THE SKELETAL ISOMERISATION OF THE N-BUTENES
CATALYST PERFORMANCE AND KINETIC INVESTIGATION

by

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DECLARATION

I, Stefan Mathias Harms hereby declare that the work presented in this thesis is my work, except where otherwise indicated. I further declare that this work has not been submitted to any other institution for purposes of obtaining a degree.

Stefan Mathias Harms
1 October 1998

CLASSIFICATION

Please note that this thesis entitled "THE SKELETAL ISOMERISATION OF THE N-BUTENES CATALYST PERFORMANCE AND KINETIC INVESTIGATION" is classified for a period of 5 years. Subject to evaluation, this period may be extended.

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ABSTRACT

With the advent of catalytic converters being placed in the exhaust systems of motor vehicles, in an attempt to reduce pollution, the use of tetra ethyl lead as an anti-knock additive to fuel was no longer acceptable. Lead is a poison for the exhaust catalysts used and so an alternative had to be found. At present the ethers, particularly methyl tertiary butyl ether (MTBE), are being used as a substitute for lead. The limiting factor in the production of the ethers is the availability of isobutene. Isobutene may be produced using a number of complex processes and feedstocks. One route that has not been commercialised is the direct conversion of the linear butenes to isobutene via skeletal isomerisation.

In the present study, using a specially constructed bench scale reactor system and a pilot plant, it was shown that an amorphous silica alumina catalyst could be used for the skeletal isomerisation of the n-butenes to isobutene. By investigating the effects of the residence time, n-butene partial pressure, total system pressure, system temperature and water to hydrocarbon molar ratio, a commercially suitable operating and regeneration procedure was developed. The effects of the various feed and product constituents, that build-up in the recycled hydrocarbon and process water streams, such as n-butane, isobutene, pentene, 1,3-butadiene and acetone, on the performance of the catalyst were also quantified. The long-term stability of the material, during repeated on-line and regeneration cycles, was determined.

To allow the rigorous design of a commercial reactor, a suitable rate equation is required. Hence, a detailed kinetic investigation was conducted using the bench scale reactor system, the suitability of which for such a study was first investigated and confirmed. For the mono-molecular mechanism with either a single step or multiple steps controlling the overall reaction rate, and including the law of mass action, a total of eight cases were considered. Although the overall reaction mechanism could not be identified, a suitable rate equation was developed. The robustness of the rate equation was confirmed by its ability to predict accurately the performance of the pilot plant reactor system.

UITTREKSEL

Met die koms van katalitiese omsetters wat tans in motors se uitlaatstelsels geïnstalleer word in 'n poging om besoedeling te bekamp, is die gebruik van tetra-etiel-lood as 'n anti-klopmiddel nie meer aanvaarbaar nie. Lood vergiftig die katalisatore en daarom word 'n alternatiewe anti-klopmiddel benodig. Tans word die eters, spesifiek metiel tersiêre butiel eter (MTBE), gebruik in plaas van lood. Die beskikbaarheid van isobuteen is egter beperkend in die vervaardiging van hierdie eter. Isobuteen kan vervaardig word deur middel van 'n aantal ingewikkelde prosesse en verskillende uitgangstowwe. Die direkte omskakeling van die n-buteen na isobuteen is 'n roete wat nog nie kommersieel bedryf word nie.

In hierdie studie, deur gebruik van 'n spesiale loodsaanleg en 'n bankskaal reaktor-sisteem, is bewys dat 'n amorfe silika alumina katalisator geskik is vir die direkte omskakeling van die n-buteen na isobuteen. Deur die invloed van die verblyfstyd n-buteen parsiële druk, totaal druk, sisteem temperatuur en water tot koolwaterstowwe mol-verhouding te ondersoek, is 'n bedryf en regenerasieprosedure, wat ook geskik is vir 'n kommersiële proses, ontwikkel. Die effek van verskillende voer en produkkomponente, wat in die hersirkulasie koolwaterstof- en proseswaterstroom sal opbou, op die werksverrigting van die katalisator, is ook gekwantifiseer. Die volgende komponente is ondersoek : n-butaan, isobuteen, 1-penteen, 1,3-butadieen en asetoon. Die lang termyn werksverrigting van die katalisator gedurende op-lyn en regenerasie siklusse, is ook bepaal.

Om 'n kommersiële reaktor te ontwerp word 'n geskikte reaksiesnelheidsvergelyking benodig. Daarom is die kinetika ondersoek in die bankskaal reaktorsisteem. Die geskiktheid van hierdie sisteem vir so 'n ondersoek is vooraf bevestig. Die mono-molekulêre meganisme, met 'n enkel of veelvoudige snelheidsbepalende stappe as ook die wet van massawerking, is ondersoek. In totaal is agt gevalle ondersoek. Alhoewel die reaksie meganisme nie geïdentifiseer kon word nie, is 'n bruikbare reaksiesnelheids-vergelyking opgestel. Die geskiktheid van die model is verder bevestig deur die werkverrigting van die loodsaanleg suksesvol te voorspel.

RÉSUMÉ

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, to develop an appropriate operating procedure, and to generate data suitable for the design of a commercial n-butene skeletal isomerisation unit. Hence, this study included not only quantifying the effects of the operating parameters on the performance of the catalyst, but also a detailed kinetic investigation.

The final use of the isobutene is as a fuel additive in the form of a tertiary ether (Unzelman et al., 1971:47; Unzelman, 1989a:44, 1989b:33). A number of alternative processes, using a variety of raw materials for the production of isobutene are available as discussed by, among others, Muddarris and Pettman (1980:92), Logwinuk and Graig (1964:66), Vors et al., (1981:1) and Remirez, 1987:21). However, the complexity of these processes and availability of the feed stocks prevent their use at Sasol Chemical Industries. Hence, the feasibility of the skeletal isomerisation of the n-butenes to isobutene was investigated. This promised to be a possible way, due to feedstock availability and a relatively simple process flow sheet, to prepare a suitable feed stock for the etherification plant.

An investigation as to the reactions that can take place during the bond and skeletal isomerisation of 1-butene, and an analysis of the reactivity of the various products during the preparation of the tertiary ether, were carried out. It was found that the by-products formed consisted mainly of the linear butene isomers, C_4 paraffins and lighter (C_3) and heavier (C_5) components (Kirk and Othmer, 1984:356, Choudhary and Doraiswamy, 1971:230, Andy et al., 1998:322). Examining the affinity of these components for reactions with an alcohol, at the conditions traditionally used for the preparation of ethers, it was found that all of these, including the linear butenes, i.e., 1-butene, *cis*-2- and *trans*-2-butene, were inert. Hence, high yields of the desired tertiary ethers could be achieved without costly purification of the products from the isomerisation plant being required (Ancillotti and Pescarollo, 1986:1; Tejero et al., 1989:1269). An examination of the thermodynamics showed that even if the only by-products formed were *cis*-2- and

trans-2-butene, the maximum yield of isobutene possible, at the optimum temperature of 520°C, is 36.6 mass % (Kilpatrick et al., 1946:559). However, as isobutene can be removed from the products via etherification, a high yield of isobutene may be achieved by recycling the gaseous products from the etherification reactor to the isomerisation reactor. The successful implementation of this closed loop system requires that the formation of the by-products other than *cis*-2- and *trans*-2-butene be kept as low as possible. The build-up of the lighter and heavier by-products in the recycled stream could best be prevented by venting some of the gaseous material. Unfortunately, this will also lead to the loss of valuable feed stocks and should thus be avoided. Hence, a suitable skeletal isomerisation catalyst will firstly have to exhibit a high selectivity to isobutene, and secondly a high conversion of the n-butenes per pass.

A search of the literature was conducted in the attempt to locate a suitable catalyst. The results from the literature survey are given in Chapter 2. Searching the literature for details of a suitable catalyst and a kinetic equation that could be used for the rigorous design of a skeletal isomerisation reactor, it was noted that little information was available. What was found was that the law of mass action could be used to describe the rate of n-butene conversion and the formation of by-products (Choudhary and Doraiswamy, 1971:55, Bianchi et al., 1994:554, Simon et al., 1994:480, Szabo et al., 1993:319) and that silanised alumina catalysts were the most suitable for this application.

Examining the bond isomerisation mechanism over a catalyst containing predominantly Lewis acid sites, it was concluded that both an acid and base site were required, and that the rearrangement of the olefin proceeds via the hydrogen switch mechanism (Gerberich and Hall, 1966:107). It was also established that Lewis sites are not capable of catalising skeletal isomerisation and are thus not suitable for this reaction (Condon, 1958:44). In the case of Brønsted acids, it was found that the rearrangement of the olefin proceeds via the classical cation mechanism (Choudhary and Doraiswamy, 1975:253). The rearrangement of the butyl cation from the secondary to the less stable primary butyl cation, the dehydrogenation of which results in the formation of isobutene, can only be accommodated if it is assumed that the butyl cation assumes the methyl bridged configuration after formation (Carneiro et al. 1990:4065). Alternatively, a by-molecular mechanism consisting of dimerisation, isomerisation followed by cracking to the desired products, was proposed (Mooiweer et al., 1994:2330). However, the validity of this mechanism is still being debated in the literature (Houžvička et al., 1996:288, Mériaudeau et al., 1997:L).

Examining the nature of the active sites on alumina and silica alumina, it was found that in the case of the former the required Brønsted sites were absent (Knözinger and Kaerlein, 1972:438). The required sites may be created either by halogenating alumina with fluorine (Holm and Clark, 1963:38; Gerberich et al., 1966:216) or chlorine (Tanaka and Ogasawara, 1970:162; Ayame and Sawada, 1989:3055) or by silanising the material with tetra-ethoxysilane (Buonomo et al., 1977:1; Manara et al., 1977:1, Nielsen et al., 1986:338). To establish which of these materials, including silica alumina prepared in the conventional way, was suitable for use in a commercial application, the results achieved by other workers were reviewed. It was found that in most cases the catalyst deactivated during the on-line period. However, the initial performance could usually be recovered by regenerating the material, i.e., by burning off the coke deposited on the catalyst during the on-line period (Choudhary and Doraiswamy, 1971:56). From this it may be concluded that in a commercial plant a multi-reactor system will be required to guarantee that the composition of the products from the isomerisation reactors remains stable. A stable product stream will be required to enable the uninterrupted operation of the etherification plant and other down stream processes. It was further found that the period between regenerations could be extended by protecting the Brønsted acid sites present on the surface of the catalyst. The most effective manner in which this could be done was to co-feed water (Choudhary and Doraiswamy, 1971:59; Gerhard et al., 1980:3). The water co-fed interacted with the Lewis acid sites to form the required Brønsted acid sites (Hughes et al., 1969:58).

In the case of fluorinated or chlorinated alumina, the loss of the halogen to the water could be counteracted by spiking the water with a suitable halogen compound such as HF or HCl. The corrosive nature of these materials and their presence in the final product may be undesirable. Hence, it may be concluded that halogenated aluminas are not suitable for use in a commercial skeletal isomerisation plant.

Examining the results achieved by other workers using silica alumina for the skeletal isomerisation of the n-butenes to isobutene, it was found that the material had little to no activity (Choudhary and Doraiswamy, 1971:59; Nielsen et al., 1986:341). Silanised alumina, prepared using tetraethoxysilane was found to be a highly active material for this reaction (Hsing, 1984:1, Nilsen et al., 1986:338). It was further noted that the activity and stability of the material was largely dependent on the procedure used during the pre-treatment of the alumina support and the water to hydrocarbon ratio used during the on-line period. In addition to this, it was established that silanising alumina enhanced the resistance of the material to thermal sintering, particularly in the presence of water, making it suitable for use in a commercial process (Beguin et al., 1991:603). An attempt to locate the intrinsic kinetic equation particular to this type of catalyst, suitable for the rigorous design of the skeletal isomerisation reactor, was not successful. However, a proprietary, experimental amorphous silica alumina catalyst could be obtained from a supplier of refinery technology and was used during this study. The performance of the material was evaluated and an intrinsic kinetic equation suitable for use in the design of a commercial skeletal isomerisation reactor developed during this study. Unfortunately, although some of the physical characteristics of this material are presented in this thesis, a full characterisation may not be included.

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

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- 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, was 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 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 per pass through the isomerisation reactor at 520°C is 36.6 mass % (Kilpatrick et al., 1946:559), 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 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 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.

The kinetics of this reaction were investigated in an attempt to identify the reaction mechanism and to develop the intrinsic kinetic equation. The necessary experimental data was 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 had to be established. Using various theoretical techniques as discussed by, among others, Smith (1981:557), Mears (1971:544), Froment and Bischoff (1979:451) and Carberry (1981:76), the significance of both radial and axial heat and mass transfer limitations were quantified. It was concluded that the flow patterns in both the pilot plant and the bench reactor system did not deviate sufficiently from ideal plug flow to warrant the use of a two-dimensional reactor model. Also, from a theoretical as well as experimental investigation, using the techniques proposed by, among others, Mears (1971:128), Everson et al. (1996:238) and Froment and Bischoff (1990:173), it was concluded that mass and heat transfer limitations in and around the catalyst particle were not significant. Hence, it was concluded that a one-dimensional pseudo-homogeneous reactor model may be used to describe the reactor system, while heterogeneous models to describe heat and mass transfer effects in and around the particle, were not required. Furthermore, all results recorded were due to the catalyst, as homogeneous gas phase reactions did not take place and the reactor and packing material were inert. Finally, as the reactor systems were operated isothermally, in both the axial and the radial direction, isobarically in the axial direction, and as the molar flow rate remained constant throughout, the superficial linear velocity in both the pilot plant reactor system and the bench scale reactor systems were independent of the axial position in the catalyst bed, allowing further simplification of the reactor model.

It is, of course, not possible to investigate the kinetics of a system in which the composition of the products is independent of the operating conditions, as is the case if the products are at thermodynamic equilibrium. During the kinetic investigation, only results for which the isobutene to n-butene ratio in the product gas was less than 75 % of the theoretical value predicted from thermodynamics, were used. The thermodynamic equilibrium composition of the butenes as a function of temperature was obtained from the literature (Kilpatric et al., 1946:559) and calculated using two process engineering modelling packages, ProII and AspenPlus. The influence of the thermodynamic equilibrium on the suitability of the data for kinetic studies was not previously reported in the literature.

The molar ratios of the linear butenes, on the other hand, were independent of the operating conditions. In all cases the recorded ratios were as predicted from thermodynamics. This permitted that the linear butenes, 1-butene, *cis*-2- and *trans*-2-butene could be treated as a pseudo-component, n-butene, during the kinetic study. Similarly, the by-products, formed via the disproportionation of the butenes (Andy et al., 1998:322), were treated as a single pseudo-component as was previously done by Choudhary and Doraiswamy (1975:228). The rate equations required, based on the mono-molecular mechanism (Choudhary and Doraiswamy, 1975:235) when a single step, or multiple steps, control the overall reaction rate, were developed, as discussed in Chapter 6 and Appendix 3 (Froment and Bischoff, 1979:73). To fit the various rate equations to the experimental data, i.e., to identify the optimum values of the unknown parameters, the necessary FORTRAN program was set up. Attempting to model the n-butene skeletal isomerisation reaction using a multi-step approach, was not previously reported in the literature.

To allow discrimination between rival models, a number of statistical techniques (Sarup and Wojchiehowski, 1989:70, Draper and Smith, 1981:533, Box et al., 1978:43) were employed. Confidence intervals and confidence contours, about the optimum values of the unknown parameters required by the various rate equations, were also generated. Using a fictitious data set, the ability of the procedures developed to discriminate between rival models was also confirmed. The use of confidence contours to confirm that the optimum value of the unknown parameters was indeed located in each case was not previously reported for this system in the literature.

Using the bench scale reactor system, the rate of the n-butene skeletal isomerisation to isobutene, in the absence of other resistances, was measured. The various rate equations, based on the mono-molecular mechanism (Choudhary and Doraiswamy, 1975:235), when a single step, or multiple steps, controls the overall reaction rate, were developed (See also Appendix 3). Using the FORTRAN program set up (See Appendix 5), the optimum values of the unknown parameters for each of the rate equations were determined. That in each case the optimum values of the unknown parameters were found, was confirmed by an examination of the confidence contours set up. It was found that the seven mechanistic rate equations developed, and the law of mass action, were equally capable of predicting the performance of the bench scale reactor system. Discrimination on a statistical basis, using various procedures (Sarup and Wojchiehowski, 1989:70, Draper and Smith, 1981:533, Box et al., 1978:43) was not possible.

However, it was found that for a given reaction step, the absolute values of the pre-exponential factors and the activation energies 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 was thus concluded 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 view of this, the fact that it was not possible to discriminate between models developed by assuming that a specific reaction step(s) controls the overall rate, may be understood. Using multi-step modelling to identify the n-butene skeletal isomerisation mechanism has not previously been reported in the literature.

From an examination of the confidence profiles generated, it was found that in each case the model was equally sensitive to increases or decreases in the values of the parameters used to describe the rate of n-butene adsorption (Step 1 in Figure 6.1). 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. This mechanism was previously proposed by Choudhary and Doraiswamy (1975:234) while studying a fluorinated alumina catalyst at temperatures below 435°C. At higher temperatures, they observed a switch in the mechanism, with isobutene desorption becoming the rate controlling step. For the other two forward reactions, the optimum values of the unknown parameters were also found in each case. However, taking a global view of the confidence contours, suggested that the rate of the n-butene to isobutene surface reaction, and the desorption of isobutene, have 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 the rate 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. The use of confidence contours to confirm that the optimum values of the unknown parameters had been found, or to assist in identifying the most significant reaction step, was not previously proposed in the literature.

During this investigation, the ratios of the n-butene, *cis*-2-, *trans*-2- and 1-butene in the flue gas were at values as predicted from thermodynamics. Hence, the linear butenes were treated as a single component, n-butene. This approach was previously used by, among others, Bianchi et al. (1994:554), Simon et al. (1994:480) and Choudhary and Doraiswamy (1971:55). This approach was not used by Szabo et al. (1993:323), who set up a set of elementary first order reactions to describe the bond as well as the skeletal isomerisation of the butenes. What has not previously been reported in the literature is an attempt to identify the overall reaction mechanism, using multi-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 (Bianchi et al., 1994:556, Houžvička et al., 1996:288, Mériaudeau et al, 1997:L1), and are routinely treated as a single pseudo-component.

Hence, as discrimination between rival models was not possible, the simplest form of the rate equations considered, the law of mass action to describe the skeletal isomerisation of the n-butene to isobutene, was adopted. This approach was previously used by (Choudhary and Doraiswamy, 1971:55, Bianchi et al., 1994:554, Simon et al., 1994:480, Szabo et al., 1993:319). The robustness of the rate equation developed and its suitability for the rigorous design of a commercial n-butene skeletal isomerisation reactor was further confirmed by the ability of this model to predict the performance of the pilot plant. The final form of the rate equations, together with the appropriate values of the unknown parameters, are repeated below.

The net rate of n-butene formation may be calculated using

$$r_{n-C_4^=} = -r_{ISOM} - r_{BP}$$

with the rate of the n-butene skeletal isomerisation using

$$r_{ISOM} = k'_1 \cdot \exp\left(\frac{-E'_1}{R \cdot T}\right) \cdot P_{n-C_4^=} - k'_2 \cdot \exp\left(\frac{-E'_2}{R \cdot T}\right) \cdot P_{i-C_4^=}$$

and the formation of by-products using

$$r_{BP} = k'' \cdot \exp\left(\frac{-E''}{R \cdot T}\right) \cdot P^{m}_{n-C_4^=}$$

where

k''	is the frequency factor for the by-product reaction, $k'' = 0.072$ mol·kg^{-1}·s^{-1}·kPa^{-m},
E''	is the activation energy for the by-product formation reaction, $E'' = 13425$ cal·mol^{-1},
m	is the order of the by-product formation equation, $m = 0.778$,
k'_1	is the frequency factor for the forward n-butene skeletal isomerisation reaction, $k'_1 = 0.095$ (+7.93e-4 / -7.22e-4) mol·kg^{-1}·s^{-1}·kPa^{-1},
k'_2	is the frequency factor for the backward n-butene skeletal isomerisation reaction, $k'_2 = 0.631$ (+2.68e-2 / -2.48e-2) mol·kg^{-1}·s^{-1}·kPa^{-1},
E'_1	is the activation energy for the forward n-butene skeletal isomerisation reaction, $E'_1 = 11785$ (+3.31 / - 0.96) cal·mol^{-1},
E'_2	is the activation energy for the backward n-butene skeletal isomerisation reaction, $E'_2 = 12979$ (+25.7 / -94.5)cal·mol^{-1},
T	is the system temperature, K,
R	is the universal gas constant, $R = 1.987$ cal·mol^{-1}·K^{-1},
$P_{n\text{-}C4}$	is the n-butene partial pressure, kPa(a) and
$p_{i\text{-}C4}$	is the isobutene partial pressure, kPa(a).

Extreme care was taken during this study to ensure that the kinetics were measured in the absence of other resistances. This, and the fact that the values of the forward ($E_1 = 11785$ cal·mole^{-1} = 49.3 kJ·mole^{-1}) and reverse ($E_2 = 12979$ cal·mole^{-1} = 54.33 kJ·mole^{-1}) activation energy, are of a magnitude similar to those reported previously in the literature, (35.2 kJ·mol^{-1} to 113 kJ·mole^{-1}), confirms that they represent the true intrinsic activation energy for the n-butene skeletal isomerisation reaction over the silica alumina catalyst used. The enthalpy and entropy for the adsorption equilibrium constants in the Hougen-Watson type rate equations, were not evaluated during this study. This is an area where further work is required. See also Boudart and Loffler (1990:317) and Arthur et al. (1991:8521).

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LIST OF SYMBOLS

CHAPTER 2

k	is the rate constant, gmole·hr^{-1}·g^{-1}·atm^{-1}
K	is the equilibrium constant, -
K_A	is the adsorption equilibrium coefficient of n-butene, -
K_B	is the adsorption equilibrium coefficient of isobutene, -
K_p	is the equilibrium constant, -
P_A	is the partial pressure of n-butene, atm
P_B	is the partial pressure of isobutene, atm
r_B	is the rate of formation of isobutene, gmole·hr^{-1}·g^{-1}
r_C	is the rate of conversion of isobutene to poly isobutene, gmole·hr^{-1}·g^{-1}
T	is the temperature, °C

CHAPTER 5

C_i	is the concentration of component i at the reaction conditions, mol·m^{-3}
$C_{i,in}$	is the concentration of component i in the feed at the reaction conditions, mol·m^{-3}
err	is the sum of errors at the optimum solution, -
err'	is the sum of errors away from the optimum solution, -
F(n-p-m,m)	is the tabulated F-test values, -, (Draper and Smith, 1981:533)
i	is the experiment number, -
L	is the total bed length, m.
m	is the number of experiments, -
m	is the number of degrees of freedom associated with the pure error variance, -
n	is the total number of experimental points, -
p	is the number of parameters being estimated, -
$p^a_{i\text{-}C4}$	is the actual isobutene partial pressure in the product gas, kPa(a)

$p^{a}_{n\text{-}C4}$	is the actual n-butene partial pressure in the product gas, kPa(a)
$p^{c}_{i\text{-}C4}$	is the calculated isobutene partial pressure in the product gas, kPa(a)
$p^{c}_{n\text{-}C4}$	is the calculated n-butene partial pressure in the product gas, kPa(a)
R^2	is the coefficient of determination, -
r_i	is the global rate of disappearance of reactant per unit mass of catalyst, $mol{\cdot}s^{-1}{\cdot}kg^{-1}$
SSQ	is the sum of the residual squared at the optimum solution, -
u	is the superficial velocity in the axial direction, $m{\cdot}s^{-1}$
Y_{Ai}	is the actual value for experiment i, -
Y_{Pi}	is the predicted value for experiment i, -
$\overline{y}$	is the average of the actual values, -
z	is the height of the element, m
δ^2	is the pure error variance calculated from repeat data collected at the same reaction conditions, -
ρ_B	is the density of the catalyst in the bed, $kg{\cdot}m^{-3}$

CHAPTER 6

E_i	is the activation energy for the reaction step under consideration, $cal{\cdot}mole^{-1}$
E"	is the activation energy for the by-product formation reaction, $cal{\cdot}mole^{-1}$
E'_1	is the activation energy for the forward n-butene skeletal isomerisation reaction, $cal{\cdot}mole^{-1}$
E'_2	is the activation energy for the backward n-butene skeletal isomerisation reaction, $cal{\cdot}mole^{-1}$
f(x)	is the dependent variable, -
i	is the reaction under consideration, -
i-C4	represents a molecule of isobutene in the gas phase, -
$(i\text{-}C_4^{=}{\cdot}S)$	represents a molecule of isobutene on the surface of the catalyst, -
k"	is the frequency factor for the by-product reaction, $mol{\cdot}kg^{-1}{\cdot}s^{-1}{\cdot}kPa^{-m}$
k'_1	is the frequency factor for the forward n-butene skeletal isomerisation reaction, $mol{\cdot}kg^{-1}{\cdot}s^{-1}{\cdot}kPa^{-1}$

k'_2	is the frequency factor for the backward n-butene skeletal isomerisation reaction, $mol \cdot kg^{-1} \cdot s^{-1} \cdot kPa^{-1}$
k'_j	are the frequency factors for Case 1, j=1 or 2, $mol \cdot kg^{-1} \cdot s^{-1} \cdot kPa^{-1}$
k_i	is the forward frequency factor for the reaction, $mol \cdot kg^{-1} \cdot s^{-1} \cdot kPa^{-1}$
k_i	are the frequency factors for Case 2 to Case 8, i=1 to 6, $mol \cdot kg^{-1} \cdot s^{-1} \cdot kPa^{-1}$
k_i^o	is the frequency factor for the reaction step under consideration, $mol \cdot kg^{-1} \cdot s^{-1} \cdot kPa^{-1}$
m	is the order of the by-product formation equation, -
$(n\text{-}C_4^{=} \cdot S)$	represents a molecule of n-butene on the surface of the catalyst, -
n-C4	represents a molecule of n-butene in the gas phase, -
n_t	is the total number of data points under consideration, $n_t = 392$
n_x	is the number of data point at X
R	is the universal gas constant, $R = 1.987\ cal \cdot mol^{-1} \cdot K^{-1}$
T	is the system temperature, K
(S)	is a vacant surface site, -
x	is the independent multiplier, $-0.9625 \leq x \leq 1.0375$

APPENDIX 1

CB	is the 1-butene conversion, mass %
CT	is the total conversion of the n-butenes to isobutene and all other by-products, mass %
D_W	is the density of the water which was fixed at 1 $g \cdot ml^{-1}$ in this study
$F_{G\ tn,tn+1}$	is the average flow rate of gaseous products over the time interval, $g \cdot hr^{-1}$
$F_{H\ tn,tn+1}$	is the average hydrocarbon flow rate over the time interval, $g \cdot hr^{-1}$
$F_{L\ tn,tn+1}$	is the average flow rate of liquid products over the time interval, $g \cdot hr^{-1}$
$F_{W\ tn,tn+1}$	is the average water flow rate over the time interval, $g \cdot hr^{-1}$
F_X	is the average of two successive flow rates, $g \cdot hr^{-1}$ with X equal to W, H, L or G depending on which stream is being examined
HR	is the total time on-line, hr
LB	is the loss of butenes, mass %

LHSV	is the average liquid hourly space velocity of the hydrocarbons, hr^{-1}
LHSV$_{After}$	is the LHSV of the hydrocarbons assuming that all mass loss occurred after the reactor, hr^{-1}
LHSV$_{Before}$	is the LHSV of the hydrocarbons assuming that all mass loss occurred before the reactor, hr^{-1}
MB	is the average mass balance, mass %
M$_{C\ tn+1}$	is the mass of the feed cylinder at the end of the interval, g
M$_{C\ tn}$	is the mass of the feed cylinder at the start of the interval, g
M$_{L\ tn,tn+1}$	is the total mass of liquid collected over the time interval, g
Mo$_{H,OUT}$	is the average molar mass of the gaseous products, Mo$_{H,OUT}$ = 56 g·gmol^{-1}
Mo$_{H,OUT}$	is the average molar mass of the hydrocarbon feed, Mo$_{H,OUT}$ = 56 g·gmol^{-1}
Mo$_{H,IN}$	is the average molar mass of the hydrocarbon feed, Mo$_{H,IN}$ = 56 g·g mol^{-1}
Mo$_{H,IN}$	is the average molar mass of the hydrocarbon feed, 56 g·gmol^{-1}
Mo$_{i,x}$	is the molar mass of component i, g·gmol^{-1}
Mo$_{out}$	is the average molar mass of the product gas, g·mol^{-1}
Mo$_{W}$	is the molar mass of water, Mo$_{W}$ = 18 g·g mol^{-1}
Mo$_{W}$	is the molar mass of water, 18 g·gmol^{-1}
Mp	is the average water to butenes, mole %
Mp$_{After}$	is the water to butene mole % assuming that all mass was lost after the reactor, mole %
Mp$_{Before}$	is the water to butene mole % assuming that all mass loss occurred before the reactor, mole %
p	is the ambient pressure, p = 85 kPa
p$_{R}$	is the reactor pressure, kPa(a)
R	is the universal gas constant, R = 8314 kPa·cm^{3}·mol^{-1}·K^{-1}
R	is the universal gas constant, R = 8.314 kPa·l·K^{-1}·mol^{-1}
RT	is the average residence time of the reactants, s
RT$_{After}$	is the RT of the reactants assuming that all mass loss occurred after the reactor, s
RT$_{Before}$	is the RT of the reactants assuming that all mass loss occurred before the reactor, s
SC	is the cracking selectivity, mass %

SH	is the hydrogen transfer selectivity, mass %
SI	is the isobutene selectivity, mass %
SO	is the oligomerisation selectivity, mass %
T	is the ambient temperature, $T = 298$ K.
$t_{n,n+1}$	is the mid point of the time interval, hr
t_n	is the time at the start of the time interval, hr
t_n	is the time at the start of the interval, hr
t_{n+1}	is the time at the end of the interval, hr
t_{n+1}	is the time at the end of the time interval, hr
T_R	is the reactor temperature, K
$V_{C\,tn+1}$	is the feed cylinder volume at the end of the time interval, ml
$V_{c\,tn}$	is the feed cylinder volume at the start of the time interval, ml
V_{tn}	is the WGFM reading at the start of the time interval, l
V_{tn+1}	is the WGFM reading at the end of the time interval, l
W/H_{Before}	is the water to hydrocarbon ratio assuming that all mass was lost before the reactor, molar
W/H_{After}	is the water to hydrocarbon ratio assuming that all mass was lost after the reactor, molar
W/H	is the average water to hydrocarbon ratio, molar
W_C	is the mass of catalyst, g
$WF_{<C4,OUT}$	is the mass fraction of lights in the product gas, -
$WF_{<C4,IN}$	is the mass fraction of lights in the feed gas, -
$WF_{>C4,IN}$	is the mass fraction of heavies in the feed gas, -
$WF_{>C4,OUT}$	is the mass fraction of heavies in the product gas, -
$WF_{1,3\text{-}C4'''',IN}$	is the mass fraction of dienes in the feed gas, -
$WF_{1,3\text{-}C4'''',OUT}$	is the mass fraction of dienes in the product gas, -
$WF_{1\text{-}C4'',OUT}$	is the mass fraction of 1-butene in the product gas, -
$WF_{1\text{-}C4'',IN}$	is the mass fraction of 1-butene in the feed gas, -
$WF_{C4'',OUT}$	is the mass fraction of the four isomers of butene in the product, -
$WF_{C4'',IN}$	is the mass fraction of the four isomers of butene in the feed, -
$WF_{C4'',OUT}$	is the mass fraction of the four isomers of butene in the product, -
$WF_{C4',IN}$	is the mass fraction of n-butane and isobutane in the feed gas, -

$WF_{C4',OUT}$	is the mass fraction of n + isobutane in the product gas, -
$WF_{i,x}$	is the mass fraction of component i in the gas, -, with X=OUT for the gaseous products and X=IN for the hydrocarbon feed
$WF_{I\text{-}C4'',OUT}$	is the mass fraction of isobutene in the product gas, -
$WF_{I\text{-}C4'',IN}$	is the mass fraction of isobutene in the feed gas, -
WHSV	is the average weight hourly space velocity of the butenes, hr^{-1}
$WHSV_{After}$	is the WHSV of the butenes assuming that all mass loss occurred after the reactor, hr^{-1}
$WHSV_{Before}$	is the WHSV of the butenes assuming that all mass loss occurred before the reactor, hr^{-1}
z	is the compressibility factor, -
ρ_C	is the bulk density of the catalyst, $g{\cdot}ml^{-1}$. This is 0.85 $g{\cdot}ml^{-1}$ for Catalyst A and 0.65 $g{\cdot}ml^{-1}$ for Catalyst B
ρ_H	is the liquid density of the butenes at 25°C of 0.59 $g{\cdot}ml^{-1}$
ΣF_G	is the total mass of gas produced during the on-line period, g
ΣF_H	is the total mass of hydrocarbons used during the on-line period, g
ΣF_L	is the total mass of liquid collected during the on-line period, g
ΣF_W	is the total mass of water used during the on-line period, g
3600	is a conversion factor from hr to s

APPENDIX 3

$(i\text{-}C_4^{=}{\cdot}S)$	represents a molecule of isobutene on the surface of the catalyst, -
$(n\text{-}C_4^{=}{\cdot}S)$	represents a molecule of n-butene on the surface of the catalyst, -
(S)	represents a vacant surface site, -
$(S)_t$	is the total number of active sites, -
i-C4	represents a molecule of isobutene in the gas phase, -
k'_j	are the frequency factors for Case 1, j=1 or 2, $mol{\cdot}kg^{-1}{\cdot}s^{-1}{\cdot}kPa^{-1}$
k_i	are the frequency factors for Case 2 to Case 8 with i=1 to 6 and with $k_i = k'_j$ with j = 1 or 2, for Case 1, $mol{\cdot}kg^{-1}{\cdot}s^{-1}{\cdot}kPa^{-1}$,
k_i^1	is the pre-exponential factor, traditionally represented by k_i^o, $mol{\cdot}kg^{-1}{\cdot}s^{-1}{\cdot}kPa^{-1}$

k_i^2	is the activation energy, traditionally represented by E, $cal \cdot mol^{-1}$
n-C4	represents a molecule of n-butene in the gas phase, -
$P_{i\text{-}C4}$	is the bulk partial pressure of isobutene, kPa(a)
$P_{n\text{-}C4}$	is the bulk partial pressure of n-butene, kPa(a)
r_a	is the overall rate of adsorption, $mol \cdot s^{-1} \cdot kg^{-1}$
r_d	is the overall rate of desorption, $mol \cdot s^{-1} \cdot kg^{-1}$
r_s	is the overall surface reaction rate, $mol \cdot s^{-1} \cdot kg^{-1}$

APPENDIX 4

a, b, ·	are the stoichiometric coefficients of the reactants, -
A, to D_i	are constants in the ideal gas heat capacity equation for component i, -
A_i to D_i	are constants specific for component i in the ideal gas thermal conductivity equation, -
a_m	is the external area available for mass transfer, m^2
a_t	is the total particle external area, m^2
C	is the reactant concentration, $mole \cdot m^{-3}$
C_{Ao}	is the inlet concentration of reactant A, $mol \cdot m^{-3}$
C^b_A	is the bulk reactant concentration, $kmol \cdot m^{-3}$
C_p	is the gas heat capacity, $J \cdot kg^{-1} \cdot K^{-1}$
C_{pe}	is the effective heat capacity of the gas, $J \cdot kg^{-1} \cdot K^{-1}$
C_{Pi}	is the heat capacity of component i, $J \cdot mol^{-1} \cdot K^{-1}$
D_{ik}	is the effective diffusivity of component j in component k, $m^2 \cdot s^{-1}$
D_{jm}	is the effective binary diffusion coefficient of component j in a multi-component mixture m, $m^2 \cdot s^{-1}$
D^P_{jm}	is the effective binary diffusivity of component j in a multi-component mixture in the pore of the catalyst, $m^2 \cdot s^{-1}$
d_p	is the diameter of the particle, m
d_t	is the reactor tube diameter, m
$(D_e)_L$	is the effective diffusivity in the axial direction, $m^2 \cdot s^{-1}$
$(D_e)_r$	is the effective diffusivity in the radial direction, $m^2 \cdot s^{-1}$

E	is the activation energy, $J \cdot kmol^{-1}$
F_{ci}	is a molecular shape and polarity correction factor, -
f_D	is a correction factor
G	is the superficial mass velocity, $kg \cdot m^{-2} \cdot s$
h	is the gas to particle heat transfer coefficient, $W \cdot m^{-2} \cdot K^{-1}$
K	is the thermodynamic equilibrium constant, -
k	is the Boltzman constant, k = 1.3805e-23 $J \cdot K^{-1}$
k_1	is the reaction rate constant, $m^3_f \cdot kg^{-1}_{cat} \cdot s^{-1}$ or $moles \cdot kg_{cat}^{-1} \cdot s^{-1} \cdot kPa(a)^{-1}$
k_1	is the Carman-Kozeny constant for viscous losses, -
k_2	is the Burke-Plummer constant for kinetic losses, -
$(k_g)_{n-C4''}$	is the mass transfer coefficient for n-butene, $moles \cdot m^{-2} \cdot s^{-1}$
l	is the total catalyst bed height, m
L	is the volume (V) to surface area (S) ratio of the catalyst particle, which for spherical particle, reduces to $d_P/6$, m
M_i	is the molecular weight of component i, $g \cdot mol^{-1}$
n	is the molar density of the mixture, $mol \cdot m^{-3}$
$(Pe_r)_m$	is the radial Peclet number for mass transfer, -
$(Pe_L)_h$	is the Peclet number in the axial direction for heat transfer, -
$(Pe_L)_m$	is Peclet number for mass transfer in the axial direction, -
p	is the emissivity of the solid, -
$p_{1-C4''}$	is the isobutene partial pressure in the fluid, kPa(a)
$p^b_{n-C4''}$	is the bulk n-butene partial pressure, kPa(a)
$p_{n-C4''}$	is the n-butene partial pressure in the fluid, kPa(a)
$p^s_{n-C4''}$	is the surface n-butene partial pressure, kPa(a)
P_T	is the total pressure, bar(a)
R	is the universal gas constant, $kmol \cdot kPa(a) \cdot m^{-3} \cdot K^{-1}$
R	is the universal gas constant, $J \cdot kmol^{-1} \cdot K^{-1}$
r	is the radius of the element, m
r, s, ·	are the stoichiometric coefficients of the products, -
r_A	is the observed rate of reaction of component A, $kmol \cdot kg^{-1}_{cat} \cdot s^{-1}$
r_A^b	is the reaction rate if not slowed by diffusion, $moles \cdot kg^{-1}_{cat} \cdot s^{-1}$
r_A^p	is the reaction rate if slowed by diffusion in the pore, $moles \cdot kg^{-1}_{cat} \cdot s^{-1}$

$r^{b}_{n\text{-}C4''}$	is the bulk n-butene consumption rate, moles·kg^{-1}_{cat}·s^{-1}
$r_{n\text{-}C4''}$	is the rate of n-butene consumption, moles·kg_{cat}^{-1}·s^{-1}
r_p	is the global rate of disappearance of the reactant, mol·s^{-1}·kg^{-1}
$r^{s}_{n\text{-}C4''}$	is the surface n-butene consumption rate, moles·kg^{-1}_{cat}·s^{-1}
$(r_A)_{obs}$	is the observed reaction rate, kmol·kg^{-1}_{cat}·s^{-1}
S	is the surface area of the catalyst particle, m^2
T	is the temperature, K
T^b	is the bulk temperature, K
T_{bi}	is the normal boiling point of component i at 1 atm, K
T_{ci}	is the critical temperature of component i, K
T_o	is the inlet temperature, K
T_R	is the temperature at the centre of the reactor, K
T_W	is the temperature at the wall of the reactor, K
u	is the superficial velocity in the axial direction, m·s^{-1}
u_s	is the fluid superficial velocity, m·s^{-1}
V	is the volume of the catalyst particle, m^3
V_{bi}	is the liquid molar volume at the normal boiling point of component i, cm^3·mol^{-1}
V_{ci}	is the critical volume of component i, cm^3·mol^{-1}
X	is the fractional conversion, -
y_i	is the mole fraction of component i, -
z	is the height of the element, m
z	is the increment height, m
α_{rs}	is the solid radiation heat transfer coefficient, J·m^{-2}·s^{-1}·K^{-1}
α_{rv}	is the void radiation heat transfer coefficient, J·m^{-2}·s^{-1}·K^{-1}
α_w	is the heat transfer coefficient at the reactor wall, W·m^{-2}·K^{-1}
β	is a coefficient that depends on the particular geometry and packing density, comprised between 0.9 and 1.0 (Froment and Bischoff, 1990:455). In this study ß was assumed to be equal to 0.95.
ΔH_r	is the heat of reaction, J·$mole^{-1}$
ΔP	is the pressure drop, Pa
ΔT_{ad}	is the potential adiabatic temperature rise, -

ϵ	is the effective bed voidage, -
ϵ_s	is the solid void fraction, -
ϵ_s	is the particle internal void fraction, -
ζ_A	is the fractional conversion of component A at equilibrium, -
ζ_j	is the stoichiometric coefficient of component j, with the convention that ζ is positive for products and negative for reactants, -
η	is the effectiveness factor, -
η_i	is the dipole moment for component i, debyes.
η_{ri}	is a dimensionless dipole moment for component i, -
$(\lambda_e)_L$	is the effective axial thermal conductivity coefficient, $W \cdot m^{-1} \cdot K^{-1}$
$(\lambda_e)_r$	is the effective radial thermal conductivity coefficient, $W \cdot m^{-1} \cdot K^{-1}$
κ_i	is a special correction factor for highly polar substances, -
λ	is the fluids thermal conductivity, $kW \cdot m^{-1} \cdot K^{-1}$
λ_{eL}	is the effective axial thermal conductivity, $W \cdot m^{-1} \cdot K^{-1}$
λ_{er}	is the effective radial thermal conductivity, $W \cdot m^{-1} \cdot K^{-1}$
λ_{er}^{o}	is the static contribution to the effective thermal conductivity, $W \cdot m^{-1} \cdot K^{-1}$
λ_{er}^{t}	is the dynamic contribution to the effective thermal conductivity, $W \cdot m^{-1} \cdot K^{-1}$
λ_g	is the effective gas thermal conductivity, $W \cdot m^{-1} \cdot K^{-1}$
λ_{ge}	is the effective thermal conductivity of the fluid, $J \cdot m^{-1} \cdot s^{-1} \cdot K^{-1}$
λ_{gi}	is the thermal conductivity of component i, $W \cdot m^{-1} \cdot K^{-1}$
λ_s	is the thermal conductivity of the solid, $W \cdot m^{-1} \cdot K^{-1}$
λ_{se}	is the effective thermal conductivity of the catalyst, $W \cdot m^{-1} \cdot K^{-1}$
μ	is the fluid dynamic viscosity, $kg \cdot m^{-1} \cdot s^{-1}$
μ_f	is the dynamic viscosity. $kg \cdot m^{-1} \cdot s^{-1}$
μ_g	is the viscosity of the gas, $Pa \cdot s^{-1}$
μ_i	is the viscosity of component i, cP
μ_{pi}	is the dipole moment of component i, debyes
ρ_B	is the density of the catalyst in the bed, $kg \cdot m^{-3}$
ρ_f	is the density of the fluid, $kg \cdot m^{-3}$
ρ_g	is the fluid density, $kg \cdot m^{-3}$
ρ_{ge}	is the effective density of the reaction mixture, $kg \cdot m^{-3}$
ρ_s	is the density of the solid, $kg \cdot m^{-3}$

δ_i	is the characteristic-length parameter for component i, where i= A or B, Å
σ_{jk}	is a characteristic length, Å
τ	is the tortuosity factor, -
ϕ	is the Thiele modulus, -
Φ	is a packing specific constant, -
ω_i	is the acentric factor for component i, -
Ω_D	is the diffusion collision integral, -
$\Omega^P{}_D$	is the collision integral for a polar mixture, -
Ω_v	is the viscosity collision integral, -