study for 1-hexene is around 4-7 bar. It was found that an increase in the LHSV resulted in higher catalyst activity. The lower LHSV values gave a higher selectivity for long-chain oligomers while the higher LHSV values resulted in a more selective formation of shorter-chain oligomers. No literature data (polymerisation or oligomerisation) are available on the effect of LHSV, and hence no comparison could be made with the data obtained in this specific study.
7.1. INTRODUCTION

In the studies on the oligomerisation of 1-hexene (Chapter 6) it was found that the oligomerisation of 1-hexene catalysed by a CrO₃/SiO₂ catalyst resulted in the production of a high viscosity oil (ranging from 200 to 10,000 cSt at 40°C; and viscosity index up to 400) with carbon distributions ranging from C₁₂ to C₁₆₂. It was found that the activation conditions (calcination and reduction temperature) gave results which differed from earlier literature reports on the polymerisation reaction concerning the molecular mass distribution of the products (McDaniel & Johnson, 1982, 1987; Clark et al., 1956; Hogan & Banks, 1958). Since reduction of the catalyst after the calcination step results in the formation of the active Cr²⁺ and/or Cr³⁺ sites, this step is extremely important. It was thus decided to do a more in-depth study of the effects of reduction temperature and reduction time on the catalyst activity and the product characteristics. The statistical design approach was chosen for this purpose.

Other variables expected to have an influence on the oligomerisation reaction were reaction temperature, reaction pressure and LHSV. The effect of reaction temperature on the conversions in the oligomerisation reaction was indicated in the literature to be an important variable (Wu, 1989 a, 1993). In Chapter 6 it was found that an increase in the reaction temperature not only greatly affected the oligomerisation reaction, but also the many product characteristics. The oligomerisation results obtained by variation of the pressure were marginally different when compared to the results obtained by Hogan and Banks (1958) and Clark et al., (1956) in their studies on the polymerisation reaction. The need for more information on the effect of pressure on the

Statistical optimisation
oligomerisation reaction was thus identified as essential. Since the LHSV is a variable that has not been extensively described in the literature, it was also chosen as a variable to be investigated further. The reaction temperature, pressure and LHSV were thus variables that were identified as important and worthy of further detailed study by statistical optimisation procedures.

Although the statistical design of experiments is an approach commonly used in industry, not much literature data is available on this subject in the open literature. The typical approach normally used in an experimental procedure is the "one-factor-at-a-time" procedure. In this procedure only one variable is changed at a time while all the others are held constant. An estimate is thus provided of the effect of a single variable at selected fixed conditions on the other variables (Box et al., 1978). When following this procedure, it is necessary to assume that the effect would be the same at other settings of the other variables. This would mean that over the ranges of interest the variables would act on the response additively. The "one-factor-at-a-time" design would not be able to detect the non-additivity of variables. By contrast a factorial design would be able to detect and estimate interactions that measure any nonadditivity (Box et al., 1978).

In "one-factor-at-a-time" experiments such as those employed in Chapter 6, it is thus normally assumed that the effects of different variables are independent. The data obtained in Chapter 6 gave an indication of the variables that needed to be studied more intensively. As mentioned above, it was decided to study the effect of reduction conditions (temperature and time of reduction) and the effect of oligomerisation conditions (temperature, pressure and LHSV) by use of statistical design experiments. Such an approach would enable optimisation of the reduction conditions by taking the effect of the two variables, namely temperature and time, on each other into account. The use of a statistical design approach would also provide information for the enhancement of the oil characteristics (viscosity index and C₁₈ selectivity) in addition to optimisation of the reaction conditions (conversion, cycle time and activity). The

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optimum reduction and reaction conditions needed for the production of an oil with a high viscosity index and low C_{18} content could thus be obtained using such an approach. A further advantage of the statistical design approach is that relatively few runs are needed per factor that is studied. Maximum information is thus obtained from the smallest number of runs. Since randomization and repeatability are included in the experiments, the design is also protected from unexpected influences.

7.1.1. Statistical design experiments

7.1.1.1. General factorial designs and designs at two levels

When performing a general factorial design a fixed number of levels (or "versions") for each of the variables (factors) is selected, and experiments performed with all possible variations. For a situation with $l_1$ levels for the first variable, $l_2$ for the second and $l_k$ for the kth, there would be a total of $l_1 \times l_2 \times l_k$ experimental runs, also called a $l_1 \times l_2 \times \ldots \times l_k$ factorial design. In the same manner, a $2 \times 3 \times 5$ factorial design would require 30 runs and a $2 \times 2 \times 2$ factorial design (also known as a $2^3$ factorial design) 8 runs (Box et al., 1978). Such designs are generally known as general factorial designs. They require relatively few runs and can indicate a direction for further experimentation (Box et al., 1978).

A $2^3$ factorial design, also known as a factorial design in two levels with three variables, would have two values (high and low) for each variable under investigation. The display of the combination of values (levels) to be run is called a design matrix. If the variables to be studied are for example temperature, concentration and pressure, with a high (+) and low (-) value for each variable, the design matrix could have the appearance of the matrix shown in Table 7.1.

Statistical optimisation
Table 7.1: Example of a design matrix

<table>
<thead>
<tr>
<th>Test Number</th>
<th>Temperature (°C)</th>
<th>Concentration (%)</th>
<th>Pressure (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>160</td>
<td>20</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>180</td>
<td>20</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
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</tr>
<tr>
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<tr>
<td>6</td>
<td>180</td>
<td>20</td>
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</tr>
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<td>7</td>
<td>160</td>
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<td>10</td>
</tr>
<tr>
<td>8</td>
<td>180</td>
<td>40</td>
<td>10</td>
</tr>
</tbody>
</table>

Coded units of variables:

<table>
<thead>
<tr>
<th>Test Number</th>
<th>Temperature</th>
<th>Concentration</th>
<th>Pressure</th>
</tr>
</thead>
<tbody>
<tr>
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<td></td>
<td></td>
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<td>+</td>
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<td>4</td>
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<td>+</td>
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<tr>
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<td>-</td>
<td>+</td>
</tr>
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<td>7</td>
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<td>+</td>
</tr>
<tr>
<td>8</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

If a reaction has already been studied by means of preliminary experiments, there is often no need for such a factorial or two-level design. A composite design is then used. Before attempting a variant of the composite design called the central composite design, it is required that the most important variables are known and that the ranges in which these variables operate are known. A central composite design is a design in which further values (levels) of the variables are explored. Where the factorial design only makes use of -1 (low value) and +1 (high value) designations, a central

**Statistical optimisation**
composite design contains center points, star points and cube points. A central composite design is thus a factorial design to which star and center points have been added. The star points could typically be given by \(-\sqrt{2}\) and \(\sqrt{2}\) relative to the -1 and +1 designations which apply to the low and high values for each variable, while center points would be given as 0 relative to the designated values of -1 and +1. If the high value of a variable was given by the +1 designation (eg +1 = 100), then the very high value of the same variable would be given by \(\sqrt{2}\) relative to the high value (= 141).

A central composite design for a) 2 variables and b) 3 variables where each point represents a set of independent variables for measuring the responses under investigation can be seen in Figure 7.1 (Box et al., 1978).

**Figure 7.1:** Appearance of a central composite design with a) 2 variables and b) 3 variables (Box et al., 1978)

- Design points: Cube: 4 ; Star: 4  
  Center points: Cube: 2 ; Star: 2

- Design points: Cube: 8 ; Star: 6  
  Center points: Cube: 2 ; Star: 1

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Due to the fact that the oligomerisation of 1-hexene catalysed by the CrO$_3$/SiO$_2$ catalyst has been tested under a range of preliminary conditions (Chapter 6), the data available was sufficient for the planning of a central composite design. There was thus no need to perform a factorial design to define the variables and ranges in which to carry out the experiments.

7.1.1.2. Response surface methods

Response surface methodology consists of a group of techniques used in the empirical study of relationships between one or more measured responses with the aim of answering some of the following questions (Box et al., 1978):

1. How is a particular response affected by a given set of input values over some specified region of interest?
2. What settings of the inputs will give a product that complies to the desired specifications?
3. What input values will yield a maximum for a specific response?

A response is one of the measured outcomes of the experiment and is also called a dependant variable (eg. yield, conversion etc.). The response is usually designated by $y$.

The step-by-step procedure followed in response surface methodology when following a second order design is shown in Figure 7.2 (Box et al., 1978).

Statistical optimisation
Figure 7.2: Procedure followed in response surface methodology when planning and performing a second order design (Box et al., 1978)

A first order design is one that would allow efficient fitting and checking of the first-degree polynomial model:

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \epsilon$$  \hspace{1cm} (7.1)

where $\beta$ is a constant for which the least squares estimate is obtained and $\epsilon$ is the error (Box et al., 1978).

A second order design is one that would allow fitting of a second degree polynomial model:

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\[ y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{12} x_1 x_2 + \epsilon \] (7.2)

A second order polynomial is a model with linear, quadratic and two-factor interaction terms. The terms of the type \( \beta_{11} x_1^2 \) and \( \beta_{22} x_2^2 \) are quadratic terms which can represent curvature similar to that found in a parabola (Box et al., 1976).

7.2. **EXPERIMENTAL**

7.2.1. **Statistical optimisation of the reduction conditions for the activation of a CrO\textsubscript{2}/SiO\textsubscript{2} catalyst for 1-hexene oligomerisation**

The aim of this investigation was to develop a response surface design of the two variables: reduction time and temperature. It was decided to find the optimum time and temperature of reduction of the catalyst by use of a \( 2^2 \) second order central composite design for 2 factors. With this approach a total of 11 runs are performed. These runs correspond to 4 cube design points, 4 star design points, 2 cube center points and 1 star center point.

The equipment described in Chapter 4 was used in performing the experiments.

A minimum reduction temperature of 230°C and a maximum of 310°C were chosen while the reduction time was varied between 1 minute and 30 minutes. These specific values were chosen since reduction was performed at 270°C for 8 minutes in most of the experiments performed in the previous chapter. The experiments were randomised so as to minimise any biased effects. Complete randomisation means that every possible sequence of experimental runs is likely and every combination of variables in a run is as likely as any other (Hahn, 1977). The validity of the experiment is protected by the randomisation. Process ambiguity or even incorrect conclusions can often result if randomisation is needed in an investigation but not used. On the other hand if randomisation was not needed for a specific experiment little is lost if randomisation

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was applied (Hahn, 1978)

The design used in this work is tabulated in Table 7.2. If the designation for the reduction temperature is chosen as $x$ and the reduction time as $y$, the variable levels in coded units can be calculated as explained in the following paragraph.

If $310^\circ C$ is chosen as the very high value ($x = + 1.41$) and $270^\circ C$ as the midpoint ($m$, $x = 0$), the high value ($x = + 1$) can be calculated as $298^\circ C$. From this $s$ can be determined as

$$s = 28^\circ C \times (298^\circ C - 270^\circ C) \quad (7.3)$$

The value of $x$ can be calculated from the equation:

$$x = \frac{\text{reduction temperature} - 270^\circ C}{28} \quad (7.4)$$

and the reduction temperature can be calculated from:

$$\text{reduction temperature} = 28x + 270^\circ C \quad (7.5)$$

where $x$ is the designated value under investigation. In a similar manner, the same calculations can be done on the reduction time. If the very high value ($y = + 1.41$) is chosen as 30 and the midpoint value ($m$, $y = 0$) is 15.5 minutes, the high value ($y = 1$) can be calculated as 25.75. The value of $s$ can be determined from the equation as:

$$s = 10.25 \text{ minutes} \times (25.75 - 15.5) \quad (7.6)$$

The value of $y$ can be calculated from:

$$y = \frac{\text{reduction time} - 15.5 \text{ minutes}}{10.25} \quad (7.7)$$

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and the reduction time can thus be determined from:

\[
\text{reduction time} = 10.25 y + 15.5 \text{ minutes} \tag{7.8}
\]

where \( y \) is the designated value for the reduction time under investigation.

**Table 7.2:** Second order central composite design used for optimising the activation conditions

<table>
<thead>
<tr>
<th>Run</th>
<th>Block</th>
<th>(x)</th>
<th>(y)</th>
<th>(x) Temp (°C)</th>
<th>(y) Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>241</td>
<td>5.25</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>+1</td>
<td>-1</td>
<td>298</td>
<td>5.25</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>-1</td>
<td>+1</td>
<td>241</td>
<td>25.75</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>+1</td>
<td>+1</td>
<td>298</td>
<td>25.75</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>270</td>
<td>15.5</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>270</td>
<td>15.5</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>-1.4</td>
<td>0</td>
<td>230</td>
<td>15.5</td>
</tr>
<tr>
<td>8</td>
<td>2</td>
<td>+1.4</td>
<td>0</td>
<td>310</td>
<td>15.5</td>
</tr>
<tr>
<td>9</td>
<td>1</td>
<td>0</td>
<td>-1.4</td>
<td>270</td>
<td>1</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>0</td>
<td>+1.4</td>
<td>270</td>
<td>30</td>
</tr>
<tr>
<td>11</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>270</td>
<td>15.5</td>
</tr>
</tbody>
</table>

Except for the variation in reduction time and temperature, all 11 of the runs were performed under the same reaction conditions: The catalyst was a 1.2 ± 0.1% Cr on Davison 952 silica + 30% bentonite. Before performing the reduction step, calcination was performed in 15 NL.h\(^{-1}\) air at 470°C for 15.5 hours. The reduction step for each run was performed with 15 NL.h\(^{-1}\) CO under the reduction conditions specified in Table 7.2. Other conditions were: Feed: 1-hexene (pre-dried with molecular sieve 3A), Pressure: 8.0 bar, Temperature: 99°C, LHSV: 1.2 h\(^{-1}\) and N\(_2\)-flow: 0.15 NL.h\(^{-1}\).

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After deactivation of the catalyst, it was regenerated by drying in 15 Ni.h⁻¹ N₂ for 1 hour at the reaction temperature and atmospheric pressure. The temperature was then increased to 320°C and the catalyst dried at this temperature for 2 hours. The temperature was lowered to 200°C, and air was introduced into the system at a flow rate of 15 Ni.h⁻¹. The temperature was increased at a rate of 200°C.h⁻¹ up to 470°C and kept there for 15.5 hours. After cooling down under nitrogen, reduction of the catalyst was again performed. For each run the catalyst was regenerated twice with the result that three sets of experimental data were obtained for each run. In the interpretation of the results only the data obtained in the third run were used since it was found that the catalyst activity increased with each regeneration step, up to two regenerations and then decreased. The catalyst had thus obtained an optimum activity after the second regeneration (see Chapter 6).

The following responses were monitored as a function of the temperature and time of reduction:

a). Conversion of 1-hexene to oligomer product: The amount of oligomer was determined gravimetrically after distilling off the unreacted 1-hexene from the oligomer product. The conversion was monitored as a function of the reaction time. Due to the fact that the conversion varied with time, the conversion versus time curve had to be fitted to a suitable equation to obtain constants from which further interpretation could be done. The equation used for the fitting was the following:

\[
y = \frac{x}{(a + bx + cx^2)}
\]  
(7.9)

where y is the conversion; x is the time; a, b and c are the constants obtained after fitting of the curves to the above equation. An example of the fitting of a typical curve can be seen in Figure 7.3. The reduction conditions for this specific run were a reduction temperature of 310°C and a reduction time of 15.5 minutes. The value of R² for this fit is 0.996, which indicates that a good fit was obtained. The values obtained

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for the constants $a$, $b$ and $c$ from the fit in Figure 7.3 are the following:

$a$: $0.4432 \pm 0.017$

$b$: $-1.9492 \pm 0.005$

$c$: $0.02448 \pm 0.001$

Figure 7.3: Graph of conversion versus time

In Figure 7.4 the predicted values are plotted as a function of the actual values. From this graph it can be seen that a good fit has been obtained since the data points (actual values) are distributed evenly around the straight line (predicted values).

Statistical optimisation
Figure 7.4: Correlation between predicted and actual values for the fit in Figure 7.3

For each run a theoretical curve was plotted from which the constants a, b and c were determined. These constants were used in developing a model from which the results of a specific set of reduction conditions could be predicted.

b). Activity of the catalyst (g oligomer produced per g chromium per hour): This was determined gravimetrically after distilling off the unreacted 1-hexene from the product. The activity was monitored as a function of the reaction time. As in the case of the conversion versus time curves, fitting of these activity versus time curves was performed.

c). Selectivity of the catalyst for producing the C₆ trimer: This was determined by high temperature GC of the viscous oligomer product.

d). Viscosity index of the product: This was determined by viscosity determinations

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of the total oligomerisation product obtained in a specific cycle at a temperature of 40°C and 100°C.

7.2.2. Statistical optimisation of the reaction conditions in the oligomerisation of 1-hexene by the CrO₃/SiO₂ catalyst.

This investigation involved developing a response surface design of the oligomerisation conditions (temperature, pressure and LHSV). The design used was a 2³ order central composite design for 3 factors. A total of 17 runs were performed which included 8 cube design points, 6 star design points, 2 cube center points and 1 star center point.

The catalyst used was a 1.2 ± 0.1 % Cr on Davison SiO₂ + 30% bentonite extrudates catalyst. The activation conditions were fixed (calcination at 470°C for 15.5 hours in 15 NLh⁻¹ air and reduction at 270°C for 8 minutes in 15 NLh⁻¹ CO) while the oligomerisation conditions were varied in each run. The temperature was varied between 76°C and 136°C, the pressure between 1 bar and 9 bar and the LHSV was varied between 0.6 h⁻¹ and 17.4 h⁻¹. The feed used was 1-hexene (pre-dried with molecular sieve 3A) and a constant nitrogen flow of 0.15 NLh⁻¹ was fed through the reactor. As in the case of the optimisation of the activation conditions, the experiments were performed in a random order.

The design that was used is tabulated in Table 7.3. If the designation for the reaction temperature is chosen as x, the reaction pressure as y and the LHSV as z, the levels of the variables in coded units could be calculated as follows:

If 136°C is chosen as the very high reaction temperature (x = 1.68) and 106°C as the midpoint temperature (m; x = 0), the high value (x = 1) can be calculated as 124°C. From this s can be calculated as

\[ s = 18°C (124°C - 106°C) \]

(7.10)

Statistical optimisation
and the value of $x$ as

$$x = (\text{Reaction temperature} - 106^\circ\text{C}) \div 18$$ \hspace{1cm} (7.11)

The reaction temperature can be calculated from the equation:

$$\text{Reaction temperature} = 18x + 106^\circ\text{C}$$ \hspace{1cm} (7.12)

where $x$ is the designated value for the reaction temperature.

If 9 bar is chosen as the very high pressure ($y = 1.68$) and 5 bar as the midpoint pressure ($m; y = 0$), the high value ($y = 1$) can be calculated as 7.4 bar. From this $s$ can be calculated as

$$s = 2.4 \text{ bar} (7.4 \text{ bar} - 5 \text{ bar})$$ \hspace{1cm} (7.13)

The value of $y$ can thus be calculated from the equation:

$$y = (\text{Reaction pressure} - 5.0 \text{ bar}) \div 2.4$$ \hspace{1cm} (7.14)

and the reaction pressure from the equation:

$$\text{Reaction pressure} = 2.4y + 5.0 \text{ bar}$$ \hspace{1cm} (7.15)

where $y$ is the designated value for the pressure.

If 17.4 h⁻¹ is chosen as the very high LHSV ($z = 1.68$) and 9.0 h⁻¹ as the midpoint LHSV ($m; z = 0$), the high value ($z = 1$) can be calculated to be 14.0 bar. From this $s$ can be calculated as

$$s = 5.0 \text{ h}^{-1} (14.0 \text{ h}^{-1} - 9.0 \text{ h}^{-1})$$ \hspace{1cm} (7.16)

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The value of $z$ can thus be calculated from the formula

$$z = (\text{LHSV} - 9.0 \text{ h}^{-1}) \div 5.0$$ \hspace{1cm} (7.17)

and the LHSV from the formula:

$$\text{LHSV} = 5.0 \times z + 9 \text{ h}^{-1}$$ \hspace{1cm} (7.18)

where $z$ is the designated value for the LHSV.
Table 7.3: Second order central composite design for optimising the oligomerisation conditions.

<table>
<thead>
<tr>
<th>Run</th>
<th>Block</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>(x) Temp (°C)</th>
<th>(y) Press (bar)</th>
<th>(z) LHSV (h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>88</td>
<td>2.6</td>
<td>3.4</td>
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<td>-1</td>
<td>-1</td>
<td>124</td>
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<tr>
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<td>3</td>
<td>0</td>
<td>-1.68</td>
<td>0</td>
<td>106</td>
<td>1.0</td>
<td>9.0</td>
</tr>
<tr>
<td>14</td>
<td>3</td>
<td>0</td>
<td>1.68</td>
<td>0</td>
<td>106</td>
<td>9.0</td>
<td>9.0</td>
</tr>
<tr>
<td>15</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>-1.68</td>
<td>106</td>
<td>5.0</td>
<td>0.6</td>
</tr>
<tr>
<td>16</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>1.68</td>
<td>106</td>
<td>5.0</td>
<td>17.4</td>
</tr>
<tr>
<td>17</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>106</td>
<td>5.0</td>
<td>9.0</td>
</tr>
</tbody>
</table>

Except for the variation in the oligomerisation temperature, pressure and LHSV, all 17 runs were performed under the same reaction conditions. The temperature, pressure and LHSV of each specific run were changed according to the specifications in Table 7.3.

The catalyst was regenerated by purging with 15 Nl.h⁻¹ nitrogen for 1 hour at the

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reaction temperature and atmospheric pressure, whereafter the temperature was increased to 320°C and the catalyst dried at this temperature for 2 hours. The activation and reduction steps were then followed as mentioned in the previous paragraph. As in section 7.2.1, the results obtained in the third cycle of a run (that is after the second regeneration step) were used for analysis.

The following responses were measured as a function of the oligomerisation temperature, pressure and LHSV:

a). **Maximum conversion of 1-hexene to oligomer product**: This was determined gravimetrically after distilling off the unreacted 1-hexene from the oligomer product. The maximum conversion obtained in each run was used in the interpretation of the data.

b). **Cycle time in hours**: This was taken as the time needed for the catalyst to deactivate to conversions of below 2%.

c). **Maximum activity (g oil per g Cr per hour)**: This was determined gravimetrically. Once again the maximum activity obtained in each specific run was used.

d). **Selectivity of the catalyst for producing the C₆ trimer**: This was determined by high temperature GC of the viscous oligomer product. The selectivities obtained in the third cycle of each run were used for the evaluation.

e) **Viscosity index of the product**: This was calculated from the viscosities of the product at 40°C and 100°C respectively (See Appendix 2).

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7.3. Results and Discussion

7.3.1. Activation conditions

7.3.1.1. Conversion as a function of time

The % conversion of C₆ to oligomer product was obtained as a function of time. To simplify the interpretation of the results, each run was divided into two time spans and the average % conversion was calculated in each case. The results obtained are presented in Table 7.4.

Table 7.4: Percentage conversions obtained in each run for the two time spans

<table>
<thead>
<tr>
<th>Run number</th>
<th>% conversion 1 (Time &lt; 12 hours)</th>
<th>% conversion 2 (Time &gt; 12 hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>89.5</td>
<td>9.9</td>
</tr>
<tr>
<td>2</td>
<td>71.7</td>
<td>8.0</td>
</tr>
<tr>
<td>3</td>
<td>91.3</td>
<td>40.1</td>
</tr>
<tr>
<td>4</td>
<td>87.5</td>
<td>26.2</td>
</tr>
<tr>
<td>5</td>
<td>70.1</td>
<td>11.5</td>
</tr>
<tr>
<td>6</td>
<td>55.8</td>
<td>23.0</td>
</tr>
<tr>
<td>7</td>
<td>49.2</td>
<td>4.1</td>
</tr>
<tr>
<td>8</td>
<td>41.3</td>
<td>2.6</td>
</tr>
<tr>
<td>9</td>
<td>62.0</td>
<td>5.0</td>
</tr>
<tr>
<td>10</td>
<td>69.5</td>
<td>11.0</td>
</tr>
<tr>
<td>11</td>
<td>70.4</td>
<td>51.1</td>
</tr>
</tbody>
</table>

The data for conversion 1 and conversion 2 were fitted according to the least squares method, and three-dimensional graphs of the variables as a function of the time and
temperature of reduction were obtained. The method of least squares is often called a regression analysis. This method takes the "best fit" model as the one that comes closest to the data in the sense of minimising the quantity (Box et al., 1978):

\[ s = \sum_{u=1}^{n} (y_i - \hat{y}_i)^2 \quad (7.19) \]

The above formula is the sum of squared discrepancies between the observed values \( y_i \) and the values for \( \hat{y}_i \) given by the model

\[ \hat{y}_i = a + bx_i + cx_i^2 \quad (7.20) \]

where \( i \) is the number of experiments (1,2,.....n); \( \hat{y}_i \) is the mean value of dispersion; \( x \) is the independent variable or regressor (such as temperature or time); \( y \) is the dependent variable (such as C18 selectivity, conversion, viscosity index and activity); \( a, b, \) and \( c \) are the constants for which the least squares estimate is obtained. Thus the minimum for \( a, b \) and \( c \) respectively is given by the equation (Box et al., 1978):

\[ \text{minimum} \ (a,b,c) = \min_{(a,b,c)} \sum (y_i - \hat{y}_i)^2 \quad (7.21) \]

From these fitted three dimensional graphs the optimum reduction conditions for each specific variable could be obtained.

In the discussion of the results the term "maximum" relates to the maximum of a certain response that could be obtained under a certain set of reaction conditions while "optimum" refers to the reaction conditions that give the best possible value of a certain response without significant loss in the values of the other responses.

The graphs and the conclusions drawn from the graphs are shown/described below.

*Statistical optimisation*
Figure 7.5: Conversion 1 (Time < 12 hours) plotted as a function of time and temperature of reduction

The equation that appears above the graph in Figure 7.5 is the specific equation to which the graph had been fitted.

From Figure 7.5 it can be seen that high conversions (> 90%) are obtained at a reduction time of longer than 40 minutes over the whole reduction temperature range (180°C to 380°C). Fairly high conversions were also obtained in the shorter reduction time region of 0.1 minutes to 10 minutes especially in the middle reduction temperature range of 240°C to 320°C. At shorter reduction times of 1 to 10 minutes there was a pronounced maximum at a reduction temperature between 280°C and 320°C. Thus to obtain maximum conversions, reduction times of 45 to 50 minutes or longer are ideal and reduction temperatures between 200°C and 360°C are preferred.

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A possible explanation for the results might be that CO adsorbs onto the catalyst at the shorter reduction times, with not much time for reduction of all the sites to the lower Cr$^{2+\alpha}$ state before it is flushed off again by the introduction of nitrogen into the system. The longer reduction times allow enough time for adsorption and more complete reduction to take place. The pronounced maximum observed at the shorter reduction times and intermediate temperatures is interesting to note, although there is no explanation for the occurrence.

An indication of the accuracy of the fit can be obtained from the $r^2$ values given for each specific fit, with most of the $r^2$ values in the 0.85 - 0.95 region.

**Figure 7.6:** Conversion 2 (Time > 12 hours) plotted as a function of time and temperature of reduction

At reduction times longer than 12 hours, the highest conversions were obtained for

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reduction temperatures of between 200°C and 280°C and reduction times of 30 to 50 minutes or longer. The results for conversion 2 are thus in agreement with conversion 1 in the sense that the longer reduction times of 40 to 50 minutes produce the highest conversions. The conversion 1 results are optimal between temperatures of 220°C and 320°C. A lower reduction temperature thus results in the formation of a catalyst that retains its activity for longer reaction times to a greater extent than when high reduction temperatures are used.

A further interesting fact to note is that short reduction times (10 minutes or less) result in less than 5% conversions over the whole reduction temperature range of 200°C to 360°C. Reduction temperatures of 340°C and higher result in total deactivation of the catalyst after 12 hours reaction time. This deactivation is seen over the whole range of reduction times.

From the conversion results it can thus be seen that the longer reduction times result in producing a catalyst which produces optimum conversions and that is relatively stable. The higher temperatures might be too extreme for the catalyst and thus result in a catalyst that does not retain its activity as long as one that has been reduced at the milder temperatures. The higher reduction temperatures might cause some structural or chemical changes in the catalyst which are responsible for the trends observed. The use of a high reduction temperature thus results in a catalyst with poor stability. This will be worth exploring in future work, but was not the major concern of this thesis. These observations correspond with the findings of Zecchina et al., (1975) that a higher reduction temperature results in rearrangement of the chromium ions to a higher coordination state which results in a decrease in catalyst activity.

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7.3.1.2.  Activity as a function of time

The activity of the catalyst for the production of the oligomer product (in g oil produced per g chromium per hour) was obtained as a function of time. To simplify the interpretation of the results, each run was once again divided into two time spans for which the average activity was calculated in each case. The results are presented in Table 7.5.

Table 7.5:  Activities obtained for each of the runs in each of the two time spans.

<table>
<thead>
<tr>
<th>Run number</th>
<th>activity 1 (g oil.g⁻¹Cr.h⁻¹) (Time &lt; 12 hours)</th>
<th>activity 2 (g oil.g⁻¹Cr.h⁻¹) (Time &gt; 12 hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>44.0</td>
<td>7.4</td>
</tr>
<tr>
<td>2</td>
<td>30.6</td>
<td>6.2</td>
</tr>
<tr>
<td>3</td>
<td>45.8</td>
<td>21.1</td>
</tr>
<tr>
<td>4</td>
<td>42.4</td>
<td>18.5</td>
</tr>
<tr>
<td>5</td>
<td>37.1</td>
<td>5.8</td>
</tr>
<tr>
<td>6</td>
<td>18.4</td>
<td>12.0</td>
</tr>
<tr>
<td>7</td>
<td>22.1</td>
<td>2.7</td>
</tr>
<tr>
<td>8</td>
<td>21.5</td>
<td>1.7</td>
</tr>
<tr>
<td>9</td>
<td>38.4</td>
<td>3.3</td>
</tr>
<tr>
<td>10</td>
<td>63.6</td>
<td>10.3</td>
</tr>
<tr>
<td>11</td>
<td>38.3</td>
<td>33.9</td>
</tr>
</tbody>
</table>

The data were treated in the same manner as the conversion data, and various fitted response surface curves were obtained. The fitted curves were, as expected, very similar to the conversion curves obtained. The equations to which the activity 1 and activity 2 data respectively were fitted were the following:

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activity 1: \[ z = 31.28 - 2.214x + 6.156y - 3.65x^2 + 2.521xy + 10.93y^2 \] \hspace{1cm} (7.22)

activity 2: \[ z = 17.25 - 0.6469x + 4.486y - 5.341x^2 - 0.3468xy - 3.033y^2 \] \hspace{1cm} (7.23)

In the case of the activity 1 graph, maximum activities of 60-70 g oil.g\(^{-1}\) Cr. h\(^{-1}\) were obtained over the whole reduction temperature range of 180°C to 380°C. Reduction times of 35 to 50 minutes were found to give the optimum catalyst activities. In the case of the activity 2 graph, maximum activities of 20 g oil.g\(^{-1}\) Cr. h\(^{-1}\) were obtained at the milder temperatures of 260°C to 290°C and at reduction times of 25 to 40 minutes. Since the graphs (not shown) are the same as the conversion graphs in shape and trend, the same observations made under 7.3.1.1. would apply here.

7.3.1.3. \( C_{18} \) selectivity

After fitting of the \( C_{18} \) selectivity data according to the method of least squares, the fitted response surface curve with time and temperature of reduction as the independent variables, shown in Figure 7.7, was obtained.

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Figure 7.7: $C_{18}$ selectivity plotted as a function of time and temperature of reduction

The highest selectivity (40% to 50%) was found in the lower reduction temperature range ($180^\circ$C - $220^\circ$C) with reduction times of 45 to 50 minutes or longer. A decrease in the $C_{18}$ selectivity is observed with an increase in the reduction temperature, with only a very slight increase in selectivity at $360^\circ$C.

To maximize the trimer formation with the $\text{CrO}_3/\text{SiO}_2$ catalyst, it is advisable to use lower reduction temperatures ($180^\circ$C - $240^\circ$C) and a reduction time of 50 minutes. For the production of a heavy oligomer product the use of the higher reduction temperatures would be recommended, since the $C_{18}$ selectivity is then at its lowest.

7.3.1.4. Other response surface plots

Selectivity for $C_{18}$ was plotted as a function of reduction temperature and conversion 1 data (time span shorter than 12 hours) (Fig 7.8). The maximum selectivity was set
at 20 on the scale.

**Figure 7.8:** Selectivity for $C_{18}$ as a function of the reduction temperature and conversion

From Figure 7.8 it can be seen that the highest $C_{18}$ selectivities (>20%) are obtained at low reduction temperatures of 180°C to 200°C irrespective of the conversions obtained. The selectivity of the catalyst for $C_{18}$ is thus not influenced by the conversions, but more by the reduction temperature as was also observed in Figure 7.7. When comparing Figure 7.8 to Figure 7.7 it should be kept in mind that the scale in Figure 7.8 represents a total of only 10%, while a total selectivity of 50% is represented in Figure 7.7. The increase in selectivity at the higher reduction temperatures observed in Figure 7.8 would thus agree with the slight upwards tendency of the selectivity that is observed in Figure 7.7.

If it were desired to increase the specificity of the catalyst for the longer chain products

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(> C₁₈), the middle reduction temperature range (300°C) where the C₁₈ selectivity is the lowest, would probably be the ideal reduction temperature to choose. Under these conditions the selectivity shifts to production the of >C₁₈ olefins. The same conclusion can be made from the results shown in Figure 7.7.

The reason for the decrease in the C₁₈ selectivity obtained at reduction temperatures of more or less 300°C is not known. A possible reason might be that an increase in the reduction temperatures causes structural changes in the catalyst which render it more active as an oligomerisation catalyst. Another possibility is that the specific reduction conditions result in a catalyst with a very high trimerisation activity of the C₁₈ product. If the last mentioned possibility were the case, the trimerisation activity of the catalyst would be so high that all the C₁₈ that was formed would be trimerised to higher oligomers. This tendency of the catalyst to further trimerise the C₁₈ product has been observed in Chapters 5 and 6. The higher reduction temperatures might become too extreme for the catalyst, and thus reduce the ability of the catalyst to further trimerise the C₁₈ that has been formed. The result is thus a slight increase in the C₁₈ concentrations.

In Figure 7.7 the viscosity index (VI) of the product is plotted as a function of the conversion at reaction times shorter than 12 hours. The maximum VI on the scale has been set at 500 and the minimum at 50.
Figure 7.9: Viscosity index as a function of conversion 1 and the reduction temperature

The VI of the product follows more or less the same trend as the selectivity and does not depend on the conversion. Once again the high values for the viscosity index are obtained at the low (200°C) and high (320°C) reduction temperatures irrespective of the conversions obtained. In the low viscosity index range, the VI does depend slightly on the conversions obtained. Conversion lower than 50% and higher than 90% tend to produce a product with a viscosity index lower than 100, especially in the middle temperature range (240°C to 300°C).

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