CHAPTER 7. CONCLUSIONS AND RECOMMENDATIONS

Presented here are only those conclusions and recommendations that are considered to be novel. For a full set of conclusions see the end of each chapter or the résumé. The conclusions will be presented in two sections: those dealing with the synthesis performance of the catalyst, and those dealing with the modelling results.

7.1 SYNTHESIS PERFORMANCE

The primary objective of this work was to establish the suitability of a proprietary experimental catalyst, obtained from a supplier of refinery technology, for the skeletal isomerisation of the n-butenes to isobutene. This included developing an appropriate operating procedure and generating data suitable for the design and operation of a commercial n-butene skeletal isomerisation unit. During this study, not only was pure 1-butene used, but a commercially representative feed containing both light ($<C_4$) and heavy, up to and including C_6, olefinic and paraffinic components, as well. The feed was produced via the Fischer Tropsch process as operated at Sasol.

- Using the commercially representative feed, an operating and regeneration procedure suitable for commercialisation was successfully developed.

- 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. It is imperative that the influence of the thermodynamic equilibrium and the residence time be considered when interpreting the results recorded during the various performance studies.

- Operating a commercial n-butene skeletal isomerisation plant at low pressure in combination with a high pressure etherification plant, may not be economical.

Hence, the effect of the total pressure on the performance of the system was investigated. 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 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 elevated pressures by reducing 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.

- As the theoretical maximum total conversion possible per pass through the isomerisation reactor was calculated to be 36.6 % at a temperature of 520°C, the un-reacted n-butene will have to be recycled to achieve a high overall yield of isobutene. Hence, first the isobutene selectivity and secondly the total conversion per pass through the skeletal isomerisation reactor will have to be maximised, i.e., the loss of butenes minimised. This differs from the traditional approach, to maximise the yield per pass of the desired product through the reactor.

- As was stated previously, to maximise the conversion of the linear butene to isobutene, the n-butenes must be recycled. Of course, in any closed loop system the build-up of by-products has to be controlled. The effects of the various by-products were thus investigated. It was found that heavy by-products did not have an effect on the n-butene skeletal isomerisation performance of the system. Dienes and acetone also did not effect the n-butene skeletal isomerisation performance of the catalyst but had a negative effect on 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, as the activity of the catalyst could be restored upon regeneration. The build-up of these components will therefore have to be controlled.

- The long-term stability of the catalyst was monitored by regularly conducting activity checks at the base case conditions. Using the commercially representative feed, it was found that the performance of the material was stable for the first 60 on-line and regeneration cycles at which point a step change in the activity occurred. Work in the absence of water and at high temperatures, in excess of 600°C, was conducted during this period. In a separate study conducted at the base case conditions, stable operation was maintained for more than 100 on-line days.

Hence, it was concluded that the silica alumina catalyst under study, is a robust material that is ideally suited for the commercial n-butene skeletal isomerisation reaction.

7.2 MODELLING RESULTS

The kinetics of this reaction was investigated in an attempt to identify the reaction mechanism and to develop the intrinsic kinetic equation. A multi-step approach, based on the mono-molecular mechanism when a single or multiple step(s) controls the overall reaction rate, was used. The necessary experimental data were generated using the bench scale reactor system. Of course, prior to performing a kinetic study, the suitability of the experimental equipment and the complexity of the reactor model required, needed to be established.

- Discrimination between the rival models considered, using a number of statistical procedures, was not possible. However, it was found that, for a given step, the absolute values of the pre-exponential factors and the activation energies determined for the three forward and three backward elementary reaction steps considered, were similar, irrespective of the assumption made as to the nature of the rate controlling step(s). It may thus be proposed that the rates of the six elementary reaction steps considered, and hence the net rates of the adsorption, surface reaction and desorption steps, are very similar. In this way, the fact that it was not possible to discriminate between models developed by assuming that specific reaction step(s) control the overall rate may be understood.

- Confidence intervals and confidence contours, about the optimum values of the unknown parameters required by the various rate equations, were generated. From an examination of the confidence profiles, it was found that in each case the models were equally sensitive to an increase or decrease in the values of the parameters used to describe the rate of n-butene adsorption. A symmetrical confidence contour is indicative that a specific value is required. It may thus be proposed that the rate of n-butene adsorption on a single site on the surface of the catalyst is the most significant reaction step. A global view of the confidence contours suggested that the rate of the n-butene to isobutene surface reaction, as well as the desorption of isobutene, had to be larger than some limiting value. Similarly, for the reverse reactions, the adsorption of isobutene, the isobutene to n-butene surface reaction and the desorption of n-butene, it was concluded that these rates had to be smaller than some limiting value. It may be expected that the limiting value in all cases is the rate of the significant step, i.e., the adsorption of n-butene.

- As discrimination between rival models was not possible, the simplest form of the rate equations considered, the law of mass action, was adopted. The robustness of the rate equation developed and its suitability for the rigorous design of a commercial n-butene skeletal isomerisation reactor was confirmed by the ability of this model to predict the performance of the pilot plant.

During this investigation, the ratios of the n-butene, *cis*-2-, *trans*-2- and 1-butene in the flue gas were as predicted from thermodynamics. Hence, the linear butenes were treated as a single component, n-butene. What has not previously been reported in the literature is an attempt to identify the overall reaction mechanism, using mult-step modelling of the butene bond and skeletal isomerisation reactions as well as the formation of the by-products. The latter, are traditionally assumed to form via the disproportionation of the butenes and are routinely treated as a single pseudo-component. This is an area where further work is required.