CHAPTER 3. EXPERIMENTAL INVESTIGATIONS - OPERATING PROCEDURES

3.1 INTRODUCTION

The experimental work was done in two integral reactor systems, a pilot plant unit and a bench scale reactor. The pilot plant unit was primarily used to investigate the effect of changes in the operating parameters and feed composition on the n-butene skeletal isomerisation performance of the catalyst. The bench scale system was used to study the kinetics of the reaction in an attempt to develop an intrinsic rate equation. Both systems and the operating procedures used in each case will now be discussed. For details of the analytical techniques and calculation procedures used, see Appendix 1. The results obtained during the experimental investigations are discussed in Chapter 4. For details of the mathematical and computational procedures used during the kinetic investigation and a discussion of the results obtained, see Chapter 5 and Chapter 6 and Appendices 4 and 5. For a detailed review of the relevant literature, see Chapter 2.

3.2 PILOT PLANT UNIT

3.2.1 PILOT PLANT SYSTEM LAYOUT

Figure 3.1 shows a schematic representation of the pilot plant reactor system. The hydrocarbon feed, predominately n-butene, was stored under nitrogen at a pressure of 2000 kPa(a) in a LPG cylinder (1). This was done to prevent cavitation of the pump (2) used to transport the material to the reactor. Water, which was stored in one of two calibrated glass tanks (3), was pumped to the system using either a high capacity diaphragm pump (4) or a low capacity piston pump (5) depending on the flow rate required. Vaporization of the water as well as mixing and heating of the two streams to the reaction temperature was achieved using a 50 cm long packed bed containing 3 to 5 mm carborundum chips.

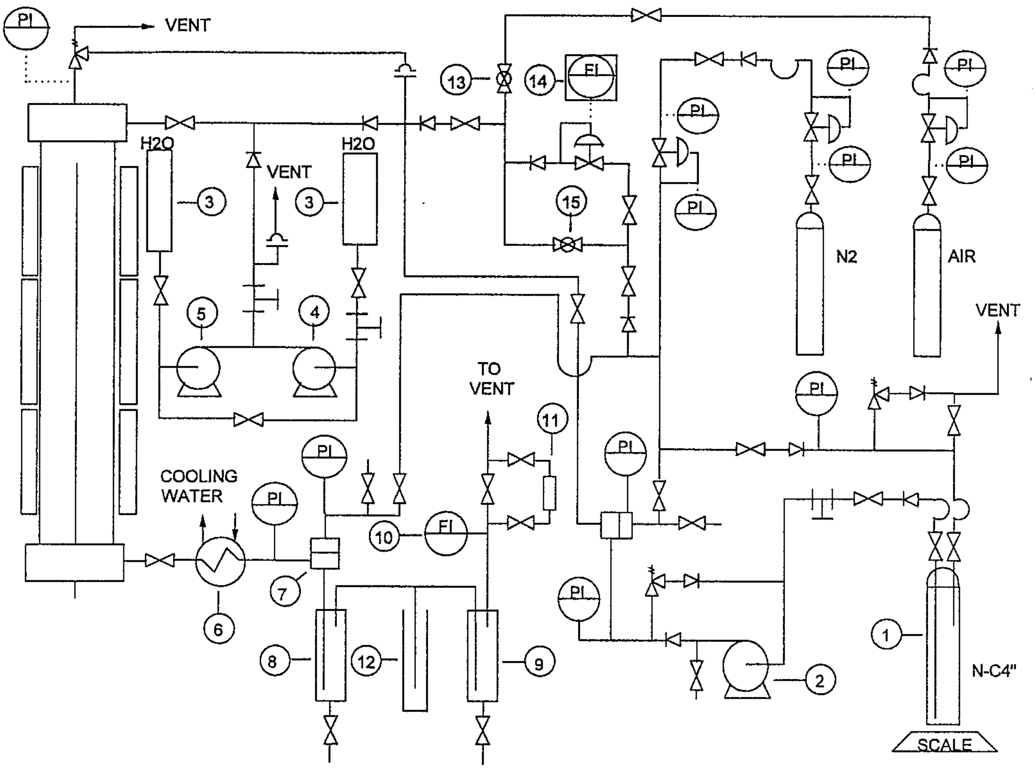


Figure 3.1 : Pilot plant reactor system

The products from the reactor were cooled using a heat exchanger (6) before being released to atmospheric pressure via a gas loaded Grove back pressure regulator (7). To prevent freezing of the products, due to Joule Thompson expansion and hence, failure of the back pressure regulator, it was heated electrically to 50°C. Separation of the gaseous and liquid products was achieved using a metal (8) and a glass (9) catch pot. This effectively prevented carry over of liquid products to the gas flow meter (10), gas sample loop (11) and vent. The gas flow meter and glass catch pot were protected from over pressure by a water seal (12) while a combination of relieve valves and bursting discs were used to ensure the safety of the entire reactor system. To re-activate the catalyst, i.e., to burn off the coke deposited on the catalyst during the on-line period, a specially developed regeneration procedure was used. Maintaining a constant water flow rate the air flow was incrementally (step wise) increased throughout the regeneration. The air flow was controlled by means of a needle valve (13). The flow of nitrogen, which was used to purge air from the catalyst bed after regeneration, was controlled using either a Brooks flow controller (14) or a needle valve (15).

3.2.2 PILOT PLANT FLOW MEASUREMENTS

The flows of the process streams, into and out of the system, were monitored for mass balance calculation purposes. Over a fixed period the hydrocarbon flow rate was recorded by measuring the change in mass of the feed cylinder, which stood on a suitable scale. The feed cylinder was connected to the rest of the system via flexible high pressure hoses. Simultaneously, the water flow rate was calculated by noting the volume that was pumped from the calibrated feed pot into the system. The flow rate of the gas leaving the reactor was recorded by means of a wet gas flow meter while the liquid products were collected and weighed. The flow of nitrogen and air into the system was controlled by means of a Brooks flow controller and calibrated needle valve respectively.

3.2.3 PILOT PLANT REACTOR CONFIGURATION

Shown in Figure 3.2 is a schematic representation of the reactor and catalyst bed configuration. The final reactor tube, constructed from SS-321, was 120 cm long and had an inner diameter of 2.54 cm. To ensure uniform distribution of the heat supplied, i.e., isothermal operation of the unit, a brass sleeve was strapped to the outside of the tube. The unit was heated using three, separately controllable, 1 kW heating elements strapped to the outside of the brass sleeve. The temperature of the reactor was controlled using three independent temperature controllers. The controlling thermocouples were placed on the outside wall of the reactor tube in the centre of each of the heating blocks. The temperature of the catalyst bed was monitored using six thermocouples in a centrally located thermowell with an outside diameter of 0.635 cm.

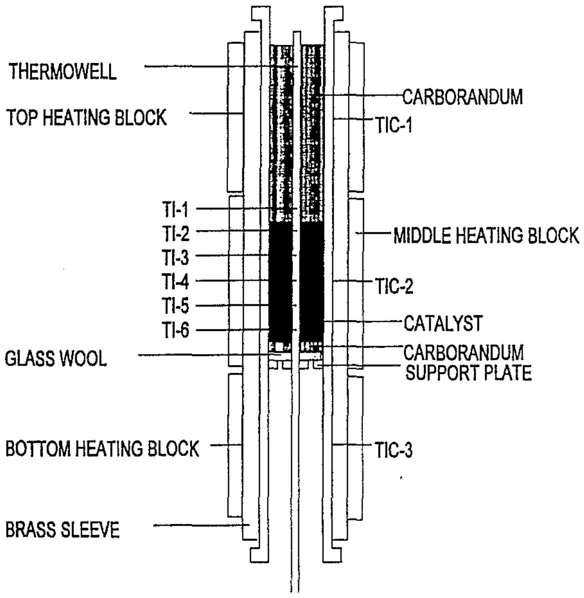


Figure 3.2 : Pilot plant reactor detail

To prevent heat loss the entire unit was insulated using an asbestos substitute that was in turn covered with a zinc sheet.

The catalyst bed was supported in the centre of the middle heating block by a bed support plate fixed to the thermowell. To prevent the spherical catalyst particles of between 1.19 mm and 2 mm, with a weighted average diameter of 1.25 mm, from falling through the bed support plate and to ensure the location of the catalyst bed in the centre of the middle heating block, a plug of quartz wool and a small amount of carborundum was first placed on the bed support. Next, 50 g of catalyst, corresponding to a bed height of ± 15 cm, was loaded, followed by a 50 cm long bed of 3 to 5 mm carborundum chips. In this way heating of the reactants was achieved before they reached the catalyst bed. This was confirmed by the measured temperature profile, as shown in Section 3.2.4.

3.2.4 AXIAL TEMPERATURE PROFILE - PILOT PLANT

Shown in Figure 3.3, is the temperature profile recorded during an experiment at the base case conditions (See Section 3.5) using the pilot plant reactor system. As may be seen from this figure isothermal behaviour throughout the ±15 cm long catalyst bed and beyond was achieved. That isothermal operation was maintained at all times was confirmed by routine checks of the temperature profile during the various experimental investigations performed.

3.2.5 HOMOGENEOUS REACTION ACTIVITY - PILOT PLANT

To confirm that the preheater and reactor material were inert and that homogeneous reactions did not take place, a blank tube experiment was conducted. In this case no catalyst was loaded but the quantity of preheat material, silica carbide (carborundum), increased to fill the volume normally occupied by the catalyst bed. Operating the system at a temperature of 530°C, pressure of 85 kPa(a), hydrocarbon LHSV of 2 and water to hydrocarbon mole ratio of 1 to 1, the formation of methane and free carbon was observed.

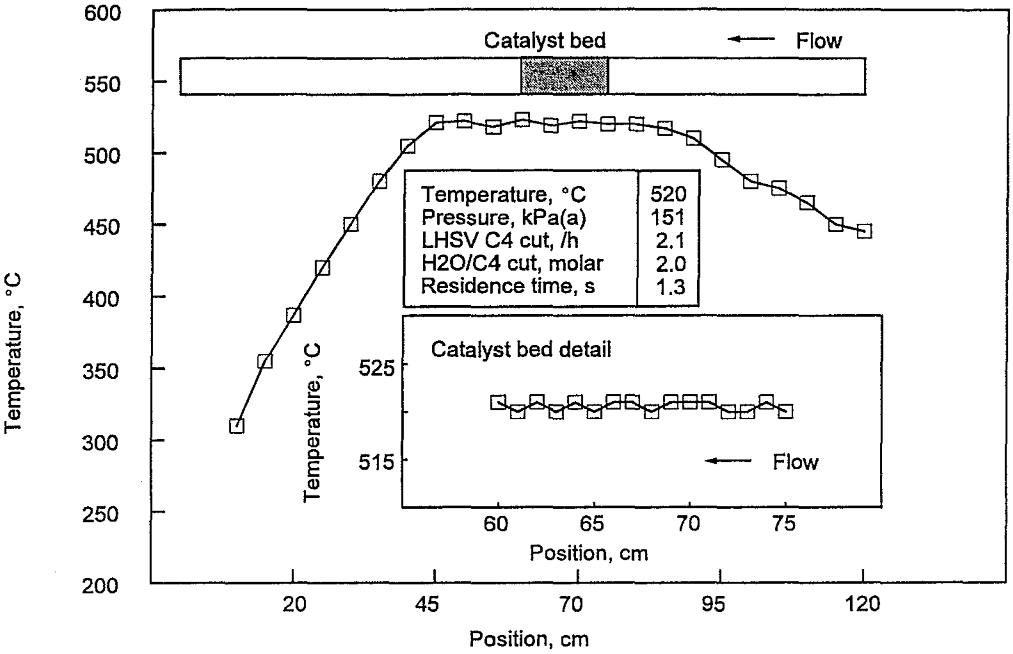


Figure 3.3 : Axial temperature profile in the pilot plant reactor system

It was subsequently established that the reactor was made of Inconel 600, a material rich in nickel. This material was not inert but reacted with the hydrocarbons forming graphitic carbon and methane via a process known as metal dusting. In this process either carburization or graphitization, or both, of the hydrocarbons occurs, resulting in the formation of methane and a carbon / hydrocarbon complex containing metal particles. As butene skeletal isomerisation was conducted at 530°C the temperature sensitivity of this reaction was examined. It was found by Hochman and Burson (1966:342) that the rate of metal dusting, for Inconel 600, was highest at temperatures between 500°C and 950°C. An analysis of the carbonaceous material collected showed that the ratios of nickel, chrome and iron present in the material were similar to those of Inconel 600. Switching to a reactor constructed from SS-321 with a nominal composition of 72 % Fe, 18 % Cr and 10 % Ni together with trace amounts of C, Ti and Cb, eliminated this problem.

In this latter unit, using the same conditions as before, an average total n-butene conversion of less than 2 mass % was observed during a 30 hr on-line period. Examining the product spectrum it was found that both the quantity of light, $<C_4$ and heavy $>C_4$ components increased and that some thermal double bond isomerisation had occurred.

No evidence of skeletal isomerisation was observed and so the reactor system and preheat material were considered to be inert.

3.3 BENCH SYSTEM

3.3.1 BENCH SYSTEM LAYOUT

Shown in Figure 3.4 is a schematic representation of the bench scale system.

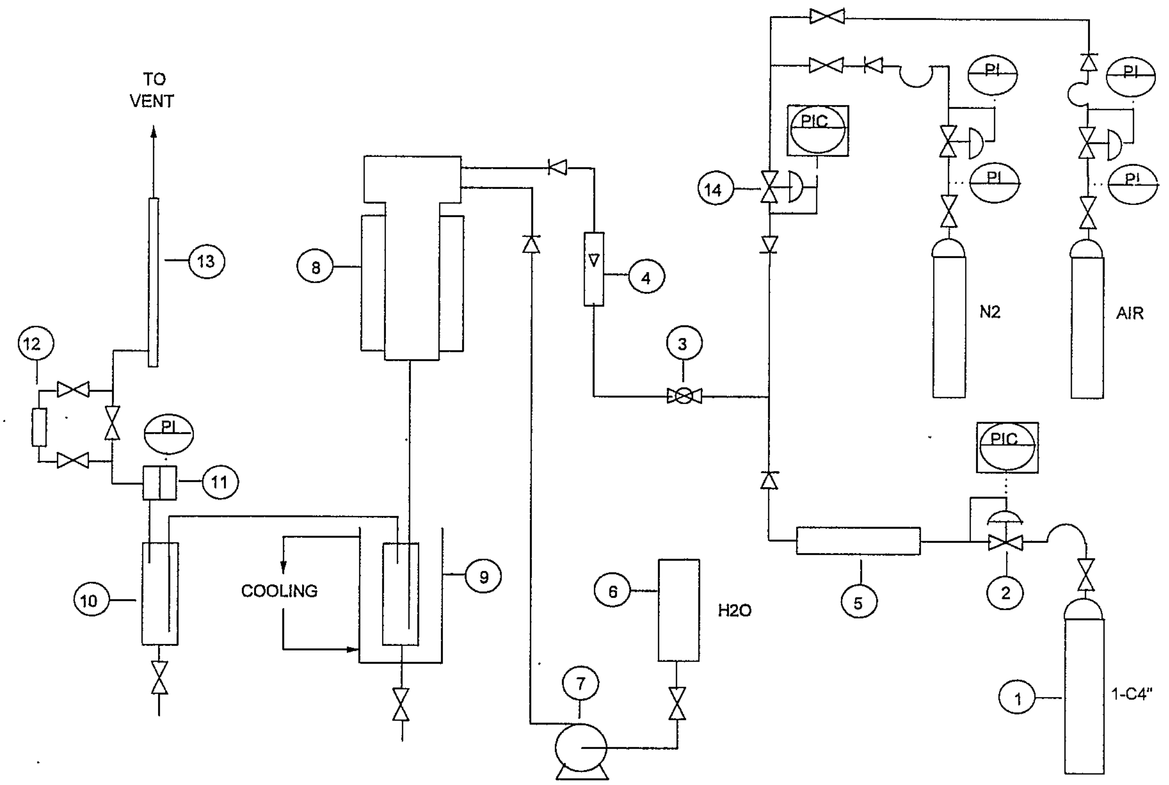


Figure 3.4 : Bench reactor system

The hydrocarbon feed was stored in a number 7 Cadac cylinder (1) mounted in the upright position. Using an in-line regulator (2) the pressure in the lines was maintained at 185 kPa(a), i.e., below the vapour pressure of the hydrocarbons of 295 kPa at 25°C, preventing condensation of the feed in the lines. The flow of the hydrocarbons was controlled using a needle valve (3) and monitored using a rotameter (4). A 1 l tank (5) was installed in the gas line to dampen fluctuations in the gas flow. The water feed rate was monitored using a calibrated feed pot (6) and controlled by adjusting the stroke of the water pump (7). The water and hydrocarbon streams were combined in the reactor (8) in a free space above the preheat material, in a co-current manner. The water and liquid products from the reactor were cooled and condensed in a catch pot (9) submerged in glycol at approximately 0°C. The gaseous products were passed through a second knockout pot (10) to ensure trouble free operation of the spring loaded back pressure regulator (11) used to control the pressure of the system.

The composition of the products was determined by passing the material through a gas sample loop (12) that could be removed from the system for later analysis. Finally, the gaseous products passed through a soap bubble meter (13) used to measure the flow rate before being vented. To purge the system, nitrogen and to regenerate the catalyst air plus water was used. The line pressure of these was controlled using an in-line regulator (14) while the flow rate was set and monitored using the same needle valve (3) and rotameter (4) and soap bubble meter (13) as before.

3.3.2 BENCH SYSTEM FLOW MEASUREMENT

The flows of the process streams, into and out of the system, were monitored for mass balance calculation purposes. Over a fixed period of time the hydrocarbon feed rate was measured by means of a calibrated rotameter. Simultaneously, the water flow rate was calculated by noting the volume that was pumped from a calibrated feed pot into the system. The flow rate of the gases leaving the reactor was recorded by means of an instantaneous reading using a soap bubble meter while the liquid products were collected over a known time period and weighed. The flow of nitrogen and air used during the regeneration of the catalyst were controlled and measured in a similar manner.

3.3.3 BENCH SYSTEM REACTOR CONFIGURATION

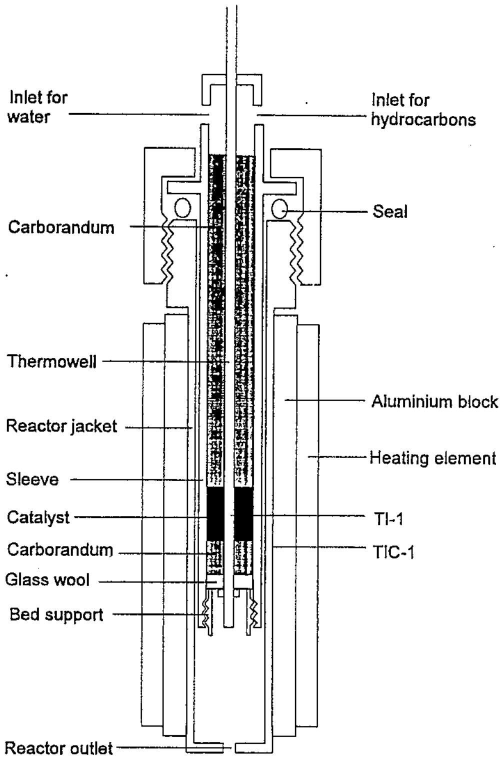


Figure 3.5 : Bench reactor detail

The reactor system consisted of a specially constructed, stainless steel (SS-321), single seal unit consisting of an outer jacket and an inner sleeve. A cross sectional view of the reactor is shown in Figure 3.5. The internal diameter of the inner sleeve was 1.31 cm and the external diameter of the centrally located thermowell 0.3 cm, with the overall length of the unit being 45 cm. To ensure equal distribution of the heat supplied to the reactor, an aluminum sleeve was wrapped around the outside of the outer jacket. In this way isothermal operation over more than half the unit length was achieved. Heat was supplied to the unit using a 1 kW element, the temperature of which was controlled by a temperature controller with a thermocouple placed on the outside wall of the reactor jacket. The temperature of the catalyst bed and preheat material was monitored using a mobile thermocouple in the centrally located thermowell. To prevent heat loss the entire unit was encased in a special insulating cement.

The catalyst bed was supported near the bottom of the heating block by a bed support plate screwed into the bottom of the inner sleeve. To prevent the spherical catalyst particles of between 1.19 mm and 2 mm, with a weighted average diameter of 1.25 mm, from falling through the bed support plate and to ensure the location of the catalyst bed a plug of quartz wool and a small amount of carborundum was placed on the bed support. Next, between 4 g (bed height of 5 cm) and 13 g (bed height of 15 cm) was loaded, followed by a bed of 3 to 5 mm carborundum chips. A small open space of approximately

0.5 cm was left at the top of the reactor where the water and hydrocarbon streams enter the unit. In this way vaporization of the water, mixing and heating of the reactants was achieved before these reach the catalyst bed.

3.3.4 AXIAL TEMPERATURE PROFILE - BENCH SCALE REACTOR SYSTEM

Shown in Figure 3.6 are the temperatures recorded over the entire bench scale reactor during a typical experiment performed at the base case conditions (See Section 3.5). It may be seen from Figure 3.6 that isothermal operation was achieved over a total length of 15 cm allowing for a maximum of 13 g of catalyst to be loaded if isothermal conditions are to be maintained.

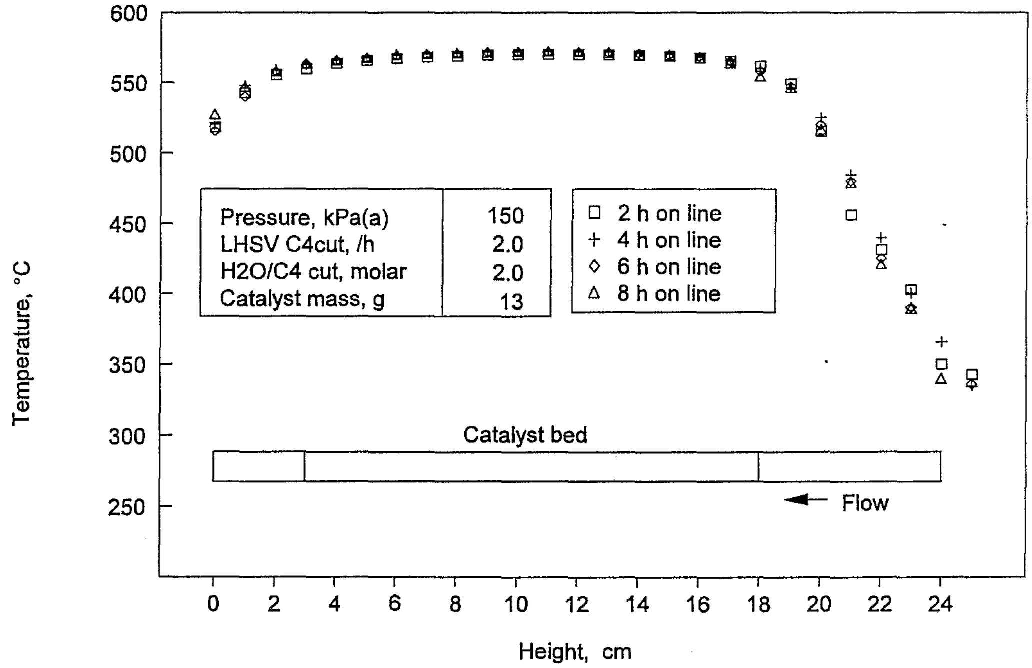


Figure 3.6 : Axial temperature profile in the bench scale reactor system

3.3.5 HOMOGENEOUS REACTION ACTIVITY - BENCH SCALE REACTOR SYSTEM

To ensure that the results obtained during the experimental investigations were due to the catalyst and not the preheat or reactor material, a series of blank tube experiments were conducted. In this case no catalyst was loaded but the quantity of preheat material, carborundum, expanded to fill the volume normally occupied by the catalyst bed. Hence, the catalytic activity of the reactor and packing material, at extremes as well as average operating conditions, could be established.

TABLE 3.1 : HOMOGENEOUS REACTION ACTIVITY CHECK - BENCH SYSTEM

Test		1	2	3	4	5	6	7	8	9
Temperature, °C		548	568	537	547	562	563	563	554	599
Pressure, kPa(a)		152	149	149	150	150	85	216	150	154
WHSV C4", hr^{-1}		3.2	1.8	1.8	2.0	1.6	1.5	1.6	2.3	1.6
H2O/C4" ratio, molar		2.8	0.9	2.6	4.3	2.1	2.1	1.3	2.0	2.4
Composition	**Feed**	**Products**								
lights, %	0.0	0.0	0.3	0.1	0.0	0.1	0.1	0.1	0.1	0.4
butane, %	0.2	0.2	0.1	0.2	0.2	0.2	0.2	0.2	0.1	0.3
n-butene, %	99.7	99.2	99.2	99.5	99.6	99.3	99.5	99.4	99.6	98.1
isobutene, %	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
1,3-butadiene, %	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.1	0.0	0.2
heavies, %	0.0	0.5	0.2	0.1	0.1	0.3	0.1	0.1	0.1	0.9
Results	-	1	2	3	4	5	6	7	8	9
Total Conversion, %		0.5	0.5	0.2	0.2	0.4	0.2	0.3	0.1	1.6

As may be seen from Table 3.1 the average total conversion after 5 h on line was less than 0.5 mass % in all cases, except when operating the reactor system at 600°C. Examining the product spectra it was found that at this extreme, the quantity of light by-products (C_1 to C_3 hydrocarbons) had increased at the expense of the n-butenes. The percentage of isobutene however had not changed during this or any of the other tests conducted. From this study it was concluded that the packing material and the bench scale reactor system were inert, i.e., that the rate of homogeneous skeletal isomerisation reaction is negligible. Hence, the results obtained from this system may exclusively be ascribed to the performance of the catalyst and not the packing material nor the reactor system as such.

3.4 CALCINATION PROCEDURE

Prior to use, the catalyst was calcined. This should preferably be done in-situ, but due to equipment limitations was done ex-situ during this study. The catalyst was activated by heating at a rate of 100°C/h to a final value of 700°C and maintaining this temperature for 1 hour. Throughout this process dry air was passed through the catalyst bed at a rate of 50 $l_n \cdot h^{-1}$, i.e., at 1 $l_n \cdot h^{-1} \cdot g^{-1}$ of catalyst.

To confirm the need for calcination, the performance of a catalyst calcined in-situ at 520°C was recorded during the first eleven on line and regeneration cycles. The results obtained, together with the performance achieved during the first on-line period when using a catalyst calcined ex-situ at 700°C, are shown in Figure 3.7 .

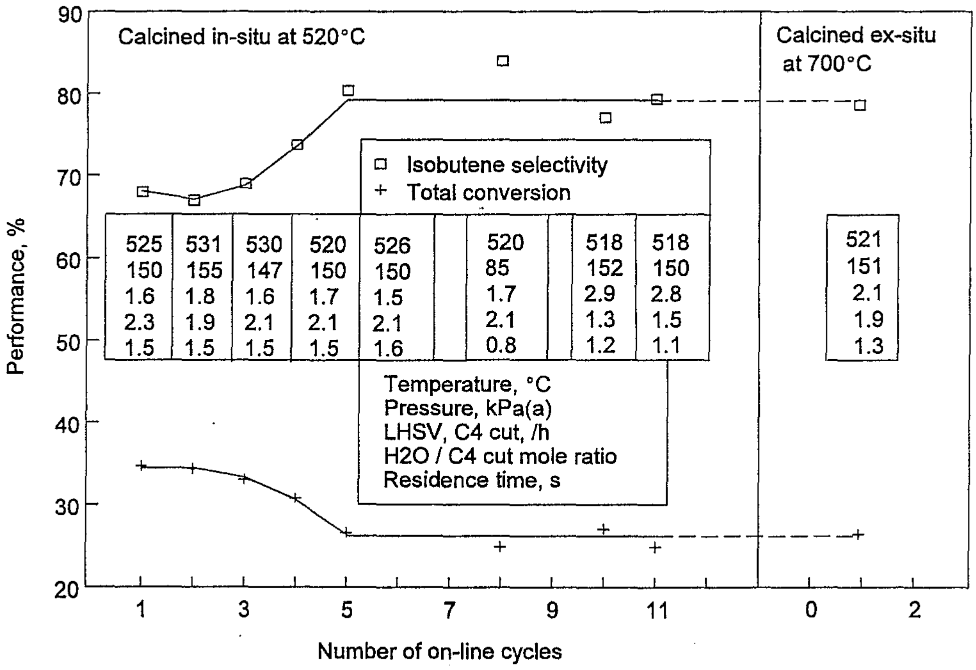


Figure 3.7 : Effect of calcination temperature on the performance of the catalyst

As can be seen from Figure 3.7, for the catalyst calcined in-situ, the selectivity increases and the conversion decreases over the first 5 cycles before finally levelling off. For the catalyst calcined ex-situ at 700°C, no induction period was present. That no further changes in the performance of the ex-situ calcined catalyst took place was confirmed during the various activity checks performed throughout this study, as discussed in

Chapter 4, Section 4.13. Hence, to ensure optimum performance from the start, ex-situ calcination at 700°C will have to form part of the catalyst activation procedure in any commercial process.

Shown in Table 3.2, are surface area, pore volume and average pore diameters for a catalyst calcining and steaming at 520°C and 700°C and for an un-calcined catalyst. Comparing the results obtained for the un-calcined catalyst with those recorded after dry calcination at either 520°C of 700°C, suggest that little to no change occurred during dry calcination. Comparing the properties recorded for the calcined and steamed catalyst with those recorded for the un-calcined catalyst, a decrease in the surface area and increase in the average pore diameter and pore volume was recorded. Traditionally, an increase in the average pore diameter, while the surface area and pore volume remain approximately constant, suggest that the smaller pores have sintered. As in this study the pore volume increased, the results are inconclusive and can not be used to account for the trends observed in Figure 3.7.

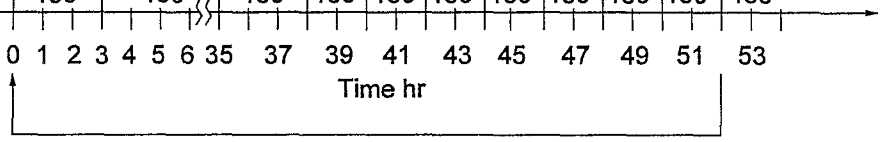
TABLE 3.2 : PHYSICAL PROPERTIES OF UN-CALCINED AND CALCINED CATALYST

Parameter	Un-calcined	Calcined at 520°C Not steamed	Calcined and steamed at 520°C	Calcined at 700°C Not steamed	Calcined and steamed at 700°C
BET surface area, m^2/g	193.9	191.3	186.2	189.4	180.7
Pore volume, cm^3/g	0.514	0.526	0.520	0.503	0.518
Pore diameter, Å	106.1	110.1	112.3	106.3	114.6

3.5 OPERATING CYCLE

Only the final version of the operating and regeneration procedure used will be discussed here, as this was one of the parameters that had to be optimised (See Chapter 4). Details of the actual operating parameters used are also given in each figure presented so that deviations from the norm may be recognized. Figure 3.8 shows the base case temperatures, pressures and flow rates of the various materials used during the on-line and regeneration cycle. A brief discussion of the operating cycle is given below.

	Purge	Reaction	Purge	Regeneration							Standby
Air, l/hr				2.5	5	10	20	40	70	100	
Nitrogen, l/hr	50		50								50
Water, g/hr	59.3	59.3	59.3	59.3	59.3	59.3	59.3	59.3	59.3	59.3	59.3
C4 Cut, g/hr		92.3									
Temperature, °C	520	520	520	520	520	520	520	520	520	520	300
Pressure, kPa(a)	150	150	150	150	150	150	150	150	150	150	150



Notes

Mass of catalyst	:	50 g
Bulk density of Catalyst B	:	0.65 g/cm^3
Liquid density of C4 Cut	:	0.6 g/cm^3
Molar weight C4 Cut	:	56 g/gmole
Molar weight water	;	18 g/gmole

Base case conditions

Temperature	:	520 °C
Pressure	:	150 kPa (a)
Water flowrate	:	59.3 g/hr
C4 Cut flowrate	:	92.3 g/hr
LHSV C4 Cut	:	2.0 /hr
H2O/C4 Cut ratio	;	2.0 molar

Figure 3.8 : Operating and regeneration procedure

The air that remained in the system at the end of the regeneration had to be purged from the catalyst bed before the reactor could be brought on line. This was done using nitrogen at a flow rate of 50 $l_n{\cdot}hr^{-1}$ and steam at a rate of 59.3 $g{\cdot}hr^{-1}$, a ratio of 0.678 mol N_2/mol H_2O, over a period of 2 hrs. The temperature and pressure were held at 520°C and 150 kPa(a) respectively during this operation. Next, if necessary, the system temperature and pressure were adjusted to the reaction conditions over a period of 1 hr. Once the desired conditions had been reached the hydrocarbon feed was introduced at the desired flow rate and the nitrogen flow stopped. Once the system had stabilized, the water flow rate was set to give the correct water to hydrocarbon ratio and the system maintained at these conditions for the duration of the on-line period, of between 8 and 33 hrs. Upon the completion of the reaction period the hydrocarbon flow was discontinued and the reactor purged using nitrogen at a flow rate of 50 $l_n{\cdot}hr^{-1}$ and steam at a rate of 59.3 $g{\cdot}hr^{-1}$, a ratio of 0.678 mol N_2/mol H_2O, for a period of 3 hrs. During this operation the system pressure was reset, if required to 150 kPa(a) and the temperature adjusted, if required, to 520°C.

It was found that during the on-line period the catalyst loses activity, due to the deposition of coke resulting in the blockage of the pores / active sites. Traditionally, coke is removed by treating the catalyst with air at an elevated temperature thereby converting the coke to CO_2 and / or CO. To prevent uncontrolled combustion, which could lead to the formation of hot-spots that may damage the catalyst, the composition of the gases has to be controlled. In this work, increases in the bed temperature were prevented by diluting the air with steam. The catalyst was regenerated using a constant water flow rate of 59.3 $g \cdot hr^{-1}$ and increasing the air flow rate, i.e., the concentration of air, in two hourly intervals from 3.3 mol % to 57.5 mol % over a period of 12 hrs. During the final stage of the regeneration the flue gas was tested for CO and CO_2. If these were detected the system was held at the final set of conditions for an additional period of 2 hrs. This procedure was repeated until no more CO_2 or CO was detected. The flows used during a typical regeneration are shown in Figure 3.9. No CO was ever detected and the majority of the carbon was removed after 2 hrs with the regeneration being complete after 10 hrs.

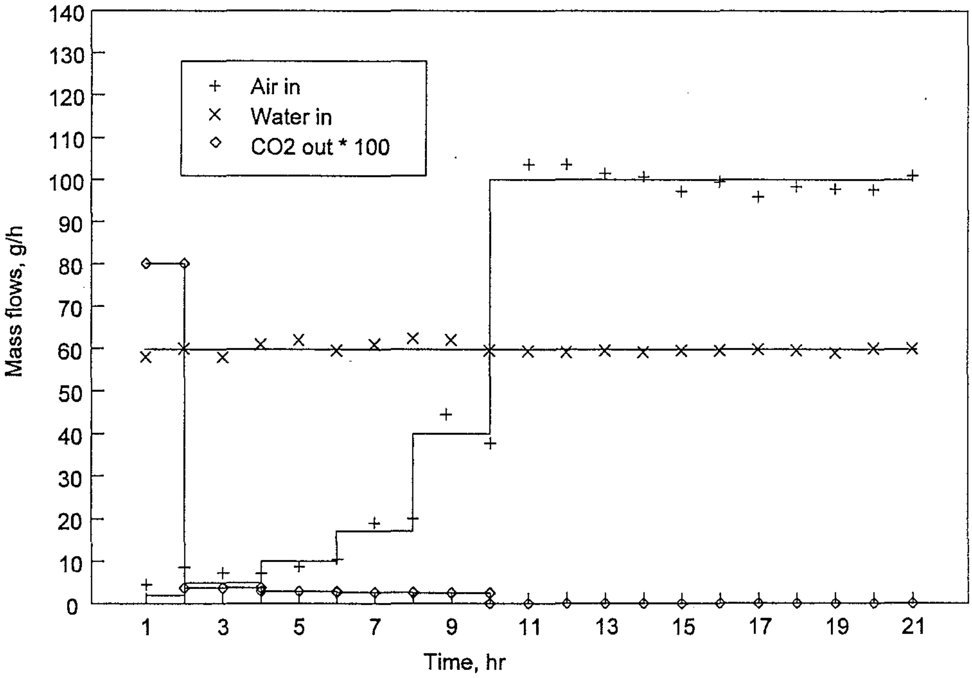


Figure 3.9 : Air, water and carbon dioxide flows recorded during a typical regeneration

Upon the completion of the regeneration step, nitrogen at a rate of 50 $l_n \cdot hr^{-1}$ was substituted for air and the system either placed on standby, in which case the temperature was decreased to 300°C or prepared for the next on-line period, i.e., the cycle was repeated.

3.6 FEED COMPOSITION

A number of feeds were used during this study. In some cases these were prepared using commercially available pure components such as 1-butene, isobutene, n-butane, 1,3-butadiene or 1-pentene. Also used was the overhead product from a commercial debutaniser column (Feed A) and a C4 cut from a cracker called Raffinate III (Feed B). The average composition of Feed A and Feed B used during this study are shown in Table 3.3. Details of the specially prepared feeds using pure components are given in each of the relevant sections.

TABLE 3.3 : AVERAGE COMPOSITIONS OF FEED A AND FEED B

Species	**Feed A**	**Feed B**
methane, mass %	0.00	0.00
ethane, mass %	0.00	0.01
ethene, mass %	0.00	0.03
propane, mass %	0.89	0.01
propene, mass %	1.29	0.11
isobutane, mass %	1.71	22.02
n-butane, mass %	9.40	13.98
trans-2-butene, mass %	2.01	19.75
1-butene, mass %	73.58	28.29
isobutene, mass %	8.46	0.65
cis-2-butene, mass %	2.09	14.10
1,3-butadiene, mass %	0.03	0.12
C_5's, mass %	0.53	0.91
C_6's, mass %	0.00	0.02

3.7 CALCULATION PROCEDURES

During the skeletal isomerisation of the n-butenes to isobutene, apart from the desired product, isobutene, a number of by-products were also formed. To quantified the by-products formed in terms of the n-butene converted, the cracking, hydrogenation and oligomerisation selectivities were calculated. The cracking selectivity was calculated using the quantity of the C_1 to C_3 hydrocarbons formed, the hydrogenation selectivity was calculated using the quantity of n-butane and isobutane as well as the quantity of butadiene formed and the oligomerisation selectivity was calculated using the quantities of C_5^+ formed. The small quantity of oil formed, less than 0.01 mass % of the water added during the on-line period of 33 h, was not included. For a details of the equations used to calculate the various parameters, see Appendix 1. A detailed sample calculation is given in Appendix 2.

3.8 GAS CHROMATOGRAPHIC ANALYSIS PROCEDURE

To quantify the effect of the operating conditions and the feed composition on the performance of the material the composition of the product and feed gas had to be determined. This was done using a Varian 3400 gas chromatograph whose responses from the flame ionization detector (FID) were monitored by an on-board integrator. The column used to separate the gases into the separate components was a porous layer open tubular (PLOT) capillary column. The column of fused silica was 50 m long with a inner diameter of 0.53 mm the inside wall of which was coated with Al_2O_3/KCl. The conditions used to operate the chromatograph and a typical result obtained are given in Appendix 1.

3.9 CATALYST COMPOSITION

The amorphous silica alumina catalyst used during this study, was an experimental, proprietary catalyst supplied by a licensor of refinery technology. Hence, although some of the physical characteristics of this material are discussed in this study, a detailed analysis may not be included. However, based on information in the literature (Buonomo et al., 1977:1, Manara et al., 1977:1, Hising, 1984:1, Nielsen et al., 1986:338), it may be proposed that the material under consideration is an alumina, modified with tetra ethoxy silane. See also Chapter 2, Sections 2.5.7 and 2.6.7 for further details.

3.10 SUMMARY

To enable the development of a commercial, n-butene to isobutene skeletal isomerisation process, the necessary experimental, analytical and data manipulation procedures needed to be set up. This was done during this study. The necessary pilot plant and bench scale reactor systems were constructed and commissioned. Operating and in-situ catalyst regeneration procedures, both suitable for commercialisation, as well as analytical and data manipulation procedures (see Appendix 1 for details of the latter) were developed. From a series of measurements the isothermal operation of the units in the axial direction was confirmed while a series of blank tests further confirmed the inertness of the system and the absence of homogeneous gas phase reactions. That these systems are also suitable for the measurement of the intrinsic kinetics of the n-butene to isobutene skeletal isomerisation reaction and that they could be modelled using a one dimensional pseudo-homogeneous reactor model, is shown in Chapter 5 and Appendix 4.