CHAPTER 4. PERFORMANCE STUDY - RESULTS AND DISCUSSION

4.1 INTRODUCTION

Having identified that one of the viable routes to isobutene is via the skeletal isomerisation of the n-butenes, a suitable catalyst was sought. As established during the review of the literature, a commercially proven catalyst was not available. Therefore, Sasol entered a co-operative agreement with a supplier of refinery technology to develop the process. An experimental, proprietary catalyst was supplied.

In this chapter, the effect of the operating parameters such as the residence time, operating temperatures, system pressure and water to hydrocarbon ratio on the performance of the catalyst were examined. The need to co-feed water was further examined, in an attempt to reconcile the performance of the system with the nature of the acid sites of the catalyst. In addition, the effect of feeding inert diluents such as nitrogen and hydrogen during the on-line period was determined, as was the effect of hydrocarbon feed contaminants, in particular oxygenates. The effect of the build-up of by-products such as, 1,3-butadiene and pentenes, on the performance of the catalyst was also determined. Activity checks were regularly performed at the 'base case' conditions to monitor the long-term stability of the catalyst. This was done to ensure that the results recorded during the various studies were a result of the operating conditions and not changes in the catalyst.

A break down of the calculation procedures and definitions used in manipulating the data is given in Appendix 1. The average values of the raw data collected during an experiment conducted at the base case conditions, together with the results calculated, are given in Appendix 2. Some of the properties of the catalyst are presented in Chapter 3 and Chapter 4. In all cases, unless otherwise stated, the results presented in Chapter 4 were generated using the pilot plant reactor, after 5 h on line. The bench reactor system was used during the kinetic investigations. For details of the modelling performed in an attempt to develop a rigorous rate equation, see Chapter 5 and Chapter 6 as well as Appendices 3 to 5.

4.2 THERMODYNAMIC AND KINETIC EFFECTS

The butene skeletal and bond isomerisation reactions are reversible. It is therefore conceivable that the performance of the catalyst may be thermodynamically as well as kinetically limited. In an attempt to quantify this, the effect of increasing the residence time was investigated. In this study, the flows of the hydrocarbons and water were adjusted but all else held constant. The effect of changing the residence time on the partial pressure ratios of the butene isomers in the product is shown in Table 4.1 and Figure 4.1, on the overall performance of the catalysts in Figure 4.2, and on the various selectivities in Table 4.2 and Figure 4.3.

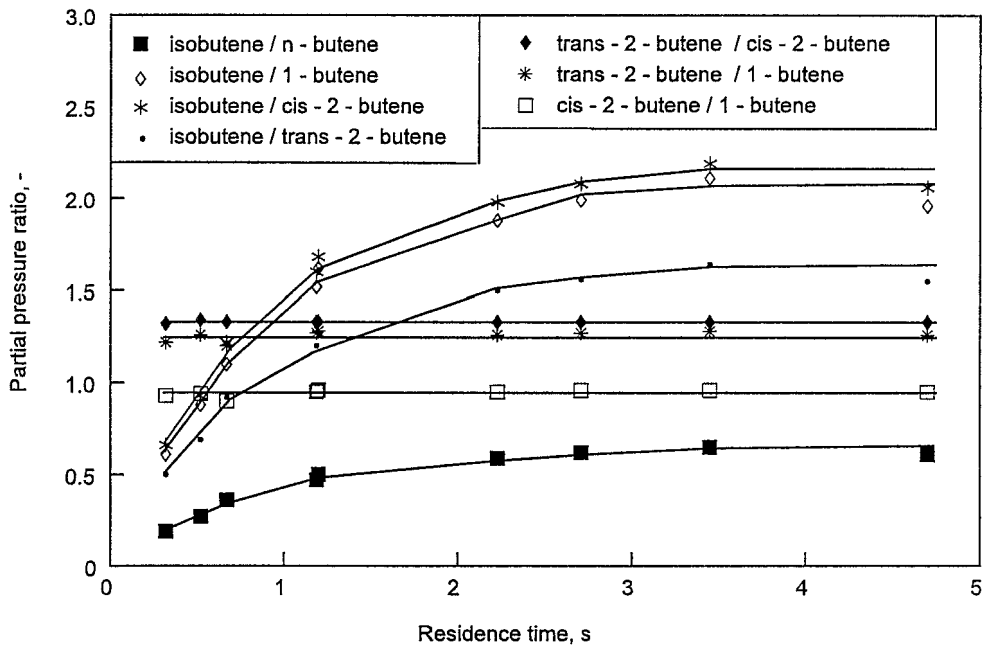

Figure 4.1 : Effect of the residence time on the butene partial pressure ratios in the product gas

It may be seen from Figure 4.1 that the partial pressure ratios of the linear butenes in the product gas were independent of the residence time, and as shown in Table 4.1, at equilibrium. From this, it may be concluded that the butene double bond isomerisation performance of the catalyst was thermodynamically and not kinetically limited. Similar results were reported previously. Szabo et al. (1993:329) found that the inter-conversion amongst the linear butenes was not effected by the activity of the catalyst while Bianchi et

al. (1994:556) showed that these reactions could best be represented by first order reversible reactions, with identical rate constants. Hence, during this study, as is done elsewhere in the literature, (Simon et al., 1994:480, Choudhary and Doraiswamy, 1971:55) the linear butene are treated as a single pseud component, namely n-butene. Examining the ratio of isobutene to the linear butenes, either individually or combined, it may be seen from Figure 4.1 that these approach a constant value as the residence time was increased. From this, it may be concluded that both thermodynamics and kinetics influence the skeletal isomerisation performance of the catalyst with the net reaction rate decreasing as the thermodynamic limit is approached. The actual residence times / hydrocarbon liquid hourly space velocity used, the butene partial pressure ratios in the product achieved as well as the ratios at 530°C, as measured by Kilpatrick et al. (1946:559) and labled 'Limit', are also shown in Table 4.1. For a detailed discussion of the procedure used to calculate the thermodynamic equilibrium, See Section 2.3.6. Examining the data presented in Table 4.1, it may be concluded that the transition from predominately kinetic control to thermodynamic effects limiting the net reaction rate occurs at residence times of between 1.2 s, and 2.2 s. This transition point may be expected to shift with temperature and the isobutene content of the feed. See also Chapter 5, where the effects of residence time using pure 1-butene are presented.

TABLE 4.1 : PRODUCT GAS BUTENE PARTIAL PRESSURE RATIOS

Residence time, s	0.32	0.52	0.67	1.19	1.20	2.23	2.71	3.45	4.70	Limit
C4 cut LHSV, h^{-1}	5.51	5.09	3.27	1.96	1.96	1.04	0.80	0.55	0.52	-
isobutene / n-butene	0.19	0.27	0.36	0.47	0.50	0.59	0.62	0.65	0.61	0.6
isobutene / 1-butene	0.61	0.88	1.1	1.52	1.62	1.88	1.99	2.11	1.96	1.8
isobutene / *cis*-2-butene	0.66	0.93	1.22	1.60	1.68	1.98	2.08	2.19	2.06	2.0
isobutene / *trans*-2-butene	0.50	0.69	0.92	1.20	1.27	1.50	1.56	1.64	1.55	1.5
trans-2-butene / *cis*-2-butene	1.32	1.34	1.33	1.33	1.33	1.33	1.33	1.33	1.33	1.3
trans-2-butene / 1-butene	1.22	1.26	1.20	1.28	1.28	1.26	1.27	1.28	1.26	1.2
cis-2-butene / 1-butene	0.93	0.94	0.90	0.96	0.96	0.95	0.96	0.96	0.95	1.0

Shown in Figure 4.2 are the selectivity to isobutene, the total conversion as well as the loss of butenes recorded as a function of the residence time. As can be seen from this figure

as the residence time was increased from 0.32 s to 4.7 s, the isobutene selectivity decreased and the total conversion and loss of butenes increased with the residence time.

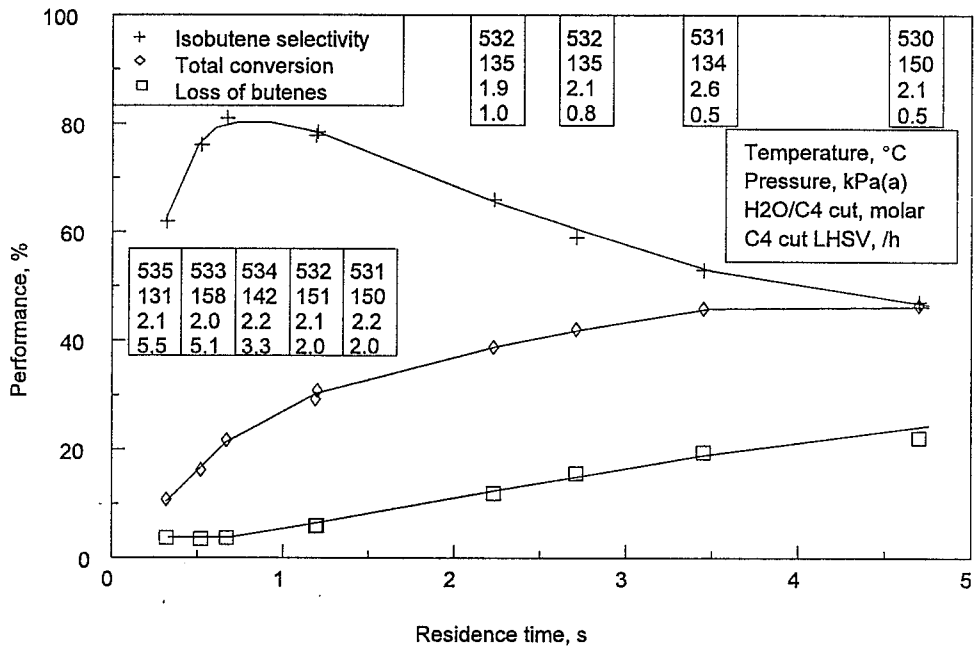

Figure 4.2 : Effect of the residence time on the isobutene selectivity, total n-butene conversion and loss of butenes

With an increase in the total conversion and particularly the loss of butenes, the n-butene partial pressure in the product stream must decrease. As at residence times in excess of 2.2 s the isobutene to n-butene partial pressure ratio in the product gas remained constant (See Table 4.1), this implies that the partial pressure of isobutene present in the product gas must also decrease at the same rate, i.e., the trend observed in Figure 4.2 , a decrease in the isobutene selectivity with increasing residence time, is as expected. (See also Appendix 1 for details of the calculation procedure used.)

Shown in Figure 4.3 and Table 4.2 are the various selectivities, calculated using the n-butene converted, as a function of the residence time. It was found that as the residence time was increased so the isobutene selectivity decreased, while the cracking and oligomerisation selectivities increased and the hydrogenation selectivity first decreased before levelling off. That 1-butene could undergo reversible bond isomerisation, i.e., the

formation of *cis*-2- and *trans*-2-butene, skeletal isomerisation to isobutene, as well as oligomerisation, cracking and hydrogenation was previously demonstrated (Condon, 1958:98). Choudhary and Doraiswamy (1971:230) found that the by-products consisted mainly of C_3 and C_5 hydrocarbons that they assumed were formed via the dimerisation of isobutene, followed by cracking to the various by-products. Szabo et al. (1994:323) proposed a dimerisation / cracking mechanism involving both the n-butene and isobutenes, while Bianchi et al. (1994:556), feeding pure isobutene obtained n-butene as the main product even at high conversion levels of as high as 50 %. From this, and their kinetic data they concluded that the by-products were formed exclusively via the n-butenes. This was further confirmed by Cheng and Ponec (1994:345), who feeding n-octene obtained the characteristic by-products as well as by Simon et al. (1994:485) from an examination of the composition of the polymer stream. (See also Section 2.3.3 for further details). This together with the trends observed during this study, i.e., an increase in both the cracking and oligomerisation selectivity with increasing residence time, strongly suggests that the lighter and heavy by-products were indeed formed via the dimerisation of the butenes followed by cracking. Of course, as the butene skeletal isomerisation reaction is reversible, it is not possible to distinguish whether the light and heavy by-products were formed via the n-butenes, isobutenes or a combination of both. From an examination of the coke profile (See Section 4.14), it could be concluded that coking was a function of the reaction products, i.e., the isobutene and / or the other by-products formed. Examining the hydrogenation selectivity it was found that this first decreased before levelling off as the residence time was increased. Although the catalyst has some hydrogenation activity, (See Section 4.3) it also may be proposed that some hydrogen and the paraffins, n-butane, isobutane, propane and ethane (See also Appendix 2), are formed during the formation of coke. Unfortunately, the degree of coking as a function of the residence time was not determined. The role of the water to hydrocarbon ratio on the performance of the catalyst is discussed in Section 4.4. In a commercial system the un-reacted n-butenes would be recycled to the isomerisation reactor after removal of the isobutene and by-products. The isomers of butene demonstrate quite different reactivities for simple electrophilic type addition reactions (Fajula and Gault, 1976:7691). This allows the selective removal of the isobutene from a mixture of its the isomers via the reaction with an alcohol to form a tertiary butyl ether. The build-up of the by-products would however have to be controlled via a

purge, also resulting in the loss of n-butenes. Hence, to minimise losses of n-butene, first the isobutene selectivity and second the total conversion per pass has to be maximised while the loss of butenes must be minimised. In this study performed at an average water to hydrocarbon ratio of 2.1, temperature of 531°C and pressure of 148 kPa(a), this was achieved at a hydrocarbon LHSV of 2.1 hr^{-1}, i.e., residence time of 1.2 seconds.

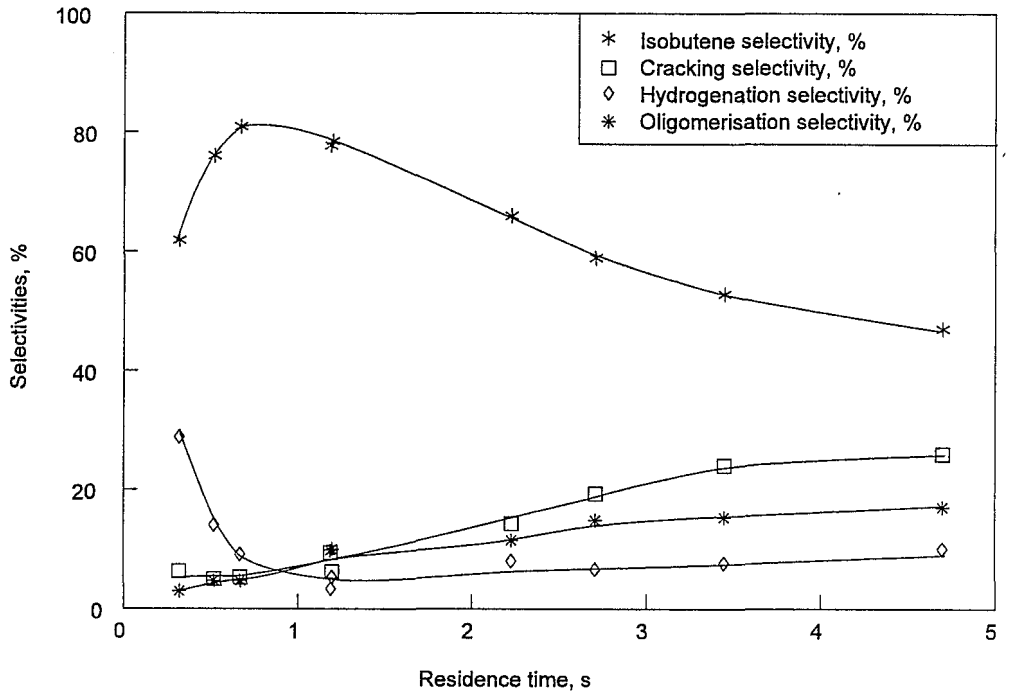

Figure 4.3 : Effect of the residence time on the isobutene, hydrogenation, cracking and oligomerisation selectivities

TABLE 4.2 : N-BUTENE ISOMERISATION SELECTIVITIES VS RESIDENCE TIME

Residence Time, s	0.32	0.52	0.67	1.19	1.20	2.23	2.71	3.45	4.70
C4 Cut LHSV, h^{-1}	5.51	5.01	3.27	1.96	1.96	1.04	0.80	0.55	0.52
n-Butene Conversion, %	10.8	16.2	21.7	29.3	30.9	38.8	42.1	45.9	46.7
Isobutene Yield, %	6.7	12.3	17.5	22.8	24.3	25.6	24.8	24.3	22.0
Loss of Butenes, %	3.7	3.5	3.7	5.9	6.0	11.1	15.6	19.5	22.2
Isobutene Selectivity, %	61.9	76.1	80.9	77.8	78.5	66.1	59.0	52.9	47.2
Cracking Selectivity, %	6.3	5.0	5.3	9.4	6.2	14.3	19.3	24.1	26.0
Hydrogenation Selectivity, %	28.9	14.1	9.1	9.5	9.9	8.1	6.7	7.7	10.1
Oligomerisation Selectivity, %	2.9	4.7	4.7	3.3	5.4	11.5	14.9	15.4	17.0

Finally, if the products are at equilibrium, the performance of the catalyst is thermodynamically as opposed to kinetically limited. In this case, it will not be possible to identify the reaction mechanism of the n-butene skeletal isomerisation reaction. The results from a detailed inspection of the data used while attempting to identify the reaction mechanism, as discussed in detail in Chapter 6, are presented in Chapter 5.

4.3 EFFECT OF N-BUTENE PARTIAL PRESSURE

The effect of the n-butene partial pressure in the combined feed on the n-butene skeletal isomerisation activity of the catalyst was investigated. Two separate studies were performed using either n-butane or hydrogen as a diluent. In the latter case the existence of a hydrogenation / dehydrogenation step in the n-butene skeletal isomerisation mechanism was also investigated.

Using n-butane as a diluent, a variety of hydrocarbon feed mixtures were prepared. Maintaining a constant total hydrocarbon LHSV of 2 h^{-1} and water to total hydrocarbon ratio of one, the effect of the n-butene partial pressure in the combined feed on the n-butene skeletal isomerisation activity of the catalyst was quantified. Of course, adjusting the composition of the hydrocarbon feed while maintaining a constant residence time, will result in a change in the actual water to n-butene ratio while the n-butene LHSV will also change. The actual values used in this study are shown in Table 4.3 while selected results obtained are shown in Figure 4.4. Examining the data shown in Figure 4.4, it may be proposed that the isomerisation performance of the catalyst is independent of the n-butene partial pressure in the combined feed, if this is between 20 kPa(a) and 60 kPa(a). The residence times used during this study of 1.8 s is in close to the limit of 2.2 s identified previously (See Section 4.2), beyond which the n-butene skeletal isomerisation performance of the catalyst is predominately thermodynamically as opposed to kinetically limited. That during this study the performance of the catalyst was indeed thermodynamically as opposed to kinetically limited was further confirmed by the fact that the partial pressure ratios of isobutene to n-butene in the product gas were between 0.57 and 0.62 throughout this study. The value measured at these conditions by Kilpatrick et

al. (1946:559) being 0.6. Hence, the independence of the butene isomerisation performance of the catalyst from the n-butene partial pressure in the feed is not surprising as the performance of the catalyst was thermodynamically as opposed to kinetically controlled.

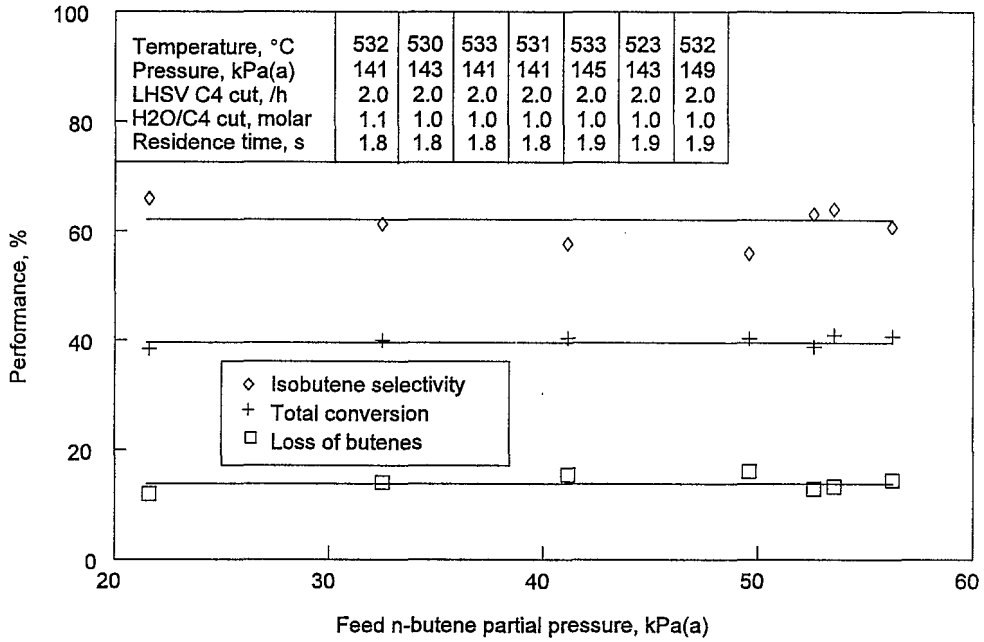

Figure 4.4 : Effect of the n-butene partial pressure in the feed on the n-butene conversion, isobutene selectivity and loss of butenes

TABLE 4.3 : EFFECT OF THE N-BUTENE PARTIAL PRESSURE ON PERFORMANCE

n-Butene Partial Pressure, kPa(a)	21.61	32.50	41.15	49.60	52.60	53.54	56.25
n-Butene LHSV, h^{-1}	0.62	0.89	1.13	1.36	1.47	1.39	1.51
H2O / n-Butene Ratio, molar	3.38	2.23	1.74	1.42	1.34	1.41	1.32
n-Butene Conversion, %	38.47	40.00	40.43	40.39	41.04	38.89	40.78
Isobutene Yield, %	25.38	24.52	23.32	22.59	24.58	26.32	24.81
Loss of Butenes, %	11.97	14.05	15.47	16.09	13.35	12.93	14.48
Isobutene Selectivity, %	65.97	61.30	57.69	55.98	64.13	63.20	60.85
Cracking Selectivity, %	19.16	20.79	21.71	27.23	21.48	22.41	22.27
Hydrogenation Selectivity, %	5.09	5.31	5.95	4.38	2.37	2.73	4.86
Oligomerisation Selectivity, %	9.77	12.59	14.64	12.40	12.05	11.63	12.52

Examining the selectivities to the by-products as shown in Table 4.3, no clear trend in the cracking, oligomerisation or hydrogenation selectivity could be observed.

The n-butene partial pressure in the feed can also be adjusted by co-feeding a permanent gas such as hydrogen. Maintaining an average hydrocarbon LHSV of 2 h^{-1}, while increasing the hydrogen flow rate, will not only result in a decrease in the n-butene partial pressure but the water partial pressure and the total residence time as well. Of course in this case, as opposed to when using n-butane as a diluent, the water to butene ratio was not effected. The actual values used / calculated during this study are shown in Table 4.4 while selected results are shown Figure 4.5.

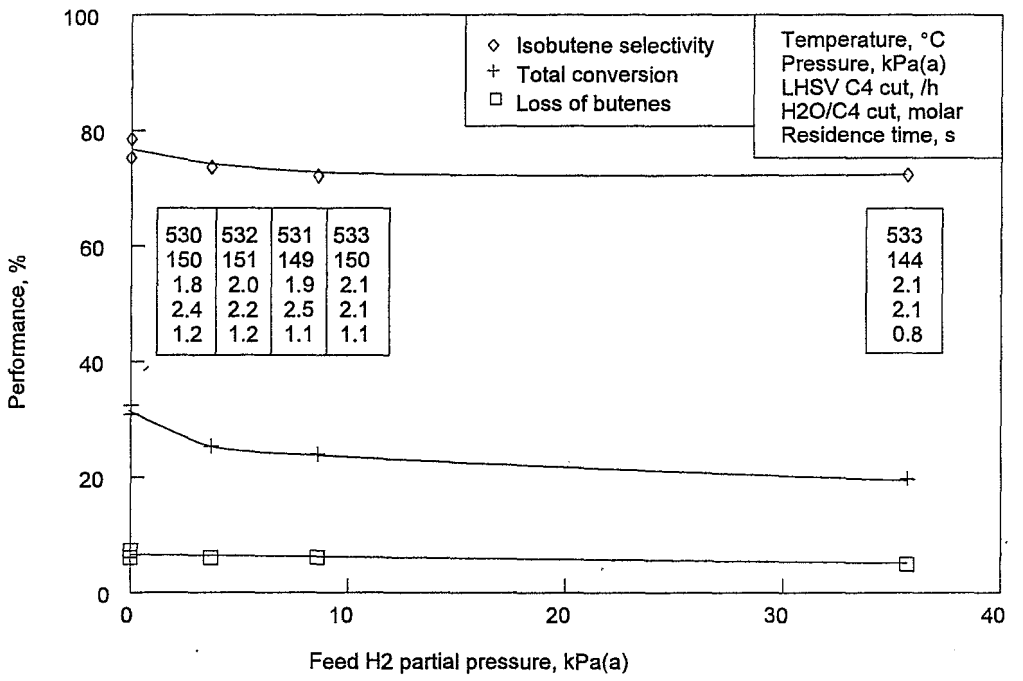

Figure 4.5 : Effect of the hydrogen partial pressure in the feed on the n-butene conversion, isobutene selectivity and loss of butenes.

The isobutene to n-butene partial pressure ratio in the product was found to increase from 0.3 to 0.5 as the n-butene partial pressure in the feed was increased. As at an isobutene to n-butene ratio in the product of below 0.5 it may be assumed that the performance of the catalyst is predominately kinetically controlled, the observed increase in the total conversion with increasing n-butene partial pressure in the feed is as expected. Similarly,

at a constant n-butene and water partial pressure in the feed of 34 kPa(a) and 104 kPa(a) respectively, it was previously shown in Section 4.2 that the isobutene selectivity and loss of butene are essentially independent of the residence time, of between 0.84 s and 1.24 s (See Figure 4.2) while the total conversion increases. Hence, the two effects are complementing each other, i.e., leading to an increase in the total conversion while the loss of butenes and the isobutene selectivity remain constant.

TABLE 4.4 : SELECTIVITIES VS HYDROGEN PARTIAL PRESSURE

Hydrogen Partial Pressure, kPa(a)	0	0	3.7	8.6	35.7
n-Butene Partial Pressure, kPa(a)	32.9	34.6	30.8	34.4	26.4
Water Partial Pressure, kPa(a)	105.6	104.1	104.1	95.6	73.0
Residence Time, s	1.24	1.19	1.11	1.08	0.84
n-Butene Conversion, %	30.9	32.5	25.3	24.0	19.7
Isobutene Yield, %	24.4	24.3	18.7	17.3	14.3
Loss of Butenes, %	7.2	6.0	6.0	6.1	5.0
Isobutene Selectivity, %	75.3	78.5	73.6	72.1	72.3
Cracking Selectivity, %	11.1	6.2	9.8	10.4	10.2
Hydrogenation Selectivity, %	10.9	10.0	12.0	12.3	14.5
Oligomerisation Selectivity, %	2.7	5.4	4.6	5.3	3.0

Examining the selectivities to the side reactions, based on the n-C4" converted it may be seen from Table 4.4 that these with the possible exception of the hydrogenation selectivity are essentially independent of the operating conditions used. As hydrogenation is thermodynamically favoured at the reaction conditions used, a more dramatic increase in the hydrogenation selectivity would be expected as the hydrogen partial pressure was increased if the catalyst contained a hydrogenation / dehydrogenation function. The slight sensitivity of the hydrogenation selectivity to the hydrogen partial pressure suggests that homogeneous hydrogenation occurred. However, this result shows that a hydrogenation / dehydrogenation step does not form part of the n-butene skeletal isomerisation mechanism. This result supports those reported in the literature as discussed below. Examining the n-butane to isobutane partial pressure ratio in the products, it was found that these remained approximately constant at 8.5 irrespective of the hydrogen partial

pressure used. The ratio of n-butane to isobutane in the feed was slightly lower at 8.0, suggesting a marginal preference for the formation of isobutane as opposed to n-butane.

The hydrogenation of the butenes, is a highly exothermic reaction with the average value for the four isomers being ΔH_{750K} = -29.86 kcal·mol^{-1}, and thermodynamically feasible, in accordance with the criteria proposed by Richardson (1980:92), with the average Gibbs free energy being ΔG_{750K} = -5.7 kcal·mol^{-1}. (See Chapter 2, Section 2.3.4 for further details). Hence, a n-butene skeletal isomerisation catalyst should not contain a hydrogenation / dehydrogenating function, as this would lead to the formation of paraffins as opposed to the desired iso-olefins if hydrogen is present. That a hydrogenation or dehydrogenation function is not required for the isomerisation reaction or by-product formation was also confirmed by Bianchi et al. (1994:557) and Simon (1994:485), who co-feeding hydrogen found no significant change in the isobutene or by-product formation rates. Bianchi et al. (1994:557) did observe hydrogen as a product during the conversion of the n-butenes to isobutene over a B/Al-BETA zeolite, but their data suggested no direct correlation between the isobutene formation and hydrogen production rates. They concluded that the hydrogen was formed via dehydrogenation during the formation of by-products. Furthermore, co-feeding hydrogen, had no effect on the isobutene formation rate, confirming that hydrogen does not participate in the bond and / or skeletal isomerisation mechanism of the butenes as was proposed previously.

4.4 EFFECT OF WATER

An amorphous silica alumina catalyst was used during this study. The most suitable form of these, are aluminas the surface of which has been modified with silica (See also Section 2.5.7 and 2.6.7). X-ray examination of this type of catalyst showed that no significant change in the physical and chemical characteristics of the starting alumina occurred during preparation (Forlani et al., 1991:243) and that active sites comparable to those on alumina and silica alumina were formed. Hence, the material will exhibit properties similar to those of alumina and silica alumina as was shown by Nilsen et al. (1986:342). A detailed review of the literature dealing with the surface properties of both alumina and silica alumina was

thus done, as presented in Chapter 2, Section 2.5. Some of the more pertinent aspects dealing with the effect of water on the nature of the acid sites on the surface of the catalyst are discussed below.

Pure alumina is activated via out gassing or calcining by which a complex variety of surface groups are formed. The primary change that occurs during the activation is the removal of most of the hydroxyl groups, with those that remain still being non-acidic but existing in a variety of coordinated states (Peri, 1965:215). Adding water to a dehydrated alumina will result in the interaction of the water with the Lewis acid site, most probably through co-ordination with an exposed aluminum ion, to form Brønsted sites. However, after co-ordination, the adsorbed water molecule may ionize and the resulting hydroxyl group may locate itself in an anionic vacancy in the oxide layer while the proton drops into a cationic vacancy in the next layer. These protons, trapped in the cationic vacancies are inactive protons. They are not readily accessible to promote surface reactions unless enough energy has been furnished so that they can dissociate themselves from the cationic vacancy. Tung and Mcininch (1964:237) found that the thermal energy required to achieve this corresponds to temperatures in excess of 400°C.

The 'deactivating' effect of water on the double bond isomerisation activity of alumina was also observed by Gerberich and Hall (1966:103). They found that as the water content of the alumina catalyst was increased, so the 1-butene bond isomerisation activity decreased. They concluded from this that the Lewis acid sites on the surface of the alumina react with water to form Brønsted acids, which are trapped in the cationic vacancies and are thus unable to partake in the reactions. Their results further suggest that bond isomerisation of 1-butene over pure alumina is catalised by Lewis acidity while Brønsted acidity is required to catalise n-butene skeletal isomerisation. Hughes et al. (1969:64), also showed that the exposure of the dehydrated surface of a fluorinated alumina to water vapour resulted in an increase in the concentration of Brønsted acid sites at the expense of Lewis acid sites, i.e., that the Lewis acid sites were converted to Brønsted acid sites. Similar results have been reported for silica alumina. Tamele (1950:270) suggested that interaction between the aluminum, silicon and highly electrophilic oxygen atoms results in an increase in the strength of the Lewis acid site. These Lewis acid sites can easily be

converted to Brønsted acid by the donation of a lone pair of electrons from the oxygen atom in the water molecule. This results in the hydroxide ion being stabilized there by resulting in the heterolytic cleavage of the water. The remaining proton is only weakly held by columbic forces, i.e., a Brønsted acid site is formed.

As discussed in Chapter 2 and above, the surface of a dehydrated alumina catalyst contains mainly Lewis acid sites. According to literature, steaming the material prior to, and using water during, the on-line period results in the conversion of these Lewis acid sites to Brønsted acid sites. To confirm the effect of water on the acid sites, the strength of the acid sites, using ammonia temperature programmed desorption (NH_4-TPD), before and after steaming was determined, as discussed in Section 4.4.6. In parallel to this, the need to co-feed water during the on-line period, to ensure the desired performance, was examined in detail. The results from the various investigation performed are presented in this section.

4.4.1 WATER TO HYDROCARBON RATIO

Shown in Figure 4.6 and Table 4.5 are the isobutene selectivity and total conversion recorded during two separate experiments using a water to hydrocarbon ratio of one and two respectively. It was found that decreasing the water to hydrocarbon ratio from two to one while simultaneously increasing the residence time from 1.2 s to 1.9 s and the n-butene partial pressure from 39 kPa(a) to 62 kPa(a), resulted in a large decrease in the isobutene selectivity and a slight increase in the total conversion while the isobutene yield remained approximately constant.

As was shown previously in Section 4.3, the isomerisation activity of the catalyst is independent of the n-butene partial pressure in the feed if this is between 20 kPa(a) and 60 kPa(a). Hence, the behaviour observed can not be attributed to the increase in the butene partial pressure of the feed from 39 kPa(a) to 62 kPa(a) as the water to hydrocarbon ratio was decreased from 2 to 1. Next, examining the data presented in Section 4.2, Figure 4.2, where the effect of the residence time is shown, it may be seen

that at a water to hydrocarbon ratio of 2, increasing the residence time from 1.2 to 1.9 seconds results in a ±10 percentage point decrease in the isobutene selectivity and a ±5 percentage point increase in the total conversion.

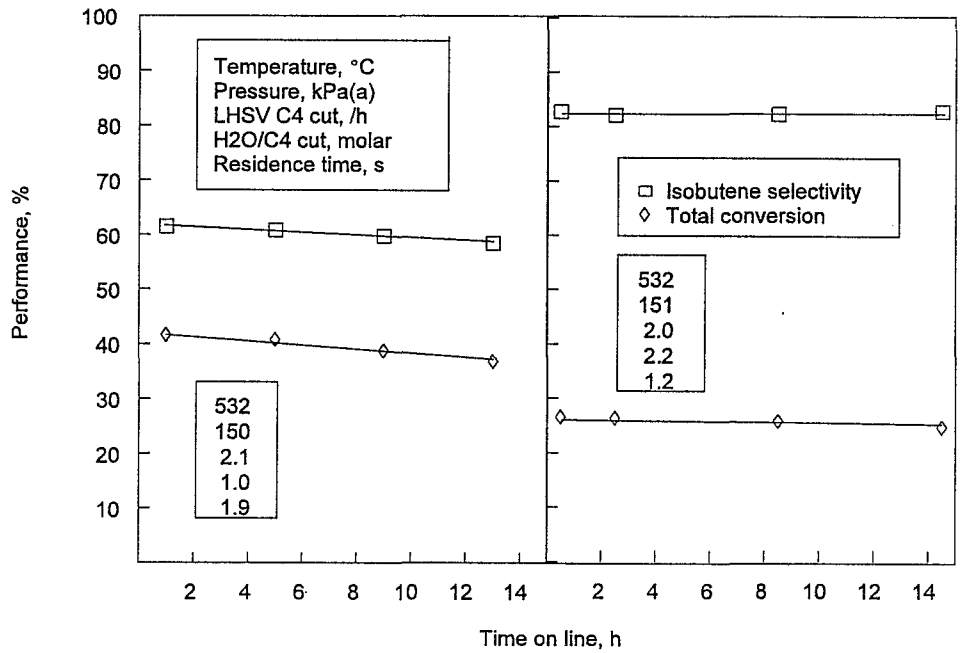

Figure 4.6 Effect of water to hydrocarbon ratio on the isobutene selectivity and total conversion

TABLE 4.5 : CATALYST PERFORMANCE VS WATER TO HYDROCARBON RATIO

Time On Line, h	1.0	5.0	9.0	13.0	0.5	2.5	8.5	14.5
n-Butene Conversion, %	41.6	40.8	38.8	36.1	26.4	26.4	25.8	25.1
Isobutene Yield, %	25.6	24.8	23.2	21.1	22.0	21.7	21.2	20.6
Loss of Butenes, %	14.3	14.5	14.3	14.0	4.2	4.2	4.1	3.8
Isobutene Selectivity, %	61.5	60.9	59.8	58.5	82.7	82.1	82.3	82.8
Cracking Selectivity, %	22.1	22.3	22.5	22.8	8.9	9.6	8.5	8.3
Hydrogenation Selectivity, %	1.2	1.9	2.4	2.9	1.9	2.6	3.1	2.9
Oligomerisation Selectivity, %	15.2	15.0	15.4	15.8	6.5	5.7	6.1	6.0
Water / hydrocarbon ratio, mol	1				2			

Comparing this to the approximately 20 percentage point decrease in the isobutene selectivity and 10 percentage point increase in the total conversion when increasing the residence time from 1.2 to 1.9 s by decreasing the water to hydrocarbon ratio from 2 to 1,

suggests that the results shown in Figure 4.6 are not entirely due to the changing residence time. Hence, it may be concluded that the changes in the performance of the catalyst may also be attributed to the changing water to hydrocarbon ratio.

Examining the selectivities to by-products as shown in Table 4.5, it may be seen that increasing the water to hydrocarbon ratio from one to two resulted in a decrease in the cracking and oligomerisation selectivities, while no clear trend in the hydrogenation selectivity was observable. From these results it may be concluded that at the lower water to hydrocarbon ratio the nature and / or strength of the acid sites changes to those favouring by-product formation. Also, at a water to hydrocarbon ratio of one, the activity of the catalyst decreased during the 13 hr on-line period, while at a ratio of two less deactivation was observed. The activity of the catalyst fully recovered after regeneration confirming that the increased rate of deactivation observed at a reduced water to hydrocarbon ratio is due to increased coking. Consequently, to ensure stable operation and a high isobutene selectivity a water to hydrocarbon ratio of two has to be used. See also Appendix 1 for the various definitions of the terms and Appendix 2 for a detailed sample analysis

4.4.2 WATER ELIMINATION

To confirm the necessity for co-feeding water, the effect of eliminating it completely from the system was investigated. Keeping all else constant, nitrogen was used as the carrier during the purging, regeneration and on-line periods. The results obtained are shown in Figure 4.7 and Table 4.6.

It may be seen by comparing the results obtained when co-feeding water, at a similar residence time and n-butene partial pressure, as shown in the right hand side of Figure 4.6 with those shown in Figure 4.7, that in the absence of water a lower than normal initial selectivity, 60 % as opposed to 82 % and similar total conversions of 25 % were achieved. However, the catalyst rapidly lost activity with the isobutene yield being about 3 mass % after 7 hours on-line as opposed to a steady 25 mass % when water was co-fed.

Examining the selectivities to by-products as shown in Table 4.6, during the seven hour on line period, isobutene selectivity decreased while cracking and hydrogenation selectivities increased. No clear trend in the oligomerisation selectivity could be observed while the loss of butene remained approximately constant.

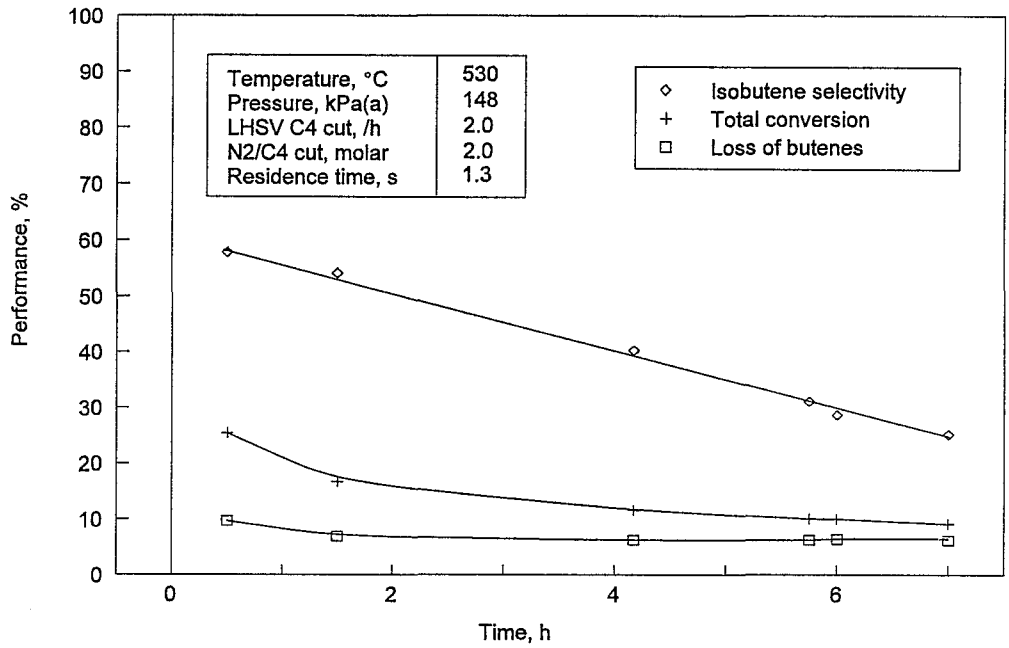

Figure 4.7 : Effect of substituting water with nitrogen during the on-line period on the isobutene selectivity, total conversion and loss of butenes

TABLE 4.6 : CATALYST PERFORMANCE VS TIME ON LINE - NO WATER ADDED

Time On Line, h	0.5	1.5	4.2	5.8	6.0	7.0
n-Butene Conversion, %	25.3	16.7	11.6	10.1	10.0	9.2
Isobutene Yield, %	14.6	9.0	4.7	3.1	2.9	2.3
Loss of Butenes, %	9.6	6.9	6.2	6.2	6.4	6.2
Isobutene Selectivity, %	57.8	54.1	40.3	31.2	28.8	25.2
Cracking Selectivity, %	25.6	31.4	35.7	39.4	39.9	42.1
Hydrogenation Selectivity, %	7.1	10.1	18.1	24.7	24.5	29.0
Oligomerisation Selectivity, %	9.5	4.3	5.8	4.7	6.9	3.7

These results confirm the proposal made previously that in the absence of water the sites on the catalyst are modified to those favouring the formation of by-products and coking. In view of the results reported by other workers, as discussed previously in Section 2.5, it

may be concluded that, the Brønsted acid sites required for the n-butene skeletal isomerisation reaction are not formed in the absence of water, and that the Lewis acid sites on the surface are responsible for the formation of the by-products and coke.

4.4.3 ACID SITE STABILITY

Using a bench reactor system containing 4.35 g of catalyst previously calcined ex-situ at 700°C for 1 hr, operated at a water to hydrocarbon mole ratio two, temperature of 520°C, hydrocarbon (1-butene) liquid hourly space velocity of 2 h^{-1} and total pressure of 150 kPa(a), the response of the catalyst to the sudden absence of water was investigated. After 7 hrs on line, the water pump was stopped, which resulted in the residence time increasing from 1.3 s to 3.8 s and the n-butene partial pressure from 50 kPa(a) to 150 kPa(a). The performance of the catalyst was monitored for an additional 15 hrs. The results from this test are shown in Figure 4.8 and Table 4.7.

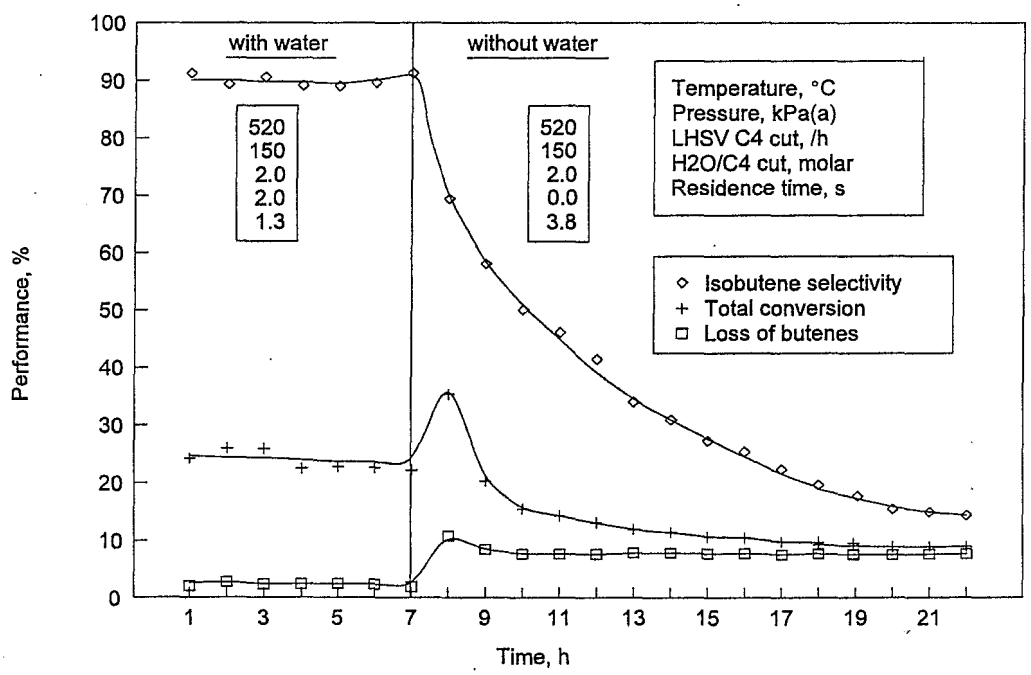

Figure 4.8 : Effect of interruption in the water flow on the isobutene selectivity, total conversion and loss of butenes

The changes in the iso-butene selectivity, the total conversion and the loss of butenes shown in Figure 4.8, from the second hour after the interruption of the water flow onwards, i.e., during the ninth to the sixteenth hour on line, were similar to those observed previously when the water was replaced by nitrogen from the start of the on-line period, i.e., the system was operated at the base case conditions, a residence time of 1.2 s and n-butene partial pressure in the feed of 40 kPa(a). Hence, it is more likely that the trends in the performance of the catalyst observed during this study are not due to the three fold increase, from 50 to 150 kPa(a) of the n-butene partial pressure in the feed or the increase in the residence time from 1.3 s to 3.8 s, but the absence of water as such.

TABLE 4.7 : EFFECT OF WATER STARVATION (BENCH REACTOR)

Time, hr	2	4	6	8	12	16	20
n-Butene Conversion, %	26.0	22.5	22.6	33.4	13.1	10.5	9.0
Isobutene Yield, %	23.2	20.1	20.3	23.2	5.4	2.7	1.4
Loss of Butenes, %	2.8	2.4	2.3	10.8	7.7	7.8	7.6
Isobutene Selectivity, %	89.4	89.2	89.7	69.4	41.4	25.5	15.5
Cracking Selectivity, %	8.5	4.1	4.6	12.9	21.7	23.9	24.1
Hydrogenation Selectivity, %	0.7	0.6	0.7	5.7	25.7	46.6	56.6
Oligomerisation Selectivity, %	1.5	6.2	5.5	11.9	11.9	4.0	3.9
Residence Time, s	1.3	1.3	1.3	3.8	3.8	3.8	3.8
Water Addition	Yes			No			

It may further be postulated that the surface of the catalyst does not respond instantaneously to the absence of water. According to the results shown in Figure 4.2, an increase in the residence time from 1.3 to 3.8 seconds, at a constant water to hydrocarbon ratio of 2, leads to a 30 percentage point decrease in the iso-butene selectivity and a 15 percentage point increase in the total conversion. Examining the data shown in Figure 4.8 similar changes in both the selectivity and total conversion were observed at the end of the first hour after stopping the water pump. These changes may therefore be attributed to the change in the residence time. However, as from than onwards the catalyst performed similarly to a material that was not hydrated prior to the introduction of the n-butene (See Section 4.4.2), it may be concluded that the surface of the catalyst is effectively dehydrated after one hour.

4.4.4 ACID SITE REGENERATION / STABILITY

To determine whether the surface of the catalyst would recover upon the re-introduction of water, the effect of interrupting the water supply, i.e., repeatedly operating the system in the absence of water at an increased hydrocarbon partial pressure of 150 kPa(a) as opposed to 50 kPa(a) and residence time of 3.8 s as opposed to 1.3 s, on the overall performance of the catalyst was examined. Selected results recorded during this investigation are shown in Figure 4.9.

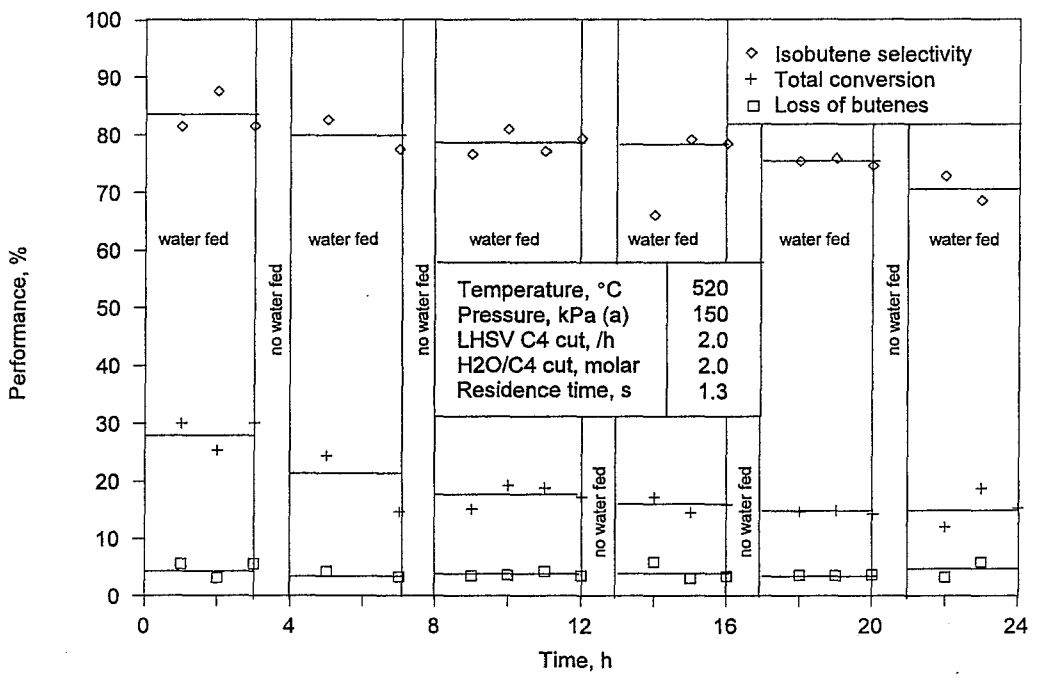

Figure 4.9 : Effect of repeated water starvation on the isobutene selectivity, total conversion and loss of butenes during the on-line period

As can be seen from Figure 4.9 the repeated interruptions in the water flow cause a continuous decrease in both the selectivity and the activity of the catalyst and that the effect was accumulative, i.e., the surface could not be regenerated by re-introduction of water. This not only supports the conclusion reached previously that the surface of the catalyst is not stable in the absence of water but also that the deactivation observed is due to the deposition of coke, i.e., that the active sites are blocked by carbonaceous deposits that require an air treatment to be removed.

4.4.5 WATER STARVED CATALYST REGENERATION

The results collected previously suggest that irrespective of the n-butene partial pressure, decreasing the water partial pressure results in an increase in the by-product formation and carbon deposition rate. Operating the catalyst in the absence of water may damage the material if the carbon deposited is of a form that can not be removed using the standard regeneration procedure. To test this, a series of experiments were performed where the catalyst was operated at the base case conditions before and after having been starved of water, i.e. operated at a higher butene partial pressure and residence time. The catalyst was then regenerated and the cycle repeated with the interruption in the water flow becoming progressively longer. The results from this investigation are shown in Figure 4.10.

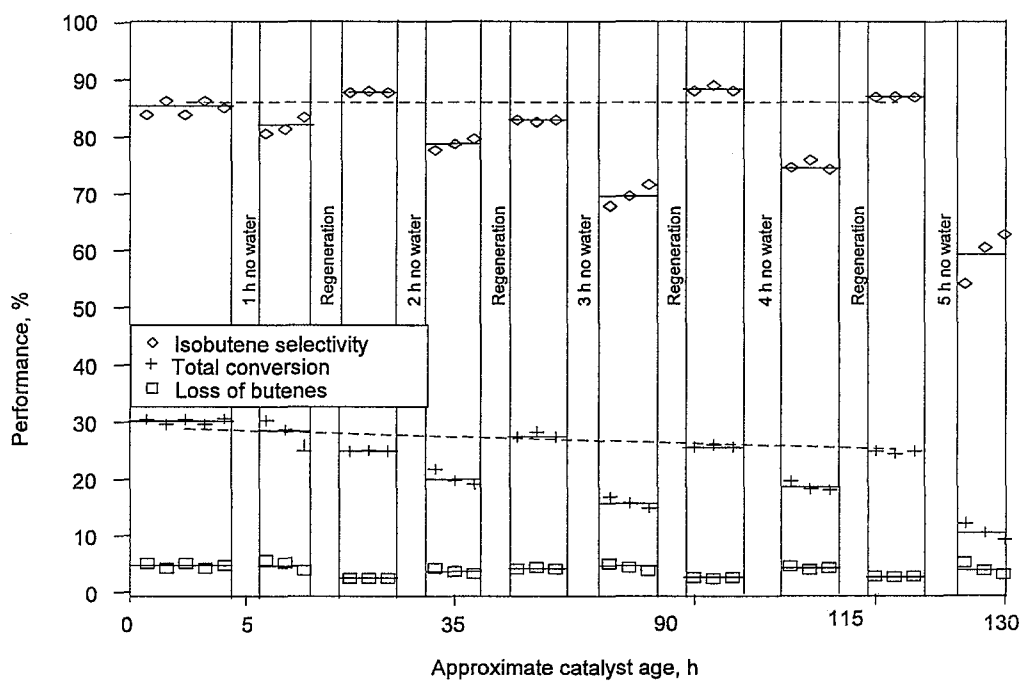

Figure 4.10 : Effect of repeated water starvation and regeneration on the isobutene selectivity, total conversion and loss of butenes

It was found, as observed previously, that an interruption of as little as 1 hour in the water flow causes a decrease in the both the activity of the catalyst and the iso-butene selectivity and that in general the severity of the decrease was proportional to the duration of the interruption in the water flow.

Examining the initial activity and iso-butene selectivity of the regenerated catalyst during consecutive on line periods, as indicated by the dashed lines in Figure 4.10, suggests that the activity of the catalyst decreased irreversibly after the catalyst was operated in the absence of water. The selectivity after regeneration was not effected by interruptions in the water flow. As the decrease in the activity observed after an interruption in the water flow was substantially greater than that observed after regeneration, it may be concluded that the changes in the performance of the catalyst in the absence of water are due to pore blockage via carbon deposits. However, the decrease in the initial activity after regeneration suggests that the catalyst was permanently altered when operated in the absence of water, possibly via sintering of the smaller pores. The change observed could be due to graphitic coke that may have been formed in the absence of water and was not removed during the subsequent regeneration, or due to sintering of the catalyst. That the catalyst did sintered during the 107 on-line and regeneration cycles, and that no graphitic coke was present on the material, was confirmed from an investigation of the physical properties of the fresh and unloaded catalyst, and a thermogravimetric investigation respectively, as discussed in detail in Section 4.13.

4.4.6 ACIDITY MEASUREMENTS

In an attempt to quantify the effect of water on the relative strength of the acid sites, before and after hydration, an ammonia temperature programmed desorption (NH_4-TPD) was performed. After calcining the catalyst at 700°C, half of the material was steamed at 520°C for 12 h before performing the NH_4-TPD studies. In addition to this, using a thermogravimetric procedure (TGA) the temperature required to remove the water from the surface of the steamed catalyst was determined.

During the NH_4-TPD studies, the material was flushed at room temperature for 10 minutes with helium at a rate of 40 ml_n/min. Next, also at room temperature, the material was flushed for 1 h, using a mixture of 4.95 mass % ammonia in helium at a rate of 40 ml_n/h. Upon the completion of this step and to remove any free ammonia, the material was once again flushed at room temperature using helium at a rate of 40 ml_n/h for 16 h. To establish

the relative strength of the acid sites, the catalyst was heated to a final temperature of 550°C under flowing helium and the ammonia concentration in the flue gas measured as a function of temperature. As an independent check, the desorbed ammonia was neutralised in a 0.1 N sulphuric acid solution. By back titration the quantity of ammonia that was present on the catalyst, determined by integrating the desorption spectra, could be confirmed. The results from this investigation are shown in Table 4.8 below.

TABLE 4.8 : EFFECT OF STEAMING ON ACID STRENGTH

Sample	Peak maxima, °C	Integrated, $mmol \cdot g^{-1}$	Titration, $mmol \cdot g^{-1}$
Dry	106	0.89	0.86
Wet	93	0.81	0.85

To confirm that the water present on the steamed catalyst was not removed while flushing the catalyst with helium, a thermogravimetric gravimetric analysis (TGA) of both the dry and hydrated sample were performed. In each case, using a temperature ramp of $20°C \cdot min^{-1}$ to a final value of 700°C, the mass loss as a function of temperature was recorded. An initial mass loss of ±4 mass %, at temperatures below 110°C was observed in both cases. This mass loss is assumed to be due to the removal of the free moisture, i.e., water adsorbed from the atmosphere. Continuing to heat the hydrated sample, a second mass loss at approximately 195°C was observed. This second mass loss was not seen in the case of the dry sample or a sample hydrated at room temperature via immersion in water. From this, it may be concluded that an elevated temperature is required to enable the interaction of the water with the surface of the catalyst. Furthermore, the result suggests that the water which interacted with the surface is not removed at temperatures below 195°C. It may therefore be concluded from the results given in Table 4.8 that the acid sites on the surface of the hydrated catalyst are weaker, if only marginal so, than those on the dry surface.

4.4.7 EFFECT OF WATER - CONCLUSIONS

A consecutive reaction mechanism, as discussed in detail in Chapter 2, Section 2.3.3, i.e., [n-butene ⇌isobutene] → by-products, has been proposed in the literature (Bianchi et al., 1994:556, Choudhary and Doraiswamy, 1971:230 etc.). When interrupting the water flow, both the iso-butene selectivity and total conversion decrease while the selectivity to the by-products, particularly cracked and paraffinic components increases. From this it may be concluded that at reduced water partial pressures the relative rate of the reactions are altered, with the formation of gaseous by-products, and in view of the reduction in lifetime, coking, being favoured. It has been shown previously (Section 4.4.6) that the acid sites on the surface of the dehydrated catalyst are marginally stronger than those on the surface after hydration. Hence, based on the results reported in this study and the literature, see Chapter 2, Section 2.5 above, it may be concluded that the water interacts with the stronger Lewis sites present on the surface of a dehydrated alumina to form weaker Brønsted acid sites. From this it may be concluded that the stronger Lewis acid sites are more active in catalising the reactions of the butenes to by-products and coking while the weaker Brønstead acid sites are more active for the n-butene skeletal isomerisation reaction. That Brønstead acidity is required for skeletal isomerisation, while double bond isomerisation may be achieved with electron pair accepting, i.e., Lewis acidity, was previously proposed by Condon (1958:44).

Furthermore, the results recorded suggest that water is required to ensure the long-term stability of the catalyst. A permanent decrease in the activity of the catalyst was observed after operating the material in the absence of water. From an investigation of the physical properties of the fresh and spent catalyst, it was concluded that the catalyst sintered when exposed to hydrocarbons in the absence of water. See also Section 4.14 for further details.

4.5 EFFECT OF PRESSURE

It is to be expected that the skeletal isomerisation of the n-butenes to isobutene is not sensitive to the operating pressure as the total number of moles does not change. However, during the formation of coke a volume contraction may occur. To quantify the effect of pressure two experiments were conducted during which the system pressure was adjusted during the on-line period. Shown in Figure 4.11 and Table 4.9 is the response of the catalyst to a decrease in the total pressure and in Figure 4.12 and Table 4.10 the response to an increase in the total pressure.

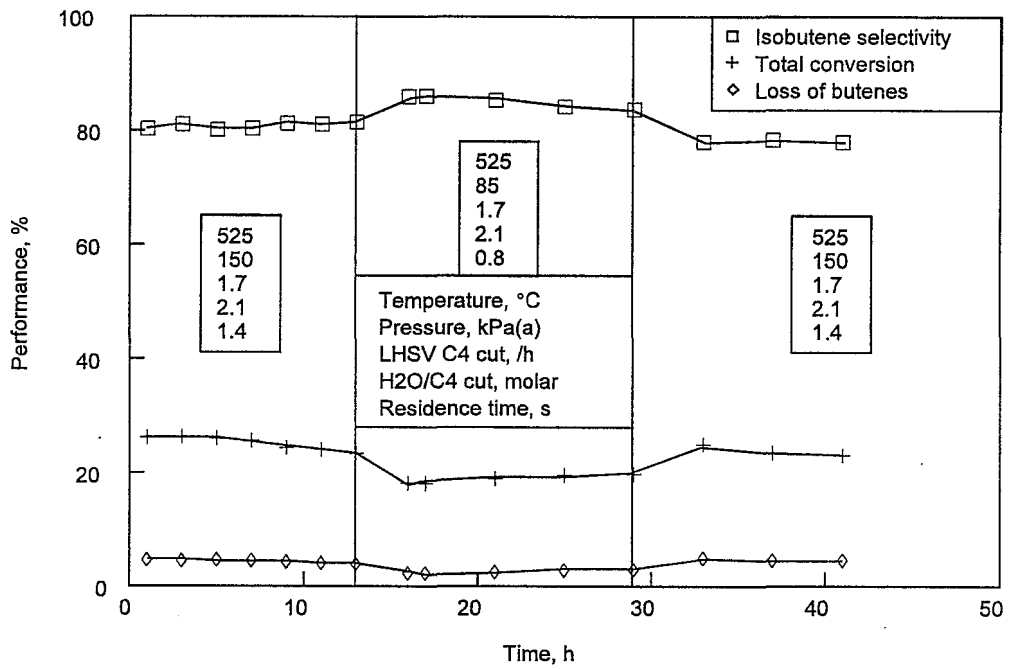

Figure 4.11 : Effect of decreasing the operating pressure on the n-butene skeletal isomerisation performance of the catalyst

As can be seen from Figure 4.11, and Table 4.9 decreasing the pressure from 150 to 85 kPa(a) and by default the residence time from 1.4 s to 0.8 s, and the n-butene partial pressure in the feed from 48 kPa(a) to 27 kPa(a), resulted in an increase in the selectivity of about 5, and a decrease in the conversion of about 6 percentage points. It was shown previously in Section 4.3 that the performance of the catalyst was not sensitive to changes in the n-butene partial pressure between 20 and 60 kPa(a). It may thus be concluded that the trends observed when decreasing the pressure could not be ascribed to changes in the n-butene partial pressure.

TABLE 4.9 : EFFECT OF DECREASING THE PRESSURE

Pressure, kPa(a)	150	85	150
Residence Time, s	1.4	0.8	1.4
n-Butene Conversion, %	25.0	18.7	22.9
Isobutene Yield, %	20.0	16.0	18.3
Loss of Butenes, %	4.3	2.5	4.3
Isobutene Selectivity, %	81	85.4	79.7
Cracking Selectivity, %	8.5	7.0	8.9
Hydrogenation Selectivity, %	3.5	3.0	4.8
Oligomerisation Selectivity, %	7.2	4.2	7.9
Isobutene to n-Butene Ratio	0.55	0.34	0.55

The effect of adjusting the residence time, with all else being held constant, was previously investigated, as discussed in Section 4.2. Comparing the results shown in Table 4.2 in Section 4.2 with those shown in Table 4.9 above, it was found that the trends observed in the performance of the catalyst when dropping the pressure and by default the decreasing the residence time, were identical to those observed when adjusting the residence time on its own. From this, it may be concluded that the trends observed during this study can be attributed to the decrease in the residence time and not the decrease in the total pressure. The effect of operating the system at a reduced pressure on the cycle lifetime, the time for the yield to drop to 90 % of the initial value, was not determined during this study. It may however be speculated that operating at reduced pressures will increase the cycle lifetime. After 33 hours on-line, the pressure was set back to 150 kPa(a), and the selectivity, conversion and the partial pressure ratios effectively returned to their initial values.

The effect of increasing the pressure from 150 to 585 kPa(a) and by default the residence time from 1.2 s to 4.7 s and the n-butene partial pressure in the feed from 33 kPa(a) to 128 kPa(a) is shown in Figure 4.12 and Table 4.10.

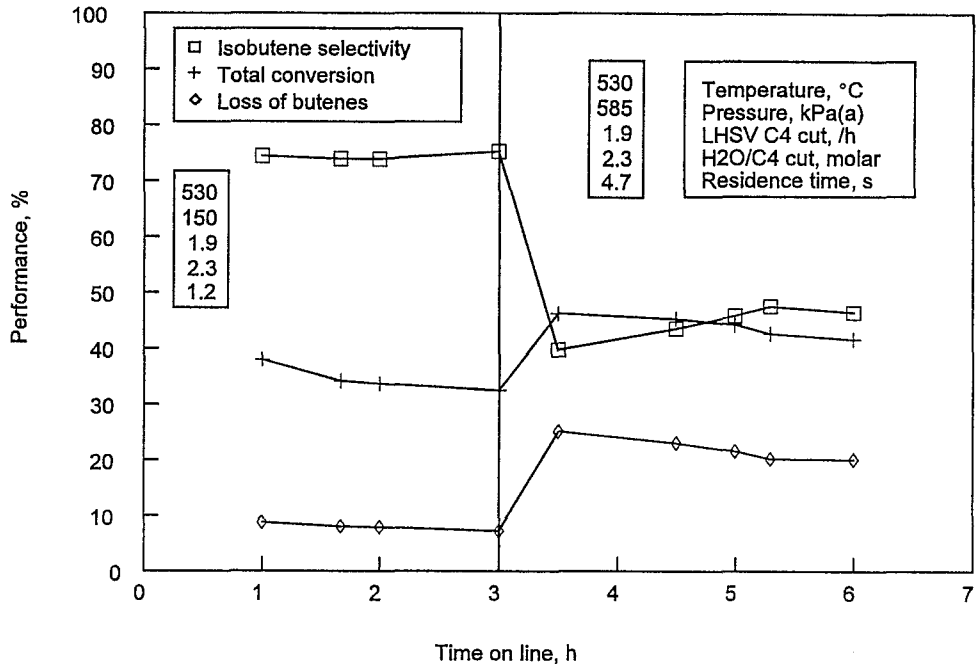

Figure 4.12 : Effect of increasing the total pressure on the isobutene selectivity, total conversion and loss of butenes

TABLE 4.10 : EFFECT OF INCREASING THE TOTAL PRESSURE ON PERFORMANCE

Pressure, kPa(a)	150				585				
Time On Line, h	1.0	1.7	2.0	3.0	3.5	4.5	5.0	5.3	6.0
n-Butene Conversion, %	37.9	34.1	33.7	32.5	46.3	45.3	44.3	42.6	41.6
Isobutene Yield, %	28.2	25.2	24.9	24.5	18.4	19.7	20.3	20.2	19.3
Loss of Butenes, %	8.8	8.0	7.9	7.2	25.1	23.0	21.6	20.2	20.1
Isobutene Selectivity, %	74.4	73.9	73.9	75.3	39.8	43.5	45.9	47.5	46.4
Cracking Selectivity, %	14.5	14.2	12.3	11.1	25.8	23.1	21.9	20.3	21.4
Hydrogenation Selectivity, %	1.5	2.5	2.6	2.7	11.6	12.3	12.4	12.7	14.2
Oligomerisation Selectivity, %	9.6	9.3	11.2	10.9	22.8	21.2	19.8	19.6	17.9

Increasing the pressure resulted in a decrease in the isobutene selectivity and an increase in the total conversion, while the isobutene to n-butene partial pressure ratio in the product gas remained unchanged at 0.50. The latter is not surprising as, at a residence time in excess of 2.2 s it was previously shown in Section 4.2 that the performance of the catalyst is predominately thermodynamically as opposed to kinetically controlled. This suggests, together with the conclusion reached previously in Section 4.2 that increasing the n-butene

partial pressure to as high as 150 kPa(a) at a residence time of 3.8 s had no effect on the skeletal isomerisation performance of the catalyst, that the changes in the performance of the catalyst observed when, increasing the total pressure can not be ascribed to the corresponding increase in the n-butene partial pressure from 33 kPa(a) to 128 kPa(a). The response to increasing the pressure must therefore be ascribed to the increase in either the residence time or the total pressure. The isobutene selectivity recovered slightly with time on-line levelling off at approximately 25 percentage points below that obtained at a pressure of 150 kPa(a).

Inspecting the results obtained six hours after increasing the total pressure and simultaneously the residence time to 4.7 s with those obtained when increasing the residence time to 4.7 s at a total pressure of 150 kPa(a), as shown in Table 4.2 in Section 4.2, it was found that almost identical results were obtained. From this it may be concluded that the changes in the performance of the catalyst are due to the change in the residence time and not the total or n-butene partial pressure. In view of the results presented when decreasing or increasing the total pressure, it may be concluded that the effect of pressure on the n-butene skeletal isomerisation performance of the catalyst is an indirect one, due to its effect on the residence time. This suggests that it may be possible to operate the catalyst at elevated pressure but reduced residence times without effecting the overall performance of the catalyst. The effect of operating at an elevated pressure but reduced residence time on the cycle lifetime, the time for the isobutene yield to drop to 90 % of its starting value, was not investigated during this study. As operation at elevated pressures would be beneficial on technical grounds, the effect of operating at elevated pressures and reduced residence times should be investigated. No references in the literature discussing the relationship between the total pressure and the residence time could be found.

4.6 EFFECT OF TEMPERATURE

After calculating the thermodynamic equilibrium composition of the four butene isomers, as discussed in Chapter 2, Section 2.3.6, it was found that to maximize the

isobutene yield, the reaction temperature should be held as low as possible. However, Frost et al. (1936:373) found that below 300°C the reaction products consisted mainly of the oligomers of butene. Choudhary and Doraiswamy (1975:227) recorded bond and skeletal isomerisation activity between 300°C and 550°C, with cracking being the main reaction at higher temperatures. The temperature limits were also studied by Tung and Mcininch (1964:233) who found that 1-butene isomerisation proceeds in stages. At lower temperatures, only bond isomerisation was observed with the products reaching equilibrium composition at approximately 200°C. This equilibrium composition prevails until 310°C when isobutene was first detected. The concentration of isobutene continues to increase with temperature until at about 475°C cracked products were first observed. It was concluded by them that these limits are valid for most acidic catalysts suitable for butene skeletal isomerisation.

The minimum temperature at which the skeletal isomerisation catalyst was active for double bond and skeletal isomerisation was also established during this study. This was achieved by increasing the reaction temperature in steps of 50°C, at two hourly intervals, from 100°C to 550°C. No attempt was made to ensure that the system reached steady state at each temperature or to control the residence time, which decreased from 2.3 s to 1.1 s as the temperature was increased, as the main objective of this study was to determine the limit for the subsequent and more detailed investigation.

From the results obtained, as shown in Figure 4.13, it can tentatively be concluded that the catalyst is inactive at temperatures below 200°C, that above 250°C double bond isomerisation occurs, with skeletal and bond isomerisation taking place at temperatures above 450°C. These results support those reported previously in the open literature.

To complete this investigation the effect of raising the temperature every 3 h by 10°C, from 490°C to 550°C, at a constant residence time of 1.5 s on the overall performance of the catalyst, was recorded. The results from this investigation are shown in Figure 4.14 and Table 4.11. As can be seen from Figure 4.14 and Table 4.11, the isobutene selectivity continuously decreased, with the exception of one point, as the temperature was increased from 490°C to 520°C while the total conversion and loss of butenes increased.

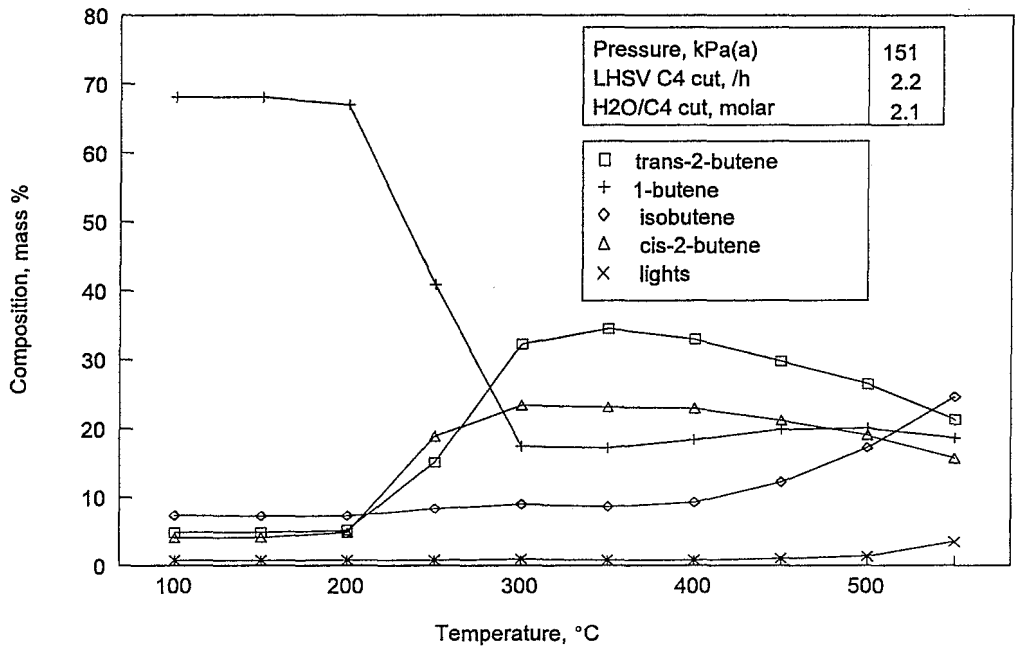

Figure 4.13 : Effect of increasing the temperature on the product gas composition

At a residence time of 1.5 s, as used in this study, the performance of the catalyst may be expected to be predominately thermodynamic as opposed to kinetically limited. (See also Section 4.2). As may be seen from Table 4.11, the actual isobutene to n-butene ratios in the product gas are similar to the theoretical values supporting this conclusion. Hence, the observed decrease in the isobutene selectivity with increasing temperature is as expected. The total conversion and loss of butenes, on the other hand, increased continuously as the temperature was raised. Examining the selectivities to the various by-products, it may be seen from Table 4.11 that the cracking selectivity increased while the hydrogenation and oligomerisation selectivities remained approximately constant as the temperature was increased.

It was further found in a separate study, where the long-term performance of the catalyst was monitored at various temperatures, that the cycle lifetime, the time for the isobutene yield to drop to 90 % of the initial value, decreased with increasing temperature. A value of approximately 12 hrs was recorded at 550°C as opposed to an average value in excess of 40 hrs at 520°C.

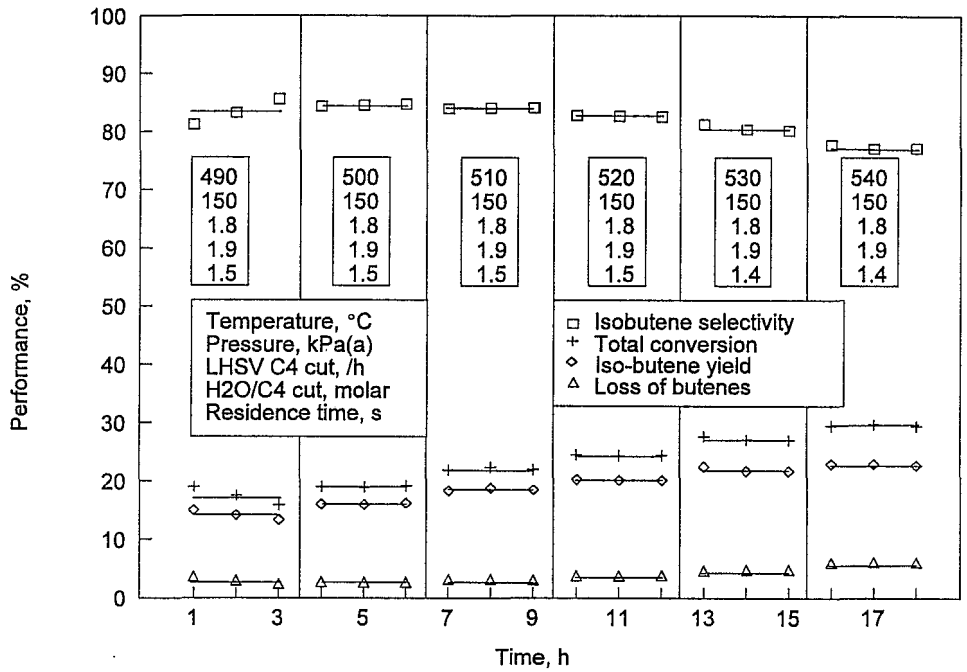

Figure 4.14 : Effect of the steady state operating temperature on the n-butene skeletal isomerisation performance of the catalyst

TABLE 4.11 : EFFECT OF TEMPERATURE

Temperature, °C	490	500	510	520	530	540
Residence Time, s	1.5	1.5	1.5	1.5	1.4	1.4
n-Butene Conversion, %	18.5	19.0	22.1	24.4	27.3	29.5
Isobutene Yield, %	15.2	16.1	18.6	20.2	22.0	22.8
Loss of Butenes, %	1.5	2.6	3.2	3.8	4.8	6.0
Isobutene Selectivity, %	82.2	84.5	84.1	82.7	80.6	77.3
Cracking Selectivity, %	9.8	5.7	6.7	7.3	9.2	10.9
Hydrogenation Selectivity, %	3.2	2.9	2.7	2.6	2.9	3.3
Oligomerisation Selectivity, %	4.7	6.8	6.5	7.4	7.3	8.4
Isobutene / n-Butene Ratio, Actual	0.58	0.62	0.59	0.57	0.57	0.58
Isobutene / n-Butene Ratio, Theory	0.60	0.60	0.59	0.58	0.57	0.56

As the cracking selectivity was found to increase with temperature the decrease in the cycle lifetime may be explained in terms of this increase in the by-product selectivities, i.e., increased coke formation with increasing temperature. Furthermore, as the total

conversion per pass through the skeletal isomerisation reactor is low, a closed loop isomerisation etherification process will have to be used to achieve high yields of the desired ether (See also Section 2.3.2). Consequently by-product formation has to be minimized and hence, a high isobutene selectivity, first and total conversion per pass, second are desired. Based on this and the cycle lifetime of the catalyst, it was concluded that the optimum operating temperature was located at 520°C.

4.7 EFFECT OF BY-PRODUCTS

In a closed loop system, the build-up of by-products has to be avoided as these could result in the poisoning of the catalyst. The simplest manner in which the level of by-products can be controlled is by purging. Unfortunately, valuable components are also lost in this way. Hence, the effect of the various by-products on the performance of the catalyst was examined in some detail. For detail of the by-products and the definitions used in calculating the various selectivities, see Appendix 1 and 2.

4.8 EFFECT OF ISOBUTENE

To investigate the effect of the isobutene partial pressure in the feed on the performance of the catalyst, pure 1-butene was spiked with isobutene. As can be seen from Figure 4.15 and Table 4.12, increasing the isobutene partial pressure in the feed results in a slight decrease in the isobutene selectivity while the total conversion and the loss of butenes appears to remain constant.

As these tests were performed at an average residence time of 1.3 s, it may be assumed that the performance of the catalyst was predominately thermodynamically as opposed to kinetically controlled, i.e., that the reaction products are close to equilibrium. This is supported by the fact that the isobutene to n-butene partial pressure ratios in the products, as shown in Table 4.12 are effectively constant and close to the theoretical value at 520°C of 0.58 (See also Section 4.2).

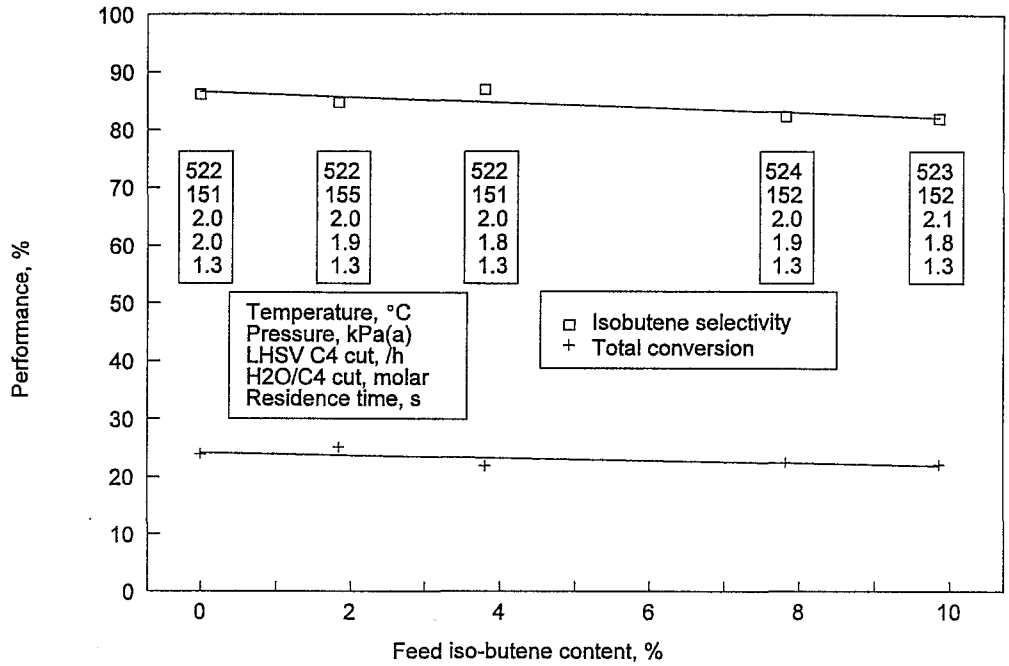

Figure 4.15 : Effect of the feed Isobutene content on the n-butene skeletal isomerisation performance

TABLE 4.12 : EFFECT OF ISOBUTENE

Isobutene,%	0.0	1.9	3.8	7.8	9.9
n-Butene Conversion, %	24.0	25.1	21.9	22.5	22.2
Isobutene Yield, %	20.7	21.3	19.0	18.5	18.2
Loss of Butenes, %	3.3	3.9	3.0	3.9	3.7
Isobutene Selectivity, %	86.2	84.8	86.9	82.4	82.0
Cracking Selectivity, %	6.5	7.8	7.2	9.0	10.3
Hydrogenation Selectivity, %	1.4	1.3	1.1	2.0	1.1
Oligomerisation Selectivity, %	3.9	6.6	5.7	7.2	7.4
Isobutene / n-Butene Ratio, -	0.51	0.48	0.53	0.55	0.54

Furthermore, in view of the procedures used to calculate the isobutene selectivity (see Appendix 1 for details), a decrease in the isobutene selectivity with an increasing isobutene content of the feed was to be expected. Examining the selectivities to the by-products, the data in Table 4.12 suggests, although not conclusively so, that as the isobutene content of the feed is increased, so the selectivities to cracked and possibly oligomerised products increases. This suggests that at the increased butene content of the feed, that these react

further via an oligomerisation / cracking type mechanism. Despite the fact that the results are inconclusive, it may be proposed that in a commercial skeletal isomerisation process the isobutene content of the feed should be kept as low as possible to minimise the formation of by-products, i.e., to ensure a high isobutene selectivity per pass. No data on the effects of the isobutene partial pressure in the feed on the overall performance of the catalyst could be found in the literature.

4.9 EFFECT OF PENTENE

To examine the effect of heavy by-products, Feed A (See Section 3.6 for details) was spiked with pentene. In this way, a number of feeds containing between zero mass % and 10.4 mass % heavies were prepared. Using a feed with increased heavies content, while maintaining a constant hydrocarbon LHSV, water to hydrocarbon ratio and average residence time of 1.3 s, will result in an increase in the actual water to n-butene ratio, a decrease in the n-butene LHSV and a decrease in the n-butene partial pressure in the feed. The actual values recorded during this study are shown in Table 4.13 and Figure 4.16

As can be seen from Figure 4.16, the isobutene selectivity was not effected while the total conversion increased, as the pentene level was raised from 0.05 mass % to 10.4 mass %. As the performance of the catalyst is not sensitive to changes in the n-butene partial pressures as used during this study, (See also Section 4.3) this increase in the conversion may be ascribed to the increase in the residence time. (See also Figure 4.2). Examining the selectivities to side reactions, as shown in Table 4.13, it was found that these were also not effected by the increasing pentene levels. Furthermore, the space time yield, i.e., the product of the selectivity, the total conversion and the n-butene flow rate remained constant as the pentene content of the feed was increased, as did the cycle lifetime which was in excess of 40 hours in all cases. It may thus be concluded that pentene, up to 10 mass %, does not effect the performance of the catalyst.

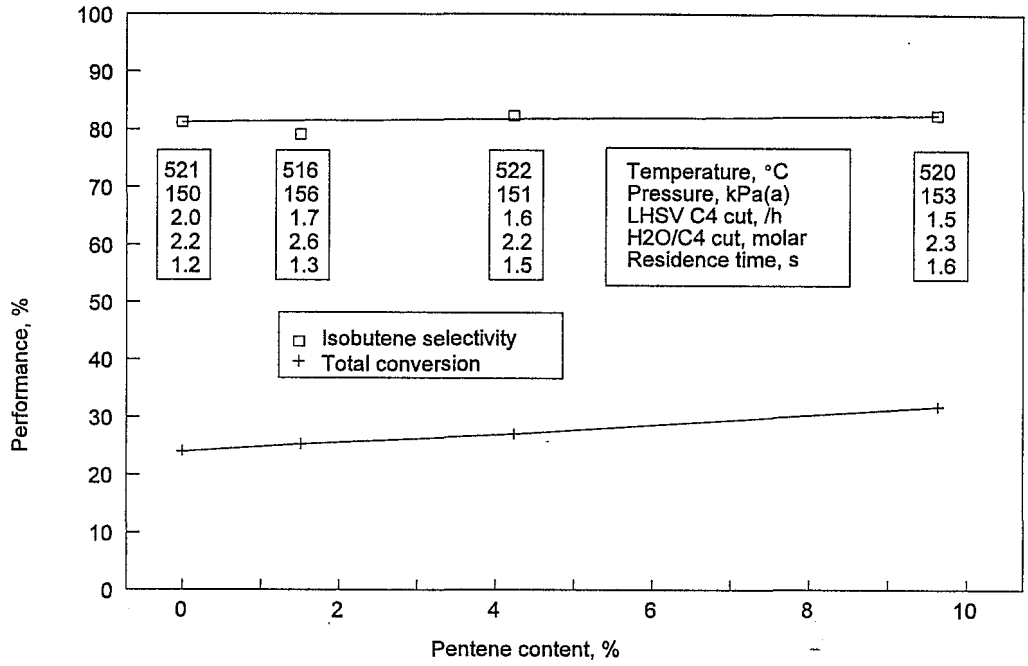

Figure 4.16 : Effect of the pentene content of the feed on the n-butene skeletal isomerisation performance

TABLE 4.13 : EFFECT OF PENTENE

Feed Heavies Content, mass %	0.05	1.51	4.24	10.4
Feed n-Butene Partial Pressure, kPa(a)	40.1	40.4	40.2	33.6
n-Butene LHSV, h^{-1}	1.4	1.2	1.1	1.0
Water / n-Butene Ratio, molar	2.6	2.6	2.7	3.0
n-Butene Conversion, %	23.8	25.3	27.2	31.8
Isobutene Yield, %	19.4	20.5	22.1	26.2
Isobutene Space Time Yield, %	14.7	13.1	13.4	13.6
Loss of Butenes, %	3.9	4.8	4.3	5.0
Isobutene Selectivity, %	81.6	81.1	81.3	82.5
Cracking Selectivity, %	8.8	13.0	9.6	9.1
Hydrogenation Selectivity, %	3.3	4.9	4.2	3.3
Oligomerisation Selectivity, %	6.3	1.0	4.9	5.1

4.10 EFFECT OF 1,3-BUTADIENE

Operating the reactor system at the base case conditions and using pure 1-butene spiked up to 0.74 mass % with 1,3-butadiene, the effect of 1,3-butadiene on the performance of the catalyst was investigated. The results from this investigation are shown in Figure 4.17 and Table 4.14. It was found that neither the isobutene selectivity and total conversion nor the loss of butenes were sensitive to the 1,3-butadiene content of the feed. Furthermore, examining the selectivities to the various side reactions, as shown in Table 4.14 no clear trend could be identified suggesting that 1,3-butadiene up to 0.74 mass % in the feed does not effect the n-butene skeletal isomerisation performance of the catalyst. However, examining the cycle lifetime, the time for the isobutene yield to drop to 90 % of the starting value, it was found that this decreased rapidly as the 1,3-butadiene level of the feed was increased. The cycle lifetimes recorded as a function of the 1,3-butadiene content of the feed are shown in Figure 4.18. As the activity of the catalyst could be fully restored via regeneration with air, it was concluded that the increased rate of deactivation observed in the presence of 1,3-butadiene was due to an increase in the coke formation rate. It may be speculated that the higher degree of unsaturation of the dienes, compared to the mono-olefins, increase their tendency to coke formation.

4.11 EFFECT OF ACETONE

After removing the oil formed, on average less than 0.01 mass % of the process water collected during a typical experiment performed at the base case conditions, acetone and butanone were the major oxygenates found together with traces of ethanol and methanol. A full analysis of the oil decanted from the process water is shown in Appendix 2. When using Feed A, the process water contained on average 1610 ppm acetone and 360 ppm butanone. The oxygenates found in Feed A are shown in Table 4.15.

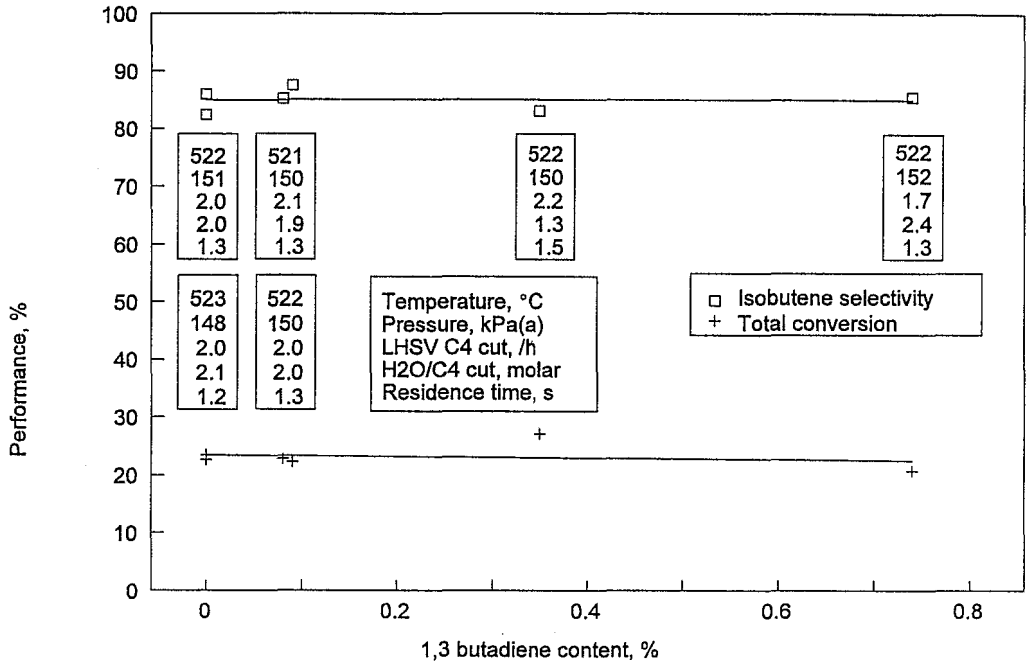

Figure 4.17 : Effect of the feed 1,3-butadiene content on the n-butene skeletal isomerisation performance

TABLE 4.14 : EFFECT OF 1,3-BUTADIENE

Feed 1,3-Butadiene, mass %	0.0	0.08	0.09	0.38	0.74
n-Butene Conversion, %	22.6	22.8	22.3	27.1	20.8
Isobutene Yield, %	18.6	19.4	19.5	22.5	17.8
Loss of Butenes, %	3.9	3.5	2.8	5.2	2.9
Isobutene Selectivity, %	82.5	85.2	87.5	83.1	84.6
Cracking Selectivity, %	6.7	6.3	6.4	9.1	9.4
Hydrogenation Selectivity, %	1.7	0.6	0.9	0.5	0.5
Oligomerisation Selectivity, %	9.1	7.9	5.2	7.3	5.5

TABLE 4.15 : FEED A OXYGENATE CONTENT

Acids, ppm as acetic acid	<100
Carbonyls, ppm as MEK	300
Alcohols, ppm as ethanol	1500
Esters, ppm as ethyl acetate	1000

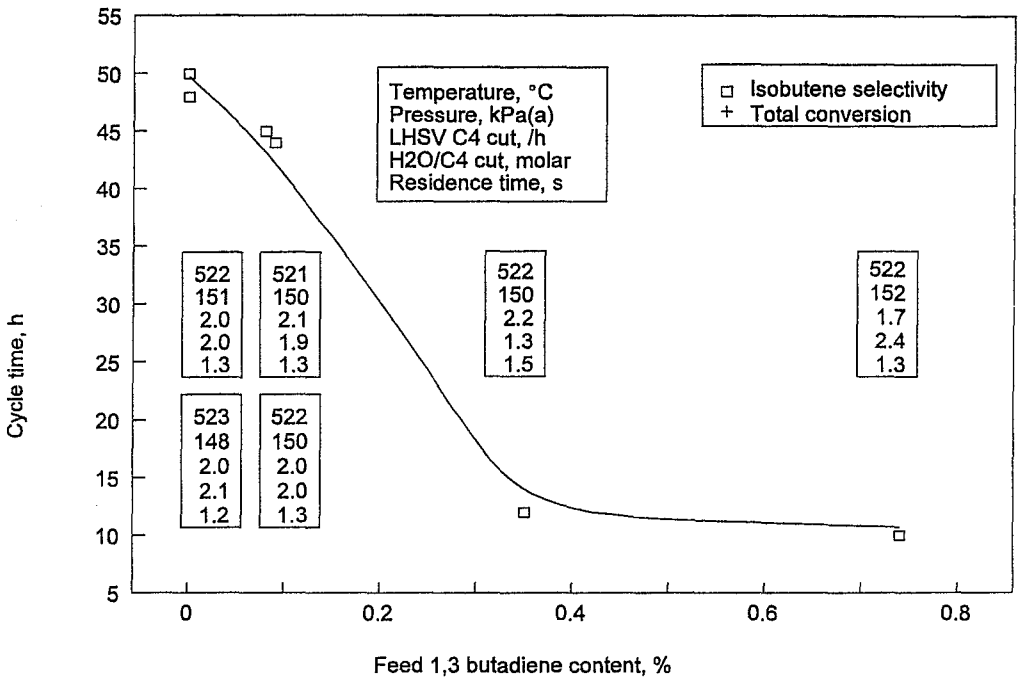

Figure 4.18 : Effect of the 1,3-butadiene content of the feed on the cycle lifetime

In an industrial process, the reaction water may be recycled. Hence, the effect of oxygenates on the performance of the catalyst was examined by spiking the feed with acetone as well as by recycling the process water. During these tests the oxygenate content of the combined feed was calculated using the total mass of reactants, i.e., both the mass of water and hydrocarbons, entering the reactor. The hydrocarbon feed, Feed A used in these tests contained a variety of oxygenates, as shown in Table 4.15 equivalent to 0.28 mass %, which reduces to 0.16 mass % when based on the combined hydrocarbon and water feed. The oxygenate content of the water was adjusted using acetone, to give the desired amount. The results recorded during this study are shown in Figure 4.19 and Table 4.16.

As can be seen from Figure 4.19 and Table 4.16 increasing the oxygenate content of the combined feed from 0.16 mass % to 3 mass % has a detrimental effect on the isobutene selectivity, a decrease of approximately 20 percentage points being recorded, while in the case of the total conversion and loss of butenes no clear trend could be identified.

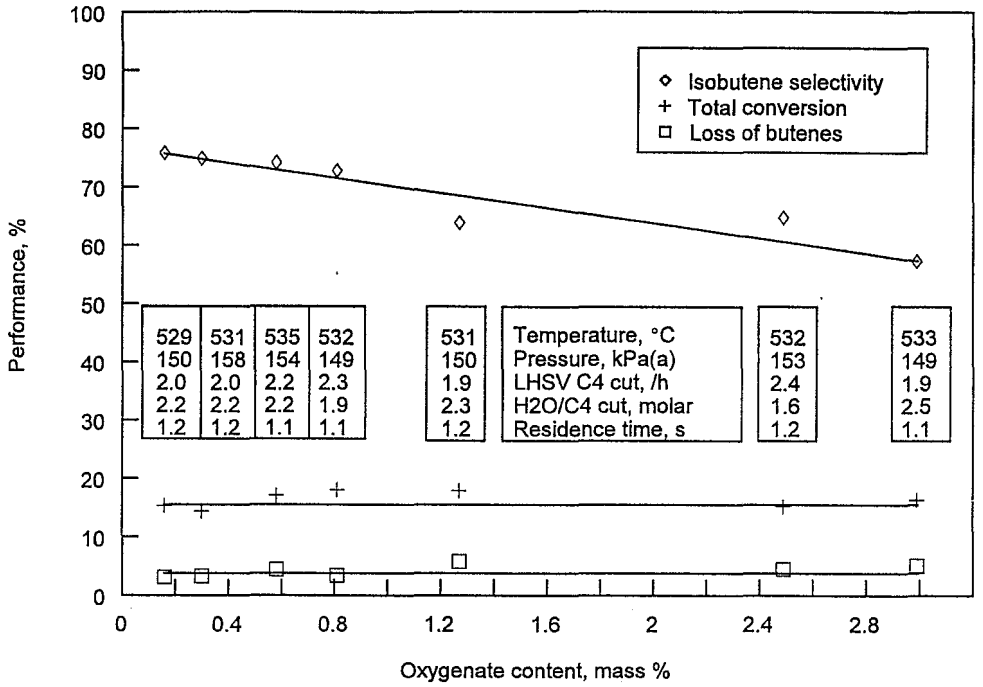

Figure 4.19 : Effect of the acetone content of the feed on the n-butene skeletal isomerisation performance

TABLE 4.16 : EFFECT OF ACETONE

Oxygenates, %	0.16	0.30	0.58	0.81	1.27	2.49[1)]	2.99[1)]
n-Butene Conversion, %	15.3	14.4	17.1	18.0	17.9	15.2	16.3
Isobutene Yield, %	11.6	10.8	12.7	13.1	11.4	9.8	9.4
Loss of butenes, %	3.1	3.3	4.4	3.4	5.8	4.5	5.1
Isobutene Selectivity, %	75.8	74.9	74.2	72.8	63.9	64.8	57.4
Cracking Selectivity, %	10.4	11.3	11.8	12.3	14.7	20.6	27.8
Hydrogenation Selectivity, %	8.8	8.5	8.9	9.3	17.0	9.8	10.4
Oligomerisation Selectivity, %	5.0	5.3	5.1	5.6	4.4	4.8	4.4

1) After 1 h on line

Examining the selectivities for the various by-products, as also shown in Table 4.16, it was found that increasing the oxygenate content resulted in an increase in the cracking and maybe hydrogenation selectivities while the oligomerisation selectivity remained approximately constant. From the cycle lifetime, the time for the isobutene yield to drop to 90 % of the starting value, as a function of the oxygenate content of the combined feed, it was found, as shown in Figure 4.20 ,that this rapidly decreases as the oxygenate content

of the combined feed was increased. However, as the activity of the catalyst could be restored via regeneration under air, it was concluded that the deactivation observed is due to increased coke formation in the presence of acetone. Note : As the catalyst rapidly lost activity at the higher acetone levels, the values at an acetone content of 2.49 % and 2.99 % shown in Table 4.16 are those collected after 1 h on line while all other data is that collected after 5 h on line.

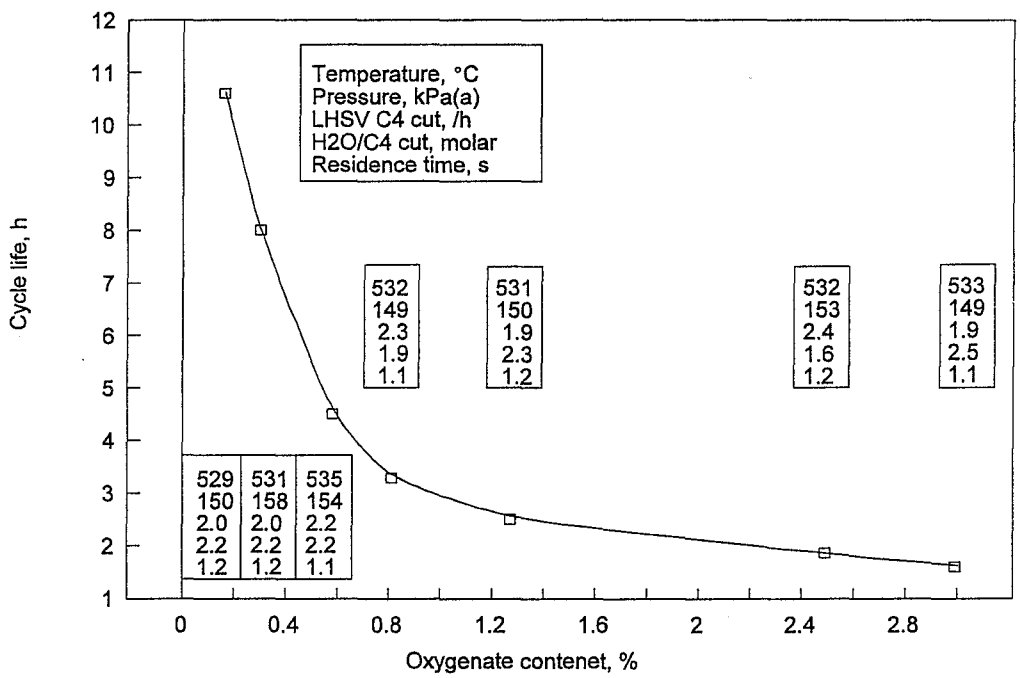

Figure 4.20 : Effect of acetone content of the feed on the cycle lifetime

From an inspection of the actual flue gas composition it was found that as the acetone content of the combined feed was increased so predominately the quantity of methane, ethane, ethene, propene and isobutane increased. It may be speculated that these components are formed during the decomposition of the acetone to coke. Hence, the increase in the lights, i.e., the cracking selectivity, is artificially inflated via a mechanism other than the decomposition of the butenes. This combined with the procedure used to calculate the various selectivities (See Appendix 1 for details) suggests that the observed decrease in the isobutene selectivity and increase in the cracking selectivity while the loss of butenes and the total conversion and isobutene yield remained approximately constant with increasing acetone in the feed, is in fact a mathematical artefact. Unfortunately,

attempts to reconcile the increase in the lights with the acetone consumed were not successful. The acetone content in the flue gas after liquid knock out, was not recorded. As acetone is a very volatile component this could account for the difficulties experienced. It may thus be postulated that the presence of acetone does not effect the n-butene skeletal isomerisation performance of the catalyst, apart from contributing to the formation of coke, resulting in the rapid deactivation of the catalyst.

4.12 EFFECT OF OXYGENATES : RECYCLING OF THE PROCESS WATER

To complete the investigation of the effect of the oxygenates, the effect of recycling the process water on the performance of the catalyst was investigated. The process water from a number of on-line periods was collected and blended, decanted to remove the oil present (See Appendix 2 for a detailed analysis) and filtered to remove any suspended material. Analysis showed that the bulk sample of water contained 1800 ppm acetone and 200 ppm butanone. The hydrocarbon feed, Feed A used in this study, in turn contained an equivalent of 2700 ppm oxygenates giving a combined oxygenate level of 2400 ppm in the combined water and hydrocarbon feed as opposed to 1600 ppm in the combined feed when using fresh water. Using process water designated as C-1 in Figure 4.21 a three on-line and regeneration cycles were performed followed by an activity check using fresh water. As can be seen from Figure 4.21 using C-1 water seemed to result in a decrease in the activity and a slight increase in the isobutene selectivity with no permanent damage done to the catalyst as normal performance was obtained after regeneration and when using fresh water. To continue the investigation of recycling the process water and to determine whether any catalyst poisons were formed during the regeneration of the catalyst, the process water collected during the on-line and regeneration periods while using C-1 water, was collected, blended and cleaned as described above. The effect of using process water during the regeneration of the catalyst, on the oxygenate content of the water, was also examined. As expected the oxygenates were removed, i.e., 'burnt up' during the regeneration decreasing from 1600 ppm to 330 ppm.

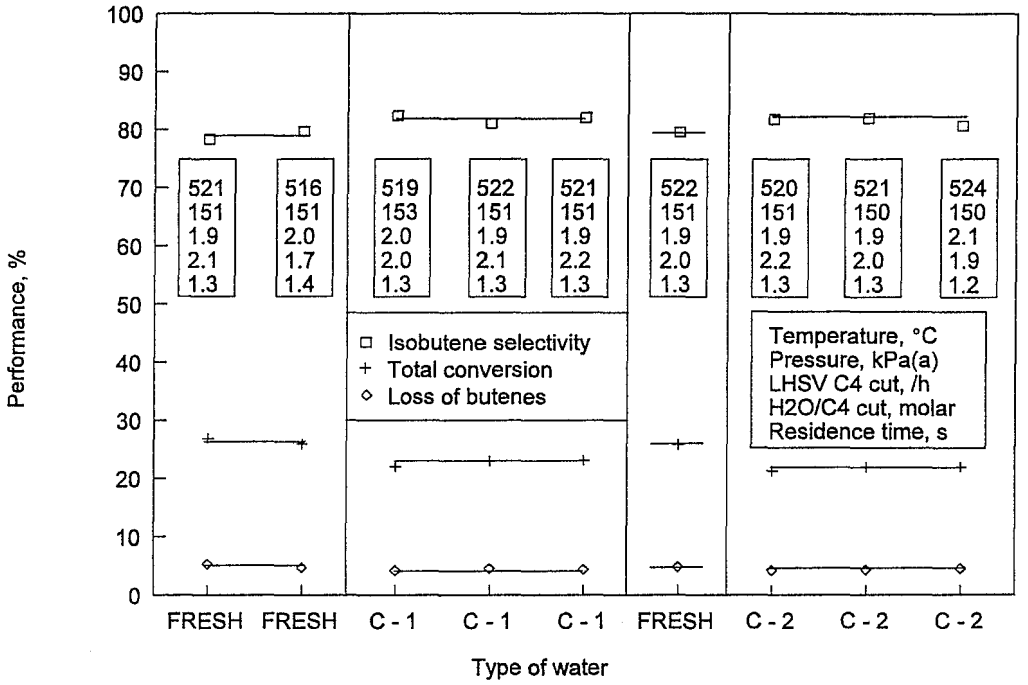

Figure 4.21 : Effect of recycling the process water on the n-butene skeletal isomerisation performance

In this way some of the process water could be cleaned thus reducing the size and hence the cost of the distillation step needed to remove the oxygenates. Next using this water, designated as C-2 water during the subsequent on-line period, resulted in a similar change in the performance of the catalyst as when using C-1 water.

From this study it was concluded that the quality of the process water does not deteriorate further by being recycled and that no catalyst poisons are formed during the regeneration of the catalyst. However, to ensure acceptable yields and cycle lifetimes the oxygenates present in the process water and preferably those in the hydrocarbon feed should be removed. This may be achieved by distillation and using part of the water during the regeneration of the catalyst followed by blending. No references in the literature discussing the effect of oxygenates on the n-butene skeletal isomerisation performance could be found.

4.13 LONG-TERM CATALYST STABILITY

During the course of this work, the catalyst was not routinely unloaded between the various experiments but regenerated according to the procedure developed, as discussed in Section 3.5. To ensure that the trends observed during the various investigations were a function of the operating parameters and not catalyst deactivation, a control experiment was regularly conducted. Two separate catalyst charges were used during this study. The history of the two pilot plant catalyst charges are discussed in this section.

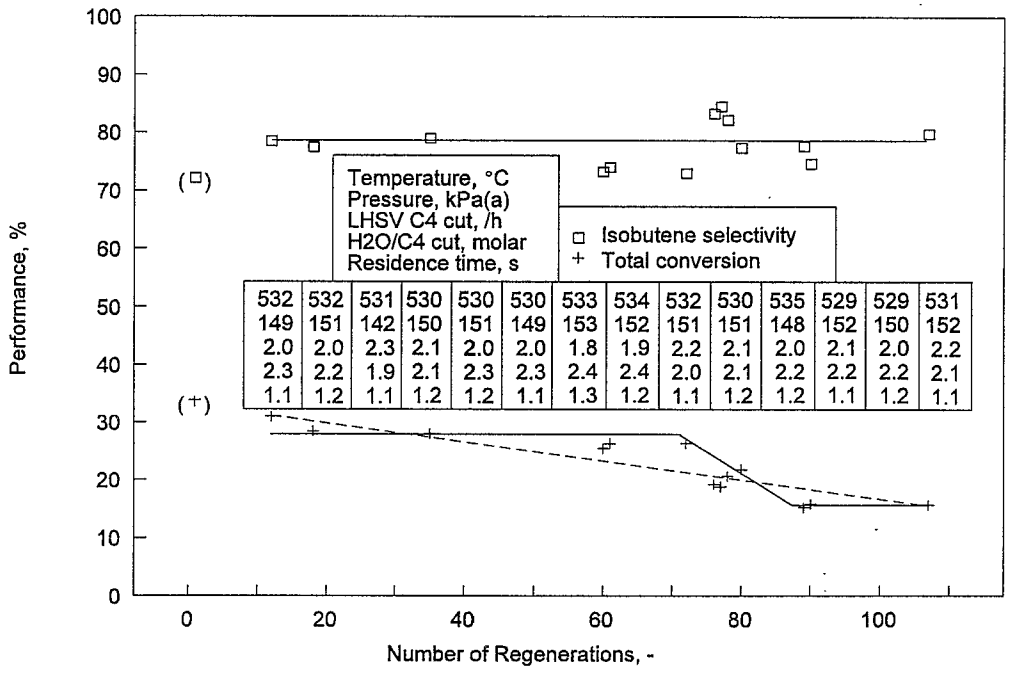

Figure 4.22 : n-Butene skeletal isomerisation performance vs number of on-line and regeneration cycles - First catalyst charge

Shown in Figure 4.22 are the results of the various activity checks for the first charge. Ignoring the first data point, it may be concluded that the selectivity remained constant throughout the 107 on-line and regeneration cycles. Examining the trend in the activity more carefully, and again ignoring the first data point, it may be concluded that the activity remained constant over the first 72 cycles at which point a change occurred followed once again by stable but decreased activity. The investigation as to the effect of decreased water to hydrocarbon ratio and some high temperature work, was conducted in the region

of the change in the activity all of which may have damaged the catalyst via sintering However, it is felt that the foregoing is not an accurate reflection of the long-term stability of the catalyst as the material was exposed to a variety of feeds, a wide range of operating conditions and occasionally starved of water. Under stable base case operating conditions, as used in a separate study, it was found that a slight, <5°C, increase in the operating temperature was required to maintain the yield at the initial value for more than 182 on-line and regeneration cycles, a total on-line time of 2840 hrs, and that the cycle lifetime did not deteriorate over this period.

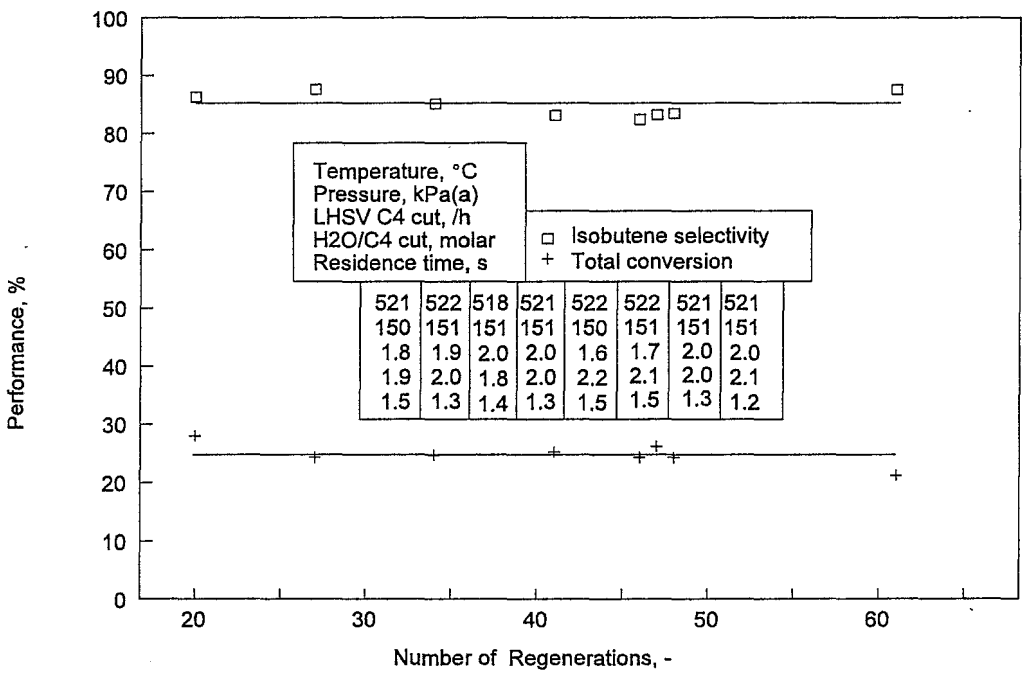

Figure 4.23 : n-Butene skeletal isomerisation performance vs number of on-line and regeneration cycles - Second catalyst charge

The activity of the second catalyst charge was also routinely checked and the results shown in Figure 4.23. As can be seen from this figure, both the activity and selectivity of the catalyst again remained approximately constant during the 61 on-line and regeneration cycles confirming the stability of the catalyst.

As all studies reported in this work were performed using a catalyst of between 10 and 60 cycles it may be concluded that the results recorded were indeed a function of the operating parameters and not catalyst deactivation.

4.14 CATALYST BED CARBON PROFILE

In an attempt to obtain an insight into the catalyst deactivation profile and mechanism the first catalyst charge, was brought on line after 107 on line and regeneration cycles for 60 h but not regenerated. Next, the reactor was unloaded in such a way as not to disturb the bed geometry. In this way it was possible to subdivide the catalyst bed into four axial regions, numbered 1 to 4 with position number 1 at the top of the bed, and to perform a number of qualitative and quantitative analysis on each region.

In each case, a Thermo-Gravimetric-Analysis (TGA) was performed. First the volatile carbonaceous components were removed by heating the sample under nitrogen to 520°C before switching to air. By recording the mass loss that occurred during each of these steps an indication of the volatile components and graphitic carbon present on the catalyst was obtained. Next the surface area, pore volume and diameter as well as a qualitative pollutant analysis on each of these 'regenerated' samples were performed. The results of the test performed on the catalyst are shown in Table 4.17, as are those of an un-used, fresh catalyst that was previously calcined ex-situ in air at 700°C and steamed using the procedure given in Section 3.5.

TABLE 4.17 : SPENT CATALYST PROPERTIES AND REACTOR CARBON PROFILE

Parameter	Calcined	'Regenerated'			
Catalyst position	-	Pos. 1	Pos. 2	Pos. 3	Pos. 4
Volatile compounds, %	-	1.8	1.9	1.7	2.3
Carbon, %	-	7.7	6.7	11.0	18.0
Surface Area, m^2/g	180.7	109	118	116	120
Pore volume, cm^3/g	0.52	0.34	0.37	0.37	0.37
Pore diameter, Å	115	124	125	127	125
Pollutants, Qualitative	-	Traces of : V, Fe, Ti, Ca, K, Zr, Cr			

Examining the coke profile of the end of run catalyst, as shown in Table 4.17, it was found that the quantity of carbon increased from 7.7 mass %, at the inlet, to 18 mass % at the outlet of the catalyst bed. A carbon profile of this type is obtained if coking takes place in series with the primary reaction. As the butene skeletal isomerisation reaction is

reversible, the effective butene partial pressure in the reactor remains constant throughout the bed. Hence, it may be concluded that coking occurs via a secondary reaction of the by-products, possibly via the cracking of the oligomers.

Examining the surface area, pore volume and average pore diameter of the 'Regenerated' catalyst, as shown in Table 4.17, no clear trend could be identified. However, comparing these results with the calcined but un-used catalyst it may be seen that the surface area and pore volume decreased while the average pore diameter increased. This suggests that either the smaller pores sintered or were blocked by refractory coke not removed during the 'regeneration'. However, no further mass loss occurred when heating a sample of 'regenerated' catalyst to 700°C under air suggesting that no refractory coke was present. Hence, the decrease in the surface area, pore volume and increase in the average pore diameter of the spent catalyst relative to the calcined and steamed but un-used catalyst, may be ascribed to sintering of the catalyst, when operated at elevated temperatures in the absence of water.

4.15 SUMMARY

As the bond and skeletal isomerisation reactions of the butenes are reversible, it is possible that the observable performance of the system may be thermodynamically or kinetically controlled. That the thermodynamic equilibrium was indeed achieved was confirmed by comparing the observed and reported ratios (Kilpatrick et al., 1946:559) of the various butene isomers. It was found that irrespective of the operating conditions, the linear butenes were always at equilibrium. A similar result was recorded previously by Szabo et al. (1993:329), who found that the inter-conversion amongst the linear butenes was not effected by the activity of the catalyst. Hence, the linear butenes, 1-butene, *cis*-2-butene and *trans*-2-butene were treated as a single pseudo-component, n-butene during this study. In the case of skeletal isomerisation, i.e., the transformation of the linear butenes to isobutene, the isobutene to n-butene ratio increased with increasing residence time before levelling off at the value predicted from theory. The cut-off point, i.e., the point beyond which the observable performance of the catalyst was predominantly

thermodynamically as opposed to kinetically controlled, at a temperature of 520°C, pressure of 150 kPa(a) and water to hydrocarbon molar ratio of 2, was found to be a residence time of 1.2 s. The influence of the thermodynamic equilibrium must be considered when interpreting the results recorded during the various studies. This was not previously reported as such in the literature.

The effect of the n-butene partial pressure on the observable performance of the catalyst, at residence times in excess of 1.2 s was examined by co-feeding a paraffin (n-butane) and a permanent gas (hydrogen). Not surprisingly, in view of the above, it was found that the performance was independent of the n-butene partial pressure in the feed. In each case the thermodynamic equilibrium had been achieved. Furthermore, as the performance of the system was only marginally effected by co-feeding hydrogen it was concluded that a hydrogenation / dehydrogenation step does not form part of the n-butene skeletal isomerisation mechanism. In fact, as the hydrogenation of the butenes at 520°C is thermodynamically very feasible, prospective butene isomerisation catalysts should not contain a hydrogenation / dehydrogenation function. This fact, that a hydrogenation / dehydrogenation step does not form part of the butene bond or skeletal isomerisation mechanism, was previously reported by Bianchi et al. (1994:557).

Adding water to the surface of a dehydrated alumina will interact with the Lewis sites present to form Brønsted acid sites. This was the conclusion reached by Peri (1965:215) and was later confirmed by a number of workers (Tung and Mcininch, 1964:237, Gerberich and Hall, 1966:103, Hughes et al., 1969:58). The effect of water, or lack thereof, on the performance of the alumina based catalyst used in this study was investigated in some detail. It was found that water was required to suppress the deactivation of the catalyst during the on-line period and to enhance the isobutene selectivity. Furthermore, it was found that the hydrated surface of the catalyst was not stable in the absence of water and that the desired sites could not be regenerated during the on-line period upon the reintroduction of water. However, as the performance of the system could be almost fully recovered by regenerating the catalyst in air, it was concluded that the rapid deactivation and shifts in selectivity observed in the absence of water could be ascribed to the formation of coke. The permanent loss in the activity of the material after exposure to hydrocarbons

in the absence of water, on the other hand, may be ascribed to sintering of the catalyst. Based on the acidity measurements of a dehydrated and hydrated alumina, together with the results quoted in the literature, it was also concluded that the stronger Lewis acid sites were more active in catalising the reactions of the butenes to by-products and coking, while the weaker Brønsted acid sites are more active for the skeletal isomerisation reaction. That Brønsted acidity is required for skeletal isomerisation while double bond isomerisation may be achieved with electron pair accepting, i.e., Lewis acidity, was previously proposed by, among others, Condon (1958:44).

Operating a commercial plant at low pressure may not be economical. Hence, the effect of the total pressure on the performance of the system was investigated. As the number of moles does not change during isomerisation, it may be expected that the performance of the system is independent of the total pressure. However, during the formation of coke, a volume contraction may occur. It was found that increasing or decreasing the total pressure, and simultaneously the residence time, had an effect on the n-butene skeletal isomerisation performance of the system. However, comparing the changes observed with those obtained when only adjusting the residence time, at a constant pressure of 150 kPa(a), it was found that the changes were identical. From this it was concluded that, as expected, pressure had no effect on the skeletal isomerisation activity of the catalyst. This does, however, suggest that it may be possible to operate the system at an elevated pressures by adjusting the residence time. This is an area where further work is required as it would be beneficial from a commercial point of view to operate at elevated pressures. The relationship between the system pressure and the residence time was not previously discussed in the literature.

Increasing the temperature, it was found, as previously reported in the literature (Tung and Mcininch 1964:237; Gerberich and Hall, 1966:103), that sufficient energy is required before the surface of a hydrated alumina catalyst becomes active for the n-butene skeletal isomerisation reaction. A temperature in excess of 400°C was found to be needed to activate the protons captured in the cationic vacancies (Tung and Mcininch, 1964:237). This was also, indirectly, confirmed by Choudhary and Doraiswamy (1975:227), who reported that over a fluorinated alumina catalysts isobutene, i.e., skeletal isomerisation

activity, was only observed at temperatures between 300°C and 550°C, and during this study, where isobutene was first observed in the product gas at temperatures in excess of 400°C. Increasing the temperature further resulted in an increase in the total conversion and the loss of butenes, while the cycle lifetime, the time for the isobutene yield to drop to 90 % of the initial value, decreased. As the theoretical maximum total conversion possible per pass through the isomerisation reactor at a temperature of 520°C, is 36.6 mass %, the un-reacted n-butene will have to be recycled to achieve a high overall yield of isobutene. Hence, firstly the isobutene selectivity, and secondly, the total conversion per pass, will have to be maximised, i.e., the loss of butenes minimised. In this study the maximum isobutene selectivity was obtained at a temperature of 520°C. The relationship between the conversion and selectivity, from a commercial view, on the overall performance was not previously discussed in the literature. In addition to this the proposal made previously that the n-butene skeletal isomerisation performance of the catalyst is predominantly thermodynamically, as opposed to kinetically, controlled was confirmed during this study. At each of the temperatures considered, the ratio of isobutene to n-butene in the flue gas was as predicted from theory (See also Chapter 2, Section 2.3.6 for further details).

As was stated previously, to maximise the conversion of the linear butene to isobutene, the n-butenes must be recycled. Similarly, as the reaction is thermodynamically limited, the isobutene partial pressure in the feed must be kept as low as possible. This may be achieved by selectively removing the isobutene from the product gas before recycling. Fortunately, this can be done while simultaneously producing the desired final product by exploiting the different activities displayed by the butene isomers for electrophilic addition type reactions such as etherification. (Fajula and Gault, 1976:7691). Of course, in any closed loop system as is being proposed, the build-up of by-products has to be controlled. A closed loop system was not operated during this study, but the effects of various by-products investigated. It was found, that heavy by-products did not have an effect on the n-butene skeletal isomerisation performance of the system. Dienes, also did not effect the n-butene skeletal isomerisation performance of the catalyst but had a negative effect the cycle lifetime the time for the yield to drop to 90 % of the starting value. The decrease in the cycle lifetime was attributed to an increase in coke formation in the presence of dienes, as the activity of the catalyst could be restored upon regeneration.

Apart from lighter and heavier hydrocarbon by-products, oxygenates were also produced. Using acetone, the effect of the oxygenates on n-butene skeletal isomerisation performance of the catalyst was investigated. A dramatic increase in the light (<C4) hydrocarbons, i.e., the cracking selectivity, and decrease in the isomerisation selectivity was observed with increasing acetone in the feed. However, the overall activity (total conversion) was not effected. From this, and in view of the procedures used to calculate the various selectivities (See Appendix 1 for details), it was concluded that acetone also had no effect on the n-butene skeletal isomerisation activity of the catalyst, i.e., the decrease in the isobutene selectivity was a mathematical artefact. Attempts to correlate the formation of lights with the acetone content of the feed were not successful. The effect of the feed contaminants were not previously discussed in the literature.

To ensure that the results recorded during this study were a function of the operating conditions and not the deterioration of the catalyst, activity checks at the base case conditions (See Chapter 3, Section 3.5 for details) were regularly performed. It was found that the performance of the material was stable for the first 60 on-line and regeneration cycles. However, in the case of the first catalyst charge a step change in the performance was then observed. Work at temperatures in excess of 600°C, and in the absence of water, was conducted during this period. However, it is felt that this is not a true reflection of the long-term performance of the material. In a separate study, conducted at the base case conditions, stable operation was maintained for more than 100 on-line days. The long-term stability of the amorphous silica alumina type catalyst and commercially available feed prepared via the Fischer Tropsch process, as used during this study, was not previously reported in the literature.

Finally, during normal operation the catalyst loses activity during the on-line period. As the activity could be fully recovered via regeneration with air, it was concluded that the deactivation was due to the deposition of coke on the active sites. In an attempt to clarify the deactivation mechanism, the first catalyst charge was brought on line but not regenerated at the end of the on-line period. By unloading the bed without disturbing the bed geometry, the carbon profile through the bed was determined. An increase in carbon content of the catalyst with increasing bed depth was observed. As the n-butene skeletal

isomerisation reaction is reversible, the effective butene partial pressure remains constant throughout the reactor. However, the by-product partial pressure increases with increasing bed depth. It may therefore be concluded that coking proceeds via the secondary reactions of the by-products formed. The most likely route to the by-products is via the oligomerisation of the butenes followed by catalytic cracking in the ß position, to give both the light and heavy by-products and the deposition of coke. It is further proposed that the hydrogenated products are also formed during coking. That the by-products are formed via a dimerisation / cracking mechanism was previously proposed by Bianchi et al. (1994:556). Hence, it may be concluded that the silica alumina catalyst under study is a robust material that is ideally suited for the n-butene skeletal isomerisation reaction.