CHAPTER 5

RESULTS AND DISCUSSION

The details of pilot plant hydrocracking studies, experimental procedures and analysis and testing methods were discussed in chapter 3. The details of kinetic and modeling schemes and their formulation, assumptions and reactions modeled were presented in chapter 4. In this chapter, the results of pilot plant hydrocracking experiments, properties of various feedstocks and hydrocracked products and the effect of operating conditions on conversion of feedstock, product yield distribution and product quality will be presented.

Different kinetic reaction schemes proposed as part of the present work and presented in chapter 4 will be validated with pilot plant experimental data using the kinetic parameters evaluated based on pilot plant yield data. Kinetic parameters for various reaction schemes for both the feedstocks used will be presented in detail. Studies on product selectivity of the hydrocracking catalysts will be presented using three different kinetic reaction schemes. Further, the pilot plant reactor will be simulated using an isothermal model and the results will be compared with the experimental data. The influence of operating conditions on conversion, product yields and product quality will be simulated using the model.

The proposed model will also be employed to simulate the performance of industrial hydrocracker unit at typical operating conditions. The conversion, product yields, product quality and the temperature profile along the length of the industrial hydrocracker reactor loaded with the same
catalyst system used in the pilot plant will be predicted based on the kinetic parameters estimated from pilot plant studies and using a scale-up factor. The catalyst deactivation will be studied considering linear increase of temperature required to obtain constant conversion with respect to time on stream.

The advantages of integration of hydrocracker unit with that of fluid catalytic cracking unit will be discussed along with some supporting pilot plant experimental data on mild hydrocracking and hydrotreating of vacuum gas oil fraction. The details of pilot plant studies, experimental procedures and analysis and testing methods for mild hydrocracking of vacuum gas oil feedstock were presented in Chapter 3. Five different kinetic reaction schemes will be presented for mild hydrocracking of vacuum gas oil fraction. The application of hydrocracking process for the manufacture of high quality lube base oils will be demonstrated based on pilot plant isodewaxing experiments and lab scale solvent dewaxing studies using hydrocracker bottoms as feedstock. The details of pilot plant isodewaxing and lab scale solvent dewaxing experiments will be presented along with the analysis and testing methods employed in the study. Finally some of the other applications of hydrocracking process will be discussed briefly.

5.1 PILOT PLANT EVALUATION OF HYDROCRACKING CATALYST

5.1.1 Feed Oil

A vacuum gas oil feedstock (Feed A) collected from crude vacuum distillation unit of Chennai Petroleum Corporation Limited was used in the present work for the first ten hydrocracking experiments. To study the effect of type of feedstock on hydrocracker conversion, product yields and product quality, a deasphalted oil (DAO) feedstock was blended with the vacuum gas
oil in the ratio of 20:80. Three hydrocracking experiments were carried out using this blend feedstock (Feed B). The properties of vacuum gas oil, deasphalted oil and the blend stream used in the present work are shown in Table 5.1.

As can be seen from Table 5.1, the vacuum gas oil feedstock used in the pilot plant studies has sulphur content of 1.62 wt%, nitrogen content of 560 ppmw, aromatic content of 44.9 wt% and Ramsbottom Carbon Residue (RCR) of 0.25 wt%. The ASTM Distillation D-1160 of the vacuum gas oil feedstock shows an initial boiling point (IBP) of 295°C and final boiling point of 569°C. The deasphalted oil fraction used in the pilot plant studies is heavier than the vacuum gas oil fraction as shown by the API gravity. Deasphalted oil has high aromatics content of 63.8 wt% and sulphur content of 2.18 wt%. The deasphalted oil has an initial boiling point of 459°C and final boiling point of 652°C indicating its heaviness and aromaticity. The deasphalted oil is also high in metals and polycyclic aromatics content compared to vacuum gas oil.

During hydrocracking experiments, a blend stream of 80% VGO and 20% DAO was used as Feed B with an objective to study the effect of feedstock quality on conversion, product yields and product quality. The Feed B is slightly heavier compared to vacuum gas oil feedstock as represented by their API gravity value. The aromatic content of Feed B is 51.6 wt% compared to 44.9 wt% for Feed A. The metals and polycyclic aromatic content also is higher for Feed B. Though the initial boiling point of both Feed A and Feed B are almost the same, the final boiling point of Feed B is very high with 649°C compared to 569°C for Feed A indicating its heavy aromatic nature.
Table 5.1 Properties of Feedstock used in Pilot Plant Studies

<table>
<thead>
<tr>
<th>Property</th>
<th>VGO</th>
<th>DAO</th>
<th>80%VGO+20%DAO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density at 15°C, gm/cc</td>
<td>0.9120</td>
<td>0.9382</td>
<td>0.9183</td>
</tr>
<tr>
<td>API Gravity</td>
<td>23.7</td>
<td>19.3</td>
<td>22.6</td>
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<tr>
<td>Viscosity at 100°C, cSt</td>
<td>6.42</td>
<td>36.62</td>
<td>9.6</td>
</tr>
<tr>
<td>Aniline Point, °C</td>
<td>88</td>
<td>112.0</td>
<td>93.0</td>
</tr>
<tr>
<td>Refractive Index</td>
<td>1.4887</td>
<td>1.4949</td>
<td>1.4899</td>
</tr>
<tr>
<td>UOP K</td>
<td>12.0</td>
<td>-</td>
<td>11.9</td>
</tr>
<tr>
<td>Pour Point, °C</td>
<td>42</td>
<td>63</td>
<td>48</td>
</tr>
<tr>
<td>Saturates, wt.%</td>
<td>55.1</td>
<td>36.2</td>
<td>48.4</td>
</tr>
<tr>
<td>Aromatics, wt.%</td>
<td>44.9</td>
<td>63.8</td>
<td>51.6</td>
</tr>
<tr>
<td>Asphaltenes, wt.%</td>
<td>0.055</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Poly Cyclic Index (PCI), wt%</td>
<td>0.2</td>
<td>&gt;1.0</td>
<td>&gt;1.0</td>
</tr>
<tr>
<td>Iron, ppm</td>
<td>0.02</td>
<td>0.212</td>
<td>0.137</td>
</tr>
<tr>
<td>Sulphur, wt.%</td>
<td>1.62</td>
<td>2.18</td>
<td>1.73</td>
</tr>
<tr>
<td>Nitrogen, ppmw</td>
<td>560</td>
<td>720</td>
<td>596</td>
</tr>
<tr>
<td>RCR, wt.%</td>
<td>0.25</td>
<td>1.3</td>
<td>0.57</td>
</tr>
<tr>
<td>Ni, ppmw</td>
<td>0.15</td>
<td>0.216</td>
<td>0.17</td>
</tr>
<tr>
<td>V, ppmw</td>
<td>0.14</td>
<td>0.20</td>
<td>0.15</td>
</tr>
<tr>
<td>Flash Point, °C</td>
<td>210</td>
<td>290</td>
<td>224</td>
</tr>
<tr>
<td><strong>ASTM D-1160 Distillation</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IBP, °C</td>
<td>295</td>
<td>459</td>
<td>289</td>
</tr>
<tr>
<td>5 vol.%., °C</td>
<td>357</td>
<td>518</td>
<td>355</td>
</tr>
<tr>
<td>10 vol.%., °C</td>
<td>378</td>
<td>536</td>
<td>378</td>
</tr>
<tr>
<td>20 vol.%., °C</td>
<td>406</td>
<td>560</td>
<td>405</td>
</tr>
<tr>
<td>30 vol.%., °C</td>
<td>424</td>
<td>575</td>
<td>426</td>
</tr>
<tr>
<td>40 vol.%., °C</td>
<td>439</td>
<td>588</td>
<td>443</td>
</tr>
<tr>
<td>50 vol.%., °C</td>
<td>451</td>
<td>600</td>
<td>458</td>
</tr>
<tr>
<td>60 vol.%., °C</td>
<td>464</td>
<td>611</td>
<td>476</td>
</tr>
<tr>
<td>70 vol.%., °C</td>
<td>477</td>
<td>622</td>
<td>504</td>
</tr>
<tr>
<td>80 vol.%., °C</td>
<td>496</td>
<td>633</td>
<td>551</td>
</tr>
<tr>
<td>90 vol.%., °C</td>
<td>522</td>
<td>643</td>
<td>598</td>
</tr>
<tr>
<td>95 vol.%., °C</td>
<td>542</td>
<td>647</td>
<td>624</td>
</tr>
<tr>
<td>FBP, °C</td>
<td>569</td>
<td>652</td>
<td>649</td>
</tr>
</tbody>
</table>
5.1.2 Catalysts

Hydrocracking catalyst system employed in the pilot plant studies comprises of a hydrotreating catalyst and a hydrocracking catalyst. These catalyst samples were procured from an industrial catalyst supplier and being currently used in many industrial hydrocracker units around the world. The hydrotreating catalyst was loaded prior to the hydrocracking catalyst to remove most of the sulphur and nitrogen compounds and partially saturate aromatic compounds. The catalyst loading pattern in the pilot plant reactors were already discussed in chapter 3.

The hydrotreating catalyst is an asymmetrical quadrilobe shaped Ni-Mo base-metal catalyst supported on alumina with an average particle diameter of 0.8 mm, surface area of 165 m$^2$/g, pore volume of 0.40 cc/g and compacted bulk density of 860 kg/m$^3$. The hydrocracking catalyst is a Ni-W base-metal catalyst containing both amorphous and zeolitic components with an average particle diameter of 0.8 mm, surface area of 285 m$^2$/g, pore volume of 0.38 cc/g and compacted bulk density of 920 kg/m$^3$. Both the catalysts were sized sufficiently by the catalyst supplier to make it suitable for pilot plant testing.

5.1.3 Operating Conditions of Pilot Plant Experiments

The experimental conditions were chosen to represent typical operating conditions of an industrial hydrocracking process. The pilot plant experiments are meant to study the performance of the catalyst system and to investigate the influence of operating conditions on conversion, product yield, product selectivity and product quality and to study different feedstock. Further the experimental data was also used to generate kinetic data, apply the kinetic data to predict the performance of the pilot plant and industrial
hydrocracker units with respect to conversion, product yields, product selectivity and product quality with change in operating conditions.

In the present work, experiments were carried out at a constant H₂/oil ratio of 845 m³/m³ as that of industrial hydrocracker unit. The operating pressures of 120 and 170 kg/cm² were used at varied reactor temperature and liquid hourly space velocity. The reactor temperature was varied from 360°C to 400°C while the liquid hourly space velocity was varied from 0.8 to 2.4 h⁻¹. The details of operating conditions employed in the pilot plant experiments are shown in Table 5.2.

**Table 5.2 Operating Conditions Employed in Pilot Plant Studies**

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Temperature, °C</th>
<th>Pressure, kg/cm²</th>
<th>LHSV, h⁻¹</th>
<th>H₂/oil Ratio, m³/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feedstock: VGO</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>360</td>
<td>170</td>
<td>0.8</td>
<td>845</td>
</tr>
<tr>
<td>2</td>
<td>380</td>
<td>170</td>
<td>0.8</td>
<td>845</td>
</tr>
<tr>
<td>3</td>
<td>400</td>
<td>170</td>
<td>0.8</td>
<td>845</td>
</tr>
<tr>
<td>4</td>
<td>380</td>
<td>120</td>
<td>0.8</td>
<td>845</td>
</tr>
<tr>
<td>5</td>
<td>360</td>
<td>170</td>
<td>1.6</td>
<td>845</td>
</tr>
<tr>
<td>6</td>
<td>380</td>
<td>170</td>
<td>1.6</td>
<td>845</td>
</tr>
<tr>
<td>7</td>
<td>400</td>
<td>170</td>
<td>1.6</td>
<td>845</td>
</tr>
<tr>
<td>8</td>
<td>360</td>
<td>170</td>
<td>2.4</td>
<td>845</td>
</tr>
<tr>
<td>9</td>
<td>380</td>
<td>170</td>
<td>2.4</td>
<td>845</td>
</tr>
<tr>
<td>10</td>
<td>400</td>
<td>170</td>
<td>2.4</td>
<td>845</td>
</tr>
<tr>
<td>Feedstock: 80% VGO + 20% DAO Blend</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>360</td>
<td>170</td>
<td>0.8</td>
<td>845</td>
</tr>
<tr>
<td>12</td>
<td>380</td>
<td>170</td>
<td>0.8</td>
<td>845</td>
</tr>
<tr>
<td>13</td>
<td>400</td>
<td>170</td>
<td>0.8</td>
<td>845</td>
</tr>
</tbody>
</table>
5.1.4 Pilot Plant Studies

The experimental data obtained from the pilot plant system along with the operating conditions are presented in Tables 5.3 to 5.26. The pilot plant conversion and product yields at various operating conditions using different feedstock are presented in Tables 5.3 to 5.6. The properties of total naphtha fraction obtained from pilot plant experiments at various operating conditions using different feedstock are presented in Tables 5.7 to 5.10. Tables 5.11 to 5.14 present the properties of aviation turbine fuel (ATF) fraction and Tables 5.15 to 5.18 present the properties of kerosene fraction obtained from pilot plant experiments. The properties of diesel fraction obtained from pilot plant experiments are presented in Tables 5.19 through 5.22. Tables 5.23 to 5.26 present the properties of unconverted oil fraction obtained from pilot plant at various operating conditions.

5.1.5 Effect of Operating Conditions on Conversion and Product Distribution

The conversion of the feedstock into desirable products can be increased either by increasing the reactor temperature or by decreasing the liquid hourly space velocity. A combination of these parameters can be used to achieve desired conversion in industrial hydrocracking units. The combination of parameters is generally referred as severity of operating conditions. The severity of operating conditions is determined based on the quality of feedstock used, desired conversion level, product yield distribution desired and design process conditions of the industrial unit. Hence it becomes important to study the influence of process variables such as reactor temperature, liquid hourly space velocity and operating pressure on conversion, product yields and product quality at a constant H₂/oil ratio.
Figure 5.1 shows the effect of temperature on 370°C- conversion at various liquid hourly space velocities. Figure 5.2 shows the effect of temperature on 370°C- conversion for different feedstocks at an operating pressure of 170 kg/cm² and LHSV of 0.8 h⁻¹. As can be seen from Tables 5.3 to 5.6 and Figures 5.1 and 5.2, the conversion of feedstock into gas, naphtha, kerosene and diesel increased with an increase in reactor temperature and decrease in liquid hourly space velocity. The highest gas oil conversion of 71.02 wt% was obtained at 400°C, 0.8 h⁻¹ liquid hourly space velocity and 170 kg/cm² total pressure in the range of operating conditions employed in the present work. The conversion of vacuum gas oil feedstock increased from 34.18 wt% to 71.02 wt% as the temperature was increased from 360 to 400°C at a constant liquid hourly space velocity of 0.8 h⁻¹. The lowest conversion of 11.50 wt% of vacuum gas oil feedstock was obtained at a temperature of 360°C, liquid hourly space velocity of 2.4 h⁻¹ and reactor pressure of 170 kg/cm².

The conversion of VGO into 370°C- products decreased with increasing liquid hourly space velocity. At a constant temperature of 360°C and pressure of 170 kg/cm², as the LHSV was increased from 0.8 to 2.4 h⁻¹, the conversion decreased from 34.18 wt% to 11.50 wt%. Similar trend was observed at other reactor temperatures also. This indicates the strong dependence of feedstock conversion on reactor temperature and liquid hourly space velocity.

The distribution of products during hydrocracking was significantly affected by operating conditions such as reactor temperature, operating pressure and liquid hourly space velocity. The yields of gas, naphtha and kerosene fractions obtained from pilot plant increased continuously with increase in reactor temperature and decrease in liquid hourly space velocity. At a constant liquid hourly space velocity of 0.8 h⁻¹, as the temperature was
Table 5.3  Pilot Plant Conversion and Product Yields at a LHSV of 0.8 h⁻¹ and $H_2$/oil ratio of 845 m³/m³ for VGO Feedstock

<table>
<thead>
<tr>
<th>Operating Conditions / Products</th>
<th>Run #1</th>
<th>Run #2</th>
<th>Run #3</th>
<th>Run #4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wt. %</td>
<td>Vol. %</td>
<td>Wt. %</td>
<td>Vol. %</td>
</tr>
<tr>
<td>Temperature, °C</td>
<td>360</td>
<td>380</td>
<td>400</td>
<td>380</td>
</tr>
<tr>
<td>Pressure, kg/cm²</td>
<td>170</td>
<td>170</td>
<td>170</td>
<td>120</td>
</tr>
<tr>
<td>$H_2S$</td>
<td>1.719</td>
<td>1.719</td>
<td>1.720</td>
<td>1.717</td>
</tr>
<tr>
<td>$NH_3$</td>
<td>0.067</td>
<td>0.068</td>
<td>0.068</td>
<td>0.066</td>
</tr>
<tr>
<td>$C_1-C_4$ Hydrocarbons</td>
<td>1.50</td>
<td>3.00</td>
<td>6.67</td>
<td>1.58</td>
</tr>
<tr>
<td>Total Naphtha, C₅-140°C</td>
<td>3.57</td>
<td>4.62</td>
<td>7.92</td>
<td>10.49</td>
</tr>
<tr>
<td>ATF, 140-250°C</td>
<td>9.85</td>
<td>11.68</td>
<td>18.92</td>
<td>22.98</td>
</tr>
<tr>
<td>Kerosene, 140-270°C</td>
<td>11.82</td>
<td>13.91</td>
<td>22.16</td>
<td>26.76</td>
</tr>
<tr>
<td>Diesel, 250-370°C</td>
<td>24.04</td>
<td>27.76</td>
<td>23.00</td>
<td>27.39</td>
</tr>
<tr>
<td>Bottoms, 370°C+</td>
<td>58.91</td>
<td>67.11</td>
<td>44.32</td>
<td>51.84</td>
</tr>
<tr>
<td>$C_{5+}$ Yield</td>
<td>113.4</td>
<td>116.5</td>
<td>118.0</td>
<td>115.6</td>
</tr>
<tr>
<td>Total yield</td>
<td>101.6</td>
<td>102.2</td>
<td>102.9</td>
<td>101.7</td>
</tr>
<tr>
<td>Conversion, 370°C-</td>
<td>34.18</td>
<td>50.48</td>
<td>71.02</td>
<td>40.13</td>
</tr>
<tr>
<td>$H_2$ Con., Nm³/m³ of feed</td>
<td>166.2</td>
<td>222.4</td>
<td>292.2</td>
<td>176.5</td>
</tr>
<tr>
<td>Sulphur, ppmw</td>
<td>25</td>
<td>18</td>
<td>10</td>
<td>42</td>
</tr>
<tr>
<td>Nitrogen, ppmw</td>
<td>8</td>
<td>BDL</td>
<td>BDL</td>
<td>15</td>
</tr>
</tbody>
</table>
Table 5.4  Pilot Plant Conversion and Product Yields at a LHSV of 1.6 h⁻¹ and H₂/oil ratio of 845 m³/m³ for VGO Feedstock

<table>
<thead>
<tr>
<th>Operating Conditions / Products</th>
<th>Run #5</th>
<th>Run #6</th>
<th>Run #7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor Temperature, °C</td>
<td>360</td>
<td>380</td>
<td>400</td>
</tr>
<tr>
<td>Reactor Pressure, kg/cm²</td>
<td>170</td>
<td>170</td>
<td>170</td>
</tr>
<tr>
<td>Hydrogen Sulfide, H₂S</td>
<td>1.702</td>
<td>1.716</td>
<td>1.719</td>
</tr>
<tr>
<td>Ammonia, NH₃</td>
<td>0.064</td>
<td>0.066</td>
<td>0.067</td>
</tr>
<tr>
<td>C₁-C₄ Hydrocarbons</td>
<td>0.72</td>
<td>1.53</td>
<td>3.05</td>
</tr>
<tr>
<td>Total Naphtha, C₅-140°C</td>
<td>1.82</td>
<td>2.30</td>
<td>3.56</td>
</tr>
<tr>
<td>ATF, 140-250°C</td>
<td>5.64</td>
<td>6.58</td>
<td>9.98</td>
</tr>
<tr>
<td>Kerosene, 140-270°C</td>
<td>6.53</td>
<td>7.52</td>
<td>11.83</td>
</tr>
<tr>
<td>Diesel, 250-370°C</td>
<td>18.49</td>
<td>20.73</td>
<td>19.45</td>
</tr>
<tr>
<td>Bottoms, 370°C+</td>
<td>71.84</td>
<td>79.80</td>
<td>63.32</td>
</tr>
<tr>
<td>C₅+ Yield</td>
<td>110.35</td>
<td>113.06</td>
<td></td>
</tr>
<tr>
<td>Total Yield</td>
<td>101.2</td>
<td>101.5</td>
<td>102.0</td>
</tr>
<tr>
<td>Conversion, 370°C-</td>
<td>19.73</td>
<td>29.25</td>
<td>45.64</td>
</tr>
<tr>
<td>H₂ Con., Nm³/m³ of feed</td>
<td>116.0</td>
<td>149.2</td>
<td>205.8</td>
</tr>
<tr>
<td>Sulphur, ppmw</td>
<td>185</td>
<td>47</td>
<td>20</td>
</tr>
<tr>
<td>Nitrogen, ppmw</td>
<td>36</td>
<td>14</td>
<td>6</td>
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Table 5.5  Pilot Plant Conversion and Product Yields at a LHSV of 2.4 h⁻¹ and H₂/oil ratio of 845 m³/m³ for VGO Feedstock

<table>
<thead>
<tr>
<th>Operating Conditions / Products</th>
<th>Run #8</th>
<th>Run #9</th>
<th>Run #10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor Temperature, °C</td>
<td>360</td>
<td>380</td>
<td>400</td>
</tr>
<tr>
<td>Reactor Pressure, kg/cm²</td>
<td>170</td>
<td>170</td>
<td>170</td>
</tr>
<tr>
<td>Hydrogen Sulfide, H₂S</td>
<td>1.638</td>
<td>1.690</td>
<td>1.712</td>
</tr>
<tr>
<td>Ammonia, NH₃</td>
<td>0.059</td>
<td>0.064</td>
<td>0.066</td>
</tr>
<tr>
<td>C₁-C₄ Hydrocarbons</td>
<td>0.44</td>
<td>0.92</td>
<td>1.96</td>
</tr>
<tr>
<td>Total Naphtha, C₅-140°C</td>
<td>1.11</td>
<td>1.39</td>
<td>2.33</td>
</tr>
<tr>
<td>ATF, 140-250°C</td>
<td>3.95</td>
<td>4.55</td>
<td>6.33</td>
</tr>
<tr>
<td>Kerosene, 140-270°C</td>
<td>4.29</td>
<td>4.92</td>
<td>7.75</td>
</tr>
<tr>
<td>Diesel, 250-370°C</td>
<td>14.12</td>
<td>15.72</td>
<td>17.36</td>
</tr>
<tr>
<td>Bottoms, 370°C+</td>
<td>79.21</td>
<td>87.23</td>
<td>71.09</td>
</tr>
<tr>
<td>C₅+ Yield</td>
<td>109.26</td>
<td>112.16</td>
<td>116.19</td>
</tr>
<tr>
<td>Total Yield</td>
<td>100.9</td>
<td>101.2</td>
<td>101.6</td>
</tr>
<tr>
<td>Conversion, 370°C-</td>
<td>11.50</td>
<td>20.57</td>
<td>33.02</td>
</tr>
<tr>
<td>H₂ Con., Nm³/m³ of feed</td>
<td>86.9</td>
<td>118.9</td>
<td>162.3</td>
</tr>
<tr>
<td>Sulphur, ppmw</td>
<td>780</td>
<td>295</td>
<td>85</td>
</tr>
<tr>
<td>Nitrogen, ppmw</td>
<td>72</td>
<td>34</td>
<td>15</td>
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Table 5.6  Pilot Plant Conversion and Product Yields at a LHSV of 0.8 h\(^{-1}\) and H\(_2\)/oil ratio of 845 m\(^3\)/m\(^3\) for 80% Vacuum Gas Oil + 20% Deasphalted Oil Blend

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<th>Run #12</th>
<th>Run #13</th>
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<td>Reactor Temperature, °C</td>
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<td>380</td>
<td>400</td>
</tr>
<tr>
<td>Reactor Pressure, kg/cm(^2)</td>
<td>170</td>
<td>170</td>
<td>170</td>
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<tr>
<td>Hydrogen Sulfide, H(_2)S</td>
<td>1.835</td>
<td>1.836</td>
<td>1.837</td>
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<tr>
<td>Ammonia, NH(_3)</td>
<td>0.071</td>
<td>0.072</td>
<td>0.072</td>
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<tr>
<td>C(_1)-C(_4) Hydrocarbons</td>
<td>1.40</td>
<td>2.89</td>
<td>6.61</td>
</tr>
<tr>
<td>Total Naphtha, C(_5)-140°C</td>
<td>3.35</td>
<td>4.33</td>
<td>7.73</td>
</tr>
<tr>
<td>ATF, 140-250°C</td>
<td>8.92</td>
<td>10.50</td>
<td>17.79</td>
</tr>
<tr>
<td>Kerosene, 140-270°C</td>
<td>10.94</td>
<td>12.85</td>
<td>20.95</td>
</tr>
<tr>
<td>Diesel, 250-370°C</td>
<td>22.51</td>
<td>25.88</td>
<td>22.26</td>
</tr>
<tr>
<td>Bottoms, 370°C+</td>
<td>61.86</td>
<td>70.27</td>
<td>46.85</td>
</tr>
<tr>
<td>C(_5)+ Yield</td>
<td>113.33</td>
<td></td>
<td>116.26</td>
</tr>
<tr>
<td>Total Yield</td>
<td>102.0</td>
<td>102.6</td>
<td>103.3</td>
</tr>
<tr>
<td>Conversion, 370°C-</td>
<td>31.11</td>
<td>47.83</td>
<td>68.35</td>
</tr>
<tr>
<td>H(_2) Con., Nm(^3)/m(^3) of feed</td>
<td>199.9</td>
<td>262.8</td>
<td>334.8</td>
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<tr>
<td>Sulphur, ppmw</td>
<td>31</td>
<td>22</td>
<td>13</td>
</tr>
<tr>
<td>Nitrogen, ppmw</td>
<td>10</td>
<td>BDL</td>
<td>BDL</td>
</tr>
</tbody>
</table>
Figure 5.1 Effect of Temperature on Conversion at various LHSV

Figure 5.2 Effect of Temperature on Conversion for Different Feedstock
increased from 360 to 380°C, the yield of gas increased from 1.50 wt% to 6.67 wt%, yield of naphtha increased from 3.57 to 16.66 wt% and the yield of kerosene increased from 11.82 to 34.70 wt% as shown in Table 5.3. The yields of gas, naphtha and kerosene increased with decrease in liquid hourly space velocity. At a reactor temperature of 360°C, the yield of gas increased from 0.44 to 1.50 wt%, yield of naphtha increased from 1.11 to 3.57 wt% and the yield of kerosene increased from 4.29 to 11.82 wt% as the liquid hourly space velocity was decreased from 2.4 to 0.8 h⁻¹. Similar trends for the effect of LHSV were observed at other temperatures also for the yield of gas, naphtha and kerosene fractions.

The yield of diesel fraction increased significantly with reactor temperature at higher liquid hourly space velocities and decreased with reactor temperature at lower liquid hourly space velocities. At the liquid hourly space velocity of 2.4 h⁻¹, as the reactor temperature was increased from 360 to 400°C, the yield of diesel increased from 14.12 to 18.12 wt% and at a constant liquid hourly space velocity of 1.6 h⁻¹, the yield of diesel increased from 18.49 to 19.45 wt%. At a lower liquid hourly space velocity of 0.8 h⁻¹, the yield of diesel constantly decreased from a value of 24.04 to 20.81 wt% as the temperature was increased from 360 to 400°C. This may be due to the fact that at higher reaction times encountered at lower space velocities, the diesel fraction undergoes secondary cracking reactions to form lower boiling products such as kerosene, naphtha and gas. At lower space velocities and higher reactor temperatures, the rate of formation of diesel fraction is significantly lower compared to the rate of secondary cracking reactions. The diesel formed by primary hydrocracking reactions starts cracking at higher rate at elevated temperatures and lower space velocities leading to the decrease in the yield of diesel fraction and increase in the formation of lower boiling products.
The yield of unconverted oil decreased continuously with increasing reactor temperature and decreasing space velocity. At a liquid hourly space velocity of 0.8 h$^{-1}$, the UCO yield decreased from 58.91 to 25.94 wt% as the temperature was increased from 360 to 400°C. At a constant reactor temperature of 360°C, the UCO yield decreased from 79.21 to 58.91 wt% as the liquid hourly space velocity was decreased from 2.4 to 0.8 h$^{-1}$.

The total yield of hydrocracked products increased with increase in reactor temperature and decrease in liquid hourly space velocity. At a liquid hourly space velocity of 0.8 h$^{-1}$, the total yield increased from 101.6 to 102.9 wt% as the temperature was increased from 360 to 400°C. At a constant reactor temperature of 360°C, the total yield increased from 100.9 to 101.6 wt% as the liquid hourly space velocity was decreased from 2.4 to 0.8 h$^{-1}$. At typical operating conditions of industrial once-through hydrocracker unit, i.e. at 380°C and 0.8 h$^{-1}$ liquid hourly space velocity, there was a 2.2 wt% addition of hydrogen to the VGO feedstock observed. The highest hydrogen addition of 2.9 wt% was observed at severe most operating conditions with a reactor temperature of 400°C, operating pressure of 170 kg/cm$^2$ and liquid hourly space velocity of 0.8 h$^{-1}$. Since hydrocracking process adds hydrogen into the feedstock, the overall yield is calculated to be more than 100 percent based on fresh feed. Hydrogen is added during hydrocracking process by the way of saturation of feed aromatic components and reaction intermediate olefinic molecules. Hydrogen also reacts with feed impurities such as sulphur and nitrogen to remove them as hydrogen sulfide and ammonia. The total yields in the present work were calculated based on fresh feed. The volumetric yields of C$_5$+ products were found to be more than 100% due to the addition of hydrogen to the feedstock during hydrocracking reactions. The volumetric swell of around 20 - 25% is generally observed during hydrocracking of vacuum gas oil under typical operating conditions.
The yields of gas, naphtha and kerosene increased with decreasing liquid hourly space velocity. The yield of diesel also increased with decreasing liquid hourly space velocity. The rate of increase of diesel yield was lower at lower space velocity. This may be due to the property of the hydrocracking catalyst to shift the conversion of feedstock towards more jet fuel at moderate values of conversion at the cost of diesel. The yield of unconverted bottoms decreased with decreasing space velocity. As the pilot plant data indicated, the yield of gas, naphtha and kerosene increased with increasing feedstock conversion levels while the unconverted bottoms decreased with conversion. But the yield of diesel fuel initially increased with conversion, but as the feedstock conversion increased at lower space velocities and higher temperatures, the yield of diesel decreased while shifting the conversion to more jet fuel.

Figure 5.3 shows the effect of temperature on product yields at 0.8 h\(^{-1}\) for Feed B. The influence of temperature and liquid hourly space velocity on naphtha-middle distillates ratio is presented in Figure 5.4 for both feedstocks. The naphtha-middle distillates ratio increased continuously with reactor temperature at all liquid hourly space velocities and for both feedstock. At typical liquid hourly space velocities employed in industrial hydrocracker units i.e. at 0.8 h\(^{-1}\), the naphtha-middle distillate ratio increased with reactor temperature significantly. At this LHSV and at a reactor temperature of 400°C, this ratio was highest at 0.32 indicating increased formation of naphtha at the cost of middle distillates at higher reaction severities. For a hydrocracker unit operated in gasoline mode of operation, increasing the severity of operation is beneficial to shift the product yield towards naphtha. But in most of the refinery cases, hydrocracker units are normally designed to produce more middle distillates having higher market demand. In such cases, optimization of operating temperature is required to achieve higher conversion of feedstock into middle distillates with lesser formation of naphtha. From the experimental data, it was observed that
Figure 5.3 Effect of Temperature on product yields at 0.8 h-1 for 80%VGO+20%DAO Feedstock

Figure 5.4 Effect of temperature and LHSV on gasoline-middle distillates ratio
operating the hydrocracker at a reactor temperature of 380°C would be a better option for producing maximum middle distillates with naphtha-middle distillate ratio of around 0.18 for the catalyst system studied in the present work.

The effect of temperature and liquid hourly space velocity on hydrogen consumption is shown in Figure 5.5 for both feedstocks. The external hydrogen consumption increased continuously with the severity of the cracking reactions at higher reactor temperatures and lower liquid hourly space velocity. The hydrogen consumption had increased from 166.2 to 292.2 Nm$^3$/m$^3$ as the reactor temperature was increased from 360 to 400°C at a constant liquid hourly space velocity of 0.8 h$^{-1}$. As the liquid hourly space velocity was increased from 0.8 to 2.4 h$^{-1}$ at a constant reactor temperature of 360°C, the hydrogen consumption decreased from 166.2 to 86.9 Nm$^3$/m$^3$.

The effect of reactor temperature and liquid hourly space velocity on product sulphur for VGO feedstock is shown in Figure 5.6 and Tables 5.3 to 5.6. Sulphur content of the hydrocracked product decreased with increase in reactor temperature for a constant liquid hourly space velocity. The sulphur content had decreased from 780 to 85 ppmw as the reactor temperature was increased from 360 to 400°C at a liquid hourly space velocity of 2.4 h$^{-1}$. The sulphur content of the hydrocracked product was found to be very low compared to feed sulphur content of 1.62 wt% for the entire range of operating conditions employed in the present work. The hydrodesulphurization generally occurs at very high rates due to higher reactor temperatures and operating pressures employed during hydrocracking process. At a constant reactor temperature of 360°C, the product sulphur increased from 25 to 780 ppmw as the liquid hourly space velocity was increased from 0.8 to 2.4 h$^{-1}$. Similar trends for product sulphur had been observed at other liquid hourly space velocities also. Reactor temperature had more pronounced effect on desulphurization compared to liquid hourly space velocity.
Figure 5.5  Effect of temperature and LHSV on hydrogen consumption

Figure 5.6  Effect of temperature and LHSV on product sulphur
The hydrodenitrogenation also showed a similar trend as that of hydrodesulphurization reactions. Under typical liquid hourly space velocity encountered during hydrocracking, most of the nitrogen compounds (99.99%) were removed. Since nitrogen compounds are poisons to acidic hydrocracking catalysts, their removal is very important during the first pretreatment step. The nitrogen content decreased from 36 to 6 ppmw as the reactor temperature was increased from 360 to 400°C at a liquid hourly space velocity of 1.6 h⁻¹. The nitrogen content of hydrocracked product decreased with decrease in liquid hourly space velocity. The hydrodenitrogenation reactions were found to be slower compared to hydrodesulphurization.

The yield of hydrogen sulphide and ammonia increased with increase in reaction severity levels. The amount of hydrogen sulphide and ammonia formed along the length of the reactor depends on the extent of sulphur and nitrogen removed during the course of hydrocracking. At typical operating conditions employed during hydrocracking, almost most of the sulphur and nitrogen compounds are removed as hydrogen sulfide and ammonia.

One hydrocracking experiment was conducted at a reactor temperature of 380°C, operating pressure of 120 kg/cm², liquid hourly space velocity of 0.8 h⁻¹ and H₂/oil ratio of 845 m³/m³ to study the effect of operating pressure on conversion, product yields and product quality during hydrocracking. The pilot plant conversion and product yields at 120 kg/cm² are presented in Table 5.3 along with data at operating pressure of 170 kg/cm² for comparing them at similar operating temperature and liquid hourly space velocity. As can be seen from Table 5.3, operating pressure had significant influence on feedstock conversion and product distribution. A reduction in the 370°C- conversion of about 10.35 wt% was observed while decreasing the operating pressure from 170 to 120 kg/cm² and maintaining other operating
conditions constant. The increased conversion at higher operating pressure might be due to increased rate of aromatic saturation and hydrocracking and also increased hydrogenation of coke precursors and cleaning of catalyst surface.

Product distribution was observed to be slightly modified by the operating pressure. The yield of unconverted bottoms product (370°C+) had increased from 44.32 to 53.58 wt% at 120 kg/cm² operating pressure due to decreased conversion levels. The yield of kerosene and diesel decreased from 22.16 to 18.86 wt% and 23.0 to 20.81 wt% respectively when decreasing the operating pressure from 170 to 120 kg/cm². Since there is lower amount of aromatic saturation at lower operating pressures, the hydrogen uptake and overall product yield decreased. The total product yield at 120 kg/cm² operating pressure was 101.7 wt% with 1.7 wt% of hydrogen addition compared to 102.2 wt% of total yield with 2.2 wt% of hydrogen addition at 170 kg/cm² operating pressure. The C₅+ yield also showed a decrease at lower operating pressure.

In addition to the effect of lower operating pressure on conversion and product yields, the quality of hydrocracked products are also significantly affected. The hydrodesulphurization and hydrodenitrogenation reactions are also affected by operating pressure. The hydrocracked product at lower pressure of 120 kg/cm² had a sulphur content of 42 ppmw compared to 18 ppmw of sulphur at 170 kg/cm². The nitrogen content of hydrocracked product at lower operating pressure was found to be 15 ppmw as opposed to very low (below detectable limits) levels of nitrogen at higher operating pressure. An increase in hydrogen partial pressure at higher operating pressures increases the rate of hydrodenitrogenation reactions. The rate of hydrodesulphurization is less sensitive to hydrogen partial pressure.
Table 5.7  Properties of Total Naphtha Fraction (C₅-140°C) Obtained from Pilot Plant Reactors for Vacuum Gas Oil Feedstock at a LHSV of 0.8 h⁻¹

<table>
<thead>
<tr>
<th>Operating Conditions / Property</th>
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<th>Run#2</th>
<th>Run#3</th>
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<tbody>
<tr>
<td>Reactor Temperature, °C</td>
<td>360</td>
<td>380</td>
<td>400</td>
<td>380</td>
</tr>
<tr>
<td>Reactor Pressure, kg/cm²</td>
<td>170</td>
<td>170</td>
<td>170</td>
<td>120</td>
</tr>
<tr>
<td>H₂/oil Ratio, m³/m³</td>
<td>845</td>
<td>845</td>
<td>845</td>
<td>845</td>
</tr>
<tr>
<td>Density at 15°C, gm/cc</td>
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<td>0.7548</td>
<td>0.7315</td>
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</tr>
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<td>API Gravity</td>
<td>51.6</td>
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<td>61.9</td>
<td>55.9</td>
</tr>
<tr>
<td>Reid Vap. Pressure, kg/cm² (a)</td>
<td>0.7</td>
<td>0.8</td>
<td>1.2</td>
<td>1.0</td>
</tr>
</tbody>
</table>

**Detailed Hydrocarbon Analysis**

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<th>Run#3</th>
<th>Run#4</th>
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<tbody>
<tr>
<td>n-Paraffins, wt.%</td>
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<td>7.6</td>
<td>13.0</td>
<td>8.4</td>
</tr>
<tr>
<td>i-Paraffins, wt.%</td>
<td>22.7</td>
<td>26.4</td>
<td>37.3</td>
<td>27.2</td>
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<tr>
<td>Naphthenes, wt.%</td>
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<td>55.8</td>
<td>46.8</td>
<td>50.9</td>
</tr>
<tr>
<td>Aromatics, wt.%</td>
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<td>10.2</td>
<td>2.9</td>
<td>13.5</td>
</tr>
<tr>
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<td>7</td>
<td>20</td>
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<tr>
<td>Mercaptans, ppmw</td>
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<td>8</td>
<td>-</td>
<td>10</td>
</tr>
<tr>
<td>Nitrogen, ppmw</td>
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<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
</tr>
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<td>&lt; 1.0</td>
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**ASTM Distillation D-86**

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<td>90 vol.% °C</td>
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<td>125</td>
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<td>FBP, °C</td>
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Table 5.8  Properties of Total Naphtha Fraction (C\textsubscript{5}-140\degree C) Obtained from Pilot Plant Reactors for Vacuum Gas Oil Feedstock at a LHSV of 1.6 h\textsuperscript{-1}

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</tr>
<tr>
<td>Reactor Pressure, kg/cm\textsuperscript{2}</td>
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<td>170</td>
<td>170</td>
</tr>
<tr>
<td>H\textsubscript{2}/oil Ratio, m\textsuperscript{3}/m\textsuperscript{3}</td>
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<td>845</td>
<td>845</td>
</tr>
<tr>
<td>Density at 15\degree C, gm/cc</td>
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<td>API Gravity</td>
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<td>Reid Vapour Pressure, kg/cm\textsuperscript{2} (a)</td>
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<td>n-Paraffins, wt.%</td>
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<td>6.6</td>
<td>9.0</td>
</tr>
<tr>
<td>i-Paraffins, wt.%</td>
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<td>Naphthenes, wt.%</td>
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<td>Aromatics, wt.%</td>
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<td>9.3</td>
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<tr>
<td>Sulphur, ppmw</td>
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<td>Mercaptans, ppmw</td>
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<td>Nitrogen, ppmw</td>
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<td>8</td>
<td>6</td>
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<td>RON, Calculated</td>
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<td>76.8</td>
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<tr>
<td>ASTM Distillation D-86</td>
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<tr>
<td>IBP, °C</td>
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<td>20 vol.%, °C</td>
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<td>30 vol.%, °C</td>
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<td>40 vol.%, °C</td>
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<td>FBP, °C</td>
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Table 5.9  Properties of Total Naphtha Fraction (C₅-140°C) Obtained from Pilot Plant Reactors for Vacuum Gas Oil Feedstock at a LHSV of 2.4 h⁻¹

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<td>Reactor Pressure, kg/cm²</td>
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<td>170</td>
</tr>
<tr>
<td>H₂/oil Ratio, m³/m³</td>
<td>845</td>
<td>845</td>
<td>845</td>
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<tr>
<td>Density at 15°C, gm/cc</td>
<td>0.7993</td>
<td>0.7804</td>
<td>0.7612</td>
</tr>
<tr>
<td>API Gravity</td>
<td>45.5</td>
<td>49.8</td>
<td>54.4</td>
</tr>
<tr>
<td>Reid Vapour Pressure, kg/cm² (a)</td>
<td>0.5</td>
<td>0.7</td>
<td>1.0</td>
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</tbody>
</table>

**Detailed Hydrocarbon Analysis:**

<table>
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<th>Component</th>
<th>Run#8</th>
<th>Run#9</th>
<th>Run#10</th>
</tr>
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<tbody>
<tr>
<td>n-Paraffins, wt.%</td>
<td>4.8</td>
<td>5.4</td>
<td>7.3</td>
</tr>
<tr>
<td>i-Paraffins, wt.%</td>
<td>16.3</td>
<td>19.0</td>
<td>24.2</td>
</tr>
<tr>
<td>Naphthenes, wt.%</td>
<td>46.4</td>
<td>50.7</td>
<td>54.3</td>
</tr>
<tr>
<td>Aromatics, wt.%</td>
<td>32.5</td>
<td>24.9</td>
<td>14.2</td>
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<tr>
<td>Sulphur, ppmw</td>
<td>120</td>
<td>62</td>
<td>32</td>
</tr>
<tr>
<td>Mercaptans, ppmw</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrogen, ppmw</td>
<td>21</td>
<td>15</td>
<td>10</td>
</tr>
<tr>
<td>RON, Calculated</td>
<td>86.8</td>
<td>84.9</td>
<td>78.4</td>
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<tr>
<td>Metals, V, Ni, Fe, Cu, ppbw</td>
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**ASTM Distillation D-86**

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<th>Run#10</th>
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</thead>
<tbody>
<tr>
<td>IBP, °C</td>
<td>79</td>
<td>75</td>
<td>59</td>
</tr>
<tr>
<td>10 vol.%, °C</td>
<td>86</td>
<td>94</td>
<td>80</td>
</tr>
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<td>20 vol.%, °C</td>
<td>90</td>
<td>101</td>
<td>89</td>
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<td>30 vol.%, °C</td>
<td>95</td>
<td>103</td>
<td>96</td>
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<td>40 vol.%, °C</td>
<td>97</td>
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<td>97</td>
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<td>50 vol.%, °C</td>
<td>107</td>
<td>107</td>
<td>106</td>
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<td>60 vol.%, °C</td>
<td>116</td>
<td>115</td>
<td>113</td>
</tr>
<tr>
<td>70 vol.%, °C</td>
<td>120</td>
<td>118</td>
<td>117</td>
</tr>
<tr>
<td>80 vol.%, °C</td>
<td>124</td>
<td>123</td>
<td>121</td>
</tr>
<tr>
<td>90 vol.%, °C</td>
<td>130</td>
<td>125</td>
<td>124</td>
</tr>
<tr>
<td>FBP, °C</td>
<td>141</td>
<td>140</td>
<td>138</td>
</tr>
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</table>
Table 5.10  Properties of Total Naphtha Fraction (C₅-140°C) Obtained from Pilot Plant Reactors for 80% Vacuum Gas Oil + 20% DAO Blend at a LHSV of 0.8 h⁻¹

<table>
<thead>
<tr>
<th>Operating Conditions / Property</th>
<th>Run#11</th>
<th>Run#12</th>
<th>Run#13</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor Temperature, °C</td>
<td>360</td>
<td>380</td>
<td>400</td>
</tr>
<tr>
<td>Reactor Pressure, kg/cm²</td>
<td>170</td>
<td>170</td>
<td>170</td>
</tr>
<tr>
<td>H₂/oil Ratio, m³/m³</td>
<td>845</td>
<td>845</td>
<td>845</td>
</tr>
<tr>
<td>Density at 15°C, gm/cc</td>
<td>0.7738</td>
<td>0.7554</td>
<td>0.7321</td>
</tr>
<tr>
<td>API Gravity</td>
<td>51.4</td>
<td>55.8</td>
<td>61.8</td>
</tr>
<tr>
<td>Reid Vapour Pressure, kg/cm² (a)</td>
<td>0.7</td>
<td>0.8</td>
<td>1.2</td>
</tr>
<tr>
<td>Detailed Hydrocarbon Analysis:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Paraffins, wt.%</td>
<td>6.1</td>
<td>7.6</td>
<td>13.2</td>
</tr>
<tr>
<td>i-Paraffins, wt.%</td>
<td>22.1</td>
<td>30.9</td>
<td>36.4</td>
</tr>
<tr>
<td>Naphthenes, wt.%</td>
<td>51.6</td>
<td>50.5</td>
<td>47.2</td>
</tr>
<tr>
<td>Aromatics, wt.%</td>
<td>20.2</td>
<td>11.0</td>
<td>3.2</td>
</tr>
<tr>
<td>Sulphur, ppmw</td>
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<td>8</td>
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<tr>
<td>Mercaptans, ppmw</td>
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<td>9</td>
<td></td>
</tr>
<tr>
<td>Nitrogen, ppmw</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>RON, Calculated</td>
<td>83.9</td>
<td>77.7</td>
<td>75.0</td>
</tr>
<tr>
<td>Metals, V, Ni, Fe, Cu, ppbw</td>
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<td>&lt;1.0</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td>ASTM Distillation D-86</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IBP, °C</td>
<td>73</td>
<td>69</td>
<td>55</td>
</tr>
<tr>
<td>10 vol.%, °C</td>
<td>84</td>
<td>81</td>
<td>80</td>
</tr>
<tr>
<td>20 vol.%, °C</td>
<td>99</td>
<td>89</td>
<td>87</td>
</tr>
<tr>
<td>30 vol.%, °C</td>
<td>102</td>
<td>98</td>
<td>93</td>
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<tr>
<td>40 vol.%, °C</td>
<td>105</td>
<td>99</td>
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<td>50 vol.%, °C</td>
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<td>60 vol.%, °C</td>
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<td>108</td>
</tr>
<tr>
<td>70 vol.%, °C</td>
<td>116</td>
<td>115</td>
<td>115</td>
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<tr>
<td>80 vol.%, °C</td>
<td>121</td>
<td>119</td>
<td>118</td>
</tr>
<tr>
<td>90 vol.%, °C</td>
<td>127</td>
<td>125</td>
<td>121</td>
</tr>
<tr>
<td>FBP, °C</td>
<td>143</td>
<td>142</td>
<td>139</td>
</tr>
</tbody>
</table>
5.1.6 Effect of Operating Conditions on Product Quality

As can be seen from Table 5.7, the density of naphtha decreased with increasing reactor temperature and decreasing LHSV due to increased saturation and cracking of feedstock and increased hydrogen addition at higher reactor severity. The Reid Vapor Pressure (RVP) of naphtha fraction increased with cracking severity due to the formation of increased amount of lighter components at higher reactor temperatures and lower liquid hourly space velocities. The sulphur content of the naphtha fraction was very low at all the operating conditions employed in the present work. The nitrogen content of naphtha fraction was found to be very low which was below detectable limit of the analytical instrument.

The concentration of n-paraffins in naphtha fraction increased with increasing reactor temperature and decreasing liquid hourly space velocity. The concentration of n-paraffins increased from 5.8 to 13.0 wt% as the reactor temperature was increased from 360 to 400°C at a constant liquid hourly space velocity of 0.8 h⁻¹ and operating pressure of 170 kg/cm². The amount of n-paraffins increased from 4.8 to 5.8 wt% as the liquid hourly space velocity was decreased from 2.4 to 0.8 h⁻¹ at a constant reactor temperature of 360°C. The concentration of isoparaffins increased with both increasing reactor temperature and decreasing liquid hourly space velocity. The isoparaffins content of naphtha increased from 22.7 to 37.3 wt% as the reactor temperature was increased from 360 to 400°C at a constant liquid hourly space velocity of 0.8 h⁻¹ and operating pressure of 170 kg/cm².

Both n-paraffins and isoparaffins showed a similar increasing trend during hydrocracking reactions at higher reaction severities. The increase in the cracking severity at higher temperatures and lower space velocity led to increased rate of aromatic saturation and subsequent cracking and
isomerization of aromatic molecules leading to increased paraffin content of the products. The concentration of isoparaffins in naphtha fractions obtained from pilot plant was higher compared to n-paraffins. This showed that isomerisation reactions are very fast during hydrocracking and that is the reason for increased amount of isomers formation with increase in cracking severity.

The concentration of naphthenes increased with reactor temperature at higher liquid hourly space velocities. As the liquid hourly space velocity was lowered, the concentration of naphthenes increased to a maximum value and then decreased slightly as the reactor temperature was further reduced. The concentration of naphthenes increased from 52.7 to 55.8 wt% as the reactor temperature was increased from 360 to 380°C at a constant liquid hourly space velocity of 0.8 h⁻¹ and then decreased to 46.8 wt% as the reactor temperature was increased to 400°C. But at the lower liquid hourly space velocity of 1.6 h⁻¹, the concentration of naphthenes increased with reactor temperature. The amount of naphthenes increased with decreasing space velocity at 360 and 380°C reactor temperatures while at 400°C the amount of naphthenes decreased with decrease in space velocity. This showed that at lower reaction times along the initial portions of the reactor, the concentration of naphthenes continually increased at the expense of aromatic saturation reactions. The concentration of naphthenes increased continuously along the length of hydrocracking reactor and reached a maximum value at higher reaction times. As the reaction time is further increased, the naphthenic molecules undergo isomerisation and cracking reactions to form both isoparaffins and smaller naphthenes. At lower cracking severities encountered at lower reactor temperatures and higher LHSV, naphthenes concentration in the product streams is lower due to lesser cracking and saturation of the feedstock aromatics. At typical operating conditions employed in industrial hydrocracking units, the concentration of isoparaffins and naphthenes are higher in naphtha fraction.
The concentration of aromatics in hydrocracked naphtha stream continuously decreased both with increasing reactor temperature and decreasing space velocity. Increasing cracking severity by increasing reactor temperature and decreasing space velocity resulted in increased rate of saturation of aromatics under higher hydrogen pressures employed during hydrocracking. The hydrotreating catalyst loaded prior to the hydrocracking catalyst saturates some of the aromatic compounds in the feedstock to facilitate cracking reactions at later hydrocracking stages. Hydrocracking catalyst also contains metal function on which hydrogenation of remaining aromatic compounds occurs. The concentration of aromatics decreased from 18.8 to 2.9 wt% as the reactor temperature was increased from 360 to 400°C at a constant liquid hourly space velocity of 0.8 h⁻¹. The concentration of aromatics increased from 18.8 to 32.5 wt% as the liquid hourly space velocity was increased from 0.8 to 2.4 h⁻¹ at a constant reactor temperature of 360°C. The research octane number (RON) of the naphtha fraction decreased with increasing temperature and decreasing liquid hourly space velocity as presented in Tables 5.7 to 5.10.

Generally under typical operating conditions employed in industrial hydrocracking process, the naphthenic rings resist cracking due to unfavorable orbital orientation of their carbon-carbon bonds. Due to this, a large portion of the naphthenic rings originally present in the vacuum gas oil will survive in the products. This is one of the reasons that naphtha produced from a hydrocracker is an excellent feedstock for catalytic reformer unit due to its higher naphthenes content (Weitkamp 1988). Also hydrocracker naphtha provides naphthenic precursor molecules for the production of BTX (Benzene, Toluene and Xylene). As can be evident from the Tables 5.7 to 5.10, most of the reactions during hydrocracking move away from the aromatic compounds to favor the production of the paraffin isomers and naphthenes. Under typical operating conditions of an industrial once-through
hydrocracker unit, i.e. at 380°C reactor temperature, 170 kg/cm² operating pressure and 0.8 h⁻¹ liquid hourly space velocity, naphtha obtained from pilot plant contained about 57.5 wt% of naphthenes. The integration of hydrocracker unit with catalytic reformer can be beneficial for the production of high quality gasoline and petrochemical feedstocks such as benzene, toluene and xylene.

Tables 5.11 to 5.14 presents the quality of Aviation Turbine Fuel (ATF) fraction obtained from pilot plant reactors for both feedstocks. The density of ATF decreased with increase in reactor temperature and decrease in LHSV due to increased hydrogen addition at higher operating severities of hydrocracking. The smoke point of ATF fraction increased from 19 to 26 mm as the reactor temperature was increased from 360 to 400°C at a constant liquid hourly space velocity of 0.8 h⁻¹ and reactor operating pressure of 170 kg/cm². The smoke point of ATF decreased with increase in liquid hourly space velocity at a constant reactor temperature. At a reactor temperature of 380°C, smoke point of ATF decreased from 25 to 17 mm as the liquid hourly space velocity was increased from 0.8 to 2.4 h⁻¹. Smoke point of ATF generally depends on aromatic content of the fuel. Aromatics contribute smoke; hence removal of aromatics increases smoke point. The increased aromatic saturation and cracking at higher severity normally leads to the formation of more saturated hydrocarbons at the expense of aromatics and result in high smoke point ATF. This was evident from the aromatic content of ATF fraction obtained from hydrocracking. The aromatic content of ATF fraction decreased from 21.6 to 4.3 wt% with increase in reactor temperature from 360 to 400°C at a constant liquid hourly space velocity of 0.8 h⁻¹. The aromatic content of the ATF decreased and the smoke point increased with reactor temperature at a constant liquid hourly space velocity and reactor operating pressure. Higher aromatic saturation and smoke point was observed with decrease in LHSV while maintaining other operating conditions constant.
Table 5.11  Properties of ATF Fraction (140 – 250°C) Obtained from Pilot Plant Reactors for Vacuum Gas Oil Feedstock at a LHSV of 0.8 h⁻¹

<table>
<thead>
<tr>
<th>Operating Conditions / Property</th>
<th>Run#1</th>
<th>Run#2</th>
<th>Run#3</th>
<th>Run#4</th>
</tr>
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<tbody>
<tr>
<td>Reactor Temperature, °C</td>
<td>360</td>
<td>380</td>
<td>400</td>
<td>380</td>
</tr>
<tr>
<td>Reactor Pressure, kg/cm²</td>
<td>170</td>
<td>170</td>
<td>170</td>
<td>120</td>
</tr>
<tr>
<td>H₂/oil Ratio, m³/m³</td>
<td>845</td>
<td>845</td>
<td>845</td>
<td>845</td>
</tr>
<tr>
<td>Density at 15°C, gm/cc</td>
<td>0.8436</td>
<td>0.8232</td>
<td>0.8013</td>
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</tr>
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<td>API Gravity</td>
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<td>40.4</td>
<td>45.1</td>
<td>40.0</td>
</tr>
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<td>Flash Point, °C</td>
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<td>47</td>
<td>&lt;27</td>
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<tr>
<td>Smoke Point, °C</td>
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<td>20</td>
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<td>Copper Strip Corrosion (2 h @ 100°C)</td>
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<td>Doctor’s Test</td>
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</tr>
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<td>4.3</td>
<td>20.8</td>
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<td>Sulphur, ppmw</td>
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<td>10</td>
<td>36</td>
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<tr>
<td>Mercaptans, ppmw</td>
<td>14</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Nitrogen, ppmw</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
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<td><strong>ASTM Distillation D-86</strong></td>
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<td></td>
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<tr>
<td>IBP, °C</td>
<td>146</td>
<td>148</td>
<td>135</td>
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<tr>
<td>10 vol.%, °C</td>
<td>179</td>
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<td>170</td>
<td>170</td>
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<td>40 vol.%, °C</td>
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<td>186</td>
<td>193</td>
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<td>50 vol.%, °C</td>
<td>206</td>
<td>197</td>
<td>194</td>
<td>201</td>
</tr>
<tr>
<td>60 vol.%, °C</td>
<td>213</td>
<td>203</td>
<td>199</td>
<td>210</td>
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<td>70 vol.%, °C</td>
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<td>209</td>
<td>207</td>
<td>215</td>
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<td>80 vol.%, °C</td>
<td>226</td>
<td>215</td>
<td>215</td>
<td>223</td>
</tr>
<tr>
<td>90 vol.%, °C</td>
<td>235</td>
<td>224</td>
<td>221</td>
<td>234</td>
</tr>
<tr>
<td>FBP, °C</td>
<td>250</td>
<td>235</td>
<td>243</td>
<td>246</td>
</tr>
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</table>
Table 5.12  Properties of ATF Fraction (140 – 250°C) Obtained from Pilot Plant Reactors for Vacuum Gas Oil Feedstock at a LHSV of 1.6 h⁻¹

<table>
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<tr>
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<th>Run#5</th>
<th>Run#6</th>
<th>Run#7</th>
</tr>
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<td>Reactor Temperature, °C</td>
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<td>380</td>
<td>400</td>
</tr>
<tr>
<td>Reactor Pressure, kg/cm²</td>
<td>170</td>
<td>170</td>
<td>170</td>
</tr>
<tr>
<td>H₂/oil Ratio, m³/m³</td>
<td>845</td>
<td>845</td>
<td>845</td>
</tr>
<tr>
<td>Density at 15°C, gm/cc</td>
<td>0.8577</td>
<td>0.8482</td>
<td>0.8206</td>
</tr>
<tr>
<td>API Gravity</td>
<td>33.5</td>
<td>35.3</td>
<td>40.9</td>
</tr>
<tr>
<td>Flash Point, °C</td>
<td>54</td>
<td>50</td>
<td>48</td>
</tr>
<tr>
<td>Smoke Point, °C</td>
<td>18</td>
<td>20</td>
<td>21</td>
</tr>
<tr>
<td>Saturates, wt.%</td>
<td>63.1</td>
<td>73.3</td>
<td>87.4</td>
</tr>
<tr>
<td>Aromatics, wt.%</td>
<td>36.9</td>
<td>26.7</td>
<td>12.6</td>
</tr>
<tr>
<td>Sulphur, ppmw</td>
<td>85</td>
<td>50</td>
<td>28</td>
</tr>
<tr>
<td>Mercaptans, ppmw</td>
<td>33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrogen, ppmw</td>
<td>9</td>
<td>6</td>
<td>BDL</td>
</tr>
<tr>
<td><strong>ASTM Distillation D-86</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IBP, °C</td>
<td>149</td>
<td>147</td>
<td>145</td>
</tr>
<tr>
<td>10 vol.%, °C</td>
<td>180</td>
<td>175</td>
<td>171</td>
</tr>
<tr>
<td>20 vol.%, °C</td>
<td>186</td>
<td>181</td>
<td>178</td>
</tr>
<tr>
<td>30 vol.%, °C</td>
<td>194</td>
<td>185</td>
<td>184</td>
</tr>
<tr>
<td>40 vol.%, °C</td>
<td>200</td>
<td>196</td>
<td>192</td>
</tr>
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<td>50 vol.%, °C</td>
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<td>205</td>
</tr>
<tr>
<td>70 vol.%, °C</td>
<td>219</td>
<td>214</td>
<td>212</td>
</tr>
<tr>
<td>80 vol.%, °C</td>
<td>226</td>
<td>218</td>
<td>219</td>
</tr>
<tr>
<td>90 vol.%, °C</td>
<td>236</td>
<td>227</td>
<td>227</td>
</tr>
<tr>
<td>FBP, °C</td>
<td>251</td>
<td>248</td>
<td>244</td>
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</table>
Table 5.13  Properties of ATF Fraction (140 – 250°C) Obtained from Pilot Plant Reactors for Vacuum Gas Oil Feedstock at a LHSV of 2.4 h⁻¹

<table>
<thead>
<tr>
<th>Operating Conditions / Property</th>
<th>Run#8</th>
<th>Run#9</th>
<th>Run#10</th>
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</thead>
<tbody>
<tr>
<td>Reactor Temperature, °C</td>
<td>360</td>
<td>380</td>
<td>400</td>
</tr>
<tr>
<td>Reactor Pressure, kg/cm²</td>
<td>170</td>
<td>170</td>
<td>170</td>
</tr>
<tr>
<td>H₂/oil Ratio, m³/m³</td>
<td>845</td>
<td>845</td>
<td>845</td>
</tr>
<tr>
<td>Density at 15°C, gm/cc</td>
<td>0.8672</td>
<td>0.8561</td>
<td>0.8250</td>
</tr>
<tr>
<td>API Gravity</td>
<td>31.7</td>
<td>33.8</td>
<td>40.0</td>
</tr>
<tr>
<td>Flash Point, °C</td>
<td>57</td>
<td>52</td>
<td>50</td>
</tr>
<tr>
<td>Smoke Point, °C</td>
<td>16</td>
<td>17</td>
<td>18</td>
</tr>
<tr>
<td>Saturates, wt.%</td>
<td>56.5</td>
<td>61.0</td>
<td>81.0</td>
</tr>
<tr>
<td>Aromatics, wt.%</td>
<td>43.5</td>
<td>39.0</td>
<td>19.0</td>
</tr>
<tr>
<td>Sulphur, ppmw</td>
<td>125</td>
<td>61</td>
<td>36</td>
</tr>
<tr>
<td>Mercaptans, ppmw</td>
<td></td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>Nitrogen, ppmw</td>
<td>15</td>
<td>12</td>
<td>8</td>
</tr>
<tr>
<td><strong>ASTM Distillation D-86</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IBP, °C</td>
<td>148</td>
<td>146</td>
<td>145</td>
</tr>
<tr>
<td>10 vol.%., °C</td>
<td>180</td>
<td>175</td>
<td>170</td>
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<tr>
<td>20 vol.%., °C</td>
<td>187</td>
<td>180</td>
<td>179</td>
</tr>
<tr>
<td>30 vol.%., °C</td>
<td>199</td>
<td>197</td>
<td>197</td>
</tr>
<tr>
<td>40 vol.%., °C</td>
<td>201</td>
<td>201</td>
<td>200</td>
</tr>
<tr>
<td>50 vol.%., °C</td>
<td>210</td>
<td>210</td>
<td>208</td>
</tr>
<tr>
<td>60 vol.%., °C</td>
<td>214</td>
<td>215</td>
<td>212</td>
</tr>
<tr>
<td>70 vol.%., °C</td>
<td>219</td>
<td>218</td>
<td>216</td>
</tr>
<tr>
<td>80 vol.%., °C</td>
<td>225</td>
<td>224</td>
<td>221</td>
</tr>
<tr>
<td>90 vol.%., °C</td>
<td>238</td>
<td>237</td>
<td>235</td>
</tr>
<tr>
<td>FBP, °C</td>
<td>251</td>
<td>250</td>
<td>249</td>
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</table>
Table 5.14  Properties of ATF Fraction (140 – 250°C) Obtained from Pilot Plant Reactors for 80% Vacuum Gas Oil + 20% DAO Blend at a LHSV of 0.8 h⁻¹

<table>
<thead>
<tr>
<th>Operating Conditions / Property</th>
<th>Run#11</th>
<th>Run#12</th>
<th>Run#13</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor Temperature, °C</td>
<td>360</td>
<td>380</td>
<td>400</td>
</tr>
<tr>
<td>Reactor Pressure, kg/cm²</td>
<td>170</td>
<td>170</td>
<td>170</td>
</tr>
<tr>
<td>H₂/oil Ratio, m³/m³</td>
<td>845</td>
<td>845</td>
<td>845</td>
</tr>
<tr>
<td>Density at 15°C, gm/cc</td>
<td>0.8492</td>
<td>0.8256</td>
<td>0.8037</td>
</tr>
<tr>
<td>API Gravity</td>
<td>35.1</td>
<td>39.9</td>
<td>44.6</td>
</tr>
<tr>
<td>Flash Point, °C</td>
<td>54</td>
<td>50</td>
<td>35</td>
</tr>
<tr>
<td>Smoke Point, °C</td>
<td>18</td>
<td>23</td>
<td>25</td>
</tr>
<tr>
<td>Copper Strip Corrosion (2 h @ 100°C)</td>
<td></td>
<td></td>
<td>1A</td>
</tr>
<tr>
<td>Doctor’s Test</td>
<td></td>
<td></td>
<td>Negative</td>
</tr>
<tr>
<td>Freezing Point, °C</td>
<td></td>
<td></td>
<td>-48</td>
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<tr>
<td>Saturates, wt.%</td>
<td>76.8</td>
<td>89.9</td>
<td>93.9</td>
</tr>
<tr>
<td>Aromatics, wt.%</td>
<td>23.2</td>
<td>10.1</td>
<td>6.1</td>
</tr>
<tr>
<td>Sulphur, ppmw</td>
<td>43</td>
<td>20</td>
<td>12</td>
</tr>
<tr>
<td>Mercaptans, ppmw</td>
<td></td>
<td></td>
<td>14</td>
</tr>
<tr>
<td>Nitrogen, ppmw</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>ASTM Distillation D-86</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IBP, °C</td>
<td>141</td>
<td>137</td>
<td>135</td>
</tr>
<tr>
<td>10 vol.%, °C</td>
<td>178</td>
<td>176</td>
<td>175</td>
</tr>
<tr>
<td>20 vol.%, °C</td>
<td>184</td>
<td>182</td>
<td>180</td>
</tr>
<tr>
<td>30 vol.%, °C</td>
<td>189</td>
<td>188</td>
<td>185</td>
</tr>
<tr>
<td>40 vol.%, °C</td>
<td>198</td>
<td>195</td>
<td>192</td>
</tr>
<tr>
<td>50 vol.%, °C</td>
<td>204</td>
<td>201</td>
<td>200</td>
</tr>
<tr>
<td>60 vol.%, °C</td>
<td>209</td>
<td>208</td>
<td>205</td>
</tr>
<tr>
<td>70 vol.%, °C</td>
<td>215</td>
<td>215</td>
<td>214</td>
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<tr>
<td>80 vol.%, °C</td>
<td>223</td>
<td>223</td>
<td>221</td>
</tr>
<tr>
<td>90 vol.%, °C</td>
<td>235</td>
<td>230</td>
<td>230</td>
</tr>
<tr>
<td>FBP, °C</td>
<td>251</td>
<td>245</td>
<td>241</td>
</tr>
</tbody>
</table>
The sulphur and nitrogen content of ATF fraction obtained by hydrocracking was found to be very low in all the hydrocracked products. As can be seen from Table 5.11, ATF obtained during hydrocracking was of very high quality with respect to other product specifications also. The freezing point of ATF fraction was −51 under typical operating conditions of hydrocracker meeting the specifications. The pilot plant data showed that the aviation turbine fuel produced from pilot plant under typical operating conditions of once-through hydrocracking unit was meeting all the specifications and could be directly used as fuel.

The properties of kerosene fraction obtained from pilot plant reactors for both the feedstock are presented in Tables 5.15 to 5.18. The density of kerosene fraction decreased with increasing reactor temperature and decrease in LHSV due to increased hydrogen uptake at higher operating severities. The effect of temperature and liquid hourly space velocity on smoke point of kerosene fraction is presented in Figure 5.7. The aromatic content of kerosene fraction decreased and the smoke point increased with increase in reactor temperature for a constant liquid hourly space velocity. At a constant reactor temperature, the aromatic content of kerosene decreased and smoke point increased with decrease in liquid hourly space velocity.

The sulphur and nitrogen content of kerosene fraction was found to be very low under all the hydrocracking conditions employed in the present work. Under typical operating conditions of industrial once-through hydrocracker unit, the kerosene fraction was found to meet all the specifications such as copper strip corrosion, smoke point (25 mm) and sulphur. The reason for better quality of kerosene from hydrocracker unit is due to increased saturation of kerosene fraction under hydrocracking conditions.
Table 5.15  Properties of Kerosene Fraction (140 - 270°C) Obtained from Pilot Plant Reactors for Vacuum Gas Oil Feedstock at a LHSV of 0.8 h⁻¹

<table>
<thead>
<tr>
<th>Operating Conditions / Property</th>
<th>Run#1</th>
<th>Run#2</th>
<th>Run#3</th>
<th>Run#4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor Temperature, °C</td>
<td>360</td>
<td>380</td>
<td>400</td>
<td>380</td>
</tr>
<tr>
<td>Reactor Pressure, kg/cm²</td>
<td>170</td>
<td>170</td>
<td>170</td>
<td>120</td>
</tr>
<tr>
<td>H₂/oil Ratio, m³/m³</td>
<td>845</td>
<td>845</td>
<td>845</td>
<td>845</td>
</tr>
<tr>
<td>Density at 15°C, gm/cc</td>
<td>0.8499</td>
<td>0.8290</td>
<td>0.8045</td>
<td>0.8325</td>
</tr>
<tr>
<td>API Gravity</td>
<td>35.0</td>
<td>39.2</td>
<td>44.4</td>
<td>38.5</td>
</tr>
<tr>
<td>Flash Point, °C</td>
<td>54</td>
<td>51</td>
<td>38</td>
<td>51</td>
</tr>
<tr>
<td>Smoke Point, °C</td>
<td>22</td>
<td>25</td>
<td>27</td>
<td>20</td>
</tr>
<tr>
<td>Colour, Saybolt</td>
<td></td>
<td>+22</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Copper Strip Corrosion (3 h @ 50°C)</td>
<td></td>
<td></td>
<td>1 A</td>
<td></td>
</tr>
<tr>
<td>Saturates, wt.%</td>
<td>81.4</td>
<td>91.5</td>
<td>96.0</td>
<td>79.8</td>
</tr>
<tr>
<td>Aromatics, wt%</td>
<td>18.6</td>
<td>8.5</td>
<td>4.0</td>
<td>20.2</td>
</tr>
<tr>
<td>Sulphur, ppmw</td>
<td>42</td>
<td>20</td>
<td>12</td>
<td>38</td>
</tr>
<tr>
<td>Mercaptans, ppmw</td>
<td></td>
<td>15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrogen, ppmw</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>ASTM Distillation D-86</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IBP, °C</td>
<td>152</td>
<td>152</td>
<td>141</td>
<td>154</td>
</tr>
<tr>
<td>10 vol.%., °C</td>
<td>183</td>
<td>178</td>
<td>173</td>
<td>176</td>
</tr>
<tr>
<td>20 vol.%., °C</td>
<td>191</td>
<td>186</td>
<td>177</td>
<td>182</td>
</tr>
<tr>
<td>30 vol.%., °C</td>
<td>199</td>
<td>193</td>
<td>186</td>
<td>193</td>
</tr>
<tr>
<td>40 vol.%., °C</td>
<td>207</td>
<td>200</td>
<td>193</td>
<td>200</td>
</tr>
<tr>
<td>50 vol.%., °C</td>
<td>216</td>
<td>208</td>
<td>205</td>
<td>207</td>
</tr>
<tr>
<td>60 vol.%., °C</td>
<td>224</td>
<td>215</td>
<td>212</td>
<td>214</td>
</tr>
<tr>
<td>70 vol.%., °C</td>
<td>231</td>
<td>223</td>
<td>220</td>
<td>219</td>
</tr>
<tr>
<td>80 vol.%., °C</td>
<td>239</td>
<td>231</td>
<td>229</td>
<td>226</td>
</tr>
<tr>
<td>90 vol.%., °C</td>
<td>251</td>
<td>240</td>
<td>237</td>
<td>243</td>
</tr>
<tr>
<td>FBP, °C</td>
<td>269</td>
<td>261</td>
<td>258</td>
<td>263</td>
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</table>
Table 5.16 Properties of Kerosene Fraction (140 - 270°C) Obtained from Pilot Plant Reactors for Vacuum Gas Oil Feedstock at a LHSV of 1.6 h⁻¹

<table>
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<tr>
<th>Operating Conditions / Property</th>
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<th>Run#6</th>
<th>Run#7</th>
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<tr>
<td>Reactor Temperature, °C</td>
<td>360</td>
<td>380</td>
<td>400</td>
</tr>
<tr>
<td>Reactor Pressure, kg/cm²</td>
<td>170</td>
<td>170</td>
<td>170</td>
</tr>
<tr>
<td>H₂/oil Ratio, m³/m³</td>
<td>845</td>
<td>845</td>
<td>845</td>
</tr>
<tr>
<td>Density at 15°C, gm/cc</td>
<td>0.8684</td>
<td>0.8558</td>
<td>0.8244</td>
</tr>
<tr>
<td>API Gravity</td>
<td>31.4</td>
<td>33.8</td>
<td>40.1</td>
</tr>
<tr>
<td>Flash Point, °C</td>
<td>58</td>
<td>56</td>
<td>51</td>
</tr>
<tr>
<td>Smoke Point, °C</td>
<td>17</td>
<td>18</td>
<td>19</td>
</tr>
<tr>
<td>Saturates, wt.%</td>
<td>61.2</td>
<td>72.3</td>
<td>87.6</td>
</tr>
<tr>
<td>Aromatics, wt.%</td>
<td>38.8</td>
<td>27.7</td>
<td>12.4</td>
</tr>
<tr>
<td>Sulphur, ppmw</td>
<td>92</td>
<td>55</td>
<td>32</td>
</tr>
<tr>
<td>Mercaptans, ppmw</td>
<td>37</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrogen, ppmw</td>
<td>11</td>
<td>8</td>
<td>5</td>
</tr>
<tr>
<td><strong>ASTM Distillation D-86</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>IBP, °C</td>
<td>153</td>
<td>152</td>
<td>149</td>
</tr>
<tr>
<td>10 vol.%, °C</td>
<td>179</td>
<td>181</td>
<td>180</td>
</tr>
<tr>
<td>20 vol.%, °C</td>
<td>191</td>
<td>193</td>
<td>188</td>
</tr>
<tr>
<td>30 vol.%, °C</td>
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<td>202</td>
<td>195</td>
</tr>
<tr>
<td>40 vol.%, °C</td>
<td>209</td>
<td>207</td>
<td>203</td>
</tr>
<tr>
<td>50 vol.%, °C</td>
<td>217</td>
<td>218</td>
<td>211</td>
</tr>
<tr>
<td>60 vol.%, °C</td>
<td>226</td>
<td>224</td>
<td>219</td>
</tr>
<tr>
<td>70 vol.%, °C</td>
<td>232</td>
<td>232</td>
<td>228</td>
</tr>
<tr>
<td>80 vol.%, °C</td>
<td>240</td>
<td>241</td>
<td>236</td>
</tr>
<tr>
<td>90 vol.%, °C</td>
<td>255</td>
<td>252</td>
<td>250</td>
</tr>
<tr>
<td>FBP, °C</td>
<td>270</td>
<td>270</td>
<td>263</td>
</tr>
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</table>
Table 5.17  Properties of Kerosene Fraction (140 - 270°C) Obtained from Pilot Plant Reactors for Vacuum Gas Oil Feedstock at a LHSV of 2.4 h⁻¹

<table>
<thead>
<tr>
<th>Operating Conditions / Property</th>
<th>Run#8</th>
<th>Run#9</th>
<th>Run#10</th>
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<tbody>
<tr>
<td>Reactor Temperature, °C</td>
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<td>380</td>
<td>400</td>
</tr>
<tr>
<td>Reactor Pressure, kg/cm²</td>
<td>170</td>
<td>170</td>
<td>170</td>
</tr>
<tr>
<td>H₂/oil Ratio, m³/m³</td>
<td>845</td>
<td>845</td>
<td>845</td>
</tr>
<tr>
<td>Density at 15°C, gm/cc</td>
<td>0.8720</td>
<td>0.8621</td>
<td>0.8302</td>
</tr>
<tr>
<td>API Gravity</td>
<td>30.8</td>
<td>32.6</td>
<td>38.9</td>
</tr>
<tr>
<td>Flash Point, °C</td>
<td>63</td>
<td>59</td>
<td>53</td>
</tr>
<tr>
<td>Smoke Point, °C</td>
<td>16</td>
<td>17</td>
<td>18</td>
</tr>
<tr>
<td>Saturates, wt.%</td>
<td>56.0</td>
<td>64.2</td>
<td>81.5</td>
</tr>
<tr>
<td>Aromatics, wt.%</td>
<td>44.0</td>
<td>35.8</td>
<td>18.5</td>
</tr>
<tr>
<td>Sulphur, ppmw</td>
<td>135</td>
<td>66</td>
<td>40</td>
</tr>
<tr>
<td>Mercaptans, ppmw</td>
<td></td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>Nitrogen, ppmw</td>
<td>20</td>
<td>16</td>
<td>10</td>
</tr>
<tr>
<td><strong>ASTM Distillation D-86</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IBP, °C</td>
<td>155</td>
<td>153</td>
<td>150</td>
</tr>
<tr>
<td>10 vol.% , °C</td>
<td>181</td>
<td>180</td>
<td>177</td>
</tr>
<tr>
<td>20 vol.% , °C</td>
<td>194</td>
<td>192</td>
<td>189</td>
</tr>
<tr>
<td>30 vol.% , °C</td>
<td>204</td>
<td>201</td>
<td>201</td>
</tr>
<tr>
<td>40 vol.% , °C</td>
<td>210</td>
<td>206</td>
<td>205</td>
</tr>
<tr>
<td>50 vol.% , °C</td>
<td>219</td>
<td>218</td>
<td>215</td>
</tr>
<tr>
<td>60 vol.% , °C</td>
<td>226</td>
<td>225</td>
<td>221</td>
</tr>
<tr>
<td>70 vol.% , °C</td>
<td>233</td>
<td>231</td>
<td>227</td>
</tr>
<tr>
<td>80 vol.% , °C</td>
<td>256</td>
<td>250</td>
<td>242</td>
</tr>
<tr>
<td>90 vol.% , °C</td>
<td>260</td>
<td>259</td>
<td>247</td>
</tr>
<tr>
<td>FBP, °C</td>
<td>270</td>
<td>270</td>
<td>269</td>
</tr>
</tbody>
</table>
Table 5.18  Properties of Kerosene Fraction (140 - 270°C) Obtained from Pilot Plant Reactors for 80% Vacuum Gas Oil + 20% DAO Blend at a LHSV of 0.8 h⁻¹

<table>
<thead>
<tr>
<th>Operating Conditions / Property</th>
<th>Run#11</th>
<th>Run#12</th>
<th>Run#13</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor Temperature, °C</td>
<td>360</td>
<td>380</td>
<td>400</td>
</tr>
<tr>
<td>Reactor Pressure, kg/cm²</td>
<td>170</td>
<td>170</td>
<td>170</td>
</tr>
<tr>
<td>H₂/oil Ratio, m³/m³</td>
<td>845</td>
<td>845</td>
<td>845</td>
</tr>
<tr>
<td>Density at 15°C, gm/cc</td>
<td>0.8516</td>
<td>0.8289</td>
<td>0.8049</td>
</tr>
<tr>
<td>API Gravity</td>
<td>34.7</td>
<td>39.2</td>
<td>44.3</td>
</tr>
<tr>
<td>Flash Point, °C</td>
<td>55</td>
<td>52</td>
<td>44</td>
</tr>
<tr>
<td>Smoke Point, °C</td>
<td>16</td>
<td>20</td>
<td>23</td>
</tr>
<tr>
<td>Colour, Saybolt</td>
<td></td>
<td>+22</td>
<td></td>
</tr>
<tr>
<td>Copper Strip Corrosion (3 h @ 50°C)</td>
<td></td>
<td>1A</td>
<td></td>
</tr>
<tr>
<td>Saturates, wt.%</td>
<td>74.1</td>
<td>89.5</td>
<td>92.7</td>
</tr>
<tr>
<td>Aromatics, wt.%</td>
<td>25.9</td>
<td>10.5</td>
<td>7.3</td>
</tr>
<tr>
<td>Sulphur, ppmw</td>
<td>45</td>
<td>23</td>
<td>15</td>
</tr>
<tr>
<td>Mercaptans, ppmw</td>
<td></td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>Nitrogen, ppmw</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td><strong>ASTM Distillation D-86</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IBP, °C</td>
<td>153</td>
<td>152</td>
<td>143</td>
</tr>
<tr>
<td>10 vol.%, °C</td>
<td>181</td>
<td>179</td>
<td>177</td>
</tr>
<tr>
<td>20 vol.%, °C</td>
<td>191</td>
<td>185</td>
<td>182</td>
</tr>
<tr>
<td>30 vol.%, °C</td>
<td>199</td>
<td>192</td>
<td>189</td>
</tr>
<tr>
<td>40 vol.%, °C</td>
<td>204</td>
<td>203</td>
<td>198</td>
</tr>
<tr>
<td>50 vol.%, °C</td>
<td>213</td>
<td>211</td>
<td>209</td>
</tr>
<tr>
<td>60 vol.%, °C</td>
<td>225</td>
<td>217</td>
<td>215</td>
</tr>
<tr>
<td>70 vol.%, °C</td>
<td>230</td>
<td>221</td>
<td>219</td>
</tr>
<tr>
<td>80 vol.%, °C</td>
<td>238</td>
<td>229</td>
<td>227</td>
</tr>
<tr>
<td>90 vol.%, °C</td>
<td>255</td>
<td>236</td>
<td>235</td>
</tr>
<tr>
<td>FBP, °C</td>
<td>270</td>
<td>265</td>
<td>265</td>
</tr>
</tbody>
</table>
The properties of diesel fraction obtained from pilot plant reactors for both the feedstock are presented in Tables 5.19 to 5.22 and Figures 5.8 to 5.10. As can be seen from Figure 5.8, the diesel fraction became lighter at higher operating severity due to increased hydrogen addition as observed with other hydrocracked products. The aromatic content of diesel fraction decreased with increase in reactor temperature for a constant liquid hourly space velocity as shown in Figure 5.9. Under typical operating conditions of hydrocracking process, an aromatic content of 5.2 wt% was observed in the diesel fraction. Under most of the operating conditions employed in the present work, the aromatic content of diesel was observed to be very low in the range of 3.2 to 19.9 wt%. The effect of temperature and liquid hourly space velocity on calculated cetane number of diesel is shown in Figure 5.10.
Table 5.19  Properties of Diesel Fraction (270 - 370°C) Obtained from Pilot Plant Reactors for Vacuum Gas Oil Feedstock at a LHSV of 0.8 h⁻¹

<table>
<thead>
<tr>
<th>Operating Conditions / Property</th>
<th>Run#1</th>
<th>Run#2</th>
<th>Run#3</th>
<th>Run#4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor Temperature, °C</td>
<td>360</td>
<td>380</td>
<td>400</td>
<td>380</td>
</tr>
<tr>
<td>Reactor Pressure, kg/cm²</td>
<td>170</td>
<td>170</td>
<td>170</td>
<td>120</td>
</tr>
<tr>
<td>H₂/oil Ratio, m³/m³</td>
<td>845</td>
<td>845</td>
<td>845</td>
<td>845</td>
</tr>
<tr>
<td>Density at 15°C, gm/cc</td>
<td>0.8661</td>
<td>0.8367</td>
<td>0.8221</td>
<td>0.8473</td>
</tr>
<tr>
<td>API Gravity</td>
<td>31.9</td>
<td>37.6</td>
<td>40.6</td>
<td>35.5</td>
</tr>
<tr>
<td>Flash Point, °C</td>
<td>154</td>
<td>132</td>
<td>125</td>
<td>134</td>
</tr>
<tr>
<td>Pour Point, °C</td>
<td>+3</td>
<td>0</td>
<td>-24</td>
<td>-6</td>
</tr>
<tr>
<td>Viscosity at 40°C, cSt</td>
<td>6.6</td>
<td>5.71</td>
<td>4.28</td>
<td>6.2</td>
</tr>
<tr>
<td>Aniline Point, °C</td>
<td>77.5</td>
<td>84</td>
<td>92.8</td>
<td>79.5</td>
</tr>
<tr>
<td>Cetane Number, Calc.</td>
<td>49.4</td>
<td>58.8</td>
<td>68.2</td>
<td>54.8</td>
</tr>
<tr>
<td>RCR, wt.%</td>
<td>0.05</td>
<td>0.03</td>
<td>0.015</td>
<td>0.05</td>
</tr>
<tr>
<td>Saturates, wt.%</td>
<td>86.2</td>
<td>94.8</td>
<td>96.8</td>
<td>80.9</td>
</tr>
<tr>
<td>Aromatics, wt.%</td>
<td>13.8</td>
<td>5.2</td>
<td>3.2</td>
<td>19.1</td>
</tr>
<tr>
<td>Sulphur, ppmw</td>
<td>33</td>
<td>15</td>
<td>8</td>
<td>40</td>
</tr>
<tr>
<td>Nitrogen, ppmw</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>5</td>
</tr>
<tr>
<td>ASTM Distillation D-86</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IBP, °C</td>
<td>266</td>
<td>260</td>
<td>255</td>
<td>261</td>
</tr>
<tr>
<td>10 vol.%, °C</td>
<td>292</td>
<td>285</td>
<td>277</td>
<td>286</td>
</tr>
<tr>
<td>20 vol.%, °C</td>
<td>297</td>
<td>291</td>
<td>281</td>
<td>292</td>
</tr>
<tr>
<td>30 vol.%, °C</td>
<td>305</td>
<td>295</td>
<td>286</td>
<td>296</td>
</tr>
<tr>
<td>40 vol.%, °C</td>
<td>314</td>
<td>301</td>
<td>293</td>
<td>302</td>
</tr>
<tr>
<td>50 vol.%, °C</td>
<td>325</td>
<td>307</td>
<td>309</td>
<td>308</td>
</tr>
<tr>
<td>60 vol.%, °C</td>
<td>331</td>
<td>315</td>
<td>315</td>
<td>316</td>
</tr>
<tr>
<td>70 vol.%, °C</td>
<td>338</td>
<td>322</td>
<td>322</td>
<td>322</td>
</tr>
<tr>
<td>80 vol.%, °C</td>
<td>343</td>
<td>329</td>
<td>331</td>
<td>329</td>
</tr>
<tr>
<td>90 vol.%, °C</td>
<td>350</td>
<td>340</td>
<td>342</td>
<td>342</td>
</tr>
<tr>
<td>FBP, °C</td>
<td>365</td>
<td>364</td>
<td>364</td>
<td>369</td>
</tr>
</tbody>
</table>
Table 5.20  Properties of Diesel Fraction (270 - 370°C) Obtained from Pilot Plant Reactors for Vacuum Gas Oil Feedstock at a LHSV of 1.6 h⁻¹

<table>
<thead>
<tr>
<th>Operating Conditions / Property</th>
<th>Run#5</th>
<th>Run#6</th>
<th>Run#7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor Temperature, °C</td>
<td>360</td>
<td>380</td>
<td>400</td>
</tr>
<tr>
<td>Reactor Pressure, kg/cm²</td>
<td>170</td>
<td>170</td>
<td>170</td>
</tr>
<tr>
<td>H₂/oil Ratio, m³/m³</td>
<td>845</td>
<td>845</td>
<td>845</td>
</tr>
<tr>
<td>Density at 15°C, gm/cc</td>
<td>0.8850</td>
<td>0.8444</td>
<td>0.8320</td>
</tr>
<tr>
<td>API Gravity</td>
<td>28.4</td>
<td>36.1</td>
<td>38.6</td>
</tr>
<tr>
<td>Flash Point, °C</td>
<td>164</td>
<td>140</td>
<td>130</td>
</tr>
<tr>
<td>Pour Point, °C</td>
<td>6</td>
<td>-6</td>
<td>-3</td>
</tr>
<tr>
<td>Viscosity at 40°C, cSt</td>
<td>8.1</td>
<td>6.5</td>
<td>4.8</td>
</tr>
<tr>
<td>Aniline Point, °C</td>
<td>75.8</td>
<td>80.0</td>
<td>84.0</td>
</tr>
<tr>
<td>Cetane Number, Calc.</td>
<td>42.9</td>
<td>55.8</td>
<td>60.9</td>
</tr>
<tr>
<td>RCR, wt.%</td>
<td>0.06</td>
<td>0.06</td>
<td>0.05</td>
</tr>
<tr>
<td>Saturates, wt.%</td>
<td>82.0</td>
<td>91.0</td>
<td>93.7</td>
</tr>
<tr>
<td>Aromatics, wt.%</td>
<td>18.0</td>
<td>9.0</td>
<td>6.3</td>
</tr>
<tr>
<td>Sulphur, ppmw</td>
<td>140</td>
<td>70</td>
<td>40</td>
</tr>
<tr>
<td>Nitrogen, ppmw</td>
<td>31</td>
<td>12</td>
<td>6</td>
</tr>
<tr>
<td><strong>ASTM Distillation D-86</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IBP, °C</td>
<td>266</td>
<td>265</td>
<td>263</td>
</tr>
<tr>
<td>10 vol.%, °C</td>
<td>302</td>
<td>290</td>
<td>280</td>
</tr>
<tr>
<td>20 vol.%, °C</td>
<td>309</td>
<td>298</td>
<td>287</td>
</tr>
<tr>
<td>30 vol.%, °C</td>
<td>314</td>
<td>307</td>
<td>292</td>
</tr>
<tr>
<td>40 vol.%, °C</td>
<td>323</td>
<td>315</td>
<td>297</td>
</tr>
<tr>
<td>50 vol.%, °C</td>
<td>328</td>
<td>326</td>
<td>306</td>
</tr>
<tr>
<td>60 vol.%, °C</td>
<td>333</td>
<td>334</td>
<td>313</td>
</tr>
<tr>
<td>70 vol.%, °C</td>
<td>336</td>
<td>339</td>
<td>321</td>
</tr>
<tr>
<td>80 vol.%, °C</td>
<td>344</td>
<td>344</td>
<td>330</td>
</tr>
<tr>
<td>90 vol.%, °C</td>
<td>350</td>
<td>350</td>
<td>338</td>
</tr>
<tr>
<td>FBP, °C</td>
<td>369</td>
<td>364</td>
<td>362</td>
</tr>
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</table>
Table 5.21 Properties of Diesel Fraction (270 - 370°C) Obtained from Pilot Plant Reactors for Vacuum Gas Oil Feedstock at a LHSV of 2.4 h⁻¹

<table>
<thead>
<tr>
<th>Operating Conditions / Property</th>
<th>Run#8</th>
<th>Run#9</th>
<th>Run#10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor Temperature, °C</td>
<td>360</td>
<td>380</td>
<td>400</td>
</tr>
<tr>
<td>Reactor Pressure, kg/cm²</td>
<td>170</td>
<td>170</td>
<td>170</td>
</tr>
<tr>
<td>H₂/oil Ratio, m³/m³</td>
<td>845</td>
<td>845</td>
<td>845</td>
</tr>
<tr>
<td>Density at 15°C, gm/cc</td>
<td>0.8981</td>
<td>0.8545</td>
<td>0.8447</td>
</tr>
<tr>
<td>API Gravity</td>
<td>26.1</td>
<td>34.1</td>
<td>36.0</td>
</tr>
<tr>
<td>Flash Point, °C</td>
<td>168</td>
<td>144</td>
<td>135</td>
</tr>
<tr>
<td>Pour Point, °C</td>
<td>0</td>
<td>0</td>
<td>-3</td>
</tr>
<tr>
<td>Viscosity at 40°C, cSt</td>
<td>9.3</td>
<td>7.4</td>
<td>5.5</td>
</tr>
<tr>
<td>Aniline Point, °C</td>
<td>74.2</td>
<td>78.1</td>
<td>79.2</td>
</tr>
<tr>
<td>Cetane Number, Calc.</td>
<td>41.1</td>
<td>52.7</td>
<td>55.2</td>
</tr>
<tr>
<td>RCR, wt.%</td>
<td>0.07</td>
<td>0.06</td>
<td>0.05</td>
</tr>
<tr>
<td>Saturates, wt.%</td>
<td>80.1</td>
<td>89.0</td>
<td>92.1</td>
</tr>
<tr>
<td>Aromatics, wt.%</td>
<td>19.9</td>
<td>11.0</td>
<td>7.9</td>
</tr>
<tr>
<td>Sulphur, ppmw</td>
<td>590</td>
<td>260</td>
<td>72</td>
</tr>
<tr>
<td>Nitrogen, ppmw</td>
<td>66</td>
<td>32</td>
<td>14</td>
</tr>
<tr>
<td><strong>ASTM Distillation D-86</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IBP, °C</td>
<td>269</td>
<td>266</td>
<td>265</td>
</tr>
<tr>
<td>10 vol.%, °C</td>
<td>284</td>
<td>286</td>
<td>286</td>
</tr>
<tr>
<td>20 vol.%, °C</td>
<td>292</td>
<td>293</td>
<td>290</td>
</tr>
<tr>
<td>30 vol.%, °C</td>
<td>305</td>
<td>307</td>
<td>306</td>
</tr>
<tr>
<td>40 vol.%, °C</td>
<td>314</td>
<td>317</td>
<td>315</td>
</tr>
<tr>
<td>50 vol.%, °C</td>
<td>322</td>
<td>322</td>
<td>321</td>
</tr>
<tr>
<td>60 vol.%, °C</td>
<td>330</td>
<td>333</td>
<td>330</td>
</tr>
<tr>
<td>70 vol.%, °C</td>
<td>341</td>
<td>340</td>
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<tr>
<td>80 vol.%, °C</td>
<td>349</td>
<td>348</td>
<td>345</td>
</tr>
<tr>
<td>90 vol.%, °C</td>
<td>354</td>
<td>352</td>
<td>351</td>
</tr>
<tr>
<td>FBP, °C</td>
<td>370</td>
<td>369</td>
<td>368</td>
</tr>
</tbody>
</table>
Table 5.22  Properties of Diesel Fraction (270 - 370°C) Obtained from Pilot Plant Reactors for 80% Vacuum Gas Oil + 20% DAO Blend at a LHSV of 0.8 h⁻¹

<table>
<thead>
<tr>
<th>Operating Conditions / Property</th>
<th>Run#11</th>
<th>Run#12</th>
<th>Run#13</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor Temperature, °C</td>
<td>360</td>
<td>380</td>
<td>400</td>
</tr>
<tr>
<td>Reactor Pressure, kg/cm²</td>
<td>170</td>
<td>170</td>
<td>170</td>
</tr>
<tr>
<td>H₂/oil Ratio, m³/m³</td>
<td>845</td>
<td>845</td>
<td>845</td>
</tr>
<tr>
<td>Density at 15°C, gm/cc</td>
<td>0.8698</td>
<td>0.8519</td>
<td>0.8301</td>
</tr>
<tr>
<td>API Gravity</td>
<td>31.2</td>
<td>34.6</td>
<td>39.0</td>
</tr>
<tr>
<td>Flash Point, °C</td>
<td>159</td>
<td>139</td>
<td>126</td>
</tr>
<tr>
<td>Pour Point, °C</td>
<td>0</td>
<td>-3</td>
<td>-21</td>
</tr>
<tr>
<td>Viscosity at 40°C, cSt</td>
<td>6.8</td>
<td>5.81</td>
<td>4.40</td>
</tr>
<tr>
<td>Aniline Point, °C</td>
<td>71.1</td>
<td>80.2</td>
<td>90.0</td>
</tr>
<tr>
<td>Cetane Number, Calc.</td>
<td>45.9</td>
<td>53.9</td>
<td>64.5</td>
</tr>
<tr>
<td>RCR, wt.%</td>
<td>0.06</td>
<td>0.06</td>
<td>0.04</td>
</tr>
<tr>
<td>Saturates, wt.%</td>
<td>84.1</td>
<td>91.1</td>
<td>95.9</td>
</tr>
<tr>
<td>Aromatics, wt.%</td>
<td>15.9</td>
<td>8.9</td>
<td>4.1</td>
</tr>
<tr>
<td>Sulphur, ppmw</td>
<td>38</td>
<td>18</td>
<td>10</td>
</tr>
<tr>
<td>Nitrogen, ppmw</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>ASTM Distillation D-86</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IBP, °C</td>
<td>268</td>
<td>263</td>
<td>261</td>
</tr>
<tr>
<td>10 vol.%, °C</td>
<td>289</td>
<td>286</td>
<td>284</td>
</tr>
<tr>
<td>20 vol.%, °C</td>
<td>291</td>
<td>291</td>
<td>290</td>
</tr>
<tr>
<td>30 vol.%, °C</td>
<td>299</td>
<td>297</td>
<td>296</td>
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<tr>
<td>40 vol.%, °C</td>
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<td>303</td>
</tr>
<tr>
<td>50 vol.%, °C</td>
<td>309</td>
<td>311</td>
<td>311</td>
</tr>
<tr>
<td>60 vol.%, °C</td>
<td>323</td>
<td>319</td>
<td>317</td>
</tr>
<tr>
<td>70 vol.%, °C</td>
<td>329</td>
<td>327</td>
<td>325</td>
</tr>
<tr>
<td>80 vol.%, °C</td>
<td>337</td>
<td>336</td>
<td>335</td>
</tr>
<tr>
<td>90 vol.%, °C</td>
<td>349</td>
<td>345</td>
<td>345</td>
</tr>
<tr>
<td>FBP, °C</td>
<td>367</td>
<td>366</td>
<td>360</td>
</tr>
</tbody>
</table>
Figure 5.8  Effect of temperature and LHSV on density of diesel fraction for VGO Feedstock

Figure 5.9  Effect of temperature and LHSV on aromatic content of diesel fraction for VGO Feedstock
The cetane number of the hydrocracked diesel was found to be very high under the operating conditions studied in pilot plant. The cetane number increased with increase in reactor temperature and decrease in LHSV due to higher paraffinicity. The cetane number of the hydrocracked diesel varied from 49.4 to 68.2 as the temperature was increased from 360 to 400°C at a constant LHSV of 0.8 h⁻¹. Since the aromatic content of diesel is related to its aniline point, the aniline point decreased with increase in aromatic content.

The sulphur and nitrogen content of diesel fraction was found to be very low under all the hydrocracking conditions. Under typical operating conditions of industrial once-through hydrocracker unit, the diesel fraction obtained from pilot plant had a sulphur content of 15 ppmw with traces of nitrogen indicating very good quality. The sulphur content of diesel varied from 33 to 8 ppmw as the reactor temperature was increased from 360 to 400°C at a constant LHSV of 0.8 h⁻¹. The diesel fraction obtained from pilot plant under typical hydrocracker operating conditions was found to meet all
the specifications and could be directly blended into diesel pool without further treatment due to increased saturation and lower heteroatoms.

The properties of unconverted oil (370°C+) obtained from pilot plant reactors are presented in Tables 5.23 to 5.26. The UCO fraction became lighter with lower density due to hydrogen addition during hydrocracking. The aromatic content of UCO fraction was observed to be very low in all the hydrocracked product fractions indicating very high hydrogenation rate of aromatic compounds during hydrocracking process. The increased saturates content of UCO during hydrocracking makes it an excellent feedstock for FCC and stream cracker units. The aromatic content in the range of 12.3 to 2.7 wt% was obtained as the temperature was increased from 360 to 400°C at a constant LHSV of 0.8 h⁻¹. The increase in temperature and decrease in LHSV increased the amount of saturation of UCO fraction. In the range of operating conditions studied, the aromatic content of UCO varied from 2.7 to 20 wt%.

Due to higher saturation of feedstock in hydrocracking, the UOP K factor of the UCO fraction increased compared to the feedstock. The vacuum gas oil feedstock used in the present work had UOP K factor of 12.0 and the hydrocracked products had UOP K in the range of 12.0 to 13.0 indicating highly paraffinic nature of the hydrocracker bottom product. In addition to increased amount of saturates, the UCO fraction contained very low sulphur and nitrogen making it ideal feedstock for FCC unit. The lower sulphur content of UCO fraction will result in very low sulphur levels in FCC product fractions and making them excellent blending stocks of high quality. The sulphur content of UCO under typical operating conditions of pilot plant hydrocracking experiments was found to be around 25 ppmw and the nitrogen was found to be below detectable limits. The RCR value of UCO was very low in the range of 0.03 to 0.09 compared to the feed RCR of 0.25 wt%. The reduced RCR of UCO fraction will result in lower amount of coke in FCC unit.
Table 5.23  Properties of Unconverted Oil (370°C+) Obtained from Pilot Plant Reactors for Vacuum Gas Oil Feedstock at a LHSV of 0.8 h⁻¹

<table>
<thead>
<tr>
<th>Operating Conditions / Property</th>
<th>Run#1</th>
<th>Run#2</th>
<th>Run#3</th>
<th>Run#4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor Temperature, °C</td>
<td>360</td>
<td>380</td>
<td>400</td>
<td>380</td>
</tr>
<tr>
<td>Reactor Pressure, kg/cm²</td>
<td>170</td>
<td>170</td>
<td>170</td>
<td>120</td>
</tr>
<tr>
<td>H₂/oil Ratio, m³/m³</td>
<td>845</td>
<td>845</td>
<td>845</td>
<td>845</td>
</tr>
<tr>
<td>Density at 15°C, gm/cc</td>
<td>0.8778</td>
<td>0.8549</td>
<td>0.8282</td>
<td>0.8712</td>
</tr>
<tr>
<td>API Gravity</td>
<td>29.7</td>
<td>34.0</td>
<td>39.4</td>
<td>30.9</td>
</tr>
<tr>
<td>Flash Point, COC, °C</td>
<td>248</td>
<td>245</td>
<td>240</td>
<td>244</td>
</tr>
<tr>
<td>Pour Point, °C</td>
<td>45</td>
<td>45</td>
<td>39</td>
<td>45</td>
</tr>
<tr>
<td>Viscosity at 100°C, cSt</td>
<td>5.7</td>
<td>4.83</td>
<td>4.1</td>
<td>5.24</td>
</tr>
<tr>
<td>Aniline Point, °C</td>
<td>109.5</td>
<td>115</td>
<td>119.3</td>
<td>110.5</td>
</tr>
<tr>
<td>UOP K</td>
<td>12.3</td>
<td>12.7</td>
<td>13.0</td>
<td>12.4</td>
</tr>
<tr>
<td>Saturates, wt.%</td>
<td>87.7</td>
<td>96.9</td>
<td>97.3</td>
<td>87.0</td>
</tr>
<tr>
<td>Aromatics, wt.%</td>
<td>12.3</td>
<td>4.6</td>
<td>2.7</td>
<td>13.0</td>
</tr>
<tr>
<td>RCR, wt.%</td>
<td>0.07</td>
<td>0.05</td>
<td>0.03</td>
<td>0.06</td>
</tr>
<tr>
<td>Sulphur, ppmw</td>
<td>42</td>
<td>25</td>
<td>20</td>
<td>54</td>
</tr>
<tr>
<td>Nitrogen, ppmw</td>
<td>10</td>
<td>BDL</td>
<td>BDL</td>
<td>20</td>
</tr>
<tr>
<td>Metals, V and Ni, ppmw</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
</tr>
</tbody>
</table>

**ASTM Distillation D-1160**

| IBP, °C                        | 369    | 347    | 337    | 355    |
| 10 vol.%, °C                   | 390    | 384    | 380    | 389    |
| 20 vol.%, °C                   | 402    | 401    | 400    | 404    |
| 30 vol.%, °C                   | 413    | 416    | 413    | 418    |
| 40 vol.%, °C                   | 428    | 426    | 424    | 430    |
| 50 vol.%, °C                   | 443    | 440    | 436    | 439    |
| 60 vol.%, °C                   | 448    | 448    | 447    | 452    |
| 70 vol.%, °C                   | 469    | 462    | 461    | 465    |
| 80 vol.%, °C                   | 488    | 477    | 475    | 479    |
| 90 vol.%, °C                   | 518    | 505    | 495    | 512    |
| FBP, °C                        | 569    | 570    | 569    | 576    |
Table 5.24  Properties of Unconverted Oil (370°C+) Obtained from Pilot Plant Reactors for Vacuum Gas Oil Feedstock at a LHSV of 1.6 h⁻¹

<table>
<thead>
<tr>
<th>Operating Conditions / Property</th>
<th>Run#5</th>
<th>Run#6</th>
<th>Run#7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor Temperature, °C</td>
<td>360</td>
<td>380</td>
<td>400</td>
</tr>
<tr>
<td>Reactor Pressure, kg/cm²</td>
<td>170</td>
<td>170</td>
<td>170</td>
</tr>
<tr>
<td>H₂/oil Ratio, m³/m³</td>
<td>845</td>
<td>845</td>
<td>845</td>
</tr>
<tr>
<td>Density at 15°C, gm/cc</td>
<td>0.9003</td>
<td>0.8842</td>
<td>0.8466</td>
</tr>
<tr>
<td>API Gravity</td>
<td>25.7</td>
<td>28.5</td>
<td>35.6</td>
</tr>
<tr>
<td>Flash Point, COC, °C</td>
<td>253</td>
<td>249</td>
<td>240</td>
</tr>
<tr>
<td>Pour Point, °C</td>
<td>45</td>
<td>43</td>
<td>42</td>
</tr>
<tr>
<td>Viscosity at 100°C, cSt</td>
<td>6.62</td>
<td>5.52</td>
<td>4.55</td>
</tr>
<tr>
<td>Aniline Point, °C</td>
<td>108.7</td>
<td>112.2</td>
<td>115.5</td>
</tr>
<tr>
<td>UOP K</td>
<td>12.0</td>
<td>12.2</td>
<td>12.7</td>
</tr>
<tr>
<td>Saturates, wt.%</td>
<td>83.2</td>
<td>90.8</td>
<td>94.8</td>
</tr>
<tr>
<td>Aromatics, wt.%</td>
<td>16.8</td>
<td>9.2</td>
<td>5.2</td>
</tr>
<tr>
<td>RCR, wt.%</td>
<td>0.08</td>
<td>0.07</td>
<td>0.06</td>
</tr>
<tr>
<td>Sulphur, ppmw</td>
<td>220</td>
<td>59</td>
<td>30</td>
</tr>
<tr>
<td>Nitrogen, ppmw</td>
<td>46</td>
<td>24</td>
<td>11</td>
</tr>
<tr>
<td>Metals, V and Ni, ppmw</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>ASTM Distillation D-1160</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IBP, °C</td>
<td>375</td>
<td>373</td>
<td>370</td>
</tr>
<tr>
<td>10 vol.%, °C</td>
<td>394</td>
<td>393</td>
<td>393</td>
</tr>
<tr>
<td>20 vol.%, °C</td>
<td>402</td>
<td>404</td>
<td>403</td>
</tr>
<tr>
<td>30 vol.%, °C</td>
<td>417</td>
<td>414</td>
<td>412</td>
</tr>
<tr>
<td>40 vol.%, °C</td>
<td>429</td>
<td>423</td>
<td>420</td>
</tr>
<tr>
<td>50 vol.%, °C</td>
<td>445</td>
<td>433</td>
<td>428</td>
</tr>
<tr>
<td>60 vol.%, °C</td>
<td>460</td>
<td>443</td>
<td>437</td>
</tr>
<tr>
<td>70 vol.%, °C</td>
<td>471</td>
<td>456</td>
<td>447</td>
</tr>
<tr>
<td>80 vol.%, °C</td>
<td>488</td>
<td>472</td>
<td>460</td>
</tr>
<tr>
<td>90 vol.%, °C</td>
<td>519</td>
<td>500</td>
<td>482</td>
</tr>
<tr>
<td>FBP, °C</td>
<td>579</td>
<td>576</td>
<td>568</td>
</tr>
</tbody>
</table>
Table 5.25  Properties of Unconverted Oil (370°C+) Obtained from Pilot Plant Reactors for Vacuum Gas Oil Feedstock at a LHSV of 2.4 h⁻¹

<table>
<thead>
<tr>
<th>Operating Conditions / Property</th>
<th>Run#8</th>
<th>Run#9</th>
<th>Run#10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor Temperature, °C</td>
<td>360</td>
<td>380</td>
<td>400</td>
</tr>
<tr>
<td>Reactor Pressure, kg/cm²</td>
<td>170</td>
<td>170</td>
<td>170</td>
</tr>
<tr>
<td>H₂/oil Ratio, m³/m³</td>
<td>845</td>
<td>845</td>
<td>845</td>
</tr>
<tr>
<td>Density at 15°C, gm/cc</td>
<td>0.9081</td>
<td>0.8905</td>
<td>0.8522</td>
</tr>
<tr>
<td>API Gravity</td>
<td>24.3</td>
<td>27.4</td>
<td>34.5</td>
</tr>
<tr>
<td>Flash Point, COC, °C</td>
<td>257</td>
<td>253</td>
<td>241</td>
</tr>
<tr>
<td>Pour Point, °C</td>
<td>42</td>
<td>42</td>
<td>39</td>
</tr>
<tr>
<td>Viscosity at 100°C, cSt</td>
<td>6.94</td>
<td>5.89</td>
<td>4.78</td>
</tr>
<tr>
<td>Aniline Point, °C</td>
<td>108.2</td>
<td>108.9</td>
<td>113.2</td>
</tr>
<tr>
<td>UOP K</td>
<td>11.9</td>
<td>12.1</td>
<td>12.6</td>
</tr>
<tr>
<td>Saturates, wt.%</td>
<td>80.0</td>
<td>87.5</td>
<td>91.3</td>
</tr>
<tr>
<td>Aromatics, wt.%</td>
<td>20.0</td>
<td>12.5</td>
<td>8.7</td>
</tr>
<tr>
<td>RCR, wt.%</td>
<td>0.09</td>
<td>0.08</td>
<td>0.07</td>
</tr>
<tr>
<td>Sulphur, ppmw</td>
<td>975</td>
<td>380</td>
<td>128</td>
</tr>
<tr>
<td>Nitrogen, ppmw</td>
<td>82</td>
<td>40</td>
<td>23</td>
</tr>
<tr>
<td>Metals, V and Ni, ppmw</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td><strong>ASTM Distillation D-1160</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IBP, °C</td>
<td>372</td>
<td>370</td>
<td>365</td>
</tr>
<tr>
<td>10 vol.%, °C</td>
<td>395</td>
<td>392</td>
<td>390</td>
</tr>
<tr>
<td>20 vol.%, °C</td>
<td>405</td>
<td>400</td>
<td>398</td>
</tr>
<tr>
<td>30 vol.%, °C</td>
<td>416</td>
<td>413</td>
<td>409</td>
</tr>
<tr>
<td>40 vol.%, °C</td>
<td>425</td>
<td>423</td>
<td>419</td>
</tr>
<tr>
<td>50 vol.%, °C</td>
<td>436</td>
<td>434</td>
<td>431</td>
</tr>
<tr>
<td>60 vol.%, °C</td>
<td>444</td>
<td>443</td>
<td>440</td>
</tr>
<tr>
<td>70 vol.%, °C</td>
<td>458</td>
<td>453</td>
<td>451</td>
</tr>
<tr>
<td>80 vol.%, °C</td>
<td>476</td>
<td>477</td>
<td>477</td>
</tr>
<tr>
<td>90 vol.%, °C</td>
<td>509</td>
<td>500</td>
<td>498</td>
</tr>
<tr>
<td>FBP, °C</td>
<td>576</td>
<td>577</td>
<td>578</td>
</tr>
</tbody>
</table>
Table 5.26  Properties of Unconverted Oil (370°C+) Obtained from Pilot Plant Reactors for 80% Vacuum Gas Oil + 20% DAO Blend at a LHSV of 0.8 h⁻¹

<table>
<thead>
<tr>
<th>Operating Conditions / Property</th>
<th>Run#11</th>
<th>Run#12</th>
<th>Run#13</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor Temperature, °C</td>
<td>360</td>
<td>380</td>
<td>400</td>
</tr>
<tr>
<td>Reactor Pressure, kg/cm²</td>
<td>170</td>
<td>170</td>
<td>170</td>
</tr>
<tr>
<td>H₂/oil Ratio, m³/m³</td>
<td>845</td>
<td>845</td>
<td>845</td>
</tr>
<tr>
<td>Density at 15°C, gm/cc</td>
<td>0.8803</td>
<td>0.8576</td>
<td>0.8330</td>
</tr>
<tr>
<td>API Gravity</td>
<td>29.2</td>
<td>33.5</td>
<td>38.4</td>
</tr>
<tr>
<td>Flash Point, COC, °C</td>
<td>254</td>
<td>250</td>
<td>244</td>
</tr>
<tr>
<td>Pour Point, °C</td>
<td>42</td>
<td>42</td>
<td>39</td>
</tr>
<tr>
<td>Viscosity at 100°C, cSt</td>
<td>6.99</td>
<td>6.45</td>
<td>4.83</td>
</tr>
<tr>
<td>Aniline Point, °C</td>
<td>107.1</td>
<td>113.0</td>
<td>116.4</td>
</tr>
<tr>
<td>UOP K</td>
<td>12.3</td>
<td>12.6</td>
<td>13.0</td>
</tr>
<tr>
<td>Saturates, wt.%</td>
<td>84.1</td>
<td>92.2</td>
<td>94.0</td>
</tr>
<tr>
<td>Aromatics, wt.%</td>
<td>15.9</td>
<td>7.8</td>
<td>6.0</td>
</tr>
<tr>
<td>RCR, wt.%</td>
<td>0.09</td>
<td>0.08</td>
<td>0.05</td>
</tr>
<tr>
<td>Sulphur, ppmw</td>
<td>51</td>
<td>30</td>
<td>21</td>
</tr>
<tr>
<td>Nitrogen, ppmw</td>
<td>12</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>Metals, V and Ni, ppmw</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>ASTM Distillation D-1160</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IBP, °C</td>
<td>375</td>
<td>361</td>
<td>358</td>
</tr>
<tr>
<td>10 vol.%, °C</td>
<td>386</td>
<td>385</td>
<td>379</td>
</tr>
<tr>
<td>20 vol.%, °C</td>
<td>404</td>
<td>401</td>
<td>400</td>
</tr>
<tr>
<td>30 vol.%, °C</td>
<td>421</td>
<td>417</td>
<td>417</td>
</tr>
<tr>
<td>40 vol.%, °C</td>
<td>435</td>
<td>431</td>
<td>430</td>
</tr>
<tr>
<td>50 vol.%, °C</td>
<td>444</td>
<td>442</td>
<td>442</td>
</tr>
<tr>
<td>60 vol.%, °C</td>
<td>458</td>
<td>460</td>
<td>459</td>
</tr>
<tr>
<td>70 vol.%, °C</td>
<td>479</td>
<td>476</td>
<td>472</td>
</tr>
<tr>
<td>80 vol.%, °C</td>
<td>509</td>
<td>503</td>
<td>495</td>
</tr>
<tr>
<td>90 vol.%, °C</td>
<td>539</td>
<td>535</td>
<td>527</td>
</tr>
<tr>
<td>FBP, °C</td>
<td>640</td>
<td>631</td>
<td>627</td>
</tr>
</tbody>
</table>
The operating pressure had a significant effect on the quality of products obtained from hydrocracking. All the products obtained at lower operating pressure contained higher aromatics due to decreased saturation. As can be seen from Tables 5.11 and 5.15, the aromatic content of ATF and kerosene fractions obtained at lower operating pressure of 120 kg/cm$^2$ was higher compared to products obtained at higher operating pressure of 170 kg/cm$^2$. Due to higher aromatic content of hydrocracked ATF and kerosene fractions obtained at 120 kg/cm$^2$, the smoke points were found to be lower. The aromatic content of ATF fraction obtained at 120 kg/cm$^2$ is 20.8 wt% compared to 6.8 wt% for the product obtained at 170 kg/cm$^2$. Thus the smoke point of ATF at 120 kg/cm$^2$ was only 20 mm compared to a value of 25 mm at 170 kg/cm$^2$ while keeping other operating conditions constant. The same observation was made for kerosene also. The diesel fraction obtained at 120 kg/cm$^2$ operating pressure contained increased aromatics, sulphur and nitrogen compared to that obtained at 170 kg/cm$^2$. Due to increased aromatic content of diesel obtained at 120 kg/cm$^2$, the cetane number of diesel was lower. The aromatic content of diesel obtained at 120 kg/cm$^2$ was 19.1 wt% as compared to 5.2 wt% obtained at 170 kg/cm$^2$. The cetane number of diesel obtained at 170 kg/cm$^2$ was 58.8 compared to 54.8 at lower operating pressure of 120 kg/cm$^2$.

The quality of UCO fraction was also significantly affected by operating pressure. The UOP K factor of 12.4 was obtained at 120 kg/cm$^2$ compared to 12.7 at 170 kg/cm$^2$ indicating higher aromaticity of UCO obtained at lower operating pressure. This indicates lower saturation of unconverted bottoms at reduced pressure. The aromatic content, sulphur and nitrogen contents of UCO fraction were higher at lower operating pressure. This will have significant impact when the UCO be utilized as feedstock in FCC unit. The increased aromatic content of UCO will result in lower
conversion in FCC unit and affect FCC product quality. The pilot plant data showed that an increase in hydrogen partial pressure at higher operating pressures increased conversion and improved the quality of jet fuel, kerosene, diesel and unconverted oil products by reducing their aromatic content. The higher conversion at higher operating pressure might be due to stronger suppression of catalyst coking and increased saturation and hydrocracking of aromatics. Especially for feedstocks with higher aromatics content, lower hydrogen partial pressure will have detrimental effect on the hydrocracking conversion.

5.1.7 Effect of Feedstock on Conversion, Product Yields and Product Quality

Since feedstock composition can show significant variations, product quality will depend strongly on feedstock in industrial hydrocracking process. So it is essential to study the effect of feedstock type on conversion, product yields and product quality. As can be seen from Figure 5.2 and Tables 5.3 and 5.6, VGO feedstock (Feed A) exhibited a higher conversion compared to 80% VGO + 20% DAO blend feedstock (Feed B). For similar operating conditions, Feed B gave 2 - 3 wt% lower conversion compared to Feed A. This might be due to the heaviness of the Feed B with its higher end point and higher concentrations of aromatics and heavy polycyclic aromatic compounds as indicated by the polycyclic index. For example, at a reactor temperature of 360°C, operating pressure of 170 kg/cm² and liquid hourly space velocity of 0.8 h⁻¹, a conversion of 34.18 wt% was obtained with Feed A compared to 31.11 wt% for Feed B. Similar decrease in conversion was observed at other operating conditions also for Feed B. The above data showed that the quality of feedstock had a strong effect in influencing the hydrocracker conversion levels.
The hydrogen consumption for hydrocracking of Feed B was higher compared to Feed A at similar operating conditions studied due to increased aromatic content. At a reactor temperature of 360°C and liquid hourly space velocity of 0.8 h⁻¹, the hydrogen consumption in the case of Feed B was 199.9 Nm³/m³ compared to 166.2 Nm³/m³ for Feed A.

Generally, the main feedstock parameters affecting the processability in a hydrocracker are heaviness, end boiling point, nitrogen content and aromatic content. In general, with increasing feedstock heaviness, the amount of catalyst poisons such as metals, aromatic coke precursors, and nitrogen progressively increases. Metals cause irreversible deactivation of the first stage hydrotreating catalyst, whereas organic nitrogen compounds specifically reduce the cracking activity of the acidic second-stage hydrocracking catalysts as result of their strong adsorption. Higher boiling range feedstock would generally have more of polycyclic aromatics, which are difficult to crack and form more coke during processing. Due to the heavy aromatic nature of the Feed B compared to Feed A, the conversion obtained was lower at similar operating conditions.

Similar type of product distribution curve was obtained for Feed B as that of Feed A as shown in Figure 5.3. The change in the feedstock type did not have significant effect on product yield distribution though it has some effect on feedstock conversion. This may be due to the flexibility of the hydrocracking process with respect to feedstock type. However, there was slight decrease in the middle distillates yield for Feed B compared to Feed A.

As can be seen from Table 5.10, naphtha fraction obtained from hydrocracking of Feed B had high naphthenes and isoparaffin content and lower aromatic content as observed for the case of Feed A. The aromatic
content of the naphtha fraction obtained from hydrocracking of Feed B was found to be slightly higher compared to that obtained from Feed A for similar operating conditions. Due to higher aromatic content of naphtha obtained from Feed B, the octane number of naphtha was slightly higher. As can be seen from Table 5.14, the aromatic content of ATF obtained by hydrocracking of high aromatic Feed B was higher compared to Feed A and thus the smoke point of ATF in the case of Feed B was slightly lower compared to Feed A. At 380°C reactor temperature, 0.8 h⁻¹ LHSV and 170 kg/cm² operating pressure, the hydrocracked ATF fraction obtained from Feed A had an aromatic content of 6.8 wt% and smoke point of 25 mm. Under the same operating conditions, the aromatic content of ATF obtained from Feed B is 10.1 wt% and smoke point of 23 mm. This showed that quality of ATF fraction was slightly lower in case of high aromatic feedstock processed in hydrocracker unit compared to processing of low aromatic feedstock. Similarly, kerosene fraction obtained from hydrocracking of Feed B contained slightly higher aromatics and sulphur.

As can be seen from Tables 5.19 and 5.22, the quality of diesel obtained from Feed B was inferior compared to that obtained from Feed A. The diesel obtained from Feed B was higher in aromatic content and lower in cetane number compared to that obtained from Feed A. At a typical operating temperature of 380°C, operating pressure of 170 kg/cm² and LHSV of 0.8 h⁻¹, the aromatic content of diesel obtained from Feed B was 8.9 wt% compared to that of 5.2 wt% in case of diesel obtained from Feed A. Thus the cetane number of diesel obtained using Feed B was 53.9 compared to a value of 58.8 in case of diesel obtained from Feed A. The higher sulphur content of the diesel obtained from Feed B compared to Feed A was evident from Table 5.22. The quality of feedstock has a stronger influence on product quality in hydrocracking process. Especially a feedstock with higher aromatic content will yield poorer quality middle distillate fractions such as ATF,
kerosene and diesel. The smoke point of jet fuel and kerosene and cetane number of diesel are the important properties that are affected by the higher aromaticity of feedstock. The quality of UCO fraction obtained from Feed B was inferior with higher aromatics and sulphur compared to that obtained from Feed A.

Generally the ease of hydrocracking a specific feedstock depends on its composition and properties. The heavier feedstocks such as Feed B with higher end point requires more severe operating conditions to obtain satisfactory product yields and quality. Heavier feeds are usually processed at higher temperatures, higher hydrogen partial pressures and lower space velocities to obtain similar conversion and product yields. The addition of heavier feedstock to a lighter feedstock reduces conversion. Since hydrocracker has very good feedstock flexibility, it can still upgrade the feedstock sufficiently that the UCO can be used as FCC feedstock. This shows the flexibility of the hydrocracking process for different type of feedstock processing and product yield distribution.

Some of the important characteristics of products obtained from pilot plant experiments at typical operating conditions of industrial hydrocrackers are listed in Table 5.27.
Table 5.27  Characteristics of Products Obtained from Pilot Plant for Feed A

<table>
<thead>
<tr>
<th>Product</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total naphtha</td>
<td>• High quality reformer feedstock with very high naphthenes content (55.8 wt%) and Feedstock for the production of aromatics (BTX) for petrochemicals</td>
</tr>
<tr>
<td></td>
<td>• Calculated RON of 76.5</td>
</tr>
<tr>
<td>Jet Fuel</td>
<td>• Low in aromatics content (6.8 wt%)</td>
</tr>
<tr>
<td></td>
<td>• High smoke point (25 mm)</td>
</tr>
<tr>
<td></td>
<td>• Low freezing point (-51°C)</td>
</tr>
<tr>
<td>Kerosene</td>
<td>• Low in aromatics content (9.5 wt%)</td>
</tr>
<tr>
<td></td>
<td>• High smoke point (25 mm)</td>
</tr>
<tr>
<td></td>
<td>• Low sulphur (20 ppmw)</td>
</tr>
<tr>
<td>Diesel</td>
<td>• High cetane number (58.8)</td>
</tr>
<tr>
<td></td>
<td>• Very low sulphur content (15 ppmw)</td>
</tr>
<tr>
<td></td>
<td>• High in rich saturated hydrocarbons (94.8 wt%)</td>
</tr>
<tr>
<td>Hydrocracker bottoms</td>
<td>• Very high in saturates content (96.9 wt%)</td>
</tr>
<tr>
<td></td>
<td>• Low sulphur (25 ppmw)</td>
</tr>
<tr>
<td></td>
<td>• Low RCR (0.05 wt%)</td>
</tr>
</tbody>
</table>
5.2 KINETIC SCHEMES FOR HYDROCRACKING PROCESS

In the present work, seven different types of kinetic reaction schemes have been proposed to describe the hydrocracking process based on discrete lumping approach. These reaction schemes were already presented in detail in chapter 4. The kinetic schemes developed in the present work were applied to the experimental data obtained in a pilot plant trickle bed reactor for hydrocracking of different feedstocks over an industrial hydrocracking catalyst system. The kinetic parameters for these reaction schemes were evaluated using the experimental data obtained from pilot plant reactor. The reaction schemes were validated using the experimental data generated at varied operating conditions for both feedstocks based on the kinetic parameters evaluated from pilot plant experiments.

As presented in chapter 4, the kinetic schemes for hydrocracking process were represented using a set of first order ordinary differential equations for the change in the concentration of kinetic lumps with respect to reaction time. For each reaction scheme the differential equations are to be solved simultaneously to obtain the product yield distribution at various reaction times and reactor temperatures. As the system of differential equations cannot be solved analytically, numerical techniques are employed. Models VI and VII have some mass balance constraints along with differential equations.

In industrial hydrocracking process, hydrotreating catalyst was loaded prior to hydrocracking catalyst to remove heteroatoms such as sulfur and nitrogen and to partially saturate aromatic compounds present in the feedstock. In most of the cases, the first bed of the hydrocracking reactor is loaded with high activity NiO-MoO$_3$/Al$_2$O$_3$ hydrotreating catalyst for this purpose. The hydrotreating catalyst support material has very low acidity and
promote very small amount of cracking of feed molecules into lighter compounds. However, the cracking activity of hydrotreating catalyst is normally very less and for practical considerations, it can be neglected. So the present work neglects the hydrocracking reactions occurring over the HDT catalyst. Most of the hydrocracking reactions i.e. scission of C-C bond occur over the dual functional hydrocracking catalyst. The hydrocracking reactions are assumed to occur only over hydrocracking catalyst in the present work.

5.2.1 Kinetic Parameter Estimation

The kinetic models can be validated using the performance data evaluated in pilot plant trickle bed reactor for hydrocracking of different feedstocks only if the rate constants, or kinetic parameters are known. The rate constants represent the intrinsic property of a catalyst and feed system and indicate its ability to accomplish the desired reactions under the given operating conditions. The rate constants present the speed at which the reactions take place. The rate constants vary with the nature of the catalyst system and feedstock used and is a unique function of their composition. For a same feedstock, different catalysts having varying composition and properties will have different rate constants unique to their physical and chemical characteristics. The catalyst with higher values of rate constants for a desired reaction results in higher conversions under given operating conditions. Prior to industrial applications, pilot plant experiments were conducted to determine the intrinsic activity of a catalyst. For a given catalyst system, feedstock will also have some effect on rate constants. Feedstock with higher amounts of refractory compounds will exhibit different kinetics for the same catalyst system. But generally the effect of catalyst type is more pronounced than the effect of feedstock type on the rate constants.

The kinetic constants for the various hydrocracking reactions considered in all the reaction schemes presented in chapter 4 were estimated
using an optimization algorithm called Sequential Quadratic Programming (SQP). The objective function used in the SQP optimization algorithm to minimize the error between experimental weight fractions and the predicted weight fractions from model estimation results is shown as below:

\[
error = \sum_{i} \sum_{j} [C_{pre}(i, j) - C_{exp}(i, j)]^2
\]  

(5.1)

Where \(C_{pre}\) is the weight fraction of the each lump predicted from solving model differential equations and \(C_{exp}\) is the weight fraction of the lump estimated from experiment.

This objective error function was minimized subject to the constraint, \(k > 0\), for all the values of \(k\) in all the models presented in the present work. SQP algorithm evaluated the objective function for each lump and various reaction times such that the error was minimum for a set of data to evaluate kinetic rate constants. The initial sets of kinetic constant values were assumed and the model differential equations solved to obtain a product distribution in the proposed SQP algorithm. The values of kinetic constants converged to a value when the error between the experimental data and calculated distribution data was minimum. In all the cases the squared error was very minimum ranging from \(4.30 \times 10^{-5}\) to \(2.04 \times 10^{-11}\) indicating the validity of the proposed reaction schemes. The product distribution data at various operating conditions used in the pilot plant and the initial product distribution in the feedstock was used in the algorithm for minimization of errors.

Arrhenius temperature dependency of the rate constants was considered in the present work. The preexponential factors and activation energies for the rate constants were evaluated based on linear regression analysis of rate parameters at various temperatures. Since analytical methods cannot be employed to solve the model differential equations using the estimated kinetic parameters, ODE 45 function in MATLAB software was used to solve the differential equations to predict product distribution at various reaction times and reactor temperatures for all the reaction schemes.

In the present work the inverse of the liquid hourly space velocity is considered to be the reaction time.

5.2.2 Model I
The kinetic expressions for this model are listed in Table 5.28 for both the feedstocks along with kinetic constant at 380°C, which is the typical operating temperature of once-through hydrocracker unit. The activation energy for the hydrocracking of vacuum gas oil over the hydrocracking catalyst was found to be $2.3218 \times 10^4$ cal/gmol. The activation energy for the case of hydrocracking of Feed B was $2.4060 \times 10^4$ cal/gmol. The range of activation energies reported in the present work is inline with the values reported in the open literature. Qader and Hill (1969) reported an activation energy of 21,100 cal/gmol for hydrocracking of vacuum gas oil boiling in the range 300 to 430°C over a dual functional Ni-W/silica-alumina catalyst system. Qader and Hill (1969) in another communication, reported activation energies of 14300 and 15500 cal/gmol respectively for hydrocracking of petroleum and coal derived oils over a commercial hydrocracking catalyst system based on Ni-W/SiO$_2$-Al$_2$O$_3$. El kady (1979) obtained activation energy of 26658 cal/gmol for hydrocracking of vacuum distillate fraction using a Ni-Mo/Silica-Alumina catalyst system for first order hydrocracking reactions.

The kinetic data indicated that Feed A and Feed B both exhibit almost similar kinetic behavior under hydrocracking operating conditions, but Feed B required a slightly higher activation energy for hydrocracking reactions compared to Feed A. The higher activation energy for hydrocracking of Feed B may be due to higher amounts of heavy polycyclic aromatic compounds, which are coke precursors and refractory during hydrocracking. Due to higher activation energy for the hydrocracking of Feed B, it requires slightly higher temperature to obtain the same conversion as that obtained during hydrocracking of Feed A under identical operating conditions. It was found that an increase of around 3°C reactor temperature was required in case of Feed B compared to Feed A for obtaining same conversion during hydrocracking. The kinetic rate constants at a reactor
temperature of 380°C for both feedstocks indicated that Feed A reacted at slightly higher rate compared to Feed B during hydrocracking and the lower rate in the case of Feed B might be due to the higher end point and refractoriness of Feed B.

The effect of reactor temperature on 370°C+ yields for Feed A and Feed B at various reaction times is presented in Figures 5.11 and 5.12. The effect of reaction time on 370°C+ yields at different temperatures is presented in Table 5.29 and Figures 5.13 and 5.14 for both the feedstocks. The simulations for the effect of reactor temperature and reaction time on VGO yields were generated by solving the differential equations for Model I using the kinetic parameters presented in Table 5.28.

As can be seen from Figure 5.11, the 370°C+ yield decreased with increasing reactor temperature. The conversion of the feedstock was observed to increase with increasing reactor temperature at all reaction times. The conversion of the feedstock into 370°C- products occurred at higher rate with higher reaction times during hydrocracking. Similar trend for the 370°C+ yield with reactor temperature was observed for Feed B as shown in Figure 5.12. But the feedstock conversion in the case of Feed B was lower compared to that of Feed A in all the temperature range.

### Table 5.28 Kinetic Expression for Model I

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Kinetic expression for $k_{HC}$</th>
<th>$k_{HC}$ at 380°C, h⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacuum gas oil (VGO)</td>
<td>$4.8364 \times 10^7 \exp(-2.3218 \times 10^4 / RT)$</td>
<td>0.7988</td>
</tr>
<tr>
<td>80% VGO + 20% DAO</td>
<td>$8.5121 \times 10^7 \exp(-2.4060 \times 10^4 / RT)$</td>
<td>0.7430</td>
</tr>
</tbody>
</table>
Table 5.29  Effect of reaction time on 370°C+ yields for VGO feedstock at various temperatures - Model I

<table>
<thead>
<tr>
<th>Reaction time, h</th>
<th>370°C+ yields, wt%</th>
<th>360°C</th>
<th>380°C</th>
<th>400°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>89.5</td>
<td>89.5</td>
<td>89.5</td>
<td>89.5</td>
</tr>
<tr>
<td>0.25</td>
<td>79.66</td>
<td>72.91</td>
<td>63.13</td>
<td></td>
</tr>
<tr>
<td>0.295</td>
<td>78.00</td>
<td>79.87</td>
<td>70.27</td>
<td>71.49</td>
</tr>
<tr>
<td>0.445</td>
<td>72.74</td>
<td>72.28</td>
<td>62.13</td>
<td>63.52</td>
</tr>
<tr>
<td>0.5</td>
<td>70.90</td>
<td>59.39</td>
<td>44.54</td>
<td></td>
</tr>
<tr>
<td>0.75</td>
<td>63.10</td>
<td>48.38</td>
<td>31.42</td>
<td></td>
</tr>
<tr>
<td>0.89</td>
<td>59.11</td>
<td>59.0</td>
<td>43.13</td>
<td>44.14</td>
</tr>
<tr>
<td>1.0</td>
<td>56.16</td>
<td>39.41</td>
<td>22.16</td>
<td></td>
</tr>
<tr>
<td>1.25</td>
<td>49.98</td>
<td>32.10</td>
<td>15.63</td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>44.49</td>
<td>26.15</td>
<td>11.03</td>
<td></td>
</tr>
<tr>
<td>1.75</td>
<td>39.59</td>
<td>21.30</td>
<td>7.78</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>35.24</td>
<td>17.35</td>
<td>5.49</td>
<td></td>
</tr>
</tbody>
</table>

The 370°C+ yield decreased with increasing reaction time for all the reactor temperatures for both the feedstock as shown in Figures 5.13 and 5.14. This is due to increased conversion of feedstock with increase in reaction time for all the temperatures. It was observed that the reactor temperature and reaction time or LHSV are the most important variables affecting the feedstock conversion during hydrocracking. The effect of reactor temperature on the conversion of feedstock was more pronounced than that of LHSV.
The Arrhenius plot for hydrocracking of both feedstocks is shown in Figure 5.15 for first order hydrocracking reactions. The Eyring plot for the hydrocracking of both feedstocks is shown in Figure 5.16. The following values of enthalpies and entropies of activation were calculated from plots of log \( \log \left( \frac{k'}{T} \right) \) vs. \( 1/T \) by applying Eyring equation:

**For VGO Feedstock**

\[
\Delta H_{hc}^\ast = 21,919 \text{ cal/mol} \\
\Delta S_{hc}^\ast = -43.19 \text{ e.u.}
\]

**For 80% VGO+20% DAO Feedstock**

\[
\Delta H_{hc}^\ast = 22,763 \text{ cal/mol} \\
\Delta S_{hc}^\ast = -42.06 \text{ e.u.}
\]

Similar values of enthalpies and entropies of activation for hydrocracking as obtained in the present work were reported by other authors in the literature. Qader and Hill (1969) reported the enthalpy and entropy of activation as 19100 cal/mole and –44.18 e.u. respectively for hydrocracking a vacuum gas oil fraction over a commercial Ni-W/SiO₂-Al₂O₃ catalyst system.
Figure 5.11 Effect of Temperature on 370°C+ Yield for VGO Feedstock - Model I

Figure 5.12 Effect of Temperature on 370°C+ Yield for 80% VGO+ 20% DAO Feedstock - Model I

Figure 5.13 Effect of Reaction time on 370°C+ Yield for VGO Feedstock - Model I

Figure 5.14 Effect of Reaction time on 370°C+ Yield for 80% VGO+20% DAO Feedstock - Model I
Figure 5.15  Arrhenius plot for hydrocracking - Model I

Figure 5.16  Eyring plot for hydrocracking - Model I
El kady (1979) reported the enthalpy and entropy of activation as 24482 cal/mole and –39.84 e.u. respectively for hydrocracking of a vacuum distillate fraction over a Ni-Mo/SiO₂-Al₂O₃ catalyst system. The high negative values of $\Delta S^*$ obtained during hydrocracking of the vacuum distillate are the combined effect of many complex chemical processes occurring during the reactions as observed by Qader and Hill (1969).

The data comparing experimental and predicted yields for the conversion of both feedstocks using this model is presented in Table 5.29 for VGO feedstock. This data showed that the model predicted the 370°C+ yields very well in the range of operating conditions studied in the present work confirming the applicability of this type of kinetic analysis for hydrocracking process. This is a simple first order reaction model and can be applied to the hydrocracking process very well for predicting the conversion of the feedstock into overall lighter products.

5.2.3 Model II

There are two kinetic parameters to be estimated for this model. One for the cracking of feedstock into middle distillates fraction and another for the cracking of middle distillates into naphtha and gas fractions. The hydrogen is also involved in the hydrocracking reactions as one of the reactant, but it is not explicitly included in the hydrocracking reaction scheme since it is used in excess quantity and its concentration generally does not change during experiments. The estimated kinetic parameters for the Model II for both the feedstocks were listed in Table 5.30. The activation energy for the hydrocracking of feedstock into middle distillates was found to be 23219 cal./gmol compared to the value of 22222 cal/gmol for the hydrocracking of middle distillates into naphtha and gas. The kinetic rate constant values at a reactor temperature of 380°C indicated that the hydrocracking of feedstock into middle distillates occurred at a faster rate compared to that of the hydrocracking of middle distillates into naphtha and gas fractions for both the feedstock. Feed B required slightly higher activation energy compared to Feed A for hydrocracking reactions due to its refractory nature. The rate constants at a reactor temperature of 380°C for Feed B
indicated that the rate of VGO hydrocracking is lower for Feed B compared to Feed A.

Hydrocracking of heavier molecules will proceed easily compared to lighter stocks. Generally the kinetic constants are functions of TBP distillation of the fractions. Heavier molecules with higher TBP will have higher kinetic constants compared to lighter fractions with lower molecular weight. This observation was made in the present work also as seen from Table 5.30. The Arrhenius plot for hydrocracking was shown in Figure 5.17. The Eyring plot was shown in Figure 5.18 for the hydrocracking reactions based on the reaction scheme represented by Model II.

Table 5.30 Kinetic Expression for Model II

<table>
<thead>
<tr>
<th>Kinetic parameter</th>
<th>Kinetic expression</th>
<th>k at 380°C, h⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Feedstock: Vacuum gas oil</td>
<td></td>
</tr>
<tr>
<td>k₁</td>
<td>(4.8139 \times 10^7 \exp(-2.3219 \times 10^4/RT))</td>
<td>0.7942</td>
</tr>
<tr>
<td>k₂</td>
<td>(1.0820 \times 10^7 \exp(-2.2222 \times 10^4/RT))</td>
<td>0.3897</td>
</tr>
<tr>
<td></td>
<td>Feedstock: 80% VGO + 20% DAO Blend</td>
<td></td>
</tr>
<tr>
<td>k₁</td>
<td>(8.4622 \times 10^7 \exp(-2.4060 \times 10^4/RT))</td>
<td>0.7388</td>
</tr>
<tr>
<td>k₂</td>
<td>(2.1853 \times 10^7 \exp(-2.3108 \times 10^4/RT))</td>
<td>0.3969</td>
</tr>
</tbody>
</table>
Figure 5.17 Arrhenius plot for hydrocracking - Model II

Figure 5.18 Eyring plot for hydrocracking - Model II

Model II was represented by three simple first order ordinary differential equations for the change in the yields of VGO Feedstock, Middle Distillates and Naphtha and Gas fractions with respect to reaction time. Model
differential equations in chapter 4 were solved simultaneously to obtain product yield distribution of the three kinetic lumps with respect to reaction time using the kinetic parameters listed in Table 5.30. The effect of reactor temperature on product yields at various reaction times are presented in Figures 5.19 to 5.21. The effect of reactor temperature on product yields at a reaction time of 0.89 h is shown in Table 5.31. The effect of reaction time on product yields at various reactor temperatures is presented in Figures 5.22 to 5.24. The parity plot for all the product yield data obtained using Model II for both the feedstock is shown in Figure 5.25.

Figures 5.19 through 5.21 were generated by solving the model equations for the effect of temperature on product yield distribution at different reaction time. As can be seen from these figures, the yield of VGO Feedstock decreased as the reactor temperature was increased from 360 to 420°C while the yields of naphtha and gas (NG) constantly increased at all reaction times. The yield of VGO decreased with reactor temperature at a higher rate at higher reaction times. The rate of increase in the yields of naphtha and gas with reactor temperature is higher at higher reaction time compared to that of lower reaction time. The yield of middle distillates increased as the temperature was increased from 360 to 420°C at lower reaction time, but at higher reaction time, the yield of middle distillate fraction increased initially up to certain reactor temperature and then started decreasing with reactor temperature. This decrease in the yield of middle distillates at higher reaction severities is due to the increased rate of secondary hydrocracking reaction of middle distillate fraction already formed during hydrocracking and present in the feedstock compared to its rate of formation.
Figure 5.19 Effect of temperature on product yields at 0.295 h - Model II

Figure 5.20 Effect of temperature on product yields at 0.445 h - Model II
Figure 5.21  Effect of temperature on product yields at 0.89 h - Model II

Table 5.31  Effect of temperature on product yields at a reaction time of 0.89 h - Model II

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Product yields, wt%</th>
<th>Feedstock: VGO</th>
<th>Feedstock: 80% VGO + 20% DAO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>F</td>
<td>MD</td>
<td>NG</td>
</tr>
<tr>
<td>360</td>
<td>59.25</td>
<td>35.72</td>
<td>5.03</td>
</tr>
<tr>
<td>370</td>
<td>51.65</td>
<td>40.79</td>
<td>7.56</td>
</tr>
<tr>
<td>380</td>
<td>43.30</td>
<td>45.51</td>
<td>11.18</td>
</tr>
<tr>
<td>390</td>
<td>34.58</td>
<td>49.22</td>
<td>16.20</td>
</tr>
<tr>
<td>400</td>
<td>26.01</td>
<td>51.13</td>
<td>22.86</td>
</tr>
<tr>
<td>410</td>
<td>18.19</td>
<td>50.57</td>
<td>31.23</td>
</tr>
<tr>
<td>420</td>
<td>11.64</td>
<td>47.19</td>
<td>41.16</td>
</tr>
</tbody>
</table>
Figure 5.22 Effect of reaction time on product yields at 360°C - Model II

Figure 5.23 Effect of reaction time on product yields at 380°C - Model II
Figures 5.22 to 5.24 and Table 5.32 were generated by solving the model differential equations using the kinetic parameters evaluated for Model II for the effect of reaction time on product yields at constant reactor
temperatures. The yield of VGO feedstock decreased continuously with reaction time at a constant reactor temperature. The yield of gas and naphtha fractions increased continuously with reaction time at constant reactor temperature. But the yield of middle distillates initially increased with reaction time and then decreased at higher reaction time at constant temperatures. This is due to increased rate of hydrocracking of middle distillate fraction compared to its formation.

**Table 5.32 Effect of reaction time on product yields at 380°C - Model II**

<table>
<thead>
<tr>
<th>Reaction time, h</th>
<th>Product yields, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Feedstock: VGO</td>
</tr>
<tr>
<td></td>
<td>F</td>
</tr>
<tr>
<td>0.0</td>
<td>8.95</td>
</tr>
<tr>
<td>0.25</td>
<td>72.99</td>
</tr>
<tr>
<td>0.295</td>
<td>70.36</td>
</tr>
<tr>
<td>0.445</td>
<td>62.25</td>
</tr>
<tr>
<td>0.5</td>
<td>59.52</td>
</tr>
<tr>
<td>0.75</td>
<td>48.54</td>
</tr>
<tr>
<td>0.89</td>
<td>43.30</td>
</tr>
<tr>
<td>1.0</td>
<td>39.59</td>
</tr>
<tr>
<td>1.25</td>
<td>32.28</td>
</tr>
<tr>
<td>1.5</td>
<td>26.33</td>
</tr>
<tr>
<td>1.75</td>
<td>21.47</td>
</tr>
<tr>
<td>2.0</td>
<td>17.51</td>
</tr>
</tbody>
</table>

The kinetic simulation of hydrocracking process showed that the yield of feedstock decreased continuously with increase in reactor temperature and reaction time while the yield of gas and naphtha fractions increased continuously. This is due to increased rate of hydrocracking reactions at higher reaction severities. The yield of middle distillates showed a peak at a particular reaction severity and after that its yield started decreasing as the severity was further increased. Especially at higher reactor temperatures and reaction times, secondary hydrocracking of middle distillates was found to
dominate over the formation of middle distillates and thus the yield was decreased.

The simulation data generated using the model predicts the yields of products very well in the entire range of operating conditions as shown in Figure 5.25. The match between experimental and predicted product yields is quite close with correlation coefficient of 0.9977 indicating the applicability of this type of analysis for hydrocracking process. The simulated data also follow the general trend of hydrocracking product yield distribution at all reaction severities. As shown in Tables 5.31 and 5.32, Feed B also exhibited a similar product yield distribution during hydrocracking as that of Feed A in the entire range of operating conditions studied. The conversion of the feedstock was slightly lower in the case of Feed B compared to Feed A.

5.2.4 Model III

Since the hydrocracking of the feedstock yields both middle distillates and naphtha and gas fractions during primary cracking, there are two kinetic parameters considered for these reactions and another for the cracking of middle distillates into naphtha and gas fractions. The estimated kinetic parameters for Model III for both the feedstock were listed in Table 5.33. For the case of Feed B, the activation energy for the hydrocracking of feedstock into middle distillates was found to be 20245 cal./gmol and for the hydrocracking of feedstock into naphtha and gas was found to be 37694 cal/gmol. The activation energy for the hydrocracking of middle distillates into naphtha and gas was observed to be 41432 cal/gmol. The activation energy for the hydrocracking reaction of VGO Feedstock into middle distillates is lower than the activation energy for the formation of naphtha and gas indicating higher temperature sensitivity of the reaction leading to naphtha and gas compared to that of reaction leading to middle distillates. The activation energy for the cracking of middle distillates into naphtha and gas was higher than that of the both of the primary reactions indicating very high temperature sensitivity of the secondary cracking of middle distillates. This indicates that at higher reaction temperatures the middle distillates formed during primary cracking of the feedstock tend to crack further to form naphtha and gas.

<table>
<thead>
<tr>
<th>Kinetic parameter</th>
<th>Kinetic expression</th>
<th>k at 380°C</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Feedstock: Vacuum gas oil</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( k_1 )</td>
<td>( 1.0669 \times 10^6 \exp(-1.8616 \times 10^4/RT) )</td>
<td>0.6259</td>
</tr>
</tbody>
</table>
The kinetic rate constant values at a reactor temperature of 380°C indicated that the hydrocracking of feedstock into middle distillates occurred at a faster rate compared to that of the hydrocracking of feedstock into naphtha and gas fractions for both the feedstock. The kinetic constant for the cracking of middle distillates fraction into naphtha and gas was found to be lower compared to primary hydrocracking reactions of feedstock. This showed the higher rate of hydrocracking of heavier fractions compared to the lighter fractions. Feed B required slightly higher activation energy compared to Feed A for hydrocracking reactions due to its refractory nature. The rate constants at a reactor temperature of 380°C for Feed B indicated that the rate of VGO hydrocracking is lower for Feed B compared to Feed A.

The differential equations for this model were solved simultaneously to obtain product yield distribution of the three kinetic lumps with respect to reaction time and reactor temperature using the kinetic parameters listed in Table 5.33. The effect of reactor temperature on product yields at various reaction times are presented in Table 5.34 and Figure 5.26. The effect of reaction time on product yields at various reactor temperatures is shown in Figures 5.27 and 5.28 and Table 5.35. The parity plot for all the product yield data obtained for Model III for both the feedstock is shown in Figure 5.29.
The yield of VGO Feedstock decreased as the reactor temperature was increased from 360 to 420°C while the yields of naphtha and gas (NG) continuously increased at all reaction times. At higher reaction severities encountered at higher reaction times and reactor temperatures, the rate of hydrocracking of VGO feedstock was higher as shown by the increased yields of naphtha and gas fractions. The yield of middle distillates increased as the
Table 5.34  Effect of temperature on product yields at a reaction time of 0.445 h - Model III

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Feedstock: VGO</th>
<th>Feedstock: 80% VGO + 20% DAO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>F</td>
<td>MD</td>
</tr>
<tr>
<td>360</td>
<td>72.71</td>
<td>24.64</td>
</tr>
<tr>
<td>370</td>
<td>68.14</td>
<td>27.69</td>
</tr>
<tr>
<td>380</td>
<td>62.57</td>
<td>31.04</td>
</tr>
<tr>
<td>390</td>
<td>55.89</td>
<td>34.55</td>
</tr>
<tr>
<td>400</td>
<td>48.11</td>
<td>37.97</td>
</tr>
<tr>
<td>410</td>
<td>39.38</td>
<td>40.99</td>
</tr>
<tr>
<td>420</td>
<td>30.13</td>
<td>43.17</td>
</tr>
</tbody>
</table>

Table 5.35  Effect of reaction time on product yields at 360°C - Model III

<table>
<thead>
<tr>
<th>Reaction time, h</th>
<th>Feedstock: VGO</th>
<th>Feedstock: 80% VGO + 20% DAO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>F</td>
<td>MD</td>
</tr>
<tr>
<td>0.0</td>
<td>89.50</td>
<td>10.50</td>
</tr>
<tr>
<td>0.25</td>
<td>79.64</td>
<td>18.83</td>
</tr>
<tr>
<td>0.295</td>
<td>77.98</td>
<td>20.22</td>
</tr>
<tr>
<td>0.445</td>
<td>72.71</td>
<td>24.64</td>
</tr>
<tr>
<td>0.5</td>
<td>70.86</td>
<td>26.18</td>
</tr>
<tr>
<td>0.75</td>
<td>63.05</td>
<td>32.66</td>
</tr>
<tr>
<td>0.89</td>
<td>59.06</td>
<td>35.95</td>
</tr>
<tr>
<td>1.0</td>
<td>56.11</td>
<td>38.37</td>
</tr>
<tr>
<td>1.25</td>
<td>49.92</td>
<td>43.39</td>
</tr>
<tr>
<td>1.5</td>
<td>44.42</td>
<td>47.79</td>
</tr>
<tr>
<td>1.75</td>
<td>39.53</td>
<td>51.65</td>
</tr>
<tr>
<td>2.0</td>
<td>35.17</td>
<td>55.03</td>
</tr>
<tr>
<td>2.25</td>
<td>31.30</td>
<td>57.98</td>
</tr>
<tr>
<td>2.5</td>
<td>27.85</td>
<td>60.54</td>
</tr>
<tr>
<td>2.75</td>
<td>24.78</td>
<td>62.77</td>
</tr>
</tbody>
</table>
temperature was increased from 360 to 420°C at lower reaction times. But at higher reaction time, the yield of middle distillate fraction increased initially up to certain reactor temperature and then started decreasing with reactor temperature as shown in Figure 5.28. The yield of VGO feedstock decreased continuously while the yield of gas and naphtha fractions increased continuously with reaction time at a constant reactor temperature. But the yield of middle distillates initially increased with reaction time and then decreased at higher reaction time at constant reactor temperatures.

The kinetic simulation of hydrocracking process using Model III showed similar trend pattern for product yield distribution as that obtained for Model II. The yield of feedstock decreased continuously with increase in reactor temperature and reaction time while the yield of gas and naphtha fractions increased continuously due to increased rate of hydrocracking reactions at higher reaction severities. The decrease in the yield of middle distillates at higher reaction severities can be attributed to the increased rate of secondary hydrocracking reaction of middle distillate fraction already formed during hydrocracking and present in the feedstock compared to its rate of formation.

The simulated yield distribution data generated using Model III predicts the yields of products very well in the entire range of operating conditions studied as shown in Figure 5.29. The match between experimental and predicted product yields is quite close with correlation coefficient of 0.9984 indicating the applicability of Model III for representing hydrocracking process. As shown in Tables 5.34 and 5.35, Feed B also exhibited a similar product yield distribution during hydrocracking as that of Feed A in the entire range of operating conditions studied for Model III.
Figure 5.26 Effect of temperature on product yields at 0.89 h - Model III

Figure 5.27 Effect of reaction time on product yields at 380°C - Model III
Figure 5.28  Effect of reaction time on product yields at 400°C - Model III

Figure 5.29  Parity plot for Model III- All Exp. Data For both feedstock
5.2.5 Model IV

There are five kinetic parameters to be estimated for this four lump reaction model. The hydrocracking of the feedstock was considered to yield all the product lumps such as middle distillates, naphtha and gas fractions during primary cracking reactions and three kinetic parameters represented these reactions. The middle distillates fraction formed during the hydrocracking was considered to undergo secondary cracking to yield both naphtha and gas fractions. There are two kinetic parameters considered for the hydrocracking reaction of middle distillates. The kinetic parameters estimated for Model IV for both the feedstock were listed in Table 5.36. As can be seen from Table 5.36, the activation energies for the formation of middle distillates from VGO feedstock is lower compared to the activation energies for the formation of naphtha and gas. This indicates the higher temperature sensitivity of these two primary hydrocracking reactions leading to the formation of naphtha and gas compared to the hydrocracking reaction leading to the formation of middle distillates from the feedstock. For the case of Feed A, the activation energy for the hydrocracking of feedstock into middle distillates was found to be 21111 cal/gmol compared to the activation energies of 33489 and 32972 cal/gmol for the formation of naphtha and gas respectively from primary hydrocracking of feedstock. The activation energy for secondary hydrocracking of middle distillates fraction to form naphtha and gas was higher compared to the values of activation energies obtained for primary hydrocracking of VGO feedstock. As shown by their activation energies, the secondary hydrocracking reactions are highly temperature sensitive compared to primary hydrocracking reactions. Similar trend in activation energies was observed for the hydrocracking of Feed B also. Feed B reacted slightly slowly during hydrocracking as shown by their lower kinetic constant values compared to Feed A.

Table 5.36 Kinetic Expression for Model IV

<table>
<thead>
<tr>
<th>Kinetic parameter</th>
<th>Kinetic expression</th>
<th>k at 380°C, h⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feedstock: Vacuum gas oil</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( k_1 )</td>
<td>( 7.8919 \times 10^6 \exp\left(-2.1111 \times 10^4/RT\right) )</td>
<td>0.6767</td>
</tr>
<tr>
<td>( k_2 )</td>
<td>( 1.5847 \times 10^{10} \exp\left(-3.3489 \times 10^4/RT\right) )</td>
<td>0.0853</td>
</tr>
<tr>
<td>( k_3 )</td>
<td>( 3.8146 \times 10^9 \exp\left(-3.2972 \times 10^4/RT\right) )</td>
<td>0.0322</td>
</tr>
<tr>
<td>( k_4 )</td>
<td>( 1.0284 \times 10^{13} \exp\left(-4.2095 \times 10^4/RT\right) )</td>
<td>0.1116</td>
</tr>
</tbody>
</table>
The ordinary differential equations for this model presented in chapter 4 were solved simultaneously to obtain product yield distribution of the four kinetic lumps with respect to change in reaction time and reactor temperature using the kinetic parameters listed in Table 5.36. The initial yield distribution of the lumps in the feedstock was used as initial condition for solving the differential equations. The effect of reactor temperature on product yields at various reaction times are presented in Table 5.37 and Figures 5.30 and 5.31. The effect of reaction time on product yields at various reactor temperatures is presented in Figures 5.32 and 5.33 and Tables 5.38. The parity plot for all the product yield data obtained for Model IV for both the feedstock is shown in Figure 5.34.

Table 5.37 Effect of temperature on product yields at a reaction time of 0.295 h - Model IV

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>VGO</th>
<th>80% VGO + 20% DAO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>F</td>
<td>MD</td>
</tr>
<tr>
<td>360</td>
<td>78.02</td>
<td>20.29</td>
</tr>
<tr>
<td>370</td>
<td>74.62</td>
<td>22.82</td>
</tr>
<tr>
<td>380</td>
<td>70.43</td>
<td>25.74</td>
</tr>
<tr>
<td>390</td>
<td>65.39</td>
<td>28.96</td>
</tr>
<tr>
<td>400</td>
<td>59.45</td>
<td>32.29</td>
</tr>
<tr>
<td>410</td>
<td>52.63</td>
<td>35.44</td>
</tr>
<tr>
<td>420</td>
<td>45.09</td>
<td>37.93</td>
</tr>
</tbody>
</table>
Table 5.38  Effect of reaction time on product yields at 360°C - Model IV

<table>
<thead>
<tr>
<th>Reaction time, h</th>
<th>Product yields, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>VGO</td>
</tr>
<tr>
<td></td>
<td>F</td>
</tr>
<tr>
<td>0.0</td>
<td>89.50</td>
</tr>
<tr>
<td>0.25</td>
<td>79.67</td>
</tr>
<tr>
<td>0.295</td>
<td>72.76</td>
</tr>
<tr>
<td>0.445</td>
<td>72.76</td>
</tr>
<tr>
<td>0.5</td>
<td>70.93</td>
</tr>
<tr>
<td>0.75</td>
<td>63.14</td>
</tr>
<tr>
<td>0.89</td>
<td>59.16</td>
</tr>
<tr>
<td>1.0</td>
<td>56.21</td>
</tr>
<tr>
<td>1.25</td>
<td>50.04</td>
</tr>
<tr>
<td>1.5</td>
<td>44.54</td>
</tr>
<tr>
<td>1.75</td>
<td>39.65</td>
</tr>
<tr>
<td>2.0</td>
<td>35.30</td>
</tr>
</tbody>
</table>

The yield of VGO Feedstock decreased as the reactor temperature was increased from 360 to 420°C while the yields of naphtha (N) and gas (G) product lumps continuously increased at all reaction times. The yield of middle distillates increased as the temperature was increased from 360 to 420°C at lower reaction times. But at a reaction time of 0.89 h, the yield of middle distillate fraction increased initially up to a reactor temperature of 400°C and then started decreasing with reactor temperature as shown in Figure 5.31. The yield of VGO feedstock decreased while the yield of gas and naphtha fractions increased continuously with reaction time at a constant reactor temperature. But the yield of middle distillates initially increased with reaction time and then decreased at higher reaction time at constant reactor temperatures. For example a maximum middle distillates yield of 52.56 wt% was obtained at a reaction time of 1.25 h during hydrocracking at a constant reactor temperature of 400°C as shown in Figure 5.33.

The kinetic simulation of hydrocracking process using Model IV predicted product yield distribution during hydrocracking very well in accordance with general trend in product yields observed previously in the case of other models. Normally the yield of feedstock decreased and yields of
naphtha and gas fractions increased continuously with increase in hydrocracking severity especially at higher reactor temperature and reaction time due to increased rate of hydrocracking reactions. At higher reactor temperatures, the naphtha and gas formation was found to be very high indicating higher temperature sensitivity of the reactions leading to these fractions as indicated by their activation energies. The yield of middle distillates increased initially up to a certain reaction temperature and then decreased due to increased rate of secondary hydrocracking of middle distillates compared to its rate of formation. The same trend in the yield of middle distillates was observed with respect to reaction time at a constant reactor temperature.

Figure 5.30  Effect of temperature on product yields at 0.445 h - Model IV
Figure 5.31 Effect of temperature on product yields at 0.89 h - Model IV

Figure 5.32 Effect of reaction time on product yields at 380°C - Model IV
Figure 5.33  Effect of reaction time on product yields at 400°C- Model IV

Figure 5.34  Parity plot for Model IV - All Experimental data for both feedstock
Figure 5.34 presents the parity plot comparing the experimental and predicted product yields for all the data generated in the present work for both the feedstock. The match between experimental and predicted product yields is quite close with correlation coefficient of 0.9995 indicating the applicability of Model IV for representing hydrocracking process.

The simulated product yield distribution pattern generated using Model IV was found to be in accordance with the chemistry of hydrocracking process and represented the hydrocracking process very well in the entire range of operating conditions studied in the present work for both the feedstock. As presented in Tables 5.37 and 5.38, Feed B also exhibited a similar product yield distribution during hydrocracking as that of Feed A in the entire range of operating conditions studied for Model IV.

5.2.6 Model V

There are six kinetic parameters to be estimated for this four lump kinetic model with six hydrocracking reactions. This model is almost similar to Model IV except that it considers one additional hydrocracking reaction of naphtha formed during primary cracking of the feedstock. The kinetic parameters estimated for Model V for both the feedstock are listed in Table 5.39. As can be seen from Table 5.39, the activation energy for the formation of middle distillates from VGO feedstock is lower compared to the activation energies for the formation of naphtha and gas. This indicates the higher temperature sensitivity of the primary hydrocracking reactions leading to the formation of naphtha and gas compared to the hydrocracking reaction leading to the formation of middle distillates from the feedstock. The same observation was made for the case of Model IV also as shown earlier in this section.

The kinetic rate constants at a reactor temperature of 380°C indicated that the formation of middle distillates occurred at higher reaction rates compared to the formation of naphtha and gas fractions. The activation energy for secondary hydrocracking of middle distillates fraction to form naphtha and gas was higher compared to the values of activation energies obtained for primary hydrocracking of VGO feedstock for both feedstock. As shown by their activation energies, the secondary hydrocracking reactions are highly temperature sensitive compared to primary hydrocracking reactions.
### Table 5.39  Kinetic Expression for Model V

<table>
<thead>
<tr>
<th>Kinetic parameter</th>
<th>Kinetic expression</th>
<th>k at 380°C, h⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Feedstock: Vacuum gas oil</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_1$</td>
<td>$3.1524 \times 10^6 \exp(-1.9978 \times 10^4/RT)$</td>
<td>0.6474</td>
</tr>
<tr>
<td>$k_2$</td>
<td>$2.9548 \times 10^{11} \exp(-3.6839 \times 10^4/RT)$</td>
<td>0.1258</td>
</tr>
<tr>
<td>$k_3$</td>
<td>$5.6486 \times 10^7 \exp(-2.7597 \times 10^4/RT)$</td>
<td>0.0316</td>
</tr>
<tr>
<td>$k_4$</td>
<td>$1.8701 \times 10^{12} \exp(-4.0560 \times 10^4/RT)$</td>
<td>0.0660</td>
</tr>
<tr>
<td>$k_5$</td>
<td>$1.7239 \times 10^{13} \exp(-3.7785 \times 10^4/RT)$</td>
<td>0.0377</td>
</tr>
<tr>
<td>$k_6$</td>
<td>$5.1351 \times 10^5 \exp(-2.1066 \times 10^4/RT)$</td>
<td>0.0413</td>
</tr>
<tr>
<td><strong>Feedstock: 80% VGO + 20% DAO</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_1$</td>
<td>$1.0290 \times 10^7 \exp(-2.1584 \times 10^4/RT)$</td>
<td>0.6034</td>
</tr>
<tr>
<td>$k_2$</td>
<td>$2.1971 \times 10^{11} \exp(-3.6776 \times 10^4/RT)$</td>
<td>0.1120</td>
</tr>
<tr>
<td>$k_3$</td>
<td>$1.0693 \times 10^9 \exp(-3.1392 \times 10^4/RT)$</td>
<td>0.0327</td>
</tr>
<tr>
<td>$k_4$</td>
<td>$1.4421 \times 10^{10} \exp(-3.3381 \times 10^4/RT)$</td>
<td>0.0803</td>
</tr>
<tr>
<td>$k_5$</td>
<td>$1.5269 \times 10^{10} \exp(-3.4764 \times 10^4/RT)$</td>
<td>0.0315</td>
</tr>
<tr>
<td>$k_6$</td>
<td>$1.3201 \times 10^7 \exp(-2.5380 \times 10^4/RT)$</td>
<td>0.0378</td>
</tr>
</tbody>
</table>

Model V was represented by four simple first order ordinary differential equations for the change in the yields of VGO Feedstock, Middle Distillates, Naphtha and Gas fractions with respect to reaction time and were presented in chapter 4. These model differential equations were solved simultaneously to obtain product yield distribution of the kinetic lumps with respect to change in reaction time and reactor temperature using the kinetic parameters listed in Table 5.39. The effect of reactor temperature on product yields at various reaction times are presented in Table 5.40 and Figure 5.35. The effect of reaction time on product yields at various reactor temperatures is presented in Tables 5.41 and Figures 5.36 and 5.37. The parity plot for all the product yield data obtained for Model V for both the feedstock is shown in Figure 5.38.
Figure 5.35  Effect of temperature on product yields at 0.89 h - Model V

Figure 5.36  Effect of reaction time on product yields at 380°C - Model V
Figure 5.37 Effect of reaction time on product yields at 400°C - Model V

The product yield distribution obtained by solving the differential equations for Model V was similar to that obtained for Model IV at various operating conditions. The yield of VGO feedstock decreased and yields of
naphtha and gas fractions increased continuously with increase in hydrocracking severity especially at higher reactor temperature and reaction time due to increased rate of hydrocracking reactions. The yield of middle distillates increased initially up to a certain reaction severity and then started decreasing due to increased rate of its hydrocracking at higher reaction severity. At higher reactor temperatures, the naphtha and gas formation was found to be very high indicating higher temperature sensitivity of the reactions leading to these fractions as indicated by their activation energies.

As can be seen from Figure 5.38, the match between experimental and predicted product yields is quite close with correlation coefficient of 0.9989 indicating the applicability of Model V for representing hydrocracking process.

Table 5.40  Effect of temperature on product yields at a reaction time of 0.445 h - Model V

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Product yields, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>VGO</td>
</tr>
<tr>
<td></td>
<td>F  MD  N  G</td>
</tr>
<tr>
<td>360</td>
<td>72.53 24.57 2.16 0.74</td>
</tr>
<tr>
<td>370</td>
<td>67.81 27.79 3.34 1.06</td>
</tr>
<tr>
<td>380</td>
<td>62.12 31.31 5.05 1.52</td>
</tr>
<tr>
<td>390</td>
<td>55.43 34.93 7.47 2.17</td>
</tr>
<tr>
<td>400</td>
<td>47.80 38.30 10.80 3.10</td>
</tr>
<tr>
<td>410</td>
<td>39.43 40.94 15.24 4.39</td>
</tr>
<tr>
<td>420</td>
<td>30.71 42.22 20.91 6.17</td>
</tr>
</tbody>
</table>

Table 5.41  Effect of reaction time on product yields at 360°C - Model V

<table>
<thead>
<tr>
<th>Reaction time, h</th>
<th>Product yields, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>VGO</td>
</tr>
<tr>
<td></td>
<td>F  MD  N  G</td>
</tr>
<tr>
<td>0.0</td>
<td>89.50 10.50 0.0 0.0</td>
</tr>
<tr>
<td>0.25</td>
<td>79.53 18.80 1.26 0.42</td>
</tr>
</tbody>
</table>
Model VI was proposed based on the concept of constant stoichiometric coefficients for hydrocracking reactions. These stoichiometric coefficients are assumed to represent the product selectivity of a particular feedstock and catalyst system and thus can be termed as selectivity coefficients. These stoichiometric mass coefficients are considered to be constant for a system of hydrocracking catalyst and feedstock since the selectivity of a particular system cannot vary much for the selected reaction scheme. By introducing stoichiometric coefficients in the hydrocracking reaction scheme with mass balance constraints, the number of kinetic parameters to be estimated is rendered minimum. By applying the concepts of stoichiometry to a complex reacting mixture, the number of independent cracking reactions was minimized (Ayasse et al 1997).

There are four kinetic lumps considered in the model along with two reactions involving the hydrocracking of feedstock and middle distillates.
There are two kinetic constants and five stoichiometric coefficients to be evaluated for the model. The stoichiometric coefficients and kinetic constants estimated using a constrained optimization technique with suitable mass balance constrains are presented in Table 5.42. A single constant stoichiometry was assumed to represent a particular catalyst and feed system. Since the stoichiometry of the reaction system depends mostly on the hydrocracking catalyst, the same stoichiometric coefficients estimated for Feed A were used for Feed B also in evaluating kinetic constants.

As can be seen from Table 5.42, the stoichiometric coefficients for the hydrocracking reactions shows that the catalyst system studied in the present work is particularly very selective towards middle distillates with a coefficient of 0.8750 for the primary hydrocracking reaction of feedstock. The stoichiometric coefficients indicate the selectivity of a particular hydrocracking catalyst/feed system as mentioned earlier. The stoichiometric coefficients for the formation of naphtha and gas fractions by hydrocracking of the feedstock are 0.0890 and 0.0360 respectively indicating poor selectivity of the chosen catalyst system for naphtha and gas fractions. The reaction rate constants at a reactor temperature of 380°C indicate that the rate constant is higher for the hydrocracking reaction of VGO feedstock compared to the secondary cracking reaction of middle distillates. The first reaction for the primary cracking of VGO feedstock has a rate constant of 0.7952 h\(^{-1}\) while the reaction of middle distillate fraction has a rate constant of 0.1944 h\(^{-1}\) indicating lower reactivity of the middle distillates compared to the feedstock. The activation energy for VGO hydrocracking reaction is 23253 cal/gmol compared to the value of 43313 cal/gmol for the reaction of middle distillates indicating higher temperature sensitivity of the secondary hydrocracking reaction of middle distillates.
Table 5.42 Kinetic and stoichiometric parameters for Model VI

<table>
<thead>
<tr>
<th>Kinetic parameter</th>
<th>Kinetic expression</th>
<th>k at 380°C, h⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Feedstock: Vacuum gas oil</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( k_1 )</td>
<td>(4.9436 \times 10^7 \exp\left(-\frac{2.3253 \times 10^4}{RT}\right))</td>
<td>0.7952</td>
</tr>
<tr>
<td>( k_2 )</td>
<td>(5.5342 \times 10^{13} \exp\left(-\frac{4.3313 \times 10^4}{RT}\right))</td>
<td>0.1944</td>
</tr>
<tr>
<td><strong>Feedstock: 80% VGO + 20% DAO</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( k_1 )</td>
<td>(8.7193 \times 10^7 \exp\left(-\frac{2.4097 \times 10^4}{RT}\right))</td>
<td>0.7398</td>
</tr>
<tr>
<td>( k_2 )</td>
<td>(5.6134 \times 10^{13} \exp\left(-\frac{4.3268 \times 10^4}{RT}\right))</td>
<td>0.2017</td>
</tr>
</tbody>
</table>

**Stoichiometric Coefficients**

<table>
<thead>
<tr>
<th>( \lambda_1 )</th>
<th>( \lambda_2 )</th>
<th>( \lambda_3 )</th>
<th>( \lambda'_1 )</th>
<th>( \lambda'_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0360</td>
<td>0.0890</td>
<td>0.8750</td>
<td>0.3000</td>
<td>0.7000</td>
</tr>
</tbody>
</table>

The rate constants for the reaction of feedstock and middle distillates for hydrocracking of Feed B are 0.7398 and 0.2017 h⁻¹ respectively. The rate constant for the reaction of feedstock for the case of Feed B is lower compared to Feed A. The activation energy for the hydrocracking of feedstock and middle distillates is 24097 and 43268 cal/gmol respectively for Feed B. Feed B required a higher activation energy compared to Feed A for hydrocracking. This higher activation energy required for the hydrocracking of Feed B will make the hydrocracking unit to operate at slightly higher reactor temperature in case of this feedstock for constant conversion levels and this will result in increased secondary reactions and formation of more naphtha and gas. Also higher temperatures employed during hydrocracking of Feed B will increase the deactivation of hydrocracking catalyst and reduce unit cycle lengths.
The effect of reactor temperature on product yields at various reaction times were presented in Table 5.43 and Figure 5.39. These data were generated by solving the model differential equations presented in chapter 4 for the effect of reactor temperature on product yields at different reaction time. As can be seen from Table 5.43 and Figure 5.39, this model predicts the yield distribution of products during hydrocracking very well according to the chemistry of the hydrocracking process. The yield of VGO feedstock decreased and yield of naphtha and gas fractions increased continuously with reactor temperature at a constant reaction time. At higher reaction time of 0.89 h, the yield of middle distillates initially increased up to a maximum value and then decreased due to increased rate of secondary hydrocracking of middle distillates compared to its rate of formation. For operating a hydrocracker unit to maximize middle distillates, it is necessary to optimize the operating conditions for obtaining better yields.

Table 5.44 and Figures 5.40 and 5.41 presents the simulated effect of reaction time on product yields at various reactor temperatures. These data were generated by solving the model differential equations for the effect of reaction time on product yields at various reactor temperatures using the stoichiometric and kinetic parameters evaluated and presented in Table 5.42 for Model VI. The reactor temperature had a very pronounced effect on the conversion of feedstock compared to the reaction time. The yield of feedstock

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Product yields, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>VGO</td>
<td>80% VGO + 20% DAO</td>
</tr>
<tr>
<td>Reaction time, h</td>
<td>F</td>
</tr>
<tr>
<td>-----------------</td>
<td>-----</td>
</tr>
<tr>
<td>0.0</td>
<td>89.50</td>
</tr>
<tr>
<td>0.25</td>
<td>79.71</td>
</tr>
<tr>
<td>0.295</td>
<td>78.07</td>
</tr>
<tr>
<td>0.445</td>
<td>72.83</td>
</tr>
<tr>
<td>0.5</td>
<td>70.99</td>
</tr>
<tr>
<td>0.75</td>
<td>63.23</td>
</tr>
<tr>
<td>0.89</td>
<td>59.26</td>
</tr>
<tr>
<td>1.0</td>
<td>56.31</td>
</tr>
<tr>
<td>1.25</td>
<td>50.16</td>
</tr>
<tr>
<td>1.5</td>
<td>44.67</td>
</tr>
<tr>
<td>1.75</td>
<td>39.79</td>
</tr>
<tr>
<td>2.0</td>
<td>35.43</td>
</tr>
</tbody>
</table>

Table 5.44 Effect of reaction time on product yields at 360°C - Model VI
Figure 5.39  Effect of temperature on product yields at 0.89 h - Model VI

Figure 5.40  Effect of reaction time on product yields at 380°C - Model VI
Figure 5.41  Effect of reaction time on product yields at 400°C- Model VI

decreased continuously with reaction time at a constant reactor temperature and the yield of naphtha and gas fractions increased. The yield of middle distillates showed a maximum value at a particular reaction time and then decreased due to higher rate of secondary cracking reactions at higher reaction severity.

Figure 5.42 shows the parity plot comparing experimental and predicted product yields for all the data used in the present work for both the feedstock using Model VI. The fit between experimental and predicted product yield is very good with a correlation coefficient of 0.9995 indicating the applicability of this type of model analysis for hydrocracking process. The simulations were generated for Feed B also using the kinetic and stoichiometric parameters presented in Table 5.42 and presented in Tables 5.43 to 5.44. The product yield distributions showed almost similar trend the case of Feed B as obtained for Feed A in the entire range of operating conditions.
5.2.8 Model VII

Model VII was also proposed based on the same concept of constant stoichiometric coefficients for hydrocracking reactions as that of Model VI. In this model, there are five discrete lumps chosen to represent the hydrocracking process instead of four lumps in case of Model VI. The discrete lumps of diesel and kerosene are considered separately to predict their individual product yields instead of lumping them as middle distillates. There are three hydrocracking reactions considered to occur between these five kinetic lumps. The hydrocracking reactions of feedstock, diesel and kerosene were considered and each of the lumps is assumed to yield all the other products boiling below them during hydrocracking reactions. The reaction of naphtha to yield gas is not considered due to the fact that under normal hydrocracking reaction conditions, naphtha will not react significantly to yield other cracked products. A constant stoichiometry was assumed to represent a particular feed and catalyst system. The proposed reaction scheme and the model equations with mass balance constrains were presented in chapter 4. The stoichiometric coefficients and kinetic constants estimated using a constrained optimization technique with mass balance constrains are listed in Table 5.45 for Model VII.
Table 5.45 Kinetic and stoichiometric parameters for Model VII

<table>
<thead>
<tr>
<th>Kinetic parameter</th>
<th>Kinetic expression</th>
<th>k at 380°C, h⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Feedstock: Vacuum gas oil</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( k_1 )</td>
<td>( 4.8675 \times 10^7 \exp(-2.3233 \times 10^4/RT) )</td>
<td>0.7948</td>
</tr>
<tr>
<td>( k_2 )</td>
<td>( 8.4683 \times 10^{14} \exp(-4.5063 \times 10^4/RT) )</td>
<td>0.7836</td>
</tr>
<tr>
<td>( k_3 )</td>
<td>( 2.3133 \times 10^{15} \exp(-4.8528 \times 10^4/RT) )</td>
<td>0.1463</td>
</tr>
<tr>
<td><strong>Feedstock: 80% VGO + 20% DAO</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( k_1 )</td>
<td>( 8.6072 \times 10^7 \exp(-2.4081 \times 10^4/RT) )</td>
<td>0.7394</td>
</tr>
<tr>
<td>( k_2 )</td>
<td>( 1.4887 \times 10^{15} \exp(-4.5761 \times 10^4/RT) )</td>
<td>0.7746</td>
</tr>
<tr>
<td>( k_3 )</td>
<td>( 7.5623 \times 10^{13} \exp(-4.3887 \times 10^4/RT) )</td>
<td>0.1694</td>
</tr>
<tr>
<td><strong>Stoichiometric Coefficients</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \lambda_1 )</td>
<td>0.0360</td>
<td>0.0890</td>
</tr>
</tbody>
</table>

As can be seen from Table 5.45, the kinetic constants at a reactor temperature of 380°C showed that the reaction rate for the hydrocracking of feedstock is higher compared to hydrocracking of diesel and kerosene fractions in the case of VGO feedstock. The rate constant of 0.7948 h⁻¹ was obtained for the hydrocracking of VGO feedstock. The rate constants of 0.7836 and 0.1463 h⁻¹ were obtained for the hydrocracking of diesel and kerosene fractions. The rate constant values for the hydrocracking of VGO feedstock and diesel fraction were very close indicating the tendency of the selected catalyst system to hydrocrack these fractions at an equally higher reaction rate to form more of jet fuel. The experimental data generated for the hydrocracking of different feedstocks as part of the present work also confirms the selectivity of the catalyst system towards the formation of jet
fuel at the expense of diesel and VGO feedstock. For the case of Feed B also similar rate constant values were obtained as that of Feed A. However the rate of formation of gas and naphtha fractions was slightly higher compared to Feed A.

The activation energy of 23233 cal/gmol was obtained for the hydrocracking of feedstock in the case of feed A while an activation energy of 24081 cal/gmol was obtained for Feed B for the same reaction. Hydrocracking of Feed B required slightly higher activation energy compared to the hydrocracking of Feed A. The activation energy for the hydrocracking reactions of diesel and kerosene was found to be 45063 and 48528 cal/gmol respectively. These two reactions had higher activation energy compared to the hydrocracking reaction of VGO feedstock indicating higher temperature sensitivity of these two hydrocracking reactions. The hydrocracking reactions of kerosene and diesel will be more predominant at higher operating temperatures due to their higher activation energies and due to this there will be increased yield of unwanted naphtha and gas fractions at these higher severities. The stoichiometric coefficients generally indicate the selectivity of a particular catalyst system to form specific product fractions preferentially over other products. The stoichiometric coefficients indicate that this catalyst is very selective towards middle distillates such as diesel and kerosene and less selective towards naphtha and gas fractions.

Table 5.46 and Figures 5.43 and 5.44 presents the effect of reactor temperature on product yields at various reaction times. These data were generated by solving the model differential equations for Model VII presented in chapter 4 for the effect of reactor temperature on product yield distribution at various reaction times. As can be seen from the data, the yield of VGO feedstock decreased continuously while the yield of gas, naphtha and kerosene fractions increased with reactor temperature at all the reaction times.
As can be seen from Figure 5.43, the yield of diesel increased up to a reactor temperature of 380°C and then as the temperature was increased further, the yield of diesel decreased at a reaction time of 0.445 h. This indicated that the selected catalyst system is more selective towards middle distillates such as jet fuel and diesel. As can be seen from Figure 5.44, the yield of VGO decreased at a faster rate with reactor temperature and the yield of gas and naphtha increased continuously at a reaction time of 0.89 h. The yield of diesel increased up to a reactor temperature of 370°C and then started decreasing due to increased rate of hydrocracking of diesel compared to its rate of formation at the higher severity levels. The kerosene yield also

Table 5.46   Effect of temperature on product yields at a reaction time of 0.295 h

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>VGO</th>
<th>80% VGO + 20% DAO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>F  D  K  N  G</td>
<td>F  D  K  N  G</td>
</tr>
<tr>
<td>360</td>
<td>78.06 16.02 4.20 1.22 0.50</td>
<td>79.39 15.17 3.85 1.13 0.46</td>
</tr>
<tr>
<td>370</td>
<td>74.59 17.20 5.80 1.72 0.69</td>
<td>76.07 16.28 5.39 1.61 0.65</td>
</tr>
<tr>
<td>380</td>
<td>70.35 18.23 7.99 2.44 0.99</td>
<td>71.96 17.26 7.52 2.32 0.94</td>
</tr>
<tr>
<td>390</td>
<td>65.29 18.80 10.97 3.51 1.43</td>
<td>66.99 17.78 10.46 3.38 1.38</td>
</tr>
<tr>
<td>400</td>
<td>59.41 18.47 14.88 5.14 2.10</td>
<td>61.14 17.43 14.38 5.01 2.04</td>
</tr>
<tr>
<td>410</td>
<td>52.76 16.86 19.61 7.65 3.13</td>
<td>54.45 15.83 19.19 7.48 3.06</td>
</tr>
<tr>
<td>420</td>
<td>45.50 13.88 24.44 11.46 4.71</td>
<td>47.05 12.92 24.29 11.16 4.59</td>
</tr>
</tbody>
</table>
Figure 5.43  Effect of temperature on product yields at 0.445 h - Model VII

Figure 5.44  Effect of temperature on product yields at 0.89 h - Model VII
increased continuously up to a reactor temperature of 410°C and then it started decreasing due to higher rate of secondary cracking of kerosene compared to its rate of formation. The simulated data on the effect of reactor temperature on product yields showed the increased selectivity of the chosen catalyst system for the production of middle distillates. As the operating severity is increased further, the selectivity shifts towards the formation of jet fuel at the expense of feedstock and diesel. The selectivity of the chosen catalyst system was found to be lower for the formation of gas and naphtha fractions due to lower zeolite content of the catalyst.

The effect of reaction time on product yields at different reactor temperatures are shown in Figures 5.45 to 5.47. As can be seen from Figure 5.45, the yield of VGO feedstock decreased while the yields of gas, naphtha and kerosene fractions increased continuously with reaction time at a reactor temperature of 360°C. The yield of diesel increased to a maximum value and then started decreasing at higher reaction time. As can be seen from Figure 5.46, the same type of product yield distribution had been obtained for VGO feedstock at a reactor temperature of 380°C as that obtained at a temperature of 360°C. But the maximum value of diesel yield obtained had shown a reduction at higher reactor temperatures. As can be seen from Figure 5.47, the yield of VGO feedstock decreased at a higher rate at a reactor temperature of 400°C and the yields of gas and naphtha fractions increased continuously with reaction time. The yield of diesel showed a maximum value at lower reaction time itself compared to that obtained at lower temperatures. The yield of kerosene increased initially and then decreased at higher reaction severities. This shows that employing very high reactor temperatures and reaction time, the yields of gas and naphtha fractions increase at the expense of hydrocracking of other higher boiling fractions. Figure 5.48 presents the parity data comparing the experimental and predicted product yields for all the data generated for both feedstocks in the case of Model VII. Figure 5.48
Figure 5.45 Effect of reaction time on product yields at 360°C - Model VII
Figure 5.46  Effect of reaction time on product yields at 380°C - Model VII
Figure 5.47 Effect of reaction time on product yields at 400°C - Model VII
Figure 5.48  Parity plot for Model VII - All Exp. Data for both feedstock
shows a higher correlation coefficient of 0.9995 indicating very good fit between experimental and predicted yields from Model VII for the range of operating conditions studied in the present work.

5.2.9 Kinetics of HDS and HDN Reactions

Kinetics of hydrodesulphurization and hydrodenitrogenation reactions was studied by expressing the overall rate using simple first order kinetic equations as presented in chapter 4. Qader and Hill (1969) and El-Kady (1979) used similar type of first order rate equations for representing hydrodesulphurization and hydrodenitrogenation reactions occurring during hydrocracking. Table 5.47 presents the kinetic parameters for hydrodesulphurization and hydrodenitrogenation reactions over both hydrotreating and hydrocracking catalyst sections. Since hydrocracking catalyst is a dual functional catalyst, the metal function promotes HDS and HDN reactions along with hydrocracking. The kinetics for HDS and HDN reactions are assumed to be the same for both the feedstock type.

As can be seen from Table 5.47, the activation energy for hydrodenitrogenation reactions was higher compared to hydrodesulphurization reactions for both the catalyst systems. Generally hydrodenitrogenation occurs at a slower rate compared to hydrodesulphurization since most of the nitrogen compounds are attached to refractory aromatic compounds that are difficult to crack. Hydrodenitrogenation mostly occurs after the saturation of these refractory aromatic compounds in presence of hydrogen. During industrial hydrocracking process, most of the sulfur and nitrogen compounds are removed over hydrotreating catalyst system as shown by their higher rates.

Table 5.47 Kinetic Expression for HDS and HDN reactions
<table>
<thead>
<tr>
<th>Kinetic parameter</th>
<th>Kinetic expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrotreating Catalyst</td>
<td></td>
</tr>
<tr>
<td>$k_s$</td>
<td>$8.0900 \times 10^4 \exp\left(-1.1292 \times 10^4/RT\right)$</td>
</tr>
<tr>
<td>$k_N$</td>
<td>$9.1250 \times 10^4 \exp\left(-1.2002 \times 10^4/RT\right)$</td>
</tr>
<tr>
<td>Hydrocracking Catalyst</td>
<td></td>
</tr>
<tr>
<td>$k_s$</td>
<td>$8.3900 \times 10^4 \exp\left(-1.2315 \times 10^4/RT\right)$</td>
</tr>
<tr>
<td>$k_N$</td>
<td>$9.5214 \times 10^4 \exp\left(-1.3619 \times 10^4/RT\right)$</td>
</tr>
</tbody>
</table>

### 5.3 MECHANISM OF HYDROCRACKING REACTIONS

The product yield distribution data obtained in the present investigation for the hydrocracking of different feedstocks over an industrial hydrocracking catalyst system indicated that hydrocracking mainly produces middle distillates such as diesel and jet fuel, gasoline and gas through a mechanism involving a combination of simultaneous and consecutive cracking reactions followed by extensive isomerisation and hydrogenation of products, as reported by Qader and Hill (1969). As can be seen from Table 5.7 for the properties of total naphtha fraction obtained from pilot plant reactors, the naphtha fraction contained higher amounts of isoparaffins indicating the occurrence of extensive isomerisation reactions after cracking. The hydrocracked products contained higher amounts of saturated compounds such as paraffins and naphthenes and lower amounts of unsaturated aromatic compounds. This is evident from the higher naphthenes content of naphtha fractions and higher saturates content of kerosene, diesel and unconverted oil fractions obtained during pilot plant experiments. This shows the extensive hydrogenation of cracked products at all boiling ranges during hydrocracking.

It is evident that cracking of the C-C bonds followed by isomerisation and hydrogenation of the cracked products occurs during hydrocracking. The presence of olefins in naphtha fraction could not be detected in the present work due to very low amount of olefins in naphtha fractions that is beyond the detection limit of the instrument. It is known that olefins are formed as intermediates during C-C bond cracking and immediately hydrogenated due to their higher reactivity under normal hydrocracking reactions.

As shown by the experimental data on hydrocracking of industrial feedstocks, the long chain paraffinic compounds are found to undergo hydrocracking reactions to yield lighter paraffin molecules. Isomerization of paraffins followed by cracking also takes place under hydrocracking operating conditions. This is the reason for the increased isoparaffin content of naphtha fraction obtained by hydrocracking of VGO feedstock. The unsaturated aromatic compounds undergo hydrogenation to form naphthenes which in turn undergo naphthene ring opening (hydrodecyclization) reactions. The side chains of cyclic compounds are cracked during the reaction called...
hydrodealkylation. The naphthenic molecules are generally resistant to cracking under industrial hydrocracking operating conditions and thus end up in gasoline fraction as seen by the increased concentration of naphthenes in hydrocracked naphtha.

The experimental data showed that the mechanisms of hydrocracking reactions are essentially the carbenium ion mechanism of catalytic cracking reactions coupled with that of hydrogenation and isomerisation reactions. Although the initial cracking reactions such as C-C bond breaking are common to both hydrocracking and catalytic cracking, the presence of excessive hydrogen and of a hydrogenation component in the catalyst results in hydrogenated products and inhibits some of the secondary reactions, such as coke formation and secondary cracking. The cracking of the hydrocarbon molecules of the vacuum gas oil can be represented by the following steps as per the suggestion of Qader and Hill (1969).

\[
C_iH_{2i+2} \rightarrow C_mH_{2m+2} + C_nH_{2n}
\]  \hspace{1cm} (5.2)

\[
C_nH_{2n} \rightarrow C_iH_{2i}
\]  \hspace{1cm} (5.3)

\[
C_nH_{2n} + H_2 \rightarrow C_nH_{2n+2}
\]  \hspace{1cm} (5.4)

\[
C_iH_{2i} + H_2 \rightarrow C_iH_{2i+2}
\]  \hspace{1cm} (5.5)

\[
A + 3H_2 \rightarrow N
\]  \hspace{1cm} (5.6)

\[
AR + H_2 \rightarrow AH + RH
\]  \hspace{1cm} (5.7)

\[
NR + H_2 \rightarrow NH + RH
\]  \hspace{1cm} (5.8)

\[
AN + H_2 \rightarrow AR + R^1H
\]  \hspace{1cm} (5.9)

\[
AR + H_2 \rightarrow AH + R^1H
\]  \hspace{1cm} (5.10)

Where A and N represent fused aromatic rings and fused naphthenic rings respectively while AR and AN represent alkyl aromatic and hydroaromatic compounds respectively. NR represents alkyl naphthenic molecule. R, R^1 and
$R_{1}^{11}$ represent alkyl side chains attached to ring compounds. In Equation (5.6), $A$ represents monoaromatic compound benzene and $N$ represents corresponding six ring naphthenes. Equation (5.2) represents the cracking of paraffins giving rise to lower molecular weight paraffins and olefins. The extent of this reaction depends upon the severity of reaction and the nature of feedstock molecules. Equation (5.3) represents isomerisation of product olefins. Equations (5.4) and (5.5) represent hydrogenation reactions. Equation (5.6) represents the hydrogenation of monoaromatics to form corresponding naphthenes. Equations (5.7) and (5.10) represent dealkylation of aromatic hydrocarbons. Equation (5.8) represents dealkylation of naphthenic side chains. Equation (5.9) represents hydrocracking of hydroaromatics. The cracking reactions shown above involve the breakage of C-C bonds present in different types of hydrocarbons and the splitting mainly proceeds through the carbonium ion mechanism proposed by Greensfelder et al (1949).

Hydrodesulphurization and hydrodenitrogenation reactions involve the rupture of C-S and C-N bonds with subsequent interaction of hydrogen with fragmented molecules, forming hydrogen sulphide and ammonia respectively. Removal of sulfur and nitrogen may proceed through an accelerated radical mechanism as proposed by Qader and Hill (1969), which may be represented as follows in the present work.

\[
R_{i}H_{j}C - SR_{2} \rightarrow R_{i}H_{j}C^{*} + R_{2}S^{*} \\
(5.11)
\]

\[
R_{i}H_{j}C - NR_{4} \rightarrow R_{i}H_{j}C^{*} + R_{4}N^{*} \\
(5.12)
\]

\[
R_{2}S^{*} + H_{2} \rightarrow R_{2}H + H_{2}S \\
(5.13)
\]

\[
R_{4}N^{*} + H_{2} \rightarrow R_{4}H + NH_{3} \\
(5.14)
\]

\[
R_{i}H_{j}C^{*} + H_{2} \rightarrow R_{i}CH_{3} \\
(5.15)
\]

\[
R_{j}H_{k}C^{*} + H_{2} \rightarrow R_{j}CH_{3} \\
(5.16)
\]

Where $R_{1}$, $R_{2}$, $R_{3}$ and $R_{4}$ represent hydrocarbon radicals. Equations (5.11) and (5.12) represent the breakage of C-S and C-N bonds in all types of sulfur and nitrogen compounds present in the gas oil feedstock. Equations (5.13) to
(5.16) represent the reactions between hydrogen and fragmented heterocyclic molecules to form products. The reaction steps listed above are the principal surface reactions that can possibly occur during hydrocracking of vacuum gas oil and indicate that the overall kinetics observed in the present work can result from the sequence of these types of reactions.

It is well known that heterogeneous catalytic processes such as hydrocracking are very complex in nature involving interplay between the chemical reactions and the physical processes. Normally heterogeneous catalytic processes involve (1) diffusion of reaction molecules from the bulk phase to the catalyst surface, (2) adsorption of the reactants on the catalyst surface, (3) surface reaction of the adsorbed molecules, (4) desorption of the products formed and (5) diffusion of the desorbed products from the catalyst surface to the bulk phase. The magnitude of energies and enthalpies of activation obtained in the present work suggests that chemical reactions but not physical processes are rate controlling.

The bifunctional hydrocracking catalyst contains two types of active sites: the acidic cracking sites and the hydrogenation metal sites. The product yield data have shown that cracking, isomerisation and hydrogenation are the principle reactions during hydrocracking of vacuum gas oil feedstock. The cracking and isomerisation reactions occur on silica-alumina or zeolitic sites and the hydrogenation reactions on nickel-molybdenum or nickel-tungsten metal sites.

The product yield distribution data generated in the pilot plant suggests that hydrogenation was complete under all experimental operating conditions as shown by the negligible amounts of olefins and heterocyclic compounds in the hydrocracked products. Also the excess isoparaffin content
of naphtha fraction indicates that isomerisation reaction is also fast during hydrocracking process. Hydrogenation and isomerisation reactions cannot control the reaction rate since they occur at a faster rate. Therefore, the cracking reactions involving the rupture of C-C, C-S and C-N bonds will be rate-limiting in the hydrocracking of gas oil over the dual-functional catalyst.

This observation was also made by Qader and Hill (1989) for the hydrocracking of gas oil fraction over dual functional hydrocracking catalyst.

The kinetic analysis of hydrocracking process using various lumped reaction schemes suggests that hydrocracking of a higher molecular weight fraction occurs at random and can possibly yield all the lighter products boiling below it. The kinetic data indicate that both the feedstock used in the present work, vacuum gas oil and blend of vacuum gas oil and deasphalted oil, exhibit similar kinetic behavior under hydrocracking conditions, but the Feed B needs a slightly higher activation energy. The mechanism of hydrocracking of both the feedstocks appear to be similar, as proposed above, and the energetics suggest that chemical reactions involving the cracking of C-C, C-O, C-S and C-N bonds will control reaction rate.

Generally hydrocracking catalysts are dual-functional in nature containing both a cracking and a hydrogenation component. Since cracking is the rate-controlling step in hydrocracking, the reaction rates and product yield distribution are mainly influenced by the activity of the cracking component of the catalyst. Hydrocracking catalysts with higher zeolite content will exhibit higher activity to form more gasoline and gas while catalysts with lower zeolite content will be used for maximizing the production of middle distillates. The nature of feedstock seems to have little effect on the conversion and product yield distribution during hydrocracking.
5.4 PRODUCT SELECTIVITY DURING HYDROCRACKING PROCESS

In the era of changing market demands and increasingly stringent environmental regulations, it is essential to produce high quality products that have a higher demand. In this connection, it is essential to select a hydrocracking catalyst system or operating conditions that can give higher yield of specified products. The selectivity of a particular hydrocracking catalyst system depends on many parameters such as acidity of the catalyst, operating conditions etc. Hydrocracking catalysts with higher zeolite content have higher acidity and thus selective towards naphtha production. Hydrocracking catalysts with lower acidity such as amorphous silica-alumina containing catalysts will have higher selectivity towards the formation of middle distillates. Since the acid strength of the hydrocracking catalyst cannot be changed, the operating conditions can be tailored to maximize the production of particular products at the expense of others. Hydrocracking process has good flexibility to alter the product selectivity with proper selection of catalyst system and operating conditions for the production of specific products.

In this chapter, the product yield distribution and selectivity during hydrocracking are analyzed considering various reaction schemes. There are three reaction schemes considered in this chapter to analyze product selectivity with change in operating conditions. The selectivity of the hydrocracking catalyst system for maximizing jet fuel or kerosene, diesel and middle distillates are considered. The reaction schemes were presented in chapter 4 along with the analytical expressions for product yields, maximum yields of specific products and the time at which this maximum occurs.
5.4.1 Scheme I

The kinetic expressions for the rate constants using scheme I to represent the selectivity of kerosene, diesel and middle distillates are presented in Tables 5.48 and 5.49 for both feedstocks. These tables also present typical values of rate constants at a reactor temperature of 380°C for

<table>
<thead>
<tr>
<th>Table 5.48 Kinetic Expressions for the rate constants for Scheme I - VGO Feedstock</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Kerosene Selectivity</strong></td>
</tr>
<tr>
<td><strong>Kinetic Scheme</strong></td>
</tr>
<tr>
<td>$Feed &amp; Diesel(FD) \rightarrow k_1 \rightarrow Kerosene(K) \rightarrow k_2 \rightarrow Naphtha &amp; Gas(NG)$</td>
</tr>
<tr>
<td><strong>Kinetic Constant</strong></td>
</tr>
<tr>
<td>$k_1$</td>
</tr>
<tr>
<td>$k_2$</td>
</tr>
<tr>
<td><strong>Diesel Selectivity</strong></td>
</tr>
<tr>
<td><strong>Kinetic Scheme</strong></td>
</tr>
<tr>
<td>$Feed(F) \rightarrow k_1 \rightarrow Diesel(D) \rightarrow k_2 \rightarrow Kerosene, Naphtha &amp; Gas(KNG)$</td>
</tr>
<tr>
<td><strong>Kinetic Constant</strong></td>
</tr>
<tr>
<td>$k_1$</td>
</tr>
<tr>
<td>$k_2$</td>
</tr>
<tr>
<td><strong>Middle Distillates Selectivity</strong></td>
</tr>
<tr>
<td><strong>Kinetic Scheme</strong></td>
</tr>
<tr>
<td>$Feed(F) \rightarrow k_1 \rightarrow MiddleDistillates(MD) \rightarrow k_2 \rightarrow Naphtha &amp; Gas(NG)$</td>
</tr>
<tr>
<td><strong>Kinetic Constant</strong></td>
</tr>
<tr>
<td>$k_1$</td>
</tr>
<tr>
<td>$k_2$</td>
</tr>
</tbody>
</table>
Table 5.49  Kinetic Expressions for the rate constants for Scheme I - 80%VGO+20%DAO Feedstock

<table>
<thead>
<tr>
<th>Kinetic Scheme</th>
<th>Kinetic Expression</th>
<th>k at 380°C, h⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kerosene Selectivity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Feed &amp; Diesel(FD) → k₁ → Kerosene(K) → k₂ → Naphtha &amp; Gas(NG)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>k₁</td>
<td>6.5494×10¹⁰ exp(− 3.3412×10⁴/RT)</td>
<td>0.4228</td>
</tr>
<tr>
<td>k₂</td>
<td>9.4542×10⁴ exp(− 5.9607×10³/RT)</td>
<td>0.9273</td>
</tr>
<tr>
<td>Diesel Selectivity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Feed(F) → k₁ → Diesel(D) → k₂ → Kerosene, Naphtha &amp; Gas(KNG)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>k₁</td>
<td>8.4615×10⁷ exp(− 2.4060×10⁴/RT)</td>
<td>0.7387</td>
</tr>
<tr>
<td>k₂</td>
<td>8.8719×10⁸ exp(− 2.5961×10⁴/RT)</td>
<td>1.7722</td>
</tr>
<tr>
<td>Middle Distillates Selectivity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Feed(F) → k₁ → Middle Distillates(MD) → k₂ → Naphtha &amp; Gas(NG)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>k₁</td>
<td>8.4622×10⁷ exp(− 2.4060×10⁴/RT)</td>
<td>0.7388</td>
</tr>
<tr>
<td>k₂</td>
<td>2.1853×10⁷ exp(− 2.3108×10⁴/RT)</td>
<td>0.3969</td>
</tr>
</tbody>
</table>

the hydrocracking reactions considered in this reaction scheme. The kinetic constants for this scheme were evaluated by minimizing the squared error between experimental and predicted yields of the lumps chosen using a sequential quadratic programming algorithm discussed in chapter 4 under kinetic parameter estimation. These kinetic expressions were used to find out the concentration of various lumps in the product, their overall selectivity, maximum concentration of the lump obtained at specific operating conditions, time at which maximum concentration could occur and the rate constant ratio.
The selectivity of the specified catalyst system for maximizing kerosene or jet fuel was analyzed based on a series reaction scheme as presented in chapter 4. This reaction scheme was applied to the experimental data reported in the present work for finding the value of the yield and the overall selectivity of kerosene fraction with respect to the naphtha and gas fraction at various operating conditions. The maximum yield of kerosene obtained and the time at which this occurs were evaluated at various reactor temperatures and reaction times. The total conversion and overall selectivity at maximum yield conditions was estimated and tabulated. Using the kinetic parameters estimated from the experimental data, the yield and selectivity of the kinetic lumps was simulated for this case at different reaction times and reactor temperatures.

Figures 5.49 and 5.50 shows the effect of reaction time on product yields and kerosene selectivity at 380 and 400°C respectively for VGO Feedstock. As can be seen from Figure 5.49, the yield of VGO Feedstock and Diesel (FD) decreased with reaction time while the yield of naphtha and gas fractions increased continuously. The yield of kerosene fraction increased initially up to a certain reaction time and then its yield decreased with reaction time. The overall kerosene selectivity ratio decreased continuously with reaction time. This showed that the selectivity of a particular fraction is not maximum at higher product yields. The kerosene selectivity with respect to naphtha and gas was higher at lower kerosene yields. Therefore a compromise between the product yield and selectivity should be made for optimal operation. Figure 5.50 also showed a similar trend for kerosene yield and selectivity as that of Figure 5.49. Figure 5.51 shows the effect of reaction time and temperature on kerosene selectivity at three different temperatures of 360, 380 and 400°C respectively. The kerosene selectivity was higher at lower reaction temperatures and lower reaction time.
Figure 5.49 Effect of reaction time on product yield and kerosene selectivity at 380°C for VGO Feedstock - Scheme I

Figure 5.50 Effect of reaction time on product yields and kerosene selectivity at 400°C for VGO Feedstock - Scheme I
Tables 5.50 and 5.51 present the kerosene selectivity at maximum yield conditions for Feed A and Feed B respectively. Figure 5.52 presents the maximum yield of kerosene and beta at different reactor temperatures for consecutive reaction scheme used in the present work. As can be seen from Figure 5.52, the maximum yield of kerosene obtained increased with reactor temperature. The kerosene selectivity also increased with reactor temperature for both feedstocks at maximum yield conditions. The time at which maximum yield of kerosene obtained decreased with reactor temperature. At a reactor temperature of 360°C, a maximum concentration of 15.99 wt% of kerosene was obtained at a reaction time of 2.26 hours. At a reactor temperature of 380°C, a maximum concentration of 24.60 wt% of kerosene can be obtained at a reaction time of 1.50 hours. As can be seen from Tables 5.50 and 5.51, Feed B yielded lower kerosene yield compared to Feed A at all reactor temperatures. The selectivity for the formation of kerosene was slightly lower for Feed B compared to Feed A.
Table 5.50  Kerosene selectivity at maximum yield conditions for consecutive reactions - VGO Feedstock

<table>
<thead>
<tr>
<th>Temp, deg C</th>
<th>Beta (β)</th>
<th>t&lt;sub&gt;max&lt;/sub&gt;</th>
<th>(x&lt;sub&gt;FD&lt;/sub&gt;)&lt;sub&gt;max&lt;/sub&gt;</th>
<th>(x&lt;sub&gt;K&lt;/sub&gt;)&lt;sub&gt;max&lt;/sub&gt;</th>
<th>(x&lt;sub&gt;NG&lt;/sub&gt;)&lt;sub&gt;max&lt;/sub&gt;</th>
<th>x&lt;sub&gt;i&lt;/sub&gt;</th>
<th>x&lt;sub&gt;K&lt;/sub&gt; at 0.89 h</th>
<th>S&lt;sub&gt;0&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>360</td>
<td>3.9168</td>
<td>2.2554</td>
<td>0.6262</td>
<td>0.1599</td>
<td>0.2139</td>
<td>0.3738</td>
<td>0.1187</td>
<td>0.7475</td>
</tr>
<tr>
<td>370</td>
<td>2.8220</td>
<td>1.8402</td>
<td>0.5659</td>
<td>0.2005</td>
<td>0.2336</td>
<td>0.4341</td>
<td>0.1644</td>
<td>0.8583</td>
</tr>
<tr>
<td>380</td>
<td>2.0537</td>
<td>1.4987</td>
<td>0.5051</td>
<td>0.2460</td>
<td>0.2489</td>
<td>0.4949</td>
<td>0.2200</td>
<td>0.9883</td>
</tr>
<tr>
<td>390</td>
<td>1.5090</td>
<td>1.2185</td>
<td>0.4456</td>
<td>0.2953</td>
<td>0.2591</td>
<td>0.5544</td>
<td>0.2826</td>
<td>1.1397</td>
</tr>
<tr>
<td>400</td>
<td>1.1190</td>
<td>0.9894</td>
<td>0.3887</td>
<td>0.3474</td>
<td>0.2639</td>
<td>0.6113</td>
<td>0.3455</td>
<td>1.3164</td>
</tr>
<tr>
<td>410</td>
<td>0.8371</td>
<td>0.8025</td>
<td>0.3357</td>
<td>0.4010</td>
<td>0.2633</td>
<td>0.6643</td>
<td>0.3988</td>
<td>1.5230</td>
</tr>
<tr>
<td>420</td>
<td>0.6314</td>
<td>0.6505</td>
<td>0.2872</td>
<td>0.4549</td>
<td>0.2579</td>
<td>0.7128</td>
<td>0.4312</td>
<td>1.7639</td>
</tr>
</tbody>
</table>

Table 5.51  Kerosene selectivity at maximum yield conditions for consecutive reactions - VGO + DAO Feedstock

<table>
<thead>
<tr>
<th>Temp, deg C</th>
<th>Beta (β)</th>
<th>t&lt;sub&gt;max&lt;/sub&gt;</th>
<th>(x&lt;sub&gt;FD&lt;/sub&gt;)&lt;sub&gt;max&lt;/sub&gt;</th>
<th>(x&lt;sub&gt;K&lt;/sub&gt;)&lt;sub&gt;max&lt;/sub&gt;</th>
<th>(x&lt;sub&gt;NG&lt;/sub&gt;)&lt;sub&gt;max&lt;/sub&gt;</th>
<th>x&lt;sub&gt;i&lt;/sub&gt;</th>
<th>x&lt;sub&gt;K&lt;/sub&gt; at 0.89 h</th>
<th>S&lt;sub&gt;0&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>360</td>
<td>4.3361</td>
<td>2.3047</td>
<td>0.6442</td>
<td>0.1486</td>
<td>0.2072</td>
<td>0.3558</td>
<td>0.1094</td>
<td>0.7172</td>
</tr>
<tr>
<td>370</td>
<td>3.0882</td>
<td>1.8724</td>
<td>0.5828</td>
<td>0.1887</td>
<td>0.2285</td>
<td>0.4172</td>
<td>0.1537</td>
<td>0.8258</td>
</tr>
<tr>
<td>380</td>
<td>2.2224</td>
<td>1.5179</td>
<td>0.5203</td>
<td>0.2341</td>
<td>0.2455</td>
<td>0.4797</td>
<td>0.2085</td>
<td>0.9536</td>
</tr>
<tr>
<td>390</td>
<td>1.6153</td>
<td>1.2280</td>
<td>0.4587</td>
<td>0.2840</td>
<td>0.2573</td>
<td>0.5413</td>
<td>0.2712</td>
<td>1.1038</td>
</tr>
<tr>
<td>400</td>
<td>1.1852</td>
<td>0.9917</td>
<td>0.3995</td>
<td>0.3371</td>
<td>0.2634</td>
<td>0.6005</td>
<td>0.3352</td>
<td>1.2798</td>
</tr>
<tr>
<td>410</td>
<td>0.8776</td>
<td>0.7998</td>
<td>0.3441</td>
<td>0.3921</td>
<td>0.2637</td>
<td>0.6559</td>
<td>0.3898</td>
<td>1.4869</td>
</tr>
<tr>
<td>420</td>
<td>0.6554</td>
<td>0.6445</td>
<td>0.2934</td>
<td>0.4477</td>
<td>0.2588</td>
<td>0.7066</td>
<td>0.4229</td>
<td>1.7299</td>
</tr>
</tbody>
</table>
Selectivity of the selected catalyst system for the production of diesel fraction was studied using scheme I considering a consecutive reaction system. In this reaction scheme, the feed and diesel are lumped separately and other fractions, kerosene, naphtha and gas are lumped together as a single discrete lump. There are two reaction rate constants $k_1$ and $k_2$ in this scheme representing the hydrocracking process. The kinetic constants are presented in Tables 5.48 and 5.49 for both the feedstocks. The data on diesel selectivity at maximum yield conditions has been presented in Tables 5.52 and 5.53 respectively for both feedstocks.

The kinetic constant at a reactor temperature of 380°C for the reaction of feedstock into diesel was 0.7942 h$^{-1}$ compared to 1.7817 h$^{-1}$ for the reaction of diesel. This indicates that the catalyst system shifts the product yield pattern from diesel into kerosene fraction. Similar observation was found to be valid for the case of Feed B also as shown by the kinetic constants.
Table 5.52  Diesel selectivity at maximum yield conditions for consecutive reactions – VGO Feedstock

<table>
<thead>
<tr>
<th>Temp. deg. C</th>
<th>Beta (β)</th>
<th>$t_{max}$</th>
<th>$(x_F)_{max}$</th>
<th>$(x_D)_{max}$</th>
<th>$(x_{KNG})_{max}$</th>
<th>$x_r$</th>
<th>$x_D$</th>
<th>$S_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>360</td>
<td>2.1255</td>
<td>1.1740</td>
<td>0.5194</td>
<td>0.2444</td>
<td>0.2362</td>
<td>0.4197</td>
<td>0.2392</td>
<td>0.5902</td>
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<tr>
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<td>2.1614</td>
<td>0.8703</td>
<td>0.5229</td>
<td>0.2419</td>
<td>0.2352</td>
<td>0.4158</td>
<td>0.2419</td>
<td>0.5821</td>
</tr>
<tr>
<td>380</td>
<td>2.1968</td>
<td>0.6511</td>
<td>0.5262</td>
<td>0.2395</td>
<td>0.2343</td>
<td>0.4121</td>
<td>0.2314</td>
<td>0.5741</td>
</tr>
<tr>
<td>390</td>
<td>2.2316</td>
<td>0.4914</td>
<td>0.5294</td>
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<td>0.2334</td>
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<tr>
<td>400</td>
<td>2.2660</td>
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</tr>
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<td>0.5525</td>
</tr>
<tr>
<td>420</td>
<td>2.3332</td>
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<td>0.5386</td>
<td>0.2308</td>
<td>0.2306</td>
<td>0.3982</td>
<td>0.0825</td>
<td>0.5455</td>
</tr>
</tbody>
</table>

Table 5.53  Diesel selectivity at maximum yield conditions for consecutive reactions - VGO + DAO Feedstock

<table>
<thead>
<tr>
<th>Temp. deg. C</th>
<th>Beta (β)</th>
<th>$t_{max}$</th>
<th>$(x_F)_{max}$</th>
<th>$(x_D)_{max}$</th>
<th>$(x_{KNG})_{max}$</th>
<th>$x_r$</th>
<th>$x_D$</th>
<th>$S_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>360</td>
<td>2.3133</td>
<td>1.2350</td>
<td>0.5362</td>
<td>0.2318</td>
<td>0.2320</td>
<td>0.4029</td>
<td>0.2253</td>
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</tr>
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</tr>
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<td>0.2276</td>
<td>0.3872</td>
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<tr>
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<td>0.5589</td>
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<td>0.2247</td>
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<td>0.5087</td>
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<td>0.5631</td>
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<td>0.2233</td>
<td>0.3729</td>
<td>0.0757</td>
<td>0.4998</td>
</tr>
</tbody>
</table>

Figure 5.53 shows the effect of reaction time on product yields and diesel selectivity at a reactor temperature of 360°C for VGO Feedstock. As can be seen from Figure 5.53, the yield of VGO feedstock decreased with
reaction time while the yield of kerosene, naphtha and gas (KNG) fractions increased continuously. The yield of diesel increased initially up to a certain reaction time and then decreased with reaction time due to the increased rate of its cracking compared to its formation. The overall diesel selectivity ratio decreased continuously with reaction time. This showed that the selectivity of a particular fraction did not depend on yields. Figure 5.54 presents the yield of diesel at three different reactor temperatures of 360, 380 and 400°C respectively and its selectivity at a reactor temperature of 380°C. At all the reactor temperatures, the yield of diesel reached a maximum value at a certain reaction time before the concentration started decreasing. The maximum value of diesel yield was obtained at lower reaction times as the reactor temperature increased.

Figure 5.55 presents the maximum yield of diesel obtained and beta with respect to variation in reactor temperature for consecutive reaction scheme used in the present work. As can be seen from Figure 5.55, the maximum yield of diesel obtained decreased with reactor temperature. This showed the intrinsic property of the chosen hydrocracking catalyst system, which is more selective towards jet fuel or kerosene at the cost of diesel fraction. The diesel selectivity also decreased with reactor temperature for both feedstocks at maximum yield conditions. The time at which maximum yield of diesel obtained decreased with reactor temperature. At a reactor temperature of 360°C, a maximum concentration of 24.44 wt% of diesel was obtained at a reaction time of 1.1740 hours. At a reactor temperature of 380°C, a maximum concentration of 23.95 wt% of diesel was obtained at a reaction time of 0.6511 hours. Feed B yields lower diesel compared to Feed A at all reactor temperatures. The selectivity for the formation of diesel was also lower for Feed B compared to Feed A.
Figure 5.53  Effect of reaction time on product yields and diesel selectivity at 360°C - Scheme I

Figure 5.54  Diesel Yield and Selectivity at various operating conditions - Scheme I
Middle distillates selectivity of the hydrocracking catalyst system was analyzed using scheme I considering a consecutive reaction system involving three kinetic lumps, namely, feedstock (F), middle distillates (MD) and naphtha and gas (NG). The kinetic expressions for this case were listed in Tables 5.48 and 5.49 for both the feedstock. The kinetic constant at a reactor temperature of 380°C for the reaction of feedstock into middle distillate fraction is 0.7942 h⁻¹ compared to a value of 0.3897 h⁻¹ for the reaction of middle distillates into naphtha and gas. This indicated that the catalyst system was highly selective towards the formation of middle distillates such as kerosene and diesel fractions and less selective towards the formation of naphtha and gas fractions. The selected catalyst system was found to be highly efficient for the manufacture of high quality middle distillates. Similar
observation with respect to kinetic rate parameters was found to be valid for the case of Feed B.

Figure 5.56 shows the effect of reaction time on product yields and middle distillate selectivity at a reactor temperature of 380°C for VGO Feedstock. As can be seen from Figure 5.56, the yield of VGO feedstock decreased with reaction time while the yield of naphtha and gas fraction increased continuously. The yield of middle distillates increased initially up to a certain reaction time and then decreased due to the increased rate of its cracking compared to its formation. The overall middle distillates selectivity ratio decreased continuously with reaction time as observed in other cases. The highest selectivity of middle distillates occurred at lower product yields. The operation of the unit shall be at an optimum point to make a compromise between selectivity and product yield in the case of maximization of middle distillates.

Figure 5.57 shows the yield of middle distillates at three different reactor temperatures of 360, 380 and 400°C respectively. At all the reactor temperatures, the yield of middle distillates reached a maximum value at a certain reaction time before its concentration started decreasing. The maximum value of middle distillates yield could be obtained at lower reaction times as the reaction temperatures was increased due to increased cracking at higher severity. Figure 5.58 shows the middle distillates selectivity at different operating temperatures of 360, 380 and 400°C respectively. As can be seen from Figure 5.58, the selectivity to middle distillates decreased with increase in temperature at a constant reaction time and decreased with reaction time at a constant reactor temperature. This showed that increasing the severity of hydrocracking either by increasing reactor temperature or reaction time would tend to reduce the selectivity towards middle distillates.
and shift the selectivity towards more of lighter components such as naphtha and gas at the expense of valuable middle distillates.

Figure 5.59 shows the effect of feedstock type on middle distillate yield and selectivity with respect to change in reaction time at a reactor temperature of 380°C. The middle distillates yield and selectivity was lower for Feed B compared to Feed A. This indicates that for a same catalyst system, Feed B has lower tendency to form middle distillates compared to Feed A. However, the effect of type of feedstock on product yield and selectivity is very small during hydrocracking since hydrocracking is very flexible with respect to change in feedstock.

Tables 5.54 and 5.55 present the middle distillates selectivity at maximum yield conditions for VGO and VGO+DAO feedstock respectively. The maximum yield of middle distillates was almost constant with change in reactor temperature. This shows the intrinsic property of the catalyst system which could retain the middle distillate selectivity at various operating conditions. The middle distillates selectivity was also almost constant with reaction temperature for both feedstocks at maximum yield conditions. The time at which maximum yield of middle distillates obtained decreased with reaction temperature. In the present scheme, at a reactor temperature of 360°C, a maximum concentration of 50.29 wt% of middle distillates was obtained at a reaction time of 2.7543 hours. At a reactor temperature of 380°C, a maximum concentration of 50.75 wt% of middle distillates was obtained at a reaction time of 1.5833 hours. The Feed B yielded slightly lower middle distillates compared to Feed A at all reactor temperatures.
Figure 5.56  Product yields and selectivity of middle distillates at 380°C - Scheme I

Figure 5.57  Middle distillate yields at various operating conditions - Scheme I
Figure 5.58  Middle distillate selectivity at various operating conditions
- Scheme I

Figure 5.59  Effect of feedstock on MD yield and selectivity at 380°C -
Scheme I
Table 5.54  Middle Distillates selectivity at maximum yield conditions for consecutive reactions for VGO Feedstock – Scheme I

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<tr>
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Table 5.55  Middle Distillates selectivity at maximum yield conditions for consecutive reactions for VGO+DAO Feedstock – Scheme I

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5.4.2 Scheme II

Scheme II is used to analyze the selectivity of middle distillates during hydrocracking process. In this reaction scheme there are three kinetic lumps considered along with three significant reactions among them. Feedstock reacts to yield both middle distillates and naphtha and gas. The secondary hydrocracking of middle distillates into naphtha and gas is also considered. There are three kinetic parameters to be evaluated for this reaction scheme. The kinetic parameters for this reaction scheme has already been presented in Table 5.33 and discussed in Model III under section 5.2.4 for both the feedstock type.

Figure 5.60 shows the effect of reaction time on product yields and middle distillate selectivity at a reactor temperature of 400°C for VGO Feedstock. As can be seen from Figure 5.60, the yield of VGO feedstock decreased with reaction time while the yield of naphtha and gas (NG) fraction increased continuously. The yield of middle distillates increased initially up to a certain reaction time and then its yield decreased due to the increased rate of its cracking compared to its formation. The overall middle distillates selectivity decreased continuously with reaction time. The highest selectivity of middle distillates occurred at lower product yields. As shown in previous schemes, there shall be a compromise between the selectivity and yield for optimal operation of the unit.

Figure 5.61 shows the yield of middle distillates at three different reactor temperatures of 360, 380 and 400°C respectively. At all the reactor temperatures, the yield of middle distillates reached a maximum value at a certain reaction time before the concentration was decreasing. The maximum value of middle distillates can be obtained at lower reaction times as the reactor temperature increased. This is due to increased rate of secondary
Figure 5.60  Product yields and MD selectivity at 400°C - Scheme II

Figure 5.61  MD yields at various operating conditions - Scheme II
cracking reactions at higher operating conditions compared to lower reactor temperatures and hence the middle distillates formed due to primary hydrocracking reactions tend to hydrocrack further at increased rate decreasing its concentration continuously and shifting the selectivity towards more of lighter components such as naphtha and gas.

Tables 5.56 and 5.57 present the middle distillates selectivity at maximum yield conditions for VGO and VGO+DAO feedstock respectively. Figure 5.62 presents the middle distillate yield and selectivity at maximum yield conditions for VGO Feedstock. As can be seen from Tables 5.56 and 5.57 and Figure 5.62, the maximum yield of middle distillates decreased with increasing reactor temperature. The middle distillates selectivity was also found to decrease with reactor temperature for both feedstocks at maximum yield conditions. The time at which maximum yield of middle distillates obtained decreased with reactor temperature. In the present scheme, at a reactor temperature of 360°C, a maximum concentration of 78.50 wt% of middle distillates was obtained at a reaction time of 4.3883 hours. At a reactor temperature of 380°C, a maximum concentration of 73.24 wt% of middle distillates was obtained at a reaction time of 2.9768 hours. The Feed B was found to yield slightly lower middle distillates compared to Feed A at all reactor temperatures. The value of alpha constantly increased with reactor temperature due to the fact that increasing temperature cause increased rate of the formation of naphtha and gas from VGO feedstock. The value of beta, which is the ratio of rate constants of secondary to primary reaction, was also increasing with reactor temperature due to the same reason as mentioned above.
Table 5.56  Middle Distillate selectivity at maximum yield conditions for
Scheme II - VGO Feedstock

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Table 5.57  Middle Distillate selectivity at maximum yield conditions for
Scheme II - VGO+DAO Feedstock

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Scheme III is similar to the model presented in section 4.1.6 as Model VI for the analysis of kinetics of hydrocracking process. The kinetic and stoichiometric parameters for this reaction scheme has already been presented in Table 5.42 for both the feedstock and discussed in the section 5.2.7. The derivation of mathematical expressions for the maximum yield of middle distillates and the time at which this occurs was presented in Chapter 4. The simulations of product yields and the evaluation of maximum yields and the time at which this occurs were all done using the expressions derived analytically in chapter 4.

Figure 5.63 shows the effect of reaction time on product yields and middle distillate selectivity at a reactor temperature of 380°C for VGO Feedstock. As can be seen from Figure 5.63, the general trend observed for
the product yields and selectivity in other reaction schemes holds well for this scheme as well. The yield of VGO feedstock decreased with reaction time while the yield of naphtha and gas fractions increased continuously. The yield of middle distillates increased initially up to a certain reaction time and then decreased due to the increased rate of its cracking compared to its formation. The overall middle distillates selectivity ratio falls continuously with reaction time. As observed for Scheme II, the highest selectivity of middle distillates occurred at lowest yields of the fraction.

Figure 5.64 shows the middle distillates selectivity at various operating temperatures of 360, 380 and 400°C respectively for VGO feedstock. The middle distillates selectivity was higher at lower reactor temperatures and lower reaction time. Higher severity will tend to reduce the selectivity towards middle distillates and shift the selectivity towards more of lighter components such as naphtha and gas.

Figure 5.65 shows the yield of middle distillates at three different reactor temperatures of 360, 380 and 400°C respectively. At all the reactor temperatures, the yield of middle distillates reached a maximum value at a certain reaction time before the concentration started decreasing due to the reasons observed in other schemes.

Tables 5.58 and 5.59 present the middle distillates selectivity at maximum yield conditions for VGO and VGO+DAO feedstock respectively. Figure 5.66 shows maximum middle distillates yield, maximum time at which this occurs and beta at various reactor temperatures for VGO Feedstock. The maximum yield of middle distillates decreased with increasing reactor temperature due to higher rate of secondary cracking of middle distillates compared to its rate of formation. The middle distillates selectivity also decreased with reactor temperature for both feedstocks at maximum yield
Figure 5.63  Products yield and MD selectivity at 380°C - Scheme III

Figure 5.64  Middle Distillate selectivity at various operating conditions - Scheme II
Figure 5.65 MD yield at various operating conditions - Scheme III

Figure 5.66 Maximum middle distillate yield at various temperatures - Scheme III
Table 5.58  Middle Distillate selectivity at maximum yield conditions for
Scheme III -VGO Feedstock

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Table 5.59  Middle Distillate selectivity at maximum yield conditions for
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<td>0.5303</td>
<td>1.7829</td>
</tr>
<tr>
<td>410</td>
<td>2.1163</td>
<td>0.7631</td>
<td>0.2458</td>
<td>0.5006</td>
<td>0.2536</td>
<td>0.7263</td>
<td>0.4962</td>
<td>1.5718</td>
</tr>
<tr>
<td>420</td>
<td>1.7261</td>
<td>0.5339</td>
<td>0.2784</td>
<td>0.4623</td>
<td>0.2593</td>
<td>0.6899</td>
<td>0.4089</td>
<td>1.3895</td>
</tr>
</tbody>
</table>

conditions. The time at which maximum yield of middle distillates obtained decreased with reactor temperature. In the present scheme, at a reactor temperature of 360°C, a maximum concentration of 72.00 wt% of middle distillates was obtained at a reaction time of 4.7513 hours. At a reactor temperature of 380°C, a maximum concentration of 64.30 wt% of middle distillates was obtained at a reaction time of 2.2372 hours. The Feed B yielded lower middle distillates compared to Feed A at all reactor temperatures.
5.5 SIMULATION OF PILOT PLANT REACTOR PERFORMANCE

In the present work, the pilot plant reactor performance was modeled using the kinetic parameters estimated from pilot plant hydrocracking experimental data. Since the pilot plant reactor was operated in an isothermal mode, the temperature was kept constant throughout the length of the reactor. Thus the pilot plant reactor simulation was performed considering isothermal operation.

The differential equations representing the hydrocracker model and presented in chapter 4 were solved with the initial concentrations of the components as boundary conditions to get their concentrations at the outlet of the reactor using MATLAB ODE 45 function. The model differential equations were solved to obtain the concentrations of sulphur, nitrogen, feedstock, 370°C- products, hydrogen, hydrogen sulphide and ammonia at the outlet of the reactor.

Hydrodesulphurization and hydrodenitrogenation of the feedstock generally occurs in both hydrotreating and hydrocracking catalyst sections due to the presence of metal sites in both the catalysts. Thus, both these reactions were considered to occur along both the catalyst sections in the present work. However, under typical operating conditions of the industrial hydrocracker unit, most of the sulphur and nitrogen components are removed in the hydrotreating section itself. Hydrotreating catalyst performs most of the sulphur and nitrogen removal and aromatic saturation. Since hydrotreating catalyst also contains some acidic support material, very small amount of cracking occurs over this catalyst. But the cracking activity of hydrotreating catalyst is very low and can be neglected for simplicity. So the present work neglects the hydrocracking of the feedstock occurring over HDT catalyst.
Two types of models were used to simulate the pilot plant reactor, first to simulate overall yields of 370°C- products, sulphur, nitrogen etc and second one to predict the individual yields of product fractions along the length of the pilot plant reactor. The kinetic parameters for both VGO and 80%VGO+20%DAO feedstocks for hydrocracking reactions are given in Table 5.60. The kinetic parameters for hydrodesulphurization and hydrodenitrogenation reactions over both hydrotreating and hydrocracking catalyst sections were already presented in chapter 4. The kinetic parameters for HDS and HDN reactions are assumed to be the same for both the feedstock types.

The simulation of the pilot plant reactor was performed along the length of the reactor by solving the differential equations of the pilot plant reactor model. The simulated yields of feedstock, 370°C- products and change in hydrogen concentration along the length of the reactor is shown in Figure 5.67 at a reactor temperature of 380°C, pressure of 170 kg/cm², LHSV of 0.8 h⁻¹ and H₂/oil ratio of 845 m³/ m³. As can be seen from Figure 5.67, the yield of VGO feedstock decreased along the reactor length while the yield of 370°C- products increased continuously. The hydrogen concentration decreased along the reactor length due to its consumption for HDS, HDN and hydrocracking reactions. Figure 5.68 shows the change in the concentration of sulphur and hydrogen sulphide along the reactor length for the same operating conditions. The sulphur content of the feedstock almost decreased to ppm levels at the outlet of the hydrotreating catalyst section itself. The hydrogen sulphide concentration increased along the length of the reactor. Figure 5.69 shows the concentration of nitrogen and ammonia along the catalyst bed length under similar operating conditions as discussed above. The nitrogen content of the feedstock decreased almost to very low levels at the outlet of the hydrotreating catalyst section itself and ammonia concentration continuously increased.
Table 5.60  Kinetic parameters for pilot plant simulation

<table>
<thead>
<tr>
<th>Kinetic parameter</th>
<th>Kinetic expression</th>
<th>k at 380°C</th>
<th>α</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Feedstock: Vacuum gas oil</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( k_{HC} )</td>
<td>( 4.3864 \times 10^7 \exp\left(-2.3219 \times 10^4 / RT\right) )</td>
<td>0.7235</td>
<td>0.047</td>
</tr>
<tr>
<td><strong>Feedstock: VGO+DAO Blend</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( k_{HC} )</td>
<td>( 1.0640 \times 10^8 \exp\left(-2.4559 \times 10^4 / RT\right) )</td>
<td>0.6326</td>
<td>0.058</td>
</tr>
</tbody>
</table>

As seen from Figures 5.68 and 5.69, under typical operating conditions of industrial hydrocracking unit, most of the sulphur and nitrogen compounds are removed in the first pretreating section of the reactor itself. The hydrocracking catalyst has to work in the environment of hydrogen sulphide and ammonia instead of sulphur and nitrogen compounds. Generally basic nitrogen compounds are more poisonous to hydrocracking catalysts compared to less poisonous ammonia. Similar concentration profile was generated at a reactor temperature of 400°C while maintaining other conditions as shown in Figure 5.70. These pilot plant simulations were found to agree well with the general trend of hydrocracking process with respect to HDS, HDN and HC reactions.

Simulation of pilot plant reactor for the effect of operating conditions on 370°C- yields, sulphur, nitrogen, \( \text{H}_2 \) concentration etc were presented in Tables 5.61 to 5.63 for VGO Feedstock and compared with experimental data. Similar type of simulation data were generated for Feed B and presented in Table 5.64 at a LHSV of 0.8 h\(^{-1}\), reactor pressure of 170 kg/cm\(^2\) and \( \text{H}_2 / \text{oil} \) ratio of 845 m\(^3\)/m\(^3\) and compared with experimental data. In all the cases, the simulated product yields matches well with the
Figure 5.67  Yields along catalyst bed length in pilot plant reactor

Figure 5.68  Sulphur and H₂S Yields along Catalyst Bed length in Pilot Plant Reactor

Figure 5.69  Nitrogen and NH₃ Yields along Catalyst Bed Length in pilot plant reactor

Figure 5.70  Product Yields along Catalyst Bed length in Pilot Plant Reactor
experimental data very closely and shows the applicability of this model to the analysis of pilot plant reactor. Figure 5.71 shows the effect of reactor temperature on 370°C - yields at various liquid hourly space velocities of 0.8, 1.6 and 2.4 h⁻¹ respectively for the hydrocracking of VGO Feedstock. The solid lines represent the simulated data while the points indicate the experimental data. Figure 5.72 shows the effect of reactor temperature on total product yields at various liquid hourly space velocities of 0.8, 1.6 and 2.4 h⁻¹ respectively for VGO Feedstock. As can be seen from Figures 5.71 and 5.72, the simulated data closely matches with the experimental data for all the operating conditions.

Tables 5.65 to 5.67 presents the simulation of pilot plant reactor for the effect of operating conditions on individual product yields and compares the simulation with that of experimental data for the hydrocracking of VGO Feedstock. Table 5.68 presents the simulation of pilot plant reactor on individual product yields and compares with experimental data for Feed B at a LHSV of 0.8 h⁻¹, reactor pressure of 170 kg/cm² and H₂/oil ratio of 845 m³/m³. Tables 5.65 through 5.68 indicated that the kinetic model chosen here was able to predict the product yield pattern very well with minimum errors as seen from the difference between experimental and simulated values of product yields.

Individual product yields along the length of the pilot plant reactor was simulated based on Model VII presented in Chapter 4 under section 4.1.7. The kinetic parameters estimated for Model VII and listed under section 5.2.8 was used to simulate the product yields such as yields of gas, naphtha, kerosene, diesel and VGO Feedstock along hydrocracking catalyst bed length. The pilot plant simulation on product yield distribution along reactor length agrees well with general trend of product yields in hydrocracker units.
Table 5.61 Simulation of Pilot Plant Reactor vs. Experimental Data – Effect of Operating Conditions on 370°C- Yields, sulphur and nitrogen at a LHSV of 0.8 h⁻¹ and H₂/oil ratio of 845 m³/m³ for VGO Feedstock

<table>
<thead>
<tr>
<th>Operating Conditions / Products</th>
<th>Run #1</th>
<th>Run #2</th>
<th>Run #3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Exp. Wt.%</td>
<td>Sim. Wt.%</td>
<td>Exp. Wt.%</td>
</tr>
<tr>
<td>Reactor Temperature, °C</td>
<td>360</td>
<td>380</td>
<td>400</td>
</tr>
<tr>
<td>Reactor Pressure, kg/cm²</td>
<td>170</td>
<td>170</td>
<td>170</td>
</tr>
<tr>
<td>Feedstock, 370°C+</td>
<td>58.91</td>
<td>58.35</td>
<td>44.32</td>
</tr>
<tr>
<td>Sulphur, ppmw</td>
<td>25</td>
<td>2</td>
<td>18</td>
</tr>
<tr>
<td>Nitrogen, ppmw</td>
<td>8</td>
<td>1</td>
<td>BDL</td>
</tr>
<tr>
<td>Total Products, 370°C-</td>
<td>40.93</td>
<td>41.37</td>
<td>56.08</td>
</tr>
<tr>
<td>Hydrogen Sulfide, H₂S</td>
<td>1.72</td>
<td>1.72</td>
<td>1.72</td>
</tr>
<tr>
<td>Ammonia, NH₃</td>
<td>0.067</td>
<td>0.068</td>
<td>0.068</td>
</tr>
<tr>
<td>H₂ Con., wt% on feed</td>
<td>6.70</td>
<td>6.82</td>
<td>6.14</td>
</tr>
<tr>
<td>Total Yield, wt%</td>
<td>101.6</td>
<td>101.5</td>
<td>102.2</td>
</tr>
</tbody>
</table>

Table 5.62 Simulation of Pilot Plant Reactor vs. Experimental Data – Effect of Operating Conditions on 370°C- Yields, sulphur and nitrogen at a LHSV of 1.6 h⁻¹ and H₂/oil ratio of 845 m³/m³ for VGO Feedstock

<table>
<thead>
<tr>
<th>Operating Conditions / Products</th>
<th>Run #4</th>
<th>Run #5</th>
<th>Run #6</th>
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<tbody>
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<td></td>
<td>Exp. Wt.%</td>
<td>Sim. Wt.%</td>
<td>Exp. Wt.%</td>
</tr>
<tr>
<td>Reactor Temperature, °C</td>
<td>360</td>
<td>380</td>
<td>400</td>
</tr>
<tr>
<td>Reactor Pressure, kg/cm²</td>
<td>170</td>
<td>170</td>
<td>170</td>
</tr>
<tr>
<td>Feedstock, 370°C+</td>
<td>71.84</td>
<td>71.63</td>
<td>63.32</td>
</tr>
<tr>
<td>Sulphur, ppmw</td>
<td>185</td>
<td>183</td>
<td>47</td>
</tr>
<tr>
<td>Nitrogen, ppmw</td>
<td>36</td>
<td>24</td>
<td>14</td>
</tr>
<tr>
<td>Total Products, 370°C-</td>
<td>27.55</td>
<td>27.47</td>
<td>36.37</td>
</tr>
<tr>
<td>Hydrogen Sulfide, H₂S</td>
<td>1.70</td>
<td>1.70</td>
<td>1.72</td>
</tr>
<tr>
<td>Ammonia, NH₃</td>
<td>0.064</td>
<td>0.065</td>
<td>0.066</td>
</tr>
<tr>
<td>H₂ Con., wt% on feed</td>
<td>7.17</td>
<td>7.45</td>
<td>6.86</td>
</tr>
<tr>
<td>Total Yield, wt%</td>
<td>101.16</td>
<td>100.87</td>
<td>101.47</td>
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</table>
Table 5.63  Simulation of Pilot Plant Reactor vs. Experimental Data – Effect of Operating Conditions on 370°C- Yields, sulphur and nitrogen at a LHSV of 2.4 h\(^{-1}\) and H\(_2\)/oil ratio of 845 m\(^3\)/m\(^3\) for VGO Feedstock

<table>
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<tr>
<th>Operating Conditions / Products</th>
<th>Run #7</th>
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<th>Run #9</th>
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<td>Exp. Wt.%</td>
<td>Sim. Wt.%</td>
<td>Exp. Wt.%</td>
<td>Sim. Wt.%</td>
</tr>
<tr>
<td>Reactor Temperature, °C</td>
<td>360</td>
<td>380</td>
<td>400</td>
</tr>
<tr>
<td>Reactor Pressure, kg/cm(^2)</td>
<td>170</td>
<td>170</td>
<td>170</td>
</tr>
<tr>
<td>Feedstock, 370°C+</td>
<td>79.21</td>
<td>76.71</td>
<td>71.09</td>
</tr>
<tr>
<td>Sulphur, ppmw</td>
<td>780</td>
<td>814</td>
<td>295</td>
</tr>
<tr>
<td>Nitrogen, ppmw</td>
<td>72</td>
<td>67</td>
<td>34</td>
</tr>
<tr>
<td>Total Products, 370°C-</td>
<td>19.95</td>
<td>22.15</td>
<td>28.36</td>
</tr>
<tr>
<td>Hydrogen Sulfide, H(_2)S</td>
<td>1.64</td>
<td>1.63</td>
<td>1.69</td>
</tr>
<tr>
<td>Ammonia, NH(_3)</td>
<td>0.059</td>
<td>0.060</td>
<td>0.064</td>
</tr>
<tr>
<td>H(_2) Con., wt% on feed</td>
<td>7.47</td>
<td>7.69</td>
<td>7.13</td>
</tr>
<tr>
<td>Total Yield, wt%</td>
<td>100.9</td>
<td>100.6</td>
<td>101.20</td>
</tr>
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</table>

Table 5.64  Simulation of Pilot Plant Reactor vs. Experimental Data – Effect of Operating Conditions on 370°C- Yields, sulphur and nitrogen at a LHSV of 0.8 h\(^{-1}\) and H\(_2\)/oil ratio of 845 m\(^3\)/m\(^3\) for Feed B

<table>
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<tr>
<th>Operating Conditions / Products</th>
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<th>Run #13</th>
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<td>Sim. Wt.%</td>
<td>Exp. Wt.%</td>
<td>Sim. Wt.%</td>
</tr>
<tr>
<td>Reactor Temperature, °C</td>
<td>360</td>
<td>380</td>
<td>400</td>
</tr>
<tr>
<td>Reactor Pressure, kg/cm(^2)</td>
<td>170</td>
<td>170</td>
<td>170</td>
</tr>
<tr>
<td>Feedstock, 370°C+</td>
<td>61.86</td>
<td>62.08</td>
<td>46.85</td>
</tr>
<tr>
<td>Sulphur, ppmw</td>
<td>31</td>
<td>2</td>
<td>22</td>
</tr>
<tr>
<td>Nitrogen, ppmw</td>
<td>10</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>Total Products, 370°C-</td>
<td>38.20</td>
<td>37.64</td>
<td>53.83</td>
</tr>
<tr>
<td>Hydrogen Sulfide, H(_2)S</td>
<td>1.83</td>
<td>1.84</td>
<td>1.84</td>
</tr>
<tr>
<td>Ammonia, NH(_3)</td>
<td>0.071</td>
<td>0.072</td>
<td>0.072</td>
</tr>
<tr>
<td>H(_2) Con., wt% on feed</td>
<td>6.36</td>
<td>6.69</td>
<td>5.74</td>
</tr>
<tr>
<td>Total Yield, wt%</td>
<td>101.97</td>
<td>101.63</td>
<td>102.59</td>
</tr>
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</table>
Table 5.65 Simulation of Pilot Plant Reactor vs. Experimental Data – Effect of Operating Conditions on Product Yields for VGO Feedstock

<table>
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<tr>
<th>Operating Conditions / Products</th>
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<th>Run #2</th>
<th>Run #3</th>
</tr>
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<tbody>
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<td>Exp. Wt.%</td>
<td>Sim. Wt.%</td>
<td>Exp. Wt.%</td>
</tr>
<tr>
<td>Reactor Temperature, °C</td>
<td>360</td>
<td>380</td>
<td>400</td>
</tr>
<tr>
<td>Reactor Pressure, kg/cm²</td>
<td>170</td>
<td>170</td>
<td>170</td>
</tr>
<tr>
<td>LHSV, h⁻¹</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>H₂/oil ratio, m³/m³ feed</td>
<td>845</td>
<td>845</td>
<td>845</td>
</tr>
<tr>
<td>Gas</td>
<td>1.50</td>
<td>1.46</td>
<td>2.99</td>
</tr>
<tr>
<td>Naphtha</td>
<td>3.58</td>
<td>3.59</td>
<td>7.89</td>
</tr>
<tr>
<td>Kerosene</td>
<td>11.84</td>
<td>11.83</td>
<td>22.07</td>
</tr>
<tr>
<td>Diesel</td>
<td>24.08</td>
<td>23.74</td>
<td>22.91</td>
</tr>
<tr>
<td>Unconverted VGO</td>
<td>59.0</td>
<td>59.38</td>
<td>44.14</td>
</tr>
</tbody>
</table>

Table 5.66 Simulation of Pilot Plant Reactor vs. Experimental Data – Effect of Operating Conditions on Product Yields for VGO Feedstock

<table>
<thead>
<tr>
<th>Operating Conditions / Products</th>
<th>Run #4</th>
<th>Run #5</th>
<th>Run #6</th>
</tr>
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<tbody>
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<td>Exp. Wt.%</td>
<td>Sim. Wt.%</td>
<td>Exp. Wt.%</td>
</tr>
<tr>
<td>Reactor Temperature, °C</td>
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<td>380</td>
<td>400</td>
</tr>
<tr>
<td>Reactor Pressure, kg/cm²</td>
<td>170</td>
<td>170</td>
<td>170</td>
</tr>
<tr>
<td>LHSV, h⁻¹</td>
<td>1.6</td>
<td>1.6</td>
<td>1.6</td>
</tr>
<tr>
<td>H₂/oil ratio, m³/m³ feed</td>
<td>845</td>
<td>845</td>
<td>845</td>
</tr>
<tr>
<td>Gas</td>
<td>0.72</td>
<td>0.74</td>
<td>1.53</td>
</tr>
<tr>
<td>Naphtha</td>
<td>1.83</td>
<td>1.83</td>
<td>3.57</td>
</tr>
<tr>
<td>Kerosene</td>
<td>6.57</td>
<td>6.20</td>
<td>11.87</td>
</tr>
<tr>
<td>Diesel</td>
<td>18.60</td>
<td>18.33</td>
<td>19.51</td>
</tr>
<tr>
<td>Unconverted VGO</td>
<td>72.28</td>
<td>72.90</td>
<td>63.52</td>
</tr>
</tbody>
</table>
Table 5.67  Simulation of Pilot Plant Reactor vs. Experimental Data –
Effect of Operating Conditions on Product Yields for VGO
Feedstock

<table>
<thead>
<tr>
<th>Operating Conditions / Products</th>
<th>Run #7</th>
<th>Run #8</th>
<th>Run #9</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Exp. Wt.%</td>
<td>Sim. Wt.%</td>
<td>Exp. Wt.%</td>
</tr>
<tr>
<td>Reactor Temperature, °C</td>
<td>360</td>
<td>380</td>
<td>400</td>
</tr>
<tr>
<td>Reactor Pressure, kg/cm²</td>
<td>170</td>
<td>170</td>
<td>170</td>
</tr>
<tr>
<td>LHSV, h⁻¹</td>
<td>2.4</td>
<td>2.4</td>
<td>2.4</td>
</tr>
<tr>
<td>H₂/oil ratio, m³/m³ feed</td>
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<td>845</td>
<td>845</td>
</tr>
<tr>
<td>Gas</td>
<td>0.44</td>
<td>0.50</td>
<td>0.92</td>
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<tr>
<td>Naphtha</td>
<td>1.12</td>
<td>1.22</td>
<td>2.34</td>
</tr>
<tr>
<td>Kerosene</td>
<td>4.33</td>
<td>4.20</td>
<td>7.79</td>
</tr>
<tr>
<td>Diesel</td>
<td>14.24</td>
<td>16.02</td>
<td>17.46</td>
</tr>
<tr>
<td>Unconverted VGO</td>
<td>79.87</td>
<td>78.06</td>
<td>71.49</td>
</tr>
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</table>

Table 5.68  Simulation of Pilot Plant Reactor vs. Experimental Data –
Effect of Operating Conditions on Product Yields for Feed B

<table>
<thead>
<tr>
<th>Operating Conditions / Products</th>
<th>Run #1</th>
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<th>Run #3</th>
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<td></td>
<td>Exp. Wt.%</td>
<td>Sim. Wt.%</td>
<td>Exp. Wt.%</td>
</tr>
<tr>
<td>Reactor Temperature, °C</td>
<td>360</td>
<td>380</td>
<td>400</td>
</tr>
<tr>
<td>Reactor Pressure, kg/cm²</td>
<td>170</td>
<td>170</td>
<td>170</td>
</tr>
<tr>
<td>LHSV, h⁻¹</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>H₂/oil ratio, m³/m³ feed</td>
<td>845</td>
<td>845</td>
<td>845</td>
</tr>
<tr>
<td>Gas</td>
<td>1.40</td>
<td>1.37</td>
<td>2.89</td>
</tr>
<tr>
<td>Naphtha</td>
<td>3.35</td>
<td>3.38</td>
<td>7.73</td>
</tr>
<tr>
<td>Kerosene</td>
<td>10.94</td>
<td>10.92</td>
<td>20.95</td>
</tr>
<tr>
<td>Diesel</td>
<td>22.51</td>
<td>22.28</td>
<td>22.26</td>
</tr>
<tr>
<td>Unconverted VGO</td>
<td>61.86</td>
<td>62.05</td>
<td>46.85</td>
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</table>
Figure 5.71 Effect of operating conditions on 370°C-yields, Experimental vs. Simulated

Figure 5.72 Effect of operating conditions on total yields, Experimental vs. Simulated
5.6 SIMULATION OF INDUSTRIAL HYDROCRACKER UNIT

Since the industrial hydrocracking unit is operated under non-isothermal conditions due to exothermic nature of hydrocracking process, the model has to incorporate the temperature rise along the length of the reactor. A separate differential equation incorporating the heats of reactions of the individual reactions was considered in the present model. The equation representing the change in reactor temperature along the length of the reactor was already presented in chapter 4.

The kinetic parameters obtained from pilot plant reactor cannot be used directly for the simulation of industrial hydrocracker unit due to differences in their geometry and hydrodynamics. Generally industrial units operate at higher superficial velocities of liquid and gas streams and under complete wetting of catalyst particles while pilot plant reactors operate at lower fluid velocities and incomplete catalyst wetting. Due to these differences, the pilot plant reactors perform poorly compared to commercial reactors. In the present work, the kinetic constants estimated for hydrocracking and hydrotreating reactions from pilot plant reactor were used as initial guess values and fine-tuned to match the performance of industrial unit in terms of product yields and quality. The activation energy of the reactions was kept as constant and the fine tuning was done only with respect to frequency factor. It was observed that industrial unit had a higher kinetic rate constant compared to pilot plant reactor. The ratio of the two rate constants were taken as a scale-up factor and this factor was multiplied with the pilot plant rate constant to obtain industrial unit rate constant. Scale-up factor ($k_{com}/k_{pp}$) of 1.14 was obtained by fine tuning the kinetic parameters for industrial unit case. The scale-up factor was found initially for hydrocracking reaction and then the same was used to simulate HDS and HDN kinetics also for industrial unit case. The rate constants thus evaluated
for the case of industrial reactor were presented in Tables 5.69 for hydrocracking reactions.

Table 5.69 Kinetic parameters for commercial unit simulation – HC Reactions

<table>
<thead>
<tr>
<th>Kinetic parameter</th>
<th>Kinetic expression</th>
<th>k at 380°C, h⁻¹</th>
<th>α</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feedstock: Vacuum gas oil</td>
<td>( k_{HC} = 4.3864 \times 10^7 \exp\left(-2.3219 \times 10^4/RT \right) )</td>
<td>0.7235</td>
<td>0.047</td>
</tr>
<tr>
<td>Feedstock: VGO+DAO Blend</td>
<td>( k_{HC} = 1.0640 \times 10^8 \exp\left(-2.4559 \times 10^4/RT \right) )</td>
<td>0.6326</td>
<td>0.058</td>
</tr>
</tbody>
</table>

The simulation of industrial reactor was done at typical operating conditions used in an industrial hydrocracker unit. Figure 5.73 shows the yield of VGO feedstock and 370°C- products along the length of the industrial reactor under typical operating conditions of the unit. As can be seen from Figure 5.73, the yield of VGO Feedstock decreased continuously and the yield of 370°C- products increased along reactor length. Figure 5.74 presents the concentration of sulfur and hydrogen sulfide along the length of the industrial reactor. The sulfur concentration decreased to very low levels at the exit of the first reactor itself. The hydrogen sulfide concentration increased continuously along reactor length. The concentration of nitrogen and ammonia along the catalyst bed length was shown in Figure 5.75. The nitrogen content of the feedstock was almost removed at the exit of the first reactor, mostly in the HDT catalyst section itself while the ammonia concentration increased with catalyst bed length.

The temperature profile along the length of the industrial reactor was shown in Figure 5.76. Since the hydrocracking reactions are exothermic in nature, there is a huge temperature rise along the catalyst beds. Due to the
large exothermic temperature increase, intermittent hydrogen quench is provided in industrial units to reduce the temperatures. The simulated product yield distribution along the hydrocracking catalyst section was shown in Figure 5.77 for industrial unit. The Model VII was used in the simulations with kinetic parameters estimated from pilot plant experiments and using the scale-up factor for industrial reactor. The yields of gas, naphtha and kerosene increased continuously while the yield of VGO decreased sharply along industrial unit length. The yield of diesel increased sharply initially and then remained constant along reactor length due to its secondary cracking to other products.

Table 5.70 compares the simulated values of product yields and the actual industrial unit yield pattern at typical operating conditions used in the industrial unit. The percent deviation in all cases was found to be within acceptable limits considering the complex nature of hydrocracking reactions. The model predicts the yields of naphtha, kerosene, diesel and unconverted VGO very well while it predicts slightly higher gas yield as seen from the percent deviation. The delta temperature across the second catalyst bed was slightly lower compared to actual temperature rise in industrial reactor.

Simulations were also performed for the effect of operating conditions such as feed rate and reactor temperature on product yield and quality for industrial hydrocracker reactor. Table 5.71 presents the industrial unit simulations at a catalyst bed inlet temperature of 360°C (for all catalyst beds), LHSV of 0.8 h⁻¹, reactor pressure of 170 kg/cm² and H₂/oil ratio of 845 m³/m³. Figure 5.78 shows the effect of feed rate on 370°C – yields for various temperatures. As can be seen from Figure 5.78, the 370°C- yield decreased with increasing feed rate for all the temperatures. The yield of 370°C- products increased with increase in reactor temperature in the industrial unit. The proposed model predicts the industrial unit performance
satisfactorily and can be used for prediction of product yields in industrial hydrocracker unit.

Figure 5.73  Commercial unit simulation at typical operating conditions
Figure 5.74  Commercial unit simulation at typical operating conditions - Sulphur and H$_2$S

Figure 5.75  Commercial unit simulation at typical operating conditions - Nitrogen and NH$_3$
Figure 5.76  Temperature profile along the reactor length

![Temperature profile along the reactor length](image)

Figure 5.77  Product yield distribution along hydrocracking catalyst section

![Product yield distribution along hydrocracking catalyst section](image)
Figure 5.78  Effect of feed rate on 370ºC-yields

Table 5.70  Industrial unit simulation results at typical operating conditions

<table>
<thead>
<tr>
<th></th>
<th>Actual</th>
<th>Simulated</th>
<th>%Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>2.57</td>
<td>3.14</td>
<td>-19.23</td>
</tr>
<tr>
<td>Naphtha</td>
<td>8.52</td>
<td>7.70</td>
<td>9.62</td>
</tr>
<tr>
<td>Kerosene</td>
<td>23.13</td>
<td>21.83</td>
<td>5.62</td>
</tr>
<tr>
<td>Diesel</td>
<td>23.77</td>
<td>21.93</td>
<td>7.74</td>
</tr>
<tr>
<td>Unconverted Oil</td>
<td>44.51</td>
<td>45.40</td>
<td>-1.99</td>
</tr>
<tr>
<td>(\Delta T) across RIBI</td>
<td>26</td>
<td>26.6</td>
<td>-2.31</td>
</tr>
<tr>
<td>(\Delta T) across RIBII</td>
<td>11.2</td>
<td>8.4</td>
<td>25.0</td>
</tr>
<tr>
<td>(\Delta T) across RIIBI</td>
<td>27</td>
<td>28</td>
<td>-3.70</td>
</tr>
</tbody>
</table>

Table 5.71  Industrial unit simulation at 360ºC bed inlet temperature

VGO in Feedstock - 93.36 wt%
370ºC- in Feedstock - 5.017 wt%
Feed Sulfur - 1.56 wt%  Feed Nitrogen - 0.0590 wt%

Hydrogen – 8.3296 wt% (Based on Feed)

<table>
<thead>
<tr>
<th></th>
<th>RIBI</th>
<th>RIBII</th>
<th>RIIBI</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Feed Rate – 186 m³/hr</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Product sulfur, wt%</td>
<td>0.0005</td>
<td>0.0002</td>
<td>-</td>
</tr>
<tr>
<td>Product Nitrogen, wt%</td>
<td>0.00004</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>H2 consumption, wt%</td>
<td>8.2195</td>
<td>7.8279</td>
<td>5.6262</td>
</tr>
<tr>
<td>ΔT across bed, °C</td>
<td>26.7</td>
<td>6.0</td>
<td>33.7</td>
</tr>
</tbody>
</table>

| **Feed Rate – 248 m³/hr** |        |        |        |
| Product sulfur, wt%  | 0.0039 | 0.0018 | -      |
| Product Nitrogen, wt%| 0.0003 | 0.0002 | -      |
| H2 consumption, wt%  | 8.2198 | 7.9286 | 6.2350 |
| ΔT across bed, °C    | 26.6   | 4.5    | 25.98  |

| **Feed Rate – 310 m³/hr** |        |        |        |
| Product sulfur, wt%  | 0.014  | 0.0076 | 0.0002 |
| Product Nitrogen, wt%| 0.0009 | 0.0006 | 0.00007|
| H2 consumption, wt%  | 8.2205 | 7.9883 | 6.6260 |
| ΔT across bed, °C    | 26.5   | 3.7    | 21.0   |
5.7 CATALYST DEACTIVATION IN INDUSTRIAL HYDROCRAKERS

The hydrocracking catalyst system in industrial hydrocrackers usually gets deactivated gradually over time due to slow deposition of coke, metals etc on the active catalyst surface. To compensate for the loss in the catalyst activity over run time, the reactor temperature is normally increased at a slower rate for getting same conversion from the industrial unit for the same liquid hourly space velocity. Normally the feed rate of the unit is not changed because reducing the throughput of the industrial unit will decrease the yield of products. In the present work, the catalyst deactivation was modeled assuming a simple linear relation between the temperature increase required for obtaining same conversion in the industrial unit and time on stream. Usually the catalyst deactivation is faster during the initial stages of catalyst exposure to feedstock and then it gradually stabilizes. But to consider this type of analysis, accelerated catalyst deactivation testing should be done at severe operating conditions in the pilot plant reactor continuously for many months. The pilot plant data will then be correlated with the industrial deactivation data using some models. Procedures for carrying out accelerated deactivation testing are very scarce in the open literature and also mostly proprietary. This type of accelerated testing is not possible in most cases since it involves continuous running of pilot plants for many months. Also correlations relating the accelerated deactivation of pilot plant catalysts and real deactivation in the industrial unit are also not reliable due to changes in feedstock and operating conditions in the industrial units.

Generally the life of a catalyst will be evaluated by the catalyst supplier based on the design feedstock properties provided by the buyer and operating conditions fixed for that type of feedstock to attain design conversion levels. But the industrial units are generally operated using various
feedstocks having widely varying properties such as feed end point, metals content, CCR, aromatics content etc. In such cases there will be some variation in the operating conditions of the unit and the conversions. The present analysis assumed that the same feedstock as in the design case would be used throughout the cycle for which the supplier evaluated the life.

In the present work, the catalyst deactivation was modeled considering a simple first order reaction for hydrocracking and linear relation between temperature requirement for constant conversion and time on stream. The life of the hydrocracking catalyst system was assumed to be that given by the catalyst supplier. Generally, hydrocracking catalysts have a life of around 5 years, with regenerations between cycles. There will be three cycles of catalyst use with in the life of the catalyst. Two years of initial cycle is assumed in the present case.

The following first order hydrocracking reaction is considered with a rate constant $k_{HC}$ along with the differential equation for the feedstock

$$F \xrightarrow{k_{HC}} \text{Products}$$

(5.17)

$$\frac{dC_F}{dt} = -k_{HC}C_F$$

(5.18)

The Equation (5.18) can be solved using the initial boundary conditions for the concentration of feedstock and time. The following equation gives the concentration of feedstock at any given time
\[ C_F = (C_F)_0 e^{-kt} \]

(5.19)

This equation can be written in terms of conversion of the feedstock as follows

\[ C_F = (C_F)_0 (1 - X_F) \]

(5.20)

Substitution of these equations in Equation (5.18) and integrating using boundary conditions will give

\[ k_{HC} = -(LHSV) \ln(1 - X_F) \]

(5.21)

The kinetic rate constant can also be written using Arrhenius expression

\[ k_{HC} = \psi k_0 e^{-E/RT} \]

(5.22)

Where \( \psi \) is the ‘Catalyst Activity Parameter’ for the hydrocracking catalyst system. \( \psi \) will continuously decrease with time on stream of the catalyst operation due to deactivation.

These two expressions for the rate constant can be equated as follows
Generally at Start Of Run (SOR) conditions the value of $\psi$ is 1. As the catalyst is exposed to the feedstock over time, the value of $\psi$ will decrease continuously and the conversion also decreases subsequently due to deactivation of the catalyst. In industrial hydrocracking operations, the catalyst temperature is constantly increased to get the same conversion levels as that of SOR conditions. The problem here is to evaluate this deactivation constant $\psi$.

From Equation (5.23) we can define $\psi$ as

$$\psi = - \frac{(LHSV) \ln(1 - X_F)}{k_0 e^{-E/RT}}$$

(5.24)

In the present work, the value of $\psi$ was estimated using the design catalyst life cycle and the SOR and EOR conditions specified by the catalyst supplier in the design package. The values would have been arrived by the supplier based on some pilot plant evaluation at accelerated deactivation conditions at his facilities and correlating them with industrial data. The slope of the plot between time on stream (single life cycle of the catalyst) and the temperature range of operation (SOR and EOR) will yield the temperature rise required to attain the same conversion for a particular time period, e.g. after one month of operation. A linear relationship was assumed between the temperature rise required and time on stream. The life cycle of the catalyst as given by the vendor is two years for this particular catalyst for the first cycle. The slope of the curve was found to be
\( \text{slope}(m) = \frac{\Delta T_{X_r}}{t_{os}} \)

(5.25)

where \( \Delta T_{X_r} \) is the temperature increase required for maintaining the same conversion \( X_F \), and \( t_{os} \) is the time on stream.

When the temperature rise required for a time on stream is known from the slope \( m \), the required temperature of operation for obtaining the constant conversion level can be evaluated as follows

\[ T_{\text{reqd}} = \text{SOR} + \Delta T_{X_r} \]

(5.26)

Then the value of the \( \psi \) can be easily found from Equation (5.24) for constant conversion level, LHSV and known kinetic parameters. \( \psi \) will constantly decrease as the time on stream increases. Once the value of \( \psi \) is known for various time on stream, it can be plotted against time on stream for easy reading. From the plot of time on stream versus \( \psi \), the temperature required to maintain a constant conversion \( X_F \) at the same liquid hourly space velocity can be easily found from the following expressions

\[ T_{\text{reqd}} = \frac{-E}{R \cdot \ln \text{factor}} \]

(5.27)

\[ \ln \text{factor} = \ln \left( \frac{- \text{LHSV} \ln(1 - X_F)}{\psi k_0} \right) \]

(5.28)
For example considering the case of an industrial hydrocracker unit, the catalyst was designed for a life of five years with two regenerations in between. The hydrocracker operates for 330 on stream days for one year. For the first cycle there is two years of life cycle. Considering two year life cycle of hydrocracking catalyst with 330 stream days of operation per year and a feed rate of 248 m$^3$/hr of industrial hydrocracker unit, the catalyst supplier has given the SOR temperature and EOR temperature as 378 and 396°C respectively. Using these temperatures, and considering a linear increase of temperature with respect to operating time in hours, a linear relationship was obtained for the increase in reactor temperature required to maintain a constant conversion of 54% with respect to hours of operation. The rate constant parameters were taken from Model I for industrial hydrocracker unit as presented earlier. The SOR activity of the catalyst was assumed to be 1.0 since the catalyst was fresh after presulphiding. The following rate constant values were used for both the feedstocks in the present analysis

Rate constants for VGO Feedstock

\[
k_0 = 5.4978 \times 10^7
\]
\[
E = 2.3218 \times 10^4
\]

Rate constants for VGO+DAO Feedstock

\[
k_0 = 9.6761 \times 10^7
\]
\[
E = 2.4060 \times 10^4
\]

Using these kinetic parameter values, catalyst activity curves were generated for the hydrocracking catalyst system for both feedstocks using the linear relationship between temperature rise and hours of operation and shown in Figures 5.79 and 5.80 respectively. The following linear relationship was obtained for VGO Feedstock
\[ T = 0.001136 t + \text{SOR} \]

(5.29)

Where \( T \) is the reactor temperature required to obtain a constant conversion of 54\%, \( t \) is the time of operation and \( \text{SOR} \) is the start-of-run temperature.

From this linear relationship and from equations derived above, the catalyst activity parameter was estimated and plotted in Figure 5.79 for Feed A. Figure 5.79 can be used to find out the temperature required to obtain a constant conversion of 54\% with the VGO feedstock of certain quality and a constant LHSV at various operation time. The catalyst activity parameter increased with operation time from 1.0 at SOR conditions and to around 0.6 at EOR conditions. At the value of 0.6, it is wise to regenerate the catalyst for regaining its activity almost to fresh catalyst levels and then reuse it in the industrial unit in a next fresh cycle. Below this value of catalyst activity parameter, it is not advisable to operate the industrial unit. Below the value of 0.6, the catalyst will require much higher temperatures to obtain similar conversion level which will not be feasible or economical. Further operation beyond these values of catalyst activity parameter may require increased operating temperature for maintaining same conversion and lead to more coke and gas formation and increased deactivation rates. This will further deactivate the catalyst faster and damage the catalyst irreversibly. From Figure 5.79, the temperature required to obtain a 54\% conversion increased with operating time due to coke formation and deactivation of the catalyst system. In the present work, the value of \( \psi \) varies between 0.6 and 1.0 for Feed A. After the value of \( \psi \) reaches the lowest value in the cycle, the catalyst will be regenerated and used as before in another cycle.
Similar type of catalyst activity curve was generated for Feed B and shown in Figure 5.80 using the kinetic parameters presented before. However, Feed B required about 3°C higher SOR reactor temperature for obtaining the same 54% conversion of feedstock due to increased amounts of refractory polycyclic aromatics in the feedstock. Due to this the catalyst life will decrease when coprocessing this refractory feedstock along with the virgin VGO feedstock. Generally 16% reduction in catalyst life was observed in the case of processing this refractory feedstock (80%VGO+20%DAO) along with VGO feedstock.

![Catalyst Activity Curve for the Hydrocracking Catalyst System - Feed A](image)

**Figure 5.79** Catalyst Activity Curve for the Hydrocracking Catalyst System - Feed A
Figure 5.80 Catalyst Activity Curve for the Hydrocracking Catalyst System - Feed B
5.8 INTEGRATION OF HYDROCRACKER WITH FCC UNIT

In view of increasing importance of hydrocracking process as FCC feed preparation unit, pilot plant studies were conducted to evaluate the option of mild hydrocracking for FCC feed pretreatment. Pilot plant data on mild hydrocracking of FCC feedstock were compared with the data obtained for hydrotreating of FCC feedstock. Experiments were conducted on industrially available catalyst samples using high nitrogenous vacuum gas oil as feedstock. MAT experiments were also carried out to compare the conversions and yields of untreated, hydrotreated and MHC VGO at constant operating conditions. The effect of operating conditions on the conversion and quality of MHC VGO was also studied.

5.8.1 Feed Oil

A vacuum gas oil feedstock originated from Escravos crude source and collected from industrial FCC unit of Chennai Petroleum Corporation Limited (CPCL) was used in the pilot plant study. The detailed properties of VGO are presented in Table 5.72. As can be seen from Table 5.72, the VGO contains about 0.17 wt% nitrogen, 0.29 wt% sulfur and about 42 wt% of aromatics.

The vacuum gas oil used in the pilot plant studies is characterized by its high nitrogen content and thus it is essential to pretreat the vacuum gas oil before passing over an acidic mild hydrocracking catalyst. High nitrogen content of VGO, especially basic nitrogen is known to cause catalyst poisoning in FCCU and has detrimental effect on conversion and product yields.
Table 5.72 Characteristics of VGO feedstock

<table>
<thead>
<tr>
<th>Properties</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density at 15°C, gm/cc</td>
<td>0.9196</td>
</tr>
<tr>
<td>Gravity, degree API</td>
<td>22.4</td>
</tr>
<tr>
<td>Kinematic Viscosity at 100°C, cSt</td>
<td>8.06</td>
</tr>
<tr>
<td>Refractive Index at 70°C</td>
<td>1.48842</td>
</tr>
<tr>
<td>Pour point, °C</td>
<td>39</td>
</tr>
<tr>
<td>Aniline Point, °C</td>
<td>86.2</td>
</tr>
<tr>
<td>Flash Point, °C</td>
<td>217</td>
</tr>
<tr>
<td>Aromatics, wt.%</td>
<td>41.9</td>
</tr>
<tr>
<td>Saturates, wt.%</td>
<td>58.1</td>
</tr>
<tr>
<td>Sulphur, ppmw</td>
<td>2880</td>
</tr>
<tr>
<td>Nitrogen, ppmw</td>
<td>1711</td>
</tr>
</tbody>
</table>

**Simulated Distillation (ASTM D 2887)**

<table>
<thead>
<tr>
<th>IBP, °C</th>
<th>310</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 wt%, °C</td>
<td>409</td>
</tr>
<tr>
<td>50 wt%, °C</td>
<td>436</td>
</tr>
<tr>
<td>70 wt%, °C</td>
<td>460</td>
</tr>
<tr>
<td>FBP, °C</td>
<td>548</td>
</tr>
</tbody>
</table>
5.8.2 Catalysts

The catalyst system used in the pilot plant evaluation comprises of a hydrotreating (HDT) catalyst and a mild hydrocracking (MHC) catalyst. Both hydrotreating and mild hydrocracking catalysts used in the pilot plant studies were procured from same industrial catalyst supplier. Experiments were also conducted over an industrial HDT catalyst to compare the performance of HDT and MHC options for FCC feed preparation. The hydrotreating catalyst used as a pretreating catalyst for mild hydrocracking step is a trimetallic Ni-Co-Mo hydrotreating catalyst supported on alumina with higher activity for sulfur and nitrogen removal and aromatic saturation. The mild hydrocracking catalyst used is a zeolite based hydrocracking catalyst. The hydrotreating catalyst used to study the option of hydrotreating as FCC feed preparation is a latest generation, high activity NiO-MoO$_3$/Al$_2$O$_3$ catalyst with very high nitrogen removal and aromatic saturation activity.

5.8.3 Operating Conditions of Pilot Plant Experiments

Pilot plant evaluation over mild hydrocracking and hydrotreating catalyst system was carried out in a high pressure cocurrent downflow trickle bed reactor system comprising a single reactor of 500 ml volume. The reactor temperature was varied from 340°C to 400°C at various liquid hourly space velocities of 1.0 h$^{-1}$, 1.5 h$^{-1}$ and 2.0 h$^{-1}$ respectively to study the effect of reactor temperature on the quality of MHC VGO. Experiments were also conducted at different operating pressures of 60 kg/cm$^2$ and 100 kg/cm$^2$ to study the effect of pressure on the conversion, product yields and quality of MHC VGO.

Hydrotreating experiments were carried out at a reactor temperature of 340°C, operating pressure of 50 kg/cm$^2$, liquid hourly space velocity of
1.5 h\(^{-1}\) and hydrogen to oil ratio of 400 lit/lit. MAT experiments were conducted using untreated VGO, hydrotreated VGO and MHC VGO to compare conversion and yields from FCC. MAT experiments were carried out using 4 grams of catalyst sample with catalyst/oil ratio of 3. The residence time in the reactor was maintained as 75 seconds with a feed rate of 1.33 grams. The reactor temperature was kept constant at 482°C and a regenerator temperature of 650°C was used during regeneration.

### 5.8.4 Pilot Plant Studies

The properties of MHC products and pilot plant conversion and yields during mild hydrocracking of VGO fraction are presented in Tables 5.73 to 5.77 at various operating conditions.

Mild hydrocracking of vacuum gas oil feedstock was found to increase the amount of distillates produced from a refinery unit. The conversion of the feedstock into 370°C- products increased with reactor temperature at a constant liquid hourly space velocity. The conversion was also increasing with increasing liquid hourly space velocity at a constant reactor temperature. Reactor pressure also influences the conversion level of the feedstock. As can be seen from Table 5.73, the conversion of the feedstock into 370°C- products increased from 5.54 to 19.51 wt% as the reactor temperature was increased from 340 to 400°C at a constant liquid hourly space velocity of 1.0 h\(^{-1}\) and operating pressure of 60 kg/cm\(^2\). The feedstock conversion increased from 6.98 to 24.28 wt% as the operating pressure was increased from 60 to 100 kg/cm\(^2\) at a LHSV of 1.0 h\(^{-1}\) for the same temperature range. This showed that reactor operating pressure had significant influence on the conversion of the feedstock into distillate products.
The yield of VGO Feedstock decreased continuously with reactor temperature while the yields of gas, naphtha and middle distillates increased. At a constant reactor pressure of 60 kg/cm$^2$ and liquid hourly space velocity of 1.0 h$^{-1}$, the VGO yield decreased from 85.2 to 72.6 wt% while the yields of gas, naphtha and middle distillates increased from 0.5 to 3.5, 1.9 to 5.3 and 12.4 to 18.6 wt% respectively as the temperature was increased from 340 to 400°C. The increase in LHSV increased the VGO yield while the yields of gas, naphtha and middle distillates decreased. Lower LHSV and higher reactor temperatures favored improved distillate product yields during mild hydrocracking process. The middle distillates yield increased with operating pressure at a constant reactor temperature. Middle distillates yield increased with reactor temperature at a constant operating pressure.

As can be seen from Tables 5.73 to 5.75, the sulfur was found to decrease from 0.2880 wt% in the feed to 0.0125 - 0.1340 wt% in MHC VGO at an operating pressure of 60 kg/cm$^2$ in the range of operating conditions studied in the present work. The %HDS of the MHC VGO increased with increasing reactor temperature and decreasing liquid hourly space velocity. Desulphurization of VGO was found to improve with increasing operating pressure of the unit. However, the reactor temperature has more pronounced effect on desulfurization compared to liquid hourly space velocity. The effect of operating pressure on hydrodesulfurization was not very much significant compared to the effect of temperature and LHSV. The sulfur was found to decrease to 0.006 - 0.0732 wt% levels at an operating pressure of 100 kg/cm$^2$ under the operating conditions studied in the present work. Under typical operating conditions of MHC of VGO, i.e., at 400°C reactor temperature, 1.0 h$^{-1}$ liquid hourly space velocity, 60 kg/cm$^2$ operating pressure, %HDS of 95.66 was achieved. Under the same typical operating conditions, as the operating pressure was changed from 60 to 100 kg/cm$^2$,
Table 5.73 Properties of MHC products and pilot plant yields at 60 kg/cm$^2$ and 1.0 hr$^{-1}$

Pressure: 60 kg/cm$^2$
LHSV: 1.0 hr$^{-1}$
H$_2$/oil ratio: 400 lit/lit

<table>
<thead>
<tr>
<th>Properties</th>
<th>Reactor Temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>340</td>
</tr>
<tr>
<td>Density at 15°C, gm/cc</td>
<td>0.9108</td>
</tr>
<tr>
<td>Gravity, degree API</td>
<td>23.9</td>
</tr>
<tr>
<td>Kinematic Viscosity at 100°C, cSt</td>
<td>7.08</td>
</tr>
<tr>
<td>Refractive Index at 70°C</td>
<td>1.4836</td>
</tr>
<tr>
<td>Pour point, °C</td>
<td>39</td>
</tr>
<tr>
<td>Aniline Point, °C</td>
<td>90.8</td>
</tr>
<tr>
<td>Aromatics, wt.%</td>
<td>37.8</td>
</tr>
<tr>
<td>Saturates, wt.%</td>
<td>62.2</td>
</tr>
<tr>
<td>Sulphur, ppmw</td>
<td>785</td>
</tr>
<tr>
<td>Nitrogen, ppmw</td>
<td>1400</td>
</tr>
<tr>
<td>Conversion wt%, 370°C -</td>
<td>5.54</td>
</tr>
</tbody>
</table>

**Yields based on feed, wt%**

<table>
<thead>
<tr>
<th></th>
<th>340</th>
<th>360</th>
<th>380</th>
<th>400</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas (C$_1$-C$_4$)</td>
<td>0.5</td>
<td>0.9</td>
<td>1.9</td>
<td>3.5</td>
</tr>
<tr>
<td>Naphtha (C$_5$-140°C)</td>
<td>1.9</td>
<td>2.9</td>
<td>4.0</td>
<td>5.3</td>
</tr>
<tr>
<td>Middle distillates (140 – 370°C)</td>
<td>12.4</td>
<td>13.9</td>
<td>15.9</td>
<td>18.6</td>
</tr>
<tr>
<td>VGO Cut (370°C+)</td>
<td>85.2</td>
<td>82.3</td>
<td>78.2</td>
<td>72.6</td>
</tr>
<tr>
<td>% HDS</td>
<td>72.74</td>
<td>84.03</td>
<td>91.49</td>
<td>95.66</td>
</tr>
<tr>
<td>% HDN</td>
<td>18.18</td>
<td>31.33</td>
<td>49.74</td>
<td>65.52</td>
</tr>
<tr>
<td>% HDA</td>
<td>9.79</td>
<td>12.65</td>
<td>17.42</td>
<td>19.33</td>
</tr>
</tbody>
</table>
Table 5.74 Properties of MHC products and pilot plant yields at 60 kg/cm\(^2\) and 1.5 hr\(^{-1}\)

Pressure: 60 kg/cm\(^{2}\)
LHSV: 1.5 hr\(^{-1}\)
H\(_{2}\)/oil ratio: 400 lit/lit

<table>
<thead>
<tr>
<th>Properties</th>
<th>Reactor Temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>340</td>
</tr>
<tr>
<td>Density at 15°C, gm/cc</td>
<td>0.9125</td>
</tr>
<tr>
<td>Gravity, degree API</td>
<td>23.6</td>
</tr>
<tr>
<td>Kinematic Viscosity at 100°C, cSt</td>
<td>7.24</td>
</tr>
<tr>
<td>Refractive Index at 70°C</td>
<td>1.485</td>
</tr>
<tr>
<td>Pour point, °C</td>
<td>39</td>
</tr>
<tr>
<td>Aniline Point, °C</td>
<td>89</td>
</tr>
<tr>
<td>Aromatics, wt.%</td>
<td>37.8</td>
</tr>
<tr>
<td>Saturates, wt.%</td>
<td>62.2</td>
</tr>
<tr>
<td>Sulphur, ppmw</td>
<td>1080</td>
</tr>
<tr>
<td>Nitrogen, ppmw</td>
<td>1500</td>
</tr>
<tr>
<td>Conversion wt%, 370°C</td>
<td>4.21</td>
</tr>
</tbody>
</table>

**Yields based on feed, wt%**

<table>
<thead>
<tr>
<th></th>
<th>340</th>
<th>360</th>
<th>380</th>
<th>400</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas (C(<em>{1})-C(</em>{4}))</td>
<td>0.3</td>
<td>0.6</td>
<td>1.1</td>
<td>2.4</td>
</tr>
<tr>
<td>Naphtha (C(_{5})-140°C)</td>
<td>1.5</td>
<td>2.3</td>
<td>3.5</td>
<td>4.4</td>
</tr>
<tr>
<td>Middle distillates (140 – 370°C)</td>
<td>11.8</td>
<td>12.9</td>
<td>14.5</td>
<td>16.7</td>
</tr>
<tr>
<td>VGO Cut (370°C+)</td>
<td>86.4</td>
<td>84.1</td>
<td>80.9</td>
<td>76.5</td>
</tr>
<tr>
<td>% HDS</td>
<td>62.50</td>
<td>75.52</td>
<td>85.42</td>
<td>91.67</td>
</tr>
<tr>
<td>% HDN</td>
<td>12.33</td>
<td>22.85</td>
<td>37.46</td>
<td>55.29</td>
</tr>
<tr>
<td>% HDA</td>
<td>9.79</td>
<td>11.93</td>
<td>14.08</td>
<td>15.99</td>
</tr>
</tbody>
</table>
Table 5.75 Properties of MHC products and pilot plant yields at 60 kg/cm\(^2\) and 2.0 hr\(^{-1}\)

Pressure: 60 kg/cm\(^2\)
LHSV: 2.0 hr\(^{-1}\)
H\(_2\)/oil ratio: 400 lit/lit

<table>
<thead>
<tr>
<th>Properties</th>
<th>Reactor Temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>340</td>
</tr>
<tr>
<td>Density at 15°C, gm/cc</td>
<td>0.9155</td>
</tr>
<tr>
<td>Gravity, degree API</td>
<td>23.0</td>
</tr>
<tr>
<td>Kinematic Viscosity at 100°C, cSt</td>
<td>7.3</td>
</tr>
<tr>
<td>Refractive Index at 70°C</td>
<td>1.4861</td>
</tr>
<tr>
<td>Pour point, °C</td>
<td>39</td>
</tr>
<tr>
<td>Aniline Point, °C</td>
<td>88.9</td>
</tr>
<tr>
<td>Aromatics, wt.%</td>
<td>38.4</td>
</tr>
<tr>
<td>Saturates, wt.%</td>
<td>61.6</td>
</tr>
<tr>
<td>Sulphur, ppmw</td>
<td>1340</td>
</tr>
<tr>
<td>Nitrogen, ppmw</td>
<td>1570</td>
</tr>
<tr>
<td>Conversion wt%, 370°C -</td>
<td>3.55</td>
</tr>
</tbody>
</table>

**Yields based on feed, wt%**

<table>
<thead>
<tr>
<th></th>
<th>340</th>
<th>360</th>
<th>380</th>
<th>400</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas (C(_1)-C(_4))</td>
<td>0.2</td>
<td>0.4</td>
<td>1.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Naphtha (C(_5)-140°C)</td>
<td>1.3</td>
<td>2.0</td>
<td>2.8</td>
<td>3.7</td>
</tr>
<tr>
<td>Middle distillates (140 – 370°C)</td>
<td>11.5</td>
<td>12.4</td>
<td>13.7</td>
<td>15.6</td>
</tr>
<tr>
<td>VGO Cut (370°C+)</td>
<td>87.0</td>
<td>85.2</td>
<td>82.5</td>
<td>78.7</td>
</tr>
<tr>
<td>% HDS</td>
<td>53.47</td>
<td>67.71</td>
<td>79.17</td>
<td>87.50</td>
</tr>
<tr>
<td>% HDN</td>
<td>8.24</td>
<td>16.42</td>
<td>28.11</td>
<td>46.82</td>
</tr>
<tr>
<td>% HDA</td>
<td>8.35</td>
<td>10.5</td>
<td>11.7</td>
<td>15.99</td>
</tr>
</tbody>
</table>
Table 5.76 Properties of MHC products and pilot plant yields at 100 kg/cm² and 1.0 hr⁻¹

Pressure: 100 kg/cm²  
LHSV: 1.0 hr⁻¹  
\( \text{H}_2/\text{oil ratio: 400 lit/lit} \)

<table>
<thead>
<tr>
<th>Properties</th>
<th>Reactor Temperature, °C</th>
<th>340</th>
<th>360</th>
<th>380</th>
<th>400</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density at 15°C, gm/cc</td>
<td></td>
<td>0.9099</td>
<td>0.9081</td>
<td>0.9006</td>
<td>0.8796</td>
</tr>
<tr>
<td>Gravity, degree API</td>
<td></td>
<td>24.0</td>
<td>24.3</td>
<td>25.6</td>
<td>29.4</td>
</tr>
<tr>
<td>Kinematic Viscosity at 100°C, cSt</td>
<td></td>
<td>7.03</td>
<td>6.51</td>
<td>5.37</td>
<td>3.37</td>
</tr>
<tr>
<td>Refractive Index at 70°C</td>
<td></td>
<td>1.4817</td>
<td>1.48</td>
<td>1.4757</td>
<td>1.4678</td>
</tr>
<tr>
<td>Pour point, °C</td>
<td></td>
<td>39</td>
<td>39</td>
<td>39</td>
<td>36</td>
</tr>
<tr>
<td>Aniline Point, °C</td>
<td></td>
<td>90</td>
<td>89.6</td>
<td>88.8</td>
<td>88.4</td>
</tr>
<tr>
<td>Aromatics, wt.%</td>
<td></td>
<td>34.31</td>
<td>32.53</td>
<td>30.46</td>
<td>27.56</td>
</tr>
<tr>
<td>Saturates, wt.%</td>
<td></td>
<td>65.69</td>
<td>67.47</td>
<td>69.54</td>
<td>72.44</td>
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<tr>
<td>Sulphur, ppmw</td>
<td></td>
<td>445</td>
<td>240</td>
<td>115</td>
<td>60</td>
</tr>
<tr>
<td>Nitrogen, ppmw</td>
<td></td>
<td>1180</td>
<td>854</td>
<td>476</td>
<td>238</td>
</tr>
<tr>
<td>Conversion wt%, 370°C -</td>
<td></td>
<td>6.98</td>
<td>11.09</td>
<td>16.74</td>
<td>24.28</td>
</tr>
</tbody>
</table>

**Yields based on feed, wt.%**

<table>
<thead>
<tr>
<th></th>
<th>340</th>
<th>360</th>
<th>380</th>
<th>400</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas (C₁-C₄)</td>
<td>0.8</td>
<td>1.5</td>
<td>2.4</td>
<td>3.9</td>
</tr>
<tr>
<td>Naphtha (C₅-140°C)</td>
<td>2.2</td>
<td>3.3</td>
<td>5.0</td>
<td>7.0</td>
</tr>
<tr>
<td>Middle distillates (140 – 370°C)</td>
<td>13.1</td>
<td>14.9</td>
<td>17.5</td>
<td>20.8</td>
</tr>
<tr>
<td>VGO Cut (370°C+)</td>
<td>83.9</td>
<td>80.2</td>
<td>75.1</td>
<td>68.3</td>
</tr>
<tr>
<td>% HDS</td>
<td>84.55</td>
<td>91.67</td>
<td>96.01</td>
<td>97.92</td>
</tr>
<tr>
<td>% HDN</td>
<td>31.03</td>
<td>50.09</td>
<td>72.18</td>
<td>86.09</td>
</tr>
<tr>
<td>% HDA</td>
<td>18.11</td>
<td>22.36</td>
<td>27.3</td>
<td>34.22</td>
</tr>
</tbody>
</table>
Table 5.77  Properties of MHC products and pilot plant yields at
100 kg/cm² and 1.5 hr⁻¹

Pressure: 100 kg/cm²
LHSV: 1.5 hr⁻¹
H₂/oil ratio: 400 lit/lit

<table>
<thead>
<tr>
<th>Properties</th>
<th>Reactor Temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>340</td>
</tr>
<tr>
<td>Density at 15°C, gm/cc</td>
<td>0.9124</td>
</tr>
<tr>
<td>Gravity, degree API</td>
<td>23.6</td>
</tr>
<tr>
<td>Kinematic Viscosity at 100°C, cSt</td>
<td>7.21</td>
</tr>
<tr>
<td>Refractive Index at 70°C</td>
<td>1.4832</td>
</tr>
<tr>
<td>Pour point, °C</td>
<td>39</td>
</tr>
<tr>
<td>Aniline Point, °C</td>
<td>88.6</td>
</tr>
<tr>
<td>Aromatics, wt.%</td>
<td>36.42</td>
</tr>
<tr>
<td>Saturates, wt.%</td>
<td>63.58</td>
</tr>
<tr>
<td>Sulphur, ppmw</td>
<td>732</td>
</tr>
<tr>
<td>Nitrogen, ppmw</td>
<td>1315</td>
</tr>
<tr>
<td>Conversion wt%, 370°C -</td>
<td>5.88</td>
</tr>
</tbody>
</table>

Yields based on feed, wt %

| Gas (C₁-C₄)                          | 0.5        | 1.2        | 2.1        | 3.4        |
| Naphtha (C₅-140°C)                   | 2.0        | 2.9        | 4.1        | 5.9        |
| Middle distillates (140 – 370°C)     | 12.6       | 13.8       | 15.5       | 18.6       |
| VGO Cut (370°C+)                     | 84.9       | 82.1       | 78.3       | 72.1       |
| % HDS                                | 74.58      | 85.24      | 92.71      | 96.25      |
| % HDN                                | 23.14      | 40.44      | 59.21      | 77.44      |
| % HDA                                | 13.08      | 16.37      | 20.41      | 26.44      |

a %HDS of 97.92 was obtained indicating a lower dependence of sulfur removal with respect to operating pressure. MHC VGO with very low levels
of sulfur when used as FCC feedstock can reduce sulfur content in FCC gasoline and diesel blending components besides reducing SOx emissions from FCC regenerator.

As can be seen from Tables 5.73 to 5.75, the nitrogen content of VGO was found to decrease from 1711 ppmw in the feed to 590 - 1570 ppmw in the range of operating conditions studied at a constant pressure of 60 kg/cm$^2$ indicating 8.24 - 65.52 % HDN. As can be seen from Tables 5.76 and 5.77, the nitrogen content of VGO mild hydrocracked at 100 kg/cm$^2$ was found to decrease to 0.0238 - 0.1315 wt%. The %HDN increased with increasing reactor temperature and decreasing LHSV. The reactor operating pressure was found to have pronounced effect on nitrogen removal.

Under typical operating conditions of MHC unit, a %HDN of about 65.52 was obtained. It shows that hydrodenitrogenation normally proceeds at a slower rate compared to hydrodesulphurization under MHC conditions. At the same typical operating conditions, as the pressure was increased from 60 to 100 kg/cm$^2$, the %HDN increased to 86.09 indicating higher influence of operating pressure on hydrodenitrogenation. The nitrogen compounds, particularly basic nitrogen, neutralize the acidity of FCC zeolite catalyst and thus decrease conversion and yield of valuable distillates. Mild hydrocracking of VGO would result in very low nitrogen levels in the feedstock to FCCU and would result in better conversions and product yields in the unit. This is particularly beneficial while processing high nitrogenous feedstock in FCCU as that used in the pilot plant studies.

The aromatics were found to decrease from 37.8 wt.% to 33.8 wt% as the temperature was increased from 340°C to 400°C at a constant pressure of 60 kg/cm$^2$ and a LHSV of 1.0 hr$^{-1}$ indicating 9.79 to 19.3 % HDA. At the same operating conditions by increasing the operating pressure to 100 kg/cm$^2$,.
the aromatics were decreased from 34.31 to 27.6 wt% indicating 18.1 to 34.2% HDA. The pilot plant data indicates that the aromatic saturation reactions are favored at higher operating pressures.

Aromatic compounds are not easily cracked in FCC unit and the limited amount of cracking achieved produces a large amount of coke due to condensation reactions. Hydrotreating can saturate the polynuclear aromatic compounds present in the typical FCC feeds and convert them into easily cracked naphthenes and paraffins and thus help to produce valuable products.

The comparison of MAT conversions and yields are presented in Table 5.78. The yield benefits from MAT studies for hydrotreating and mild hydrocracking options are presented in Table 5.79 and Figure 5.81. As can be seen from the pilot plant data, MHC VGO resulted in higher conversions and better yields compared to HDT VGO. Processing of MHC bottoms in the MAT unit resulted in higher MAT number compared to untreated and hydrotreated VGO. The untreated VGO had resulted in a MAT number of 51 and HDT VGO 52. Mild hydrocracked VGO at 100 kg/cm² had resulted in a MAT number of 55 indicating higher conversion of the feedstock in FCC unit compared to untreated and HDT VGO. The yield of residue, coke and light gases decreased while processing MHC VGO in FCC unit and yield of LPG, gasoline and diesel increased. In the present study, the MHC product was directly used as FCC feedstock without any separation. The economic benefits from this route can be considerably higher compared to HDT option, if the distillates from MHC product are separated prior to feeding to FCC unit.
Table 5.78 Comparison of MAT Conversions and Yields

**Reactor Temperature: 482°C**  
**Catalyst/Oil ratio: 3.0**

<table>
<thead>
<tr>
<th></th>
<th>Untreated VGO</th>
<th>Hydrotreated VGO</th>
<th>Mildhydro-cracked VGO</th>
<th>Mildhydro-cracked VGO</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Temperature, ºC</strong></td>
<td>-</td>
<td>340</td>
<td>360</td>
<td>360</td>
</tr>
<tr>
<td><strong>Pressure, kg/cm²</strong></td>
<td>-</td>
<td>50</td>
<td>60</td>
<td>100</td>
</tr>
<tr>
<td><strong>LHSV, hr⁻¹</strong></td>
<td>-</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td><strong>H₂/HC ratio, lit/lit</strong></td>
<td>-</td>
<td>300</td>
<td>400</td>
<td>400</td>
</tr>
</tbody>
</table>

**Conversion and Product Yields**

<table>
<thead>
<tr>
<th>MAT No.</th>
<th>Light Gases, wt%</th>
<th>LPG, wt%</th>
<th>Gasoline, wt%</th>
<th>Diesel, wt%</th>
<th>Residue, wt%</th>
<th>Coke, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>51</td>
<td>2.9</td>
<td>10.7</td>
<td>25.4</td>
<td>27.4</td>
<td>30.0</td>
<td>3.6</td>
</tr>
<tr>
<td>52</td>
<td>2.4</td>
<td>11.2</td>
<td>25.9</td>
<td>28.6</td>
<td>28.4</td>
<td>3.5</td>
</tr>
<tr>
<td>53</td>
<td>2.3</td>
<td>11.8</td>
<td>26.3</td>
<td>29.0</td>
<td>27.2</td>
<td>3.4</td>
</tr>
<tr>
<td>55</td>
<td>2.2</td>
<td>12.4</td>
<td>26.7</td>
<td>29.5</td>
<td>26.0</td>
<td>3.2</td>
</tr>
</tbody>
</table>

Table 5.79 Yield Benefits of Mild Hydrocracking of FCC feed

<table>
<thead>
<tr>
<th>Product</th>
<th>Yield, wt%</th>
<th>Δ (HDT-Untreated) yields</th>
<th>Δ(MHC-Untreated) yields</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Untreated</td>
<td>HDT</td>
<td>MHC</td>
</tr>
<tr>
<td>LPG</td>
<td>10.7</td>
<td>11.2</td>
<td>11.8</td>
</tr>
<tr>
<td>Gasoline</td>
<td>25.4</td>
<td>25.9</td>
<td>26.3</td>
</tr>
<tr>
<td>Diesel</td>
<td>27.4</td>
<td>28.6</td>
<td>29.0</td>
</tr>
<tr>
<td>Residue</td>
<td>30.0</td>
<td>28.4</td>
<td>27.2</td>
</tr>
</tbody>
</table>
Figure 5.81 Comparison of FCC product yields

Unconverted oil obtained from MHC of VGO had resulted in higher FCC conversions due to hydrogen addition and increased saturation of the feedstock. The removal of nitrogen (especially basic) from the feed also would have contributed to higher FCC conversions. The products from FCC are expected to have very low levels of sulfur, as more than 95 wt% of sulfur has been removed during MHC step. Low sulfur FCC feed can also reduce SO$_x$ emissions from FCC regenerator and help in meeting emission standards. As can be seen from Table 5.78, the FCC yield pattern shifts towards more of fuels and less of coke and residue by using hydrotreated or MHC option for FCC feed preparation. Figure 5.81 presents integrated product yields from HDT/MHC-FCC combination of a refinery configuration. The overall yields based on fresh VGO feed also shift towards more of gasoline and diesel compared to untreated case.
5.8.5 Incremental Yields and Revenue Benefits

Table 5.80 compares data on economic analysis of different options considered in the present work. The estimations of revenue benefits were made considering a refinery configuration with a FCC unit of 22000 BPSD capacity operating for 340 days time-on-stream factor. It was assumed that additional VGO was available for upgrading to higher value fuels. The calculations were made based on TAIP (Tariff Adjusted Import Parity) prices in India during a particular month in the year 2005. It was also assumed that the VGO if not upgraded would be used for fuel oil blending.

Hydrotreating of VGO was estimated to generate additional revenues to the tune of US$ 5.5 million per annum compared to untreated case. MHC of VGO at 100 bars and feeding 370°C plus to FCC unit was estimated to result in additional revenues of US$ 10.9 million per annum compared to untreated case. These huge benefits come from the fact that additional VGO to the extent of 20% can be upgraded to valuable fuels through MHC route. For a refinery configuration with higher capacity of FCC unit, the potential benefits will be much higher.

As can be seen from the data presented here, MHC provides a profitable minimum investment route to achieve incremental vacuum gas oil conversion while producing high quality low sulfur fuels. Refiners with VGO hydrotreating units can retrofit their units for MHC operation with minimum investment to maximize refinery margins. Refineries without any feed pretreatment unit for FCCU may consider capital investments in stages by going for MHC unit instead of hydrocracker. In view of increased conversion to valuable fuels and superior quality of products, the investments made for retrofitting existing VGO hydrotreaters or building new MHC units are readily paid back.
Table 5.80  Incremental Yields and Revenue benefits: Untreated vs Hydroprocessed VGO

**Basis: 0.6 MMTPA cat-cracker**

<table>
<thead>
<tr>
<th>Operating mode</th>
<th>Untreated, Ton/day</th>
<th>$/day</th>
<th>HDT $/day</th>
<th>MHC $/day</th>
<th>$/day</th>
</tr>
</thead>
<tbody>
<tr>
<td>LPG</td>
<td>307.8</td>
<td>80149</td>
<td>368.3</td>
<td>95911</td>
<td>495.1</td>
</tr>
<tr>
<td>Naphtha</td>
<td>730.6</td>
<td>193255</td>
<td>814.5</td>
<td>215435</td>
<td>885.5</td>
</tr>
<tr>
<td>Diesel</td>
<td>788.2</td>
<td>153694</td>
<td>820.5</td>
<td>159995</td>
<td>1122.6</td>
</tr>
<tr>
<td>Fuel oil</td>
<td>862.9</td>
<td>143166</td>
<td>811.5</td>
<td>134629</td>
<td>732.1</td>
</tr>
<tr>
<td>Feed : VGO</td>
<td>-2876.5</td>
<td>-477219</td>
<td>-2994.5</td>
<td>-496785</td>
<td>-3486.4</td>
</tr>
<tr>
<td>Value Addition</td>
<td></td>
<td>93044</td>
<td>109185</td>
<td></td>
<td>125122</td>
</tr>
</tbody>
</table>

Incremental Revenue : $ \Delta (HDT – Untreated)$ - US$ 5.5 million per annum

$ \Delta (MHC – HDT)$ - US$ 5.4 million per annum

Basis: LPG - 260.4 $/Ton
Naphtha - 264.5 $/Ton
Diesel - 195 $/Ton
Fuel oil - 165.9 $/Ton
VGO - 165.9 $/Ton

In view of improved conversions, higher distillate yields, additional distillates from MHC, better FCC product qualities, many of the refiners consider revamp of their existing VGO hydrotreating units for MHC application. All over the world many refiners have successfully converted their VGO hydrotreaters for MHC application to maximize distillate yields and improving FCC product qualities. The revamped MHC units are
operating at low severity levels compared to new MHC units due to design limitations of operating pressures. Conversion of VGO hydrotreaters does not require major capital investments as the existing facilities can be used as such. The capital investments required to setup additional separation facilities to separate distillates from MHC products are justifiable with respect to higher yields distillates from the refinery with better refinery economics. The suggested process scheme for MHC option as FCC feed preparation is shown in Figure 5.82. The typical schematic diagram of MHC process is shown in Figure 5.83.

Mild hydrocracking of vacuum gas oils yields valuable distillates with lower sulfur and nitrogen contents. This process can be used to maximize the production of middle distillates from a refinery configuration with a vacuum gas oil hydrotreater and fluidized catalytic cracking units. The mild hydrocracker bottom can become a very good feedstock for FCC unit and results in significant improvements in FCC performance. Processing of mild hydrocracker bottom in FCC unit would result in better quality fuels. The mild hydrocracking of FCC feed results in the following advantages:

- Produces additional fuels in mild hydrocracking step
- Improves the quality of FCC products with respect to sulfur and nitrogen
- Increases gasoline and diesel yields from FCC unit
- Reduces the yield of residue
- Reduces Ramsbottom Carbon Residue (RCR) of the FCC feed. The reduction in RCR will greatly reduce coke make in the FCC unit by decreasing coke precursors
Figure 5.82 Hydroprocessing options for FCC feed pretreatment

Figure 5.83 Process flow diagram of MHC process
• Removes metals like Ni, V from the feed and thereby improve FCC catalyst activity and selectivity and result longer catalyst life.
• Reduces Sox emissions from FCC regenerator.

5.9 KINETICS OF MILD HYDROCRACKING PROCESS

The kinetic reaction schemes for the analysis of mild hydrocracking process and the differential equations representing them were presented in the Chapter 4. The estimation of kinetic parameters for these models was done using the same procedure as discussed under section 5.2.1 titled ‘kinetic parameter estimation’. The kinetic parameters for the Models I to IV have been presented in Table 5.81. These kinetic parameters were estimated at a reactor operating pressure of 60 kg/cm$^2$ and thus not applicable for the data generated at a reactor operating pressure of 100 kg/cm$^2$. Table 5.82 presents the kinetic parameters for mild hydrocracking reactions for the case of Model V which considers the effect of partial pressure of hydrogen.

Table 5.82 also presents the kinetics of hydrodesulfurization and hydrodenitrogenation reactions. Model V is applicable for both operating pressures since it considers the effect of operating pressure on conversion.

5.9.1 Model I

The model differential equation was solved using the kinetic parameters listed in Table 5.81 to estimate VGO yields at various operating conditions. The simulated effect of operating conditions on VGO yield at 60 kg/cm$^2$ was presented in Table 5.83. As can be seen from Table 5.83, the yield of VGO Feedstock decreased with increase in reaction time (which is considered as inverse of LHSV) and reactor temperature due to increasing cracking and disappearance of VGO Feedstock at higher severity levels. This model predicts the effect of operating conditions on the yield of VGO very well.
### Table 5.81 Kinetic parameters for mild hydrocracking reactions

<table>
<thead>
<tr>
<th>Kinetic constant</th>
<th>Kinetic Expression</th>
<th>k at 380°C, h⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Model I</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( k_{\text{MHC}} )</td>
<td>( 1.8527 \times 10^5 \exp\left(-1.8263 \times 10^4 / RT\right) )</td>
<td>0.1428</td>
</tr>
<tr>
<td><strong>Model II</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( k_1 )</td>
<td>( 1.8527 \times 10^5 \exp\left(-1.8263 \times 10^4 / RT\right) )</td>
<td>0.1428</td>
</tr>
<tr>
<td>( k_2 )</td>
<td>( 1.8605 \times 10^4 \exp\left(-1.3830 \times 10^4 / RT\right) )</td>
<td>0.4465</td>
</tr>
<tr>
<td><strong>Model III</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( k_1 )</td>
<td>( 1.6352 \times 10^5 \exp\left(-1.8895 \times 10^4 / RT\right) )</td>
<td>0.0777</td>
</tr>
<tr>
<td>( k_2 )</td>
<td>( 4.6555 \times 10^4 \exp\left(-1.7485 \times 10^4 / RT\right) )</td>
<td>0.0650</td>
</tr>
<tr>
<td>( k_3 )</td>
<td>( 2.4212 \times 10^8 \exp\left(-2.9584 \times 10^4 / RT\right) )</td>
<td>0.0333</td>
</tr>
<tr>
<td><strong>Model IV</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( k_1 )</td>
<td>( 6.1501 \times 10^4 \exp\left(-1.7711 \times 10^4 / RT\right) )</td>
<td>0.0726</td>
</tr>
<tr>
<td>( k_2 )</td>
<td>( 1.4070 \times 10^5 \exp\left(-1.8827 \times 10^4 / RT\right) )</td>
<td>0.0702</td>
</tr>
</tbody>
</table>

### Table 5.82 Kinetic parameters for mild hydrocracking reactions - Model V

<table>
<thead>
<tr>
<th>Kinetic constant</th>
<th>Pre-exponential factor (ko)</th>
<th>(E/R), K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mild hydrocracking (m=0.67, n=0.49)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( k_1+k_2 )</td>
<td>( 8.019 \times 10^4 )</td>
<td>( 7.674 \times 10^4 )</td>
</tr>
<tr>
<td>( k_1 )</td>
<td>( 2.565 \times 10^4 )</td>
<td>( 7.424 \times 10^4 )</td>
</tr>
<tr>
<td>( k_2 )</td>
<td>( 6.037 \times 10^4 )</td>
<td>( 7.907 \times 10^4 )</td>
</tr>
<tr>
<td>Hydrodesulphurisation (m=1.0, n=0.95)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( k_s )</td>
<td>( 3.234 \times 10^6 )</td>
<td>( 7.883 \times 10^4 )</td>
</tr>
<tr>
<td>Hydrodenitrogenation (m=1.0, n=1.5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( k_N )</td>
<td>( 1.466 \times 10^8 )</td>
<td>( 1.134 \times 10^8 )</td>
</tr>
</tbody>
</table>

### Table 5.83 Effect of operating conditions on VGO yield at 60 kg/cm² - Model I
<table>
<thead>
<tr>
<th>Reaction time, h</th>
<th>VGO Yield, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>340°C</td>
</tr>
<tr>
<td>0</td>
<td>90.20</td>
</tr>
<tr>
<td>0.25</td>
<td>88.92</td>
</tr>
<tr>
<td>0.5</td>
<td>87.66</td>
</tr>
<tr>
<td>0.667</td>
<td>86.83</td>
</tr>
<tr>
<td>0.75</td>
<td>86.42</td>
</tr>
<tr>
<td>1.0</td>
<td>85.19</td>
</tr>
<tr>
<td>1.25</td>
<td>83.99</td>
</tr>
<tr>
<td>1.5</td>
<td>82.79</td>
</tr>
<tr>
<td>1.75</td>
<td>81.62</td>
</tr>
<tr>
<td>2.0</td>
<td>80.46</td>
</tr>
</tbody>
</table>

### 5.9.2 Model II

Using the kinetic parameters presented in Table 5.82, the model differential equations presented in chapter 4 were solved simultaneously to generate product yield distribution data at various operating conditions. The simulated effect of operating conditions on the yield of VGO, middle distillates and naphtha and gas at 60 kg/cm² was presented in Table 5.84. As can be seen from Table 5.84, the yield of VGO Feedstock decreased with increase in reaction time due to cracking reaction of feedstock while the yields of middle distillates and naphtha and gas continuously increased with reaction time for a particular reactor temperature. The yield of VGO feedstock decreased with increase in reactor temperature due to increasing cracking and disappearance of VGO feedstock at elevated temperatures. The yield of middle distillates and naphtha and gas increased with reactor temperature for a particular reaction time. This model predicts the effect of operating
conditions on the product yields very well as seen from Figure 5.84 which shows the observed yields vs. predicted yields for Model II.

Table 5.84  Effect of operating conditions on product yields at 60 kg/cm² - Model II
Feedstock: VGO – 90.20 wt%, MD – 9.80 wt%, NG – 0.0 wt%

<table>
<thead>
<tr>
<th>Products</th>
<th>Reaction time, h</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.25</td>
</tr>
<tr>
<td>Temperature – 340°C</td>
<td></td>
</tr>
<tr>
<td>NG</td>
<td>0.56</td>
</tr>
<tr>
<td>VGO</td>
<td>88.92</td>
</tr>
<tr>
<td>Temperature – 360°C</td>
<td></td>
</tr>
<tr>
<td>NG</td>
<td>0.81</td>
</tr>
<tr>
<td>MD</td>
<td>11.03</td>
</tr>
<tr>
<td>VGO</td>
<td>88.16</td>
</tr>
<tr>
<td>Temperature – 380°C</td>
<td></td>
</tr>
<tr>
<td>NG</td>
<td>1.18</td>
</tr>
<tr>
<td>MD</td>
<td>11.79</td>
</tr>
<tr>
<td>VGO</td>
<td>87.03</td>
</tr>
<tr>
<td>Temperature – 400°C</td>
<td></td>
</tr>
<tr>
<td>NG</td>
<td>1.71</td>
</tr>
<tr>
<td>MD</td>
<td>12.86</td>
</tr>
<tr>
<td>VGO</td>
<td>85.43</td>
</tr>
</tbody>
</table>
5.9.3 Model III

The model differential equations presented in chapter 4 for this model were solved simultaneously to generate the product yields at various operating conditions using the kinetic parameters presented in Table 5.81. The simulated effect of operating conditions on the yield of VGO, middle distillates and naphtha and gas at an operating pressure of 60 kg/cm² was presented in Table 5.85. The predictions of product yields using this model are almost similar to that of Model II. Figure 5.85 shows the comparison between observed and predicted product yields for Model III. This model predicts the effect of operating conditions on the product yields very well.
Table 5.85  Effect of operating conditions on product yields at 60 kg/cm² - Model III
Feedstock: VGO – 90.20 wt%, MD – 9.80 wt%, NG – 0.0 wt%

<table>
<thead>
<tr>
<th>Products</th>
<th>Reaction time, h</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Temperature – 340°C</td>
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<td>0.63</td>
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<tr>
<td>MD</td>
<td>10.45</td>
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<tr>
<td>VGO</td>
<td>88.92</td>
</tr>
<tr>
<td></td>
<td>Temperature – 360°C</td>
</tr>
<tr>
<td>NG</td>
<td>0.99</td>
</tr>
<tr>
<td>MD</td>
<td>10.85</td>
</tr>
<tr>
<td>VGO</td>
<td>88.15</td>
</tr>
<tr>
<td></td>
<td>Temperature – 380°C</td>
</tr>
<tr>
<td>NG</td>
<td>1.53</td>
</tr>
<tr>
<td>MD</td>
<td>11.44</td>
</tr>
<tr>
<td>VGO</td>
<td>87.03</td>
</tr>
<tr>
<td></td>
<td>Temperature – 400°C</td>
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<tr>
<td>NG</td>
<td>2.31</td>
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<tr>
<td>MD</td>
<td>12.26</td>
</tr>
<tr>
<td>VGO</td>
<td>85.43</td>
</tr>
</tbody>
</table>

5.9.4  Model IV

The model differential equations presented in chapter 4 were solved simultaneously to generate product yield distribution at various operating conditions using the kinetic parameters listed in Table 5.81. As can be seen from Table 5.81, the activation energy for the formation of middle distillates is 17711 cal/gmole compared to that of 18827 cal/gmole for the reaction of feedstock into naphtha and gas indicating higher temperature sensitivity of the later reaction. The simulated effect of operating conditions on the yield of
VGO, middle distillates and naphtha and gas at an operating pressure of 60 kg/cm² is presented in Table 5.86. The prediction of product yields by this model is in accordance with the trend pattern observed for other models. This parallel reaction model predicts the effect of operating conditions on the product yields very well as seen from the Figure 5.86. The difference between the observed and predicted yields is very less indicating the applicability of a parallel reaction scheme for mild hydrocracking process.

5.9.5 Model V

The kinetic parameters for mild hydrocracking reactions in the case of Model V which considers the effect of partial pressure of hydrogen on product yields using a parallel reaction scheme is presented in Table 5.82. The estimation of kinetic parameters was done using multiple linear regression
Table 5.86  Effect of operating conditions on product yields at 60 kg/cm² - Model IV
Feedstock: VGO – 90.20 wt%, MD – 9.80 wt%, NG – 0.0 wt%

<table>
<thead>
<tr>
<th>Products</th>
<th>Reaction time, h</th>
<th>0.25</th>
<th>0.5</th>
<th>0.667</th>
<th>0.75</th>
<th>1.0</th>
<th>1.25</th>
<th>1.50</th>
<th>1.75</th>
<th>2.0</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature – 340°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>NG</td>
<td></td>
<td>0.61</td>
<td>1.21</td>
<td>1.61</td>
<td>1.81</td>
<td>2.39</td>
<td>2.97</td>
<td>3.54</td>
<td>4.10</td>
<td>4.65</td>
</tr>
<tr>
<td>VGO</td>
<td></td>
<td>88.92</td>
<td>87.66</td>
<td>86.83</td>
<td>86.42</td>
<td>85.19</td>
<td>83.98</td>
<td>82.79</td>
<td>81.62</td>
<td>80.46</td>
</tr>
<tr>
<td></td>
<td>Temperature – 360°C</td>
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<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NG</td>
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<td>0.99</td>
<td>1.96</td>
<td>2.60</td>
<td>2.91</td>
<td>3.83</td>
<td>4.74</td>
<td>5.62</td>
<td>6.49</td>
<td>7.33</td>
</tr>
<tr>
<td>MD</td>
<td></td>
<td>10.85</td>
<td>11.88</td>
<td>12.56</td>
<td>12.89</td>
<td>13.87</td>
<td>14.83</td>
<td>15.77</td>
<td>16.69</td>
<td>17.58</td>
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<tr>
<td>VGO</td>
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<td>88.16</td>
<td>86.16</td>
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<td>84.21</td>
<td>82.30</td>
<td>80.43</td>
<td>78.61</td>
<td>76.83</td>
<td>75.09</td>
</tr>
<tr>
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<td>Temperature – 380°C</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>NG</td>
<td></td>
<td>1.56</td>
<td>3.06</td>
<td>4.04</td>
<td>4.51</td>
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<td>8.57</td>
<td>9.82</td>
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</tr>
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<td>11.41</td>
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<td>14.46</td>
<td>15.91</td>
<td>17.30</td>
<td>18.65</td>
<td>19.95</td>
<td>21.20</td>
</tr>
<tr>
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<td>83.97</td>
<td>81.99</td>
<td>81.03</td>
<td>78.18</td>
<td>75.43</td>
<td>72.78</td>
<td>70.23</td>
<td>67.76</td>
</tr>
<tr>
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<td>Temperature – 400°C</td>
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<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NG</td>
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<td>4.63</td>
<td>6.06</td>
<td>6.76</td>
<td>8.78</td>
<td>10.69</td>
<td>12.50</td>
<td>14.22</td>
<td>15.84</td>
</tr>
<tr>
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<td></td>
<td>12.19</td>
<td>14.46</td>
<td>15.91</td>
<td>16.61</td>
<td>18.64</td>
<td>20.56</td>
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<td></td>
<td>85.43</td>
<td>80.91</td>
<td>78.03</td>
<td>76.64</td>
<td>72.58</td>
<td>68.75</td>
<td>65.11</td>
<td>61.67</td>
<td>58.41</td>
</tr>
</tbody>
</table>

technique for this particular case. The parallel reaction was chosen because the differential equations are very simple to solve by multiple linear regression analysis. The Equation (4.57) was linearized by putting \( k = k_1 + k_2 \) and taking logarithms on both sides. A multiple linear regression technique was employed to obtain the power terms for LHSV (m) and \( P_{H2} \) (n) and kinetic parameters (\( k_0 \) and E) for the combined rate constant \( k \). The values of \( k_{10} \), \( k_{20} \), \( E_1 \) and \( E_2 \) were obtained from the relationship of \( k_1 \) and \( k_2 \) in the equation. Power terms for LHSV and partial pressure of hydrogen were found to be 0.67 and 0.49 respectively. The activation energy for the formation of middle distillates is lower compared to the formation of naphtha and gas from
the reaction of feedstock indicating higher temperature sensitivity of the reaction leading to naphtha and gas. Table 5.87 presents the effect of operating conditions such as reactor temperature, operating pressure and reaction time on product yields during mild hydrocracking of vacuum gas oil feedstock. Higher operating pressures tend to have positive effect on middle distillate yields. The effect of other operating conditions on product yields is similar to that observed for other models presented earlier. Figure 5.87 compares the observed and predicted yields for this model. The results show a good fit of the data to the MHC kinetics. Arrhenius plots for first order mild hydrocracking reactions for Model V is plotted in Figure 5.88.

5.9.6 Kinetics of HDS and HDN Reactions

The kinetic parameters for HDS and HDN reactions are listed in Table 5.82. The power term for LHSV was unity for both HDS and HDN reactions while it was observed to be 0.67 for mild hydrocracking reactions. The power terms for partial pressure of hydrogen were 0.95 and 1.5 for HDS and HDN respectively while for MHC it was 0.49. This indicates that partial pressure of hydrogen has more pronounced effect on HDN compared to HDS reactions. The effect of partial pressure of hydrogen on MHC is very lower compared to HDS and HDN reactions. The rate constants indicate that HDN occurs at slower rate compared to HDS during mild hydrocracking process. This is due to the fact that nitrogen is mostly attached to refractory aromatic compounds and removal of nitrogen requires saturation of aromatics prior to their removal as ammonia. The sulfur and nitrogen values were predicted using the kinetic parameters listed in Table 5.88 and compared with experimental data as presented in Table 5.123. The match between the experimental and predicted values is very close for both HDS and HDN reactions. The Arrhenius plots for HDS and HDN (1.5th order) for MHC catalyst are plotted in Figure 5.89.
Figure 5.86  Observed yields vs. predicted yields for Model IV

Figure 5.87  Observed yields vs. predicted yields for Model V
Figure 5.88 Arrhenius plots of MHC (first order) reactions

Figure 5.89 Arrhenius plots of HDS and HDN (1.5\textsuperscript{th} order) reactions
Table 5.87 Simulated effect of operating conditions on product yields – Model V

Feedstock: VGO – 90.20 wt%, MD – 9.80 wt%, NG – 0.0 wt%

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Pressure, MPa</th>
<th>LHSV, h⁻¹</th>
<th>VGO Feed</th>
<th>MD</th>
<th>NG</th>
</tr>
</thead>
<tbody>
<tr>
<td>340</td>
<td>6</td>
<td>1.0</td>
<td>85.23</td>
<td>12.40</td>
<td>2.37</td>
</tr>
<tr>
<td>360</td>
<td>6</td>
<td>1.0</td>
<td>82.35</td>
<td>13.84</td>
<td>3.81</td>
</tr>
<tr>
<td>380</td>
<td>6</td>
<td>1.0</td>
<td>78.25</td>
<td>15.87</td>
<td>5.88</td>
</tr>
<tr>
<td>400</td>
<td>6</td>
<td>1.0</td>
<td>72.67</td>
<td>18.59</td>
<td>8.74</td>
</tr>
<tr>
<td>340</td>
<td>6</td>
<td>1.5</td>
<td>86.39</td>
<td>11.79</td>
<td>1.82</td>
</tr>
<tr>
<td>360</td>
<td>6</td>
<td>1.5</td>
<td>84.15</td>
<td>12.92</td>
<td>2.93</td>
</tr>
<tr>
<td>380</td>
<td>6</td>
<td>1.5</td>
<td>80.94</td>
<td>14.51</td>
<td>4.55</td>
</tr>
<tr>
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Table 5.88  Kinetics of sulfur and nitrogen removal - Exp. Vs. Pred. values

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<th>Temperature °C</th>
<th>Pressure, MPa</th>
<th>LHSV, h⁻¹</th>
<th>Sulfur, ppmw</th>
<th>Nitrogen, ppmw</th>
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<td>1.5</td>
<td>108</td>
<td>116</td>
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</table>
5.8 INTEGRATION OF HYDROCRACKER WITH FCC UNIT

In view of increasing importance of hydrocracking process as FCC feed preparation unit, pilot plant studies were conducted to evaluate the option of mild hydrocracking for FCC feed pretreatment. Pilot plant data on mild hydrocracking of FCC feedstock were compared with the data obtained for hydrotreating of FCC feedstock. Experiments were conducted on industrially available catalyst samples using high nitrogenous vacuum gas oil as feedstock. MAT experiments were also carried out to compare the conversions and yields of untreated, hydrotreated and MHC VGO at constant operating conditions. The effect of operating conditions on the conversion and quality of MHC VGO was also studied.

5.8.1 Feed Oil

A vacuum gas oil feedstock originated from Escravos crude source and collected from industrial FCC unit of Chennai Petroleum Corporation Limited (CPCL) was used in the pilot plant study. The detailed properties of VGO are presented in Table 5.72. As can be seen from Table 5.72, the VGO contains about 0.17 wt% nitrogen, 0.29 wt% sulfur and about 42 wt% of aromatics.

The vacuum gas oil used in the pilot plant studies is characterized by its high nitrogen content and thus it is essential to pretreat the vacuum gas oil before passing over an acidic mild hydrocracking catalyst. High nitrogen content of VGO, especially basic nitrogen is known to cause catalyst poisoning in FCCU and has detrimental effect on conversion and product yields.
Table 5.72 Characteristics of VGO feedstock

<table>
<thead>
<tr>
<th>Properties</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Density at 15°C, gm/cc</td>
<td>0.9196</td>
</tr>
<tr>
<td>Gravity, degree API</td>
<td>22.4</td>
</tr>
<tr>
<td>Kinematic Viscosity at 100°C, cSt</td>
<td>8.06</td>
</tr>
<tr>
<td>Refractive Index at 70°C</td>
<td>1.48842</td>
</tr>
<tr>
<td>Pour point, °C</td>
<td>39</td>
</tr>
<tr>
<td>Aniline Point, °C</td>
<td>86.2</td>
</tr>
<tr>
<td>Flash Point, °C</td>
<td>217</td>
</tr>
<tr>
<td>Aromatics, wt.%</td>
<td>41.9</td>
</tr>
<tr>
<td>Saturates, wt.%</td>
<td>58.1</td>
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<tr>
<td>Sulphur, ppmw</td>
<td>2880</td>
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<tr>
<td>Nitrogen, ppmw</td>
<td>1711</td>
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</table>

**Simulated Distillation (ASTM D 2887)**

<table>
<thead>
<tr>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>IBP, °C</td>
</tr>
<tr>
<td>30 wt%, °C</td>
</tr>
<tr>
<td>50 wt%, °C</td>
</tr>
<tr>
<td>70 wt%, °C</td>
</tr>
<tr>
<td>FBP, °C</td>
</tr>
</tbody>
</table>
5.8.2 Catalysts

The catalyst system used in the pilot plant evaluation comprises of a hydrotreating (HDT) catalyst and a mild hydrocracking (MHC) catalyst. Both hydrotreating and mild hydrocracking catalysts used in the pilot plant studies were procured from same industrial catalyst supplier. Experiments were also conducted over an industrial HDT catalyst to compare the performance of HDT and MHC options for FCC feed preparation. The hydrotreating catalyst used as a pretreating catalyst for mild hydrocracking step is a trimetallic Ni-Co-Mo hydrotreating catalyst supported on alumina with higher activity for sulfur and nitrogen removal and aromatic saturation. The mild hydrocracking catalyst used is a zeolite based hydrocracking catalyst. The hydrotreating catalyst used to study the option of hydrotreating as FCC feed preparation is a latest generation, high activity NiO-MoO$_3$/Al$_2$O$_3$ catalyst with very high nitrogen removal and aromatic saturation activity.

5.8.3 Operating Conditions of Pilot Plant Experiments

Pilot plant evaluation over mild hydrocracking and hydrotreating catalyst system was carried out in a high pressure cocurrent downflow trickle bed reactor system comprising a single reactor of 500 ml volume. The reactor temperature was varied from 340°C to 400°C at various liquid hourly space velocities of 1.0 h$^{-1}$, 1.5 h$^{-1}$ and 2.0 h$^{-1}$ respectively to study the effect of reactor temperature on the quality of MHC VGO. Experiments were also conducted at different operating pressures of 60 kg/cm$^2$ and 100 kg/cm$^2$ to study the effect of pressure on the conversion, product yields and quality of MHC VGO.

Hydrotreating experiments were carried out at a reactor temperature of 340°C, operating pressure of 50 kg/cm$^2$, liquid hourly space velocity of
1.5 h\(^{-1}\) and hydrogen to oil ratio of 400 lit/lit. MAT experiments were conducted using untreated VGO, hydrotreated VGO and MHC VGO to compare conversion and yields from FCC. MAT experiments were carried out using 4 grams of catalyst sample with catalyst/oil ratio of 3. The residence time in the reactor was maintained as 75 seconds with a feed rate of 1.33 grams. The reactor temperature was kept constant at 482\(^{\circ}\)C and a regenerator temperature of 650\(^{\circ}\)C was used during regeneration.

5.8.4 Pilot Plant Studies

The properties of MHC products and pilot plant conversion and yields during mild hydrocracking of VGO fraction are presented in Tables 5.73 to 5.77 at various operating conditions.

Mild hydrocracking of vacuum gas oil feedstock was found to increase the amount of distillates produced from a refinery unit. The conversion of the feedstock into 370\(^{\circ}\)C- products increased with reactor temperature at a constant liquid hourly space velocity. The conversion was also increasing with increasing liquid hourly space velocity at a constant reactor temperature. Reactor pressure also influences the conversion level of the feedstock. As can be seen from Table 5.73, the conversion of the feedstock into 370\(^{\circ}\)C- products increased from 5.54 to 19.51 wt% as the reactor temperature was increased from 340 to 400\(^{\circ}\)C at a constant liquid hourly space velocity of 1.0 h\(^{-1}\) and operating pressure of 60 kg/cm\(^2\). The feedstock conversion increased from 6.98 to 24.28 wt% as the operating pressure was increased from 60 to 100 kg/cm\(^2\) at a LHSV of 1.0 h\(^{-1}\) for the same temperature range. This showed that reactor operating pressure had significant influence on the conversion of the feedstock into distillate products.
The yield of VGO Feedstock decreased continuously with reactor temperature while the yields of gas, naphtha and middle distillates increased. At a constant reactor pressure of 60 kg/cm$^2$ and liquid hourly space velocity of 1.0 h$^{-1}$, the VGO yield decreased from 85.2 to 72.6 wt% while the yields of gas, naphtha and middle distillates increased from 0.5 to 3.5, 1.9 to 5.3 and 12.4 to 18.6 wt% respectively as the temperature was increased from 340 to 400°C. The increase in LHSV increased the VGO yield while the yields of gas, naphtha and middle distillates decreased. Lower LHSV and higher reactor temperatures favored improved distillate product yields during mild hydrocracking process. The middle distillates yield increased with operating pressure at a constant reactor temperature. Middle distillates yield increased with reactor temperature at a constant operating pressure.

As can be seen from Tables 5.73 to 5.75, the sulfur was found to decrease from 0.2880 wt% in the feed to 0.0125 - 0.1340 wt% in MHC VGO at an operating pressure of 60 kg/cm$^2$ in the range of operating conditions studied in the present work. The %HDS of the MHC VGO increased with increasing reactor temperature and decreasing liquid hourly space velocity. Desulphurization of VGO was found to improve with increasing operating pressure of the unit. However, the reactor temperature has more pronounced effect on desulfurization compared to liquid hourly space velocity. The effect of operating pressure on hydrodesulfurization was not very much significant compared to the effect of temperature and LHSV. The sulfur was found to decrease to 0.006 - 0.0732 wt% levels at an operating pressure of 100 kg/cm$^2$ under the operating conditions studied in the present work. Under typical operating conditions of MHC of VGO, i.e., at 400°C reactor temperature, 1.0 h$^{-1}$ liquid hourly space velocity, 60 kg/cm$^2$ operating pressure, %HDS of 95.66 was achieved. Under the same typical operating conditions, as the operating pressure was changed from 60 to 100 kg/cm$^2$,
Table 5.73 Properties of MHC products and pilot plant yields at 60 kg/cm$^2$ and 1.0 hr$^{-1}$

Pressure: 60 kg/cm$^2$
LHSV: 1.0 hr$^{-1}$
H$_2$/oil ratio: 400 lit/lit

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<th>Properties</th>
<th>Reactor Temperature, °C</th>
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<tr>
<td>Density at 15°C, gm/cc</td>
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<td>Gravity, degree API</td>
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<td>Kinematic Viscosity at 100°C, cSt</td>
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<td>Refractive Index at 70°C</td>
<td>1.4836</td>
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<td>Pour point, °C</td>
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<tr>
<td>Aniline Point, °C</td>
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<tr>
<td>Aromatics, wt.%</td>
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<td>Saturates, wt.%</td>
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<tr>
<td>Sulphur, ppmw</td>
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<tr>
<td>Nitrogen, ppmw</td>
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<td>Conversion wt%, 370°C -</td>
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**Yields based on feed, wt%**

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<tr>
<td>Gas (C$_1$-C$_4$)</td>
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<td>1.9</td>
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<td>Naphtha (C$_5$-140°C)</td>
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<td>2.9</td>
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<td>Middle distillates (140 – 370°C)</td>
<td>12.4</td>
<td>13.9</td>
<td>15.9</td>
<td>18.6</td>
</tr>
<tr>
<td>VGO Cut (370°C+)</td>
<td>85.2</td>
<td>82.3</td>
<td>78.2</td>
<td>72.6</td>
</tr>
<tr>
<td>% HDS</td>
<td>72.74</td>
<td>84.03</td>
<td>91.49</td>
<td>95.66</td>
</tr>
<tr>
<td>% HDN</td>
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<td>49.74</td>
<td>65.52</td>
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<tr>
<td>% HDA</td>
<td>9.79</td>
<td>12.65</td>
<td>17.42</td>
<td>19.33</td>
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Table 5.74  Properties of MHC products and pilot plant yields at 60 kg/cm$^2$ and 1.5 hr$^{-1}$

Pressure: 60 kg/cm$^2$
LHSV: 1.5 hr$^{-1}$
H$_2$/oil ratio: 400 lit/lit

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<td>Aniline Point, °C</td>
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<td>Aromatics, wt.%</td>
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<td>Saturates, wt.%</td>
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<tr>
<td>Nitrogen, ppmw</td>
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**Yields based on feed, wt%**

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<th>400</th>
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<tr>
<td>Naphtha (C$_5$-140°C)</td>
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<td>2.3</td>
<td>3.5</td>
<td>4.4</td>
</tr>
<tr>
<td>Middle distillates (140 – 370°C)</td>
<td>11.8</td>
<td>12.9</td>
<td>14.5</td>
<td>16.7</td>
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<tr>
<td>VGO Cut (370°C+)</td>
<td>86.4</td>
<td>84.1</td>
<td>80.9</td>
<td>76.5</td>
</tr>
<tr>
<td>% HDS</td>
<td>62.50</td>
<td>75.52</td>
<td>85.42</td>
<td>91.67</td>
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<tr>
<td>% HDN</td>
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<td>22.85</td>
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<td>% HDA</td>
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<td>11.93</td>
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</table>
Table 5.75 Properties of MHC products and pilot plant yields at 60 kg/cm² and 2.0 hr⁻¹

Pressure: 60 kg/cm²  
LHSV: 2.0 hr⁻¹  
H₂/oil ratio: 400 lit/lit  

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<td>Density at 15°C, gm/cc</td>
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<td>Gravity, degree API</td>
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<td>Kinematic Viscosity at 100°C, cSt</td>
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<td>Refractive Index at 70°C</td>
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</tr>
<tr>
<td>Pour point, °C</td>
<td>39</td>
</tr>
<tr>
<td>Aniline Point, °C</td>
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</tr>
<tr>
<td>Aromatics, wt.%</td>
<td>38.4</td>
</tr>
<tr>
<td>Saturates, wt.%</td>
<td>61.6</td>
</tr>
<tr>
<td>Sulphur, ppmw</td>
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</tr>
<tr>
<td>Nitrogen, ppmw</td>
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<tr>
<td>Conversion wt%, 370°C -</td>
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Yields based on feed, wt%

<p>| | | | | |</p>
<table>
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<td>2.0</td>
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<tr>
<td>Naphtha (C₅-140°C)</td>
<td>1.3</td>
<td>2.0</td>
<td>2.8</td>
<td>3.7</td>
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<tr>
<td>Middle distillates (140 – 370°C)</td>
<td>11.5</td>
<td>12.4</td>
<td>13.7</td>
<td>15.6</td>
</tr>
<tr>
<td>VGO Cut (370°C+)</td>
<td>87.0</td>
<td>85.2</td>
<td>82.5</td>
<td>78.7</td>
</tr>
<tr>
<td>% HDS</td>
<td>53.47</td>
<td>67.71</td>
<td>79.17</td>
<td>87.50</td>
</tr>
<tr>
<td>% HDN</td>
<td>8.24</td>
<td>16.42</td>
<td>28.11</td>
<td>46.82</td>
</tr>
<tr>
<td>% HDA</td>
<td>8.35</td>
<td>10.5</td>
<td>11.7</td>
<td>15.99</td>
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</table>
Table 5.76  Properties of MHC products and pilot plant yields at 100 kg/cm$^2$ and 1.0 hr$^{-1}$

Pressure: 100 kg/cm$^2$
LHSV: 1.0 hr$^{-1}$
H$_2$/oil ratio: 400 lit/lit

<table>
<thead>
<tr>
<th>Properties</th>
<th>Reactor Temperature, ºC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>340</td>
</tr>
<tr>
<td>Density at 15°C, gm/cc</td>
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<tr>
<td>Gravity, degree API</td>
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<tr>
<td>Kinematic Viscosity at 100ºC, cSt</td>
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</tr>
<tr>
<td>Refractive Index at 70ºC</td>
<td>1.4817</td>
</tr>
<tr>
<td>Pour point, ºC</td>
<td>39</td>
</tr>
<tr>
<td>Aniline Point, ºC</td>
<td>90</td>
</tr>
<tr>
<td>Aromatics, wt.%</td>
<td>34.31</td>
</tr>
<tr>
<td>Saturates, wt.%</td>
<td>65.69</td>
</tr>
<tr>
<td>Sulphur, ppmw</td>
<td>445</td>
</tr>
<tr>
<td>Nitrogen, ppmw</td>
<td>1180</td>
</tr>
<tr>
<td>Conversion wt%, 370ºC -</td>
<td>6.98</td>
</tr>
</tbody>
</table>

Yields based on feed, wt%

<table>
<thead>
<tr>
<th></th>
<th>Gas (C$_1$-C$_4$)</th>
<th>Naphtha (C$_5$-140ºC)</th>
<th>Middle distillates (140 – 370ºC)</th>
<th>VGO Cut (370ºC+)</th>
<th>% HDS</th>
<th>% HDN</th>
<th>% HDA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.8</td>
<td>2.2</td>
<td>13.1</td>
<td>83.9</td>
<td>84.55</td>
<td>31.03</td>
<td>18.11</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>3.3</td>
<td>14.9</td>
<td>80.2</td>
<td>91.67</td>
<td>50.09</td>
<td>22.36</td>
</tr>
<tr>
<td></td>
<td>2.4</td>
<td>5.0</td>
<td>17.5</td>
<td>75.1</td>
<td>96.01</td>
<td>72.18</td>
<td>27.3</td>
</tr>
<tr>
<td></td>
<td>3.9</td>
<td>7.0</td>
<td>20.8</td>
<td>68.3</td>
<td>97.92</td>
<td>86.09</td>
<td>34.22</td>
</tr>
</tbody>
</table>
Table 5.77 Properties of MHC products and pilot plant yields at
100 kg/cm² and 1.5 hr⁻¹

Pressure: 100 kg/cm²
LHSV: 1.5 hr⁻¹
H₂/oil ratio: 400 lit/lit

<table>
<thead>
<tr>
<th>Properties</th>
<th>Reactor Temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>340</td>
</tr>
<tr>
<td>Density at 15°C, gm/cc</td>
<td>0.9124</td>
</tr>
<tr>
<td>Gravity, degree API</td>
<td>23.6</td>
</tr>
<tr>
<td>Kinematic Viscosity at 100°C, cSt</td>
<td>7.21</td>
</tr>
<tr>
<td>Refractive Index at 70°C</td>
<td>1.4832</td>
</tr>
<tr>
<td>Pour point, °C</td>
<td>39</td>
</tr>
<tr>
<td>Aniline Point, °C</td>
<td>88.6</td>
</tr>
<tr>
<td>Aromatics, wt.%</td>
<td>36.42</td>
</tr>
<tr>
<td>Saturates, wt.%</td>
<td>63.58</td>
</tr>
<tr>
<td>Sulphur, ppmw</td>
<td>732</td>
</tr>
<tr>
<td>Nitrogen, ppmw</td>
<td>1315</td>
</tr>
<tr>
<td>Conversion wt%, 370°C -</td>
<td>5.88</td>
</tr>
</tbody>
</table>

**Yields based on feed, wt%**

<table>
<thead>
<tr>
<th></th>
<th>340</th>
<th>360</th>
<th>380</th>
<th>400</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas (C₁-C₄)</td>
<td>0.5</td>
<td>1.2</td>
<td>2.1</td>
<td>3.4</td>
</tr>
<tr>
<td>Naphtha (C₅-140°C)</td>
<td>2.0</td>
<td>2.9</td>
<td>4.1</td>
<td>5.9</td>
</tr>
<tr>
<td>Middle distillates (140 – 370°C)</td>
<td>12.6</td>
<td>13.8</td>
<td>15.5</td>
<td>18.6</td>
</tr>
<tr>
<td>VGO Cut (370°C+)</td>
<td>84.9</td>
<td>82.1</td>
<td>78.3</td>
<td>72.1</td>
</tr>
<tr>
<td>% HDS</td>
<td>74.58</td>
<td>85.24</td>
<td>92.71</td>
<td>96.25</td>
</tr>
<tr>
<td>% HDN</td>
<td>23.14</td>
<td>40.44</td>
<td>59.21</td>
<td>77.44</td>
</tr>
<tr>
<td>% HDA</td>
<td>13.08</td>
<td>16.37</td>
<td>20.41</td>
<td>26.44</td>
</tr>
</tbody>
</table>

a %HDS of 97.92 was obtained indicating a lower dependence of sulfur removal with respect to operating pressure. MHC VGO with very low levels
of sulfur when used as FCC feedstock can reduce sulfur content in FCC gasoline and diesel blending components besides reducing SOx emissions from FCC regenerator.

As can be seen from Tables 5.73 to 5.75, the nitrogen content of VGO was found to decrease from 1711 ppmw in the feed to 590 - 1570 ppmw in the range of operating conditions studied at a constant pressure of 60 kg/cm$^2$ indicating 8.24 - 65.52 % HDN. As can be seen from Tables 5.76 and 5.77, the nitrogen content of VGO mild hydrocracked at 100 kg/cm$^2$ was found to decrease to 0.0238 - 0.1315 wt%. The %HDN increased with increasing reactor temperature and decreasing LHSV. The reactor operating pressure was found to have pronounced effect on nitrogen removal.

Under typical operating conditions of MHC unit, a %HDN of about 65.52 was obtained. It shows that hydrodenitrogenation normally proceeds at a slower rate compared to hydrodesulphurization under MHC conditions. At the same typical operating conditions, as the pressure was increased from 60 to 100 kg/cm$^2$, the %HDN increased to 86.09 indicating higher influence of operating pressure on hydrodenitrogenation. The nitrogen compounds, particularly basic nitrogen, neutralize the acidity of FCC zeolite catalyst and thus decrease conversion and yield of valuable distillates. Mild hydrocracking of VGO would result in very low nitrogen levels in the feedstock to FCCU and would result in better conversions and product yields in the unit. This is particularly beneficial while processing high nitrogenous feedstock in FCCU as that used in the pilot plant studies.

The aromatics were found to decrease from 37.8 wt.% to 33.8 wt% as the temperature was increased from 340°C to 400°C at a constant pressure of 60 kg/cm$^2$ and a LHSV of 1.0 hr$^{-1}$ indicating 9.79 to 19.3 % HDA. At the same operating conditions by increasing the operating pressure to 100 kg/cm$^2$,
the aromatics were decreased from 34.31 to 27.6 wt% indicating 18.1 to 34.2% HDA. The pilot plant data indicates that the aromatic saturation reactions are favored at higher operating pressures.

Aromatic compounds are not easily cracked in FCC unit and the limited amount of cracking achieved produces a large amount of coke due to condensation reactions. Hydrotreating can saturate the polynuclear aromatic compounds present in the typical FCC feeds and convert them into easily cracked naphthenes and paraffins and thus help to produce valuable products.

The comparison of MAT conversions and yields are presented in Table 5.78. The yield benefits from MAT studies for hydrotreating and mild hydrocracking options are presented in Table 5.79 and Figure 5.81. As can be seen from the pilot plant data, MHC VGO resulted in higher conversions and better yields compared to HDT VGO. Processing of MHC bottoms in the MAT unit resulted in higher MAT number compared to untreated and hydrotreated VGO. The untreated VGO had resulted in a MAT number of 51 and HDT VGO 52. Mild hydrocracked VGO at 100 kg/cm\(^2\) had resulted in a MAT number of 55 indicating higher conversion of the feedstock in FCC unit compared to untreated and HDT VGO. The yield of residue, coke and light gases decreased while processing MHC VGO in FCC unit and yield of LPG, gasoline and diesel increased. In the present study, the MHC product was directly used as FCC feedstock without any separation. The economic benefits from this route can be considerably higher compared to HDT option, if the distillates from MHC product are separated prior to feeding to FCC unit.
Table 5.78  Comparison of MAT Conversions and Yields

**Reactor Temperature: 482°C**  
**Catalyst/Oil ratio: 3.0**  
**WHSV: 16.0 hr⁻¹**  
Catalyst: CPCL Equilibrium Catalyst

<table>
<thead>
<tr>
<th>Operating conditions of HDT/MHC</th>
<th>Untreated VGO</th>
<th>Hydrotreated VGO</th>
<th>Mildhydro-</th>
<th>Mildhydro-</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature, °C</td>
<td>-</td>
<td>340</td>
<td>360</td>
<td>360</td>
</tr>
<tr>
<td>Pressure, kg/cm²</td>
<td>-</td>
<td>50</td>
<td>60</td>
<td>100</td>
</tr>
<tr>
<td>LHSV, hr⁻¹</td>
<td>-</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>H₂/HC ratio, lit/lit</td>
<td>-</td>
<td>300</td>
<td>400</td>
<td>400</td>
</tr>
</tbody>
</table>

**Conversion and Product Yields**

<table>
<thead>
<tr>
<th>MAT No.</th>
<th>Untreated</th>
<th>51</th>
<th>52</th>
<th>53</th>
<th>55</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light Gases, wt%</td>
<td>2.9</td>
<td>2.4</td>
<td>2.3</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>LPG, wt%</td>
<td>10.7</td>
<td>11.2</td>
<td>11.8</td>
<td>12.4</td>
<td></td>
</tr>
<tr>
<td>Gasoline, wt%</td>
<td>25.4</td>
<td>25.9</td>
<td>26.3</td>
<td>26.7</td>
<td></td>
</tr>
<tr>
<td>Diesel, wt%</td>
<td>27.4</td>
<td>28.6</td>
<td>29.0</td>
<td>29.5</td>
<td></td>
</tr>
<tr>
<td>Residue, wt%</td>
<td>30.0</td>
<td>28.4</td>
<td>27.2</td>
<td>26.0</td>
<td></td>
</tr>
<tr>
<td>Coke, wt%</td>
<td>3.6</td>
<td>3.5</td>
<td>3.4</td>
<td>3.2</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.79  Yield Benefits of Mild Hydrocracking of FCC feed

<table>
<thead>
<tr>
<th>Product</th>
<th>Yield, wt%</th>
<th>Δ (HDT-Utreated) yields</th>
<th>Δ(MHC-Utreated) yields</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Un-treated</td>
<td>HDT</td>
<td>MHC</td>
</tr>
<tr>
<td>LPG</td>
<td>10.7</td>
<td>11.2</td>
<td>11.8</td>
</tr>
<tr>
<td>Gasoline</td>
<td>25.4</td>
<td>25.9</td>
<td>26.3</td>
</tr>
<tr>
<td>Diesel</td>
<td>27.4</td>
<td>28.6</td>
<td>29.0</td>
</tr>
<tr>
<td>Residue</td>
<td>30.0</td>
<td>28.4</td>
<td>27.2</td>
</tr>
</tbody>
</table>
Unconverted oil obtained from MHC of VGO had resulted in higher FCC conversions due to hydrogen addition and increased saturation of the feedstock. The removal of nitrogen (especially basic) from the feed also would have contributed to higher FCC conversions. The products from FCC are expected to have very low levels of sulfur, as more than 95 wt% of sulfur has been removed during MHC step. Low sulfur FCC feed can also reduce \( \text{SO}_x \) emissions from FCC regenerator and help in meeting emission standards. As can be seen from Table 5.78, the FCC yield pattern shifts towards more of fuels and less of coke and residue by using hydrotreated or MHC option for FCC feed preparation. Figure 5.81 presents integrated product yields from HDT/MHC-FCC combination of a refinery configuration. The overall yields based on fresh VGO feed also shift towards more of gasoline and diesel compared to untreated case.
5.8.5 Incremental Yields and Revenue Benefits

Table 5.80 compares data on economic analysis of different options considered in the present work. The estimations of revenue benefits were made considering a refinery configuration with a FCC unit of 22000 BPSD capacity operating for 340 days time-on-stream factor. It was assumed that additional VGO was available for upgrading to higher value fuels. The calculations were made based on TAIP (Tariff Adjusted Import Parity) prices in India during a particular month in the year 2005. It was also assumed that the VGO if not upgraded would be used for fuel oil blending.

Hydrotreating of VGO was estimated to generate additional revenues to the tune of US$ 5.5 million per annum compared to untreated case. MHC of VGO at 100 bars and feeding 370°C plus to FCC unit was estimated to result in additional revenues of US$ 10.9 million per annum compared to untreated case. These huge benefits come from the fact that additional VGO to the extent of 20% can be upgraded to valuable fuels through MHC route. For a refinery configuration with higher capacity of FCC unit, the potential benefits will be much higher.

As can be seen from the data presented here, MHC provides a profitable minimum investment route to achieve incremental vacuum gas oil conversion while producing high quality low sulfur fuels. Refiners with VGO hydrotreating units can retrofit their units for MHC operation with minimum investment to maximize refinery margins. Refineries without any feed pretreatment unit for FCCU may consider capital investments in stages by going for MHC unit instead of hydrocracker. In view of increased conversion to valuable fuels and superior quality of products, the investments made for retrofitting existing VGO hydrotreaters or building new MHC units are readily paid back.
Table 5.80 Incremental Yields and Revenue benefits: Untreated vs Hydroprocessed VGO

**Basis: 0.6 MMTPA cat-cracker**

<table>
<thead>
<tr>
<th>Operating mode</th>
<th>Untreated, Ton/day</th>
<th>$/day</th>
<th>HDT $/day</th>
<th>MHC $/day</th>
<th>$/day</th>
</tr>
</thead>
<tbody>
<tr>
<td>LPG</td>
<td>307.8</td>
<td>80149</td>
<td>368.3</td>
<td>95911</td>
<td>495.1</td>
</tr>
<tr>
<td>Naphtha</td>
<td>730.6</td>
<td>193255</td>
<td>814.5</td>
<td>215435</td>
<td>885.5</td>
</tr>
<tr>
<td>Diesel</td>
<td>788.2</td>
<td>153694</td>
<td>820.5</td>
<td>159995</td>
<td>1122.6</td>
</tr>
<tr>
<td>Fuel oil</td>
<td>862.9</td>
<td>143166</td>
<td>811.5</td>
<td>134629</td>
<td>732.1</td>
</tr>
<tr>
<td>Feed : VGO</td>
<td>-2876.5</td>
<td>-477219</td>
<td>-2994.5</td>
<td>-496785</td>
<td>-3486.4</td>
</tr>
<tr>
<td>Value Addition</td>
<td></td>
<td>93044</td>
<td>109185</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Incremental Revenue: \( \Delta \) (HDT – Untreated) - US$ 5.5 million per annum
\( \Delta \) (MHC – HDT) - US$ 5.4 million per annum

Basis: LPG - 260.4 $/Ton
Naphtha - 264.5 $/Ton
Diesel - 195 $/Ton
Fuel oil - 165.9 $/Ton
VGO - 165.9 $/Ton

In view of improved conversions, higher distillate yields, additional distillates from MHC, better FCC product qualities, many of the refiners consider revamp of their existing VGO hydrotreating units for MHC application. All over the world many refiners have successfully converted their VGO hydrotreaters for MHC application to maximize distillate yields and improving FCC product qualities. The revamped MHC units are
operating at low severity levels compared to new MHC units due to design limitations of operating pressures. Conversion of VGO hydrotreaters does not require major capital investments as the existing facilities can be used as such. The capital investments required to setup additional separation facilities to separate distillates from MHC products are justifiable with respect to higher yields distillates from the refinery with better refinery economics. The suggested process scheme for MHC option as FCC feed preparation is shown in Figure 5.82. The typical schematic diagram of MHC process is shown in Figure 5.83.

Mild hydrocracking of vacuum gas oils yields valuable distillates with lower sulfur and nitrogen contents. This process can be used to maximize the production of middle distillates from a refinery configuration with a vacuum gas oil hydrotreater and fluidized catalytic cracking units. The mild hydrocracker bottom can become a very good feedstock for FCC unit and results in significant improvements in FCC performance. Processing of mild hydrocracker bottom in FCC unit would result in better quality fuels. The mild hydrocracking of FCC feed results in the following advantages:

- Produces additional fuels in mild hydrocracking step
- Improves the quality of FCC products with respect to sulfur and nitrogen
- Increases gasoline and diesel yields from FCC unit
- Reduces the yield of residue
- Reduces Ramsbottom Carbon Residue (RCR) of the FCC feed. The reduction in RCR will greatly reduce coke make in the FCC unit by decreasing coke precursors
Figure 5.82  Hydroprocessing options for FCC feed pretreatment

Figure 5.83  Process flow diagram of MHC process
• Removes metals like Ni, V from the feed and thereby improve FCC catalyst activity and selectivity and result longer catalyst life.
• Reduces Sox emissions from FCC regenerator.

5.9 KINETICS OF MILD HYDROCRACKING PROCESS

The kinetic reaction schemes for the analysis of mild hydrocracking process and the differential equations representing them were presented in the Chapter 4. The estimation of kinetic parameters for these models was done using the same procedure as discussed under section 5.2.1 titled ‘kinetic parameter estimation’. The kinetic parameters for the Models I to IV have been presented in Table 5.81. These kinetic parameters were estimated at a reactor operating pressure of 60 kg/cm² and thus not applicable for the data generated at a reactor operating pressure of 100 kg/cm². Table 5.82 presents the kinetic parameters for mild hydrocracking reactions for the case of Model V which considers the effect of partial pressure of hydrogen.

Table 5.82 also presents the kinetics of hydrodesulfurization and hydrodenitrogenation reactions. Model V is applicable for both operating pressures since it considers the effect of operating pressure on conversion.

5.9.1 Model I

The model differential equation was solved using the kinetic parameters listed in Table 5.81 to estimate VGO yields at various operating conditions. The simulated effect of operating conditions on VGO yield at 60 kg/cm² was presented in Table 5.83. As can be seen from Table 5.83, the yield of VGO Feedstock decreased with increase in reaction time (which is considered as inverse of LHSV) and reactor temperature due to increasing cracking and disappearance of VGO Feedstock at higher severity levels. This model predicts the effect of operating conditions on the yield of VGO very well.
Table 5.81 Kinetic parameters for mild hydrocracking reactions

<table>
<thead>
<tr>
<th>Kinetic constant</th>
<th>Kinetic Expression</th>
<th>k at 380°C, h⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>k_MHC</td>
<td>(1.8527 \times 10^5 \exp\left(-1.8263 \times 10^4 / RT\right))</td>
<td>0.1428</td>
</tr>
<tr>
<td>k₁</td>
<td>(1.8527 \times 10^5 \exp\left(-1.8263 \times 10^4 / RT\right))</td>
<td>0.1428</td>
</tr>
<tr>
<td>k₂</td>
<td>(1.8605 \times 10^4 \exp\left(-1.3830 \times 10^4 / RT\right))</td>
<td>0.4465</td>
</tr>
<tr>
<td>k₃</td>
<td>(1.6352 \times 10^5 \exp\left(-1.8895 \times 10^4 / RT\right))</td>
<td>0.0777</td>
</tr>
<tr>
<td>k₄</td>
<td>(4.6555 \times 10^4 \exp\left(-1.7485 \times 10^4 / RT\right))</td>
<td>0.0650</td>
</tr>
<tr>
<td>k₅</td>
<td>(2.4212 \times 10^8 \exp\left(-2.9584 \times 10^4 / RT\right))</td>
<td>0.0333</td>
</tr>
</tbody>
</table>

Table 5.82 Kinetic parameters for mild hydrocracking reactions - Model V

<table>
<thead>
<tr>
<th>Kinetic constant</th>
<th>Pre-exponential factor (ko)</th>
<th>(E/R), K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mild hydrocracking (m=0.67, n=0.49)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>k₁+k₂</td>
<td>(8.019 \times 10^4)</td>
<td>(7.674 \times 10^4)</td>
</tr>
<tr>
<td>k₁</td>
<td>(2.565 \times 10^4)</td>
<td>(7.424 \times 10^4)</td>
</tr>
<tr>
<td>k₂</td>
<td>(6.037 \times 10^4)</td>
<td>(7.907 \times 10^4)</td>
</tr>
<tr>
<td>Hydrodesulphurisation (m=1.0, n=0.95)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>k₈</td>
<td>(3.234 \times 10^8)</td>
<td>(7.883 \times 10^4)</td>
</tr>
<tr>
<td>Hydrodenitrogenation (m=1.0, n=1.5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>k₉</td>
<td>(1.466 \times 10^8)</td>
<td>(1.134 \times 10^3)</td>
</tr>
</tbody>
</table>

Table 5.83 Effect of operating conditions on VGO yield at 60 kg/cm² - Model I
Using the kinetic parameters presented in Table 5.82, the model differential equations presented in chapter 4 were solved simultaneously to generate product yield distribution data at various operating conditions. The simulated effect of operating conditions on the yield of VGO, middle distillates and naphtha and gas at 60 kg/cm² was presented in Table 5.84. As can be seen from Table 5.84, the yield of VGO Feedstock decreased with increase in reaction time due to cracking reaction of feedstock while the yields of middle distillates and naphtha and gas continuously increased with reaction time for a particular reactor temperature. The yield of VGO feedstock decreased with increase in reactor temperature due to increasing cracking and disappearance of VGO feedstock at elevated temperatures. The yield of middle distillates and naphtha and gas increased with reactor temperature for a particular reaction time. This model predicts the effect of operating
conditions on the product yields very well as seen from Figure 5.84 which shows the observed yields vs. predicted yields for Model II.

Table 5.84  Effect of operating conditions on product yields at 60 kg/cm² - Model II
Feedstock: VGO – 90.20 wt%, MD – 9.80 wt%, NG – 0.0 wt%

<table>
<thead>
<tr>
<th>Products</th>
<th>Reaction time, h</th>
<th>0.25</th>
<th>0.5</th>
<th>0.667</th>
<th>0.75</th>
<th>1.0</th>
<th>1.25</th>
<th>1.50</th>
<th>1.75</th>
<th>2.0</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature – 340°C</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NG</td>
<td></td>
<td>0.56</td>
<td>1.15</td>
<td>1.56</td>
<td>1.78</td>
<td>2.44</td>
<td>3.12</td>
<td>3.84</td>
<td>4.58</td>
<td>5.35</td>
</tr>
<tr>
<td>VGO</td>
<td></td>
<td>88.92</td>
<td>87.66</td>
<td>86.83</td>
<td>86.42</td>
<td>85.19</td>
<td>83.99</td>
<td>82.79</td>
<td>81.62</td>
<td>80.46</td>
</tr>
<tr>
<td></td>
<td>Temperature – 360°C</td>
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<td></td>
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</tr>
<tr>
<td>NG</td>
<td></td>
<td>0.81</td>
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Figure 5.84 Observed yields versus predicted yields for Model II

5.9.3 Model III

The model differential equations presented in chapter 4 for this model were solved simultaneously to generate the product yields at various operating conditions using the kinetic parameters presented in Table 5.81. The simulated effect of operating conditions on the yield of VGO, middle distillates and naphtha and gas at an operating pressure of 60 kg/cm$^2$ was presented in Table 5.85. The predictions of product yields using this model are almost similar to that of Model II. Figure 5.85 shows the comparison between observed and predicted product yields for Model III. This model predicts the effect of operating conditions on the product yields very well.
Table 5.85  Effect of operating conditions on product yields at 60 kg/cm$^2$ - Model III
Feedstock: VGO – 90.20 wt%, MD – 9.80 wt%, NG – 0.0 wt%

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5.9.4 Model IV

The model differential equations presented in chapter 4 were solved simultaneously to generate product yield distribution at various operating conditions using the kinetic parameters listed in Table 5.81. As can be seen from Table 5.81, the activation energy for the formation of middle distillates is 17711 cal/gmole compared to that of 18827 cal/gmole for the reaction of feedstock into naphtha and gas indicating higher temperature sensitivity of the later reaction. The simulated effect of operating conditions on the yield of
VGO, middle distillates and naphtha and gas at an operating pressure of 60 kg/cm² is presented in Table 5.86. The prediction of product yields by this model is in accordance with the trend pattern observed for other models. This parallel reaction model predicts the effect of operating conditions on the product yields very well as seen from the Figure 5.86. The difference between the observed and predicted yields is very less indicating the applicability of a parallel reaction scheme for mild hydrocracking process.

5.9.5 Model V

The kinetic parameters for mild hydrocracking reactions in the case of Model V which considers the effect of partial pressure of hydrogen on product yields using a parallel reaction scheme is presented in Table 5.82. The estimation of kinetic parameters was done using multiple linear regression.
Table 5.86  Effect of operating conditions on product yields at 60 kg/cm\(^2\) - Model IV
Feedstock: VGO – 90.20 wt%, MD – 9.80 wt%, NG – 0.0 wt%

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The parallel reaction was chosen because the differential equations are very simple to solve by multiple linear regression analysis. The Equation (4.57) was linearized by putting \(k = k_1 + k_2\) and taking logarithms on both sides. A multiple linear regression technique was employed to obtain the power terms for LHSV \((m)\) and \(P_{H2} (n)\) and kinetic parameters \((k_0\) and \(E)\) for the combined rate constant \(k\). The values of \(k_{10}, k_{20}, E_1\) and \(E_2\) were obtained from the relationship of \(k_1\) and \(k_2\) in the equation. Power terms for LHSV and partial pressure of hydrogen were found to be 0.67 and 0.49 respectively. The activation energy for the formation of middle distillates is lower compared to the formation of naphtha and gas from
the reaction of feedstock indicating higher temperature sensitivity of the reaction leading to naphtha and gas. Table 5.87 presents the effect of operating conditions such as reactor temperature, operating pressure and reaction time on product yields during mild hydrocracking of vacuum gas oil feedstock. Higher operating pressures tend to have positive effect on middle distillate yields. The effect of other operating conditions on product yields is similar to that observed for other models presented earlier. Figure 5.87 compares the observed and predicted yields for this model. The results show a good fit of the data to the MHC kinetics. Arrhenius plots for first order mild hydrocracking reactions for Model V is plotted in Figure 5.88.

5.9.6 Kinetics of HDS and HDN Reactions

The kinetic parameters for HDS and HDN reactions are listed in Table 5.82. The power term for LHSV was unity for both HDS and HDN reactions while it was observed to be 0.67 for mild hydrocracking reactions. The power terms for partial pressure of hydrogen were 0.95 and 1.5 for HDS and HDN respectively while for MHC it was 0.49. This indicates that partial pressure of hydrogen has more pronounced effect on HDN compared to HDS reactions. The effect of partial pressure of hydrogen on MHC is very lower compared to HDS and HDN reactions. The rate constants indicate that HDN occurs at slower rate compared to HDS during mild hydrocracking process. This is due to the fact that nitrogen is mostly attached to refractory aromatic compounds and removal of nitrogen requires saturation of aromatics prior to their removal as ammonia. The sulfur and nitrogen values were predicted using the kinetic parameters listed in Table 5.88 and compared with experimental data as presented in Table 5.123. The match between the experimental and predicted values is very close for both HDS and HDN reactions. The Arrhenius plots for HDS and HDN (1.5th order) for MHC catalyst are plotted in Figure 5.89.
Figure 5.86  Observed yields vs. predicted yields for Model IV

Figure 5.87  Observed yields vs. predicted yields for Model V
Figure 5.88 Arrhenius plots of MHC (first order) reactions

Figure 5.89 Arrhenius plots of HDS and HDN (1.5\textsuperscript{th} order) reactions
Table 5.87  Simulated effect of operating conditions on product yields – Model V

Feedstock: VGO – 90.20 wt%, MD – 9.80 wt%, NG – 0.0 wt%

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Table 5.88  Kinetics of sulfur and nitrogen removal - Exp. Vs. Pred. values

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