading pattern in pilot plant reactor.

After catalyst loading, the unit was pressure tested to check for any leaks in the system. It was pressurized with nitrogen to 10 kg/cm\(^2\) higher than the required operating pressure and then isolated from the cylinder. If the pressure loss was less than 10% of the system pressure, it was assumed that there were no leaks. Otherwise, the all the tube fittings and valves were thoroughly tested with liquid soap and leaks were arrested.

3.2.5 Catalyst Presulfiding

The hydrodesulfurization catalysts are generally supplied in the form of metal oxides on \( \gamma-\text{Al}_2\text{O}_3 \) by catalyst vendors. The catalyst is to be presulfided to convert these metal oxides into Co-Mo-S phase which can catalyze hydrotreating reactions. The following catalyst presulfiding procedure was employed in the present work.

Prior to experimental runs, the catalyst was dried and presulfided with diesel spiked with Di-methyl Di-sulfide so as to get 2.5 wt% sulfur in presulfiding medium. Initially the catalyst was purged with nitrogen at the rate of 100 litre/hr for 30 minutes at atmospheric pressure and temperature. The temperature of the catalyst bed was increased to 100\(^\circ\)C and pressurized with \( \text{H}_2 \) to 10 kg/cm\(^2\). The presulfiding medium was introduced at a liquid hourly space velocity of 2.0 hr\(^{-1}\) with a \( \text{H}_2/\text{oil} \) ratio of 120 lit/lit and maintained for 3 hours.
Figure 3.3 Schematic Diagram of Catalyst Loading Pattern in Pilot Plant Reactor

<table>
<thead>
<tr>
<th>Description</th>
<th>Volume</th>
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</thead>
<tbody>
<tr>
<td>Inert Alumina Particles (Top)</td>
<td>130 ml</td>
</tr>
<tr>
<td>Catalyst Volume</td>
<td>200 ml</td>
</tr>
<tr>
<td>Inert Alumina Particles (Bottom)</td>
<td>110 ml</td>
</tr>
</tbody>
</table>
Then the liquid hourly space velocity was reduced to 1.3 hr$^{-1}$ and the temperature was increased to 320°C at a rate of 30°C/hr. These conditions were then maintained for 3 hours to complete catalyst presulfiding. The catalyst bed was gradually cooled to ambient temperature and kept under H$_2$ atmosphere for the experiments.

3.2.6 Experimental Procedure

After presulfiding the catalysts, the experimental runs were carried out. The experimental conditions were chosen such that severe most operating conditions were employed first to avoid experimental errors arising due to product contamination with line contents.

Initially the hydrogen flow was set at required level calculated from the liquid hourly space velocity and H$_2$/oil ratio of the experimental run. The hydrogen flow to the system was controlled by an electronic mass flow controller. The pressure of the reactor was maintained by an electronic pressure sensor and solenoid valve system at the gas outlet of high pressure separator.

The feed was introduced after the system attained the required pressure for the experimental condition. The diesel feed rate was regulated at required level by a variable stroke length high pressure pump.

Then the electric furnace was switched on and required temperature was set for each zone. The shell (outer wall of the reactor) and catalyst bed temperatures were monitored. The catalyst bed temperature was monitored by four multi-point insertion thermocouples located in a thermowell mounted co-axially at the centre of the reactor. These thermocouples give the temperature of the catalyst bed at four different points along the catalyst bed length. The minimum time required for steady state condition was estimated from bed void fraction and line content of the system.
The liquid and gas product samples were collected under steady state conditions. The liquid product from high pressure separator was collected by maintaining a preset liquid level with the help of a level control valve. The product gases were metered through a wet gas meter before venting out. A gas sample was also collected for GC analysis.

The experimental runs at different conditions were repeated till a material balance of ±2 wt% was obtained. This was done to ensure that the data obtained from pilot plant studies was fairly accurate.

3.3 ANALYSIS OF FEED AND PRODUCT SAMPLES

A diesel feedstock collected from a diesel hydrodesulfurization unit of Chennai Petroleum Corporation Limited was used in the present study. The feed is a typical blend of straight run diesel fractions from atmospheric distillation columns of Crude-I and Crude-II, FCC cycle oils and Heavy Naphtha etc.

The feed and product samples were analyzed to determine their physical properties and measure sulfur, nitrogen, olefinic, poly-, di-, monoaromatic and naphthenic hydrocarbons. The products collected from pilot plant reactor hydrotreated at varied operating conditions were also subjected to detailed characterization. The products collected from industrial reactor during the test run were also analyzed. The analysis was done as per ASTM and IP standard test methods. The details of experimental procedures employed for the analysis of feed and product samples are discussed below.

3.3.1 Determination of Sulfur Content

The sulfur content of diesel samples before and after hydrotreating in pilot plant reactor was determined using a X-ray fluorescence spectrophotometer (Oxford
Lab-X 3500) as per ASTM D 4294. Each sample was purged with nitrogen to remove dissolved hydrogen sulfide before analysis.

This test method provides rapid and precise measurement of total sulfur in petroleum products with minimum of sample preparation. The sample is placed in the X-ray beam and the peak intensity of the sulfur is measured. The background intensity measured at recommended wave length is subtracted from the peak intensity. The resultant net counting rate is then compared to a previously prepared calibration curve or equation to obtain the concentration of sulfur in mass percentage.

3.3.2 Determination of Nitrogen Content

The nitrogen content of diesel samples before and after hydrotreating was determined using a chemiluminescence method as per ASTM D 4629 using Antek 703C instrument. In this method, the chemically bound nitrogen is converted to nitric oxide at a reactor temperature of 1000-1100 °C. The nitric oxide is then mixed with ozone in the detector to form an excited nitrogen oxide. The light emitted by the decay of excited molecules is sensed and quantified by a photomultiplier tube.

3.3.3 Determination of Olefin Content

The olefin content in feed and product samples was determined by measuring the bromine number of the sample as per ASTM D 1159. Bromine number is defined as the number of grams of bromine that will react with 100 g of the sample under the test conditions. A known weight of the sample dissolved in the selected solvent maintained at 0 to 5°C was titrated with standard bromide-bromide solution. The end point was indicated by a sudden change in potential on an electronic end point apparatus due to the presence of free bromine. Bromine number was calculated from the end point. The olefin content was calculated from bromine number as outlined in ASTM D 1159 standard test procedure.
3.3.4 Determination of Aromatic Content

High Performance Liquid Chromatography (HPLC) technique was used to separate total aromatics and saturates from the diesel feed and product samples as per IP 368/90 standard test method. Waters 410 instrument working as per the standard test method was used in the present work. The total aromatic portion was further separated using high performance liquid chromatography refractive index detection method, IP 391, to determine poly-, di- and monoaromatic content from total aromatic hydrocarbons. This method is applicable for petroleum fractions boiling in the range of 150 to 400°C. A fixed volume of test sample was injected in high performance liquid chromatograph fitted with a polar column. Since the column has little affinity towards non-aromatic hydrocarbons compared to aromatic hydrocarbons, the hydrocarbons were separated into distinct bands according to their ring structure. The poly-, di- and monoaromatics were desorbed by backflushing and detected using a refractive index detector.

3.3.5 Determination of Naphthene Content

After separating non-aromatics from aromatic hydrocarbons, the separated non-aromatic fraction was analyzed by Gas Chromatograph Mass Spectrometric (GC-MS) technique to determine naphthene content of saturates. A GC-MS procured from Hewlett Packard (Model: HP 5890) with Brunefeldt inlent system was used. The analysis is based on the summation of characteristic mass fragments to determine the concentration of hydrocarbon types. The average carbon numbers of the hydrocarbons are estimated from spectral data. The estimations of naphthenic hydrocarbons in the sample are made using mass spectra of standard calibration samples.
3.3.6 Determination of Light Hydrocarbons in Gas Products

The amount of light hydrocarbons in the gas product was determined by gas chromatographic technique. A refinery gas analyzer (Chromepack) was used to analyze gas samples in the present work. The weight percent and average molecular weight of gaseous components was estimated from the data obtained from gas chromatograph. The yield of light hydrocarbons based on feed was computed using gas yield of pilot plant experiments obtained from material balance.

3.3.7 Determination of Wild Naphtha in the Products.

A gas chromatographic technique (Perkin Elmer- Autosystem XL Simdist) specified by ASTM D 2887 was used to determine the extent of hydrocracking and resultant formation of naphtha range hydrocarbons in the diesel product. From the simulated distillation data obtained from gas chromatography, the weight percent of product boiling below the initial boiling point of the feed was calculated. Then the yield of wild naphtha based on feed was estimated from the liquid yield of experimental run.

3.3.8 Determination of Physical Properties

The physical properties of feed and product diesel samples were measured as per ASTM standard methods. Table 3.1 shows the list of test methods used for the analysis of feed and product samples.
Table 3.1 List of Standard Test Methods Applied

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Description</th>
<th>Method No.</th>
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<tbody>
<tr>
<td>1</td>
<td>Practice for Density, Relative Density (Specific Gravity) or API Gravity of</td>
<td>ASTM D 1298</td>
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<td></td>
<td>Crude petroleum and Liquid Petroleum Products by Hydrometer Method</td>
<td></td>
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<tr>
<td>2</td>
<td>Test Method for Kinematic Viscosity of Transparent and Opaque Liquids</td>
<td>ASTM D 445</td>
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<tr>
<td></td>
<td>(The Calculation of Dynamic Viscosity)</td>
<td></td>
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<tr>
<td>3</td>
<td>Test Method for Aniline Point and Mixed Aniline Point of Petroleum Products</td>
<td>ASTM D 611</td>
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<tr>
<td></td>
<td>and Hydrocarbon Solvents</td>
<td></td>
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<tr>
<td>4</td>
<td>Test Method for Flash Point By Pensky-Martens (Closed Cup) Tester</td>
<td>ASTM D 93</td>
</tr>
<tr>
<td>5</td>
<td>Test Method for Pour Point of Petroleum Products</td>
<td>ASTM D 97</td>
</tr>
<tr>
<td>6</td>
<td>Test Method for Ramsbottom Carbon Residue of Petroleum Products</td>
<td>ASTM D 524</td>
</tr>
<tr>
<td>7</td>
<td>Test Method for Distillation of Petroleum Products at Atmospheric Pressure</td>
<td>ASTM D 86</td>
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