Selective Hydrogenation for Industrial 1-Hexene Purification

by

Tiffany Brown

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Catalysis Research Unit
Department of Chemical Engineering
University of Cape Town

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SYNOPSIS

Previous reports identified selective catalytic hydrogenation as a possible route to the purification of industrial 1-hexene streams. Even so, reported performance has been poor and, consequently, the principal aim of this study is to adjust operating conditions so as to improve process performance to an industrially interesting level.

In particular, the influence of hydrogen excess and competitive adsorbates (CO and ethanol) on overall process performance is evaluated for representative (1,5-hexadiene and 1-hexyne) impurity removal from a 1-hexene stream over a bi-metallic Pd-Ag/titania catalyst.

Experimental tests are conducted in a down-flow trickle-bed reactor at 60 °C, 15 and 30 barg, H_2/oil ratios in the range 0.01 – 0.2 mol/mol, and oil (1-hexene) space velocities in the range 8 – 16 g/g.hr. Performance is evaluated according to a simplified pseudo-parallel first order reaction scheme where impurity removal and 1-hexene loss are treated as the two competitive reactions. Consequently, specificity, viz. the ratio of the rate of impurity removal to the rate of 1-hexene loss, is a key measure of overall process performance.

It was found that low H_2/oil ratios, accompanied by the absence of gas phase hydrogen, effect a significant improvement in process specificity, from previously reported values of around 2 to values approaching 100. Moreover, at conditions of such high specificity, the extent of impurity removal appears to be limited by hydrogen depletion. It remains, however, unclear as to what effects the enhanced specificity under these conditions although the diminished presence of a palladium β-hydride phase may be at least partially responsible.

It is further observed that the introduction of low concentrations of CO and ethanol, as competitive adsorbates to 1-hexene, does not effect a noticeable increase in process specificity. This disappointing result possibly suggests that the potential advantage of catalytic site 'dilution' is already exhausted by the presence of silver in the bi-metallic catalyst employed in this study.

It is recommended that further studies investigate means to increased overall impurity removal, at high specificity, through increased dissolved hydrogen concentrations, either via higher process pressures or via multistage operation with inter-stage replenishment of dissolved hydrogen.

Regardless of the need for additional development, the substantial increase in specificity achieved in this study makes selective catalytic hydrogenation an industrially interesting process route to the purification of 1-hexene streams.

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LIST OF SYMBOLS

Symbol	Description
$A\%_i$	Area percentage of peak of species i on gas chromatogram
C_i	Concentration of species i
F_i	Molar flow rate of species i
g_{cat}	Mass of catalyst
k_i	Reaction rate constant of species i
K	Equilibrium constant
Sp	Specificity i.e. impurity removal vs. 1-hexene loss
S	Selectivity i.e. hydrogenation vs. isomerisation
X_i	Molar conversion of species i
x_i	Molar fraction of species i
Y_i	Yield of species i

GLOSSARY

β-PdH	Beta Palladium Hydride
FIC	Flow controller
FID	Flame ionisation detector
H_2/oil	Molar hydrogen to hydrocarbon ratio
LAO	Linear alpha olefins
MCP	1-methyl-1-cyclopentene
MFC	Mass flow controller
PI	Pressure indicator
PIC	Pressure controller
ppm	parts per million
ppb	parts per billion
sccm	standard cubic centimetres per minute
SHOP	Shell Higher Olefin Process
TEM	Transmission Electron Microscopy
TI	Temperature indicator
TIC	Temperature controller
TOS	Time on stream
WHSV	Weight hourly space velocity

1 INTRODUCTION

The demand for α-olefins is rapidly increasing on a global scale *(Chemical Marketing Reporter, 1995)*. Linear α-olefins in particular are produced on the scale of several million tons per annum. They have a number of applications but are mainly used as co-monomers in the production of polymers.

The growth in the annual world demand for polyolefins is estimated to be at least 5.5% on average until 2010 *(Marcilly, 2003)*. Other applications of α-olefins include the production of synthetic lubricants, methylamines and surfactants. It was found that polymers including 1-hexene and 1-octene co-monomer are growing more than two times the rate of those including 1-butene co-monomer *(colin-houston.com)*.

Linear α-olefins are produced either by ethylene oligomerisation or recovered from Fischer-Tropsch hydrocarbon streams. The C_5-C_8 alpha olefin range is extracted from Fischer-Tropsch synthesis product streams. 1-Hexene is the more dominant α-olefin by economic value. In South Africa, Sasol is producing about 200 000 tons of 1-hexene per annum and has recently commissioned a third 1-hexene train to meet the rapidly increasing demand *(www.sasol.com)*.

The activity of the catalyst in a polymerization process is largely dependant on the purity of the feed stream. There are a host of impurities emerging in industrial 1-olefin co-monomer streams, which reduce the activity of these catalysts. Typically, the more dominant impurities are dienes, cyclic olefins and alkynes, and are present in the ppm range.

In future, it is proposed that the general trend for all catalytic processes will be the improvement of catalyst activity and especially, selectivity. This will result in a reduction in operating costs and more importantly, conform to the increasing

environmental focus of reducing emissions of catalytic processes (*Marcilly, 2003*). With respect to olefin polymerisation, this often results in an increasing sensitivity of the catalyst towards feedstock impurities and therefore requires less contaminated feedstocks.

Selective hydrogenation is successfully applied in the purification of C_2 - C_4-olefin fractions from steam cracker product streams, which successfully removes the unsaturated impurities but avoids hydrogenation to the undesired alkane. Selective catalytic hydrogenation could also be a suitable method of purification of medium to long chain 1-olefin co-monomer feedstocks. The objective is to selectively hydrogenate the impurities, but inhibit hydrogenation of the 1-olefin to the corresponding paraffin or double-bond isomerisation to internal olefins. Bimetallic palladium-based catalysts were typically shown to result in an increase in the selectivity of impurity hydrogenation *(Sales et al., 2000a)*.

Previous studies showed that a bimetallic Pd-Ag/TiO_2 catalyst was successful in hydrogenating hexadienes in a 1-hexene feed, although a significant loss of 1-hexene resulted *(Stadler et al., 1984; McPherson, 2003)*.

In *McPherson's (2003)* study, criteria were developed to characterise the quality of the selective hydrogenation. "Specificity" was defined to be the ratio of the conversion of the impurity to the conversion of the 1-hexene, while "selectivity" was defined as the rate of saturation of 1-hexene relative to the rate of double-bond isomerisation.

The specificity of hydrogenation catalysts is improved by the introduction of a second metal to the base metal, e.g. Pd-Ag for palladium. Trace amounts of co-adsorbates such as CO are also used to improve specificity *(Guczi et al., 1984; Nierlich and Obenhaus, 1986)*.

It was also shown that the presence of gas-phase hydrogen in this liquid-phase process reduced the selectivity of the catalyst in the selective hydrogenation of a C_4-olefin feedstock *(Nierlich and Obenhaus, 1986)*.

Another key issue in the system of selective hydrogenation is double bond isomerisation. This is undesired, as it results in a loss of feed in terms of 1-olefin. It was found that the acidity of the catalyst carrier plays a major role. With non-acidic carriers, such as titania, double bond isomerisation is insignificant *(Stadler et al., 1984; McPherson et al., 2000)*.

The purpose of this investigation is to control reaction pathways in such a way as to increase the specificity to impurity hydrogenation, while minimizing the loss of 1-hexene. The focus of this study is the evaluation of co-adsorbates and hydrogen pre-saturated feed over a bimetallic palladium-based catalyst for the selective hydrogenation of impurities in a 1-hexene model feedstock.

2 INDUSTRIAL BACKGROUND

Olefins are aliphatic hydrocarbons with at least one carbon-carbon double bond. The name "olefin" originated from compound's ability to form oily liquids when reacted with halogens. They are also classified as alkenes. α-Olefins are straight-chain molecules which have the double bond situated on the terminal carbon atom. They are also known as 1-olefins or 1-alkenes.

A brief introduction to the industrial relevance, production and purification of α–olefins, in particular 1-hexene, is given in this chapter. The results of previous studies on the selective hydrogenation of α-olefin streams are also outlined, including the effect of the choice of catalyst and various process variables on the reaction.

2.1 Industrial relevance of α-olefins

2.1.1 The producers of α-olefins

Linear α-olefins (LAO) in the C_4 – C_{30} range are produced on the scale of several million tons per annum via different processes. The four largest producers of LAOs include BP Chemicals, Shell, Chevron Phillips and SASOL. All processes except Sasol's are based on ethene oligomerisation, yielding even-numbered α-olefins only.

Table 2.1: LAO Production (2002) ***(Chemical Market Reporter, 2002; www.sasol.com)***

Producer	Capacity (tons per annum)
BP Chemicals	470 000
Shell	590 000
Chevron Phillips	680 000
Sasol	252 000[1]

[1] Excluding production of 1-butene.

Table 2.1 shows the high volumes of LAO's produced per year. BP, Shell and Chevron produce olefins via ethene oligomerisation using the IFP, Phillips or SHOP processes, which yields a fixed range of olefinic products. Their major challenge is to control the oligomerisation process in order to match the changing needs of the α-olefin market in terms of which α-olefin (1-butene, 1-pentene, 1-hexene, etc.) has a greater demand.

Sasol on the other hand recovers olefins from Fischer-Tropsch derived hydrocarbon streams. This process yields both even and odd-numbered α-olefins, and the carbon-number distribution is affected by the composition of the raw gasoline feedstock. The flexibility of this technology allows Sasol to meet the changing needs of the α-olefin market.

Recent and current increases in worldwide α-olefin manufacturing capacity include a new Chevron Phillips α-olefins plant in Texas *(http://www.chemexpo.com)*. In addition, Shell commissioned a new 700-million-pound-per-annum LAO plant during 2002, while BP Chemicals commissioned a new 550-million-pound-per-annum plant in Canada in 2001 *(Chemical Market Reporter, 2002)*.

A third hexene train was commissioned at Sasol in 2000 to meet the increasing demand for 1-hexene, while a new 1-octene train is scheduled to be started up towards the end of 2004. The second octene train is identical to the first one, with a capacity of 48 000 tpa. The demand of octene is expected to grow at a rate of about 6 – 8% per year *(ww.sasol.com)*.

2.1.2 The uses of α-olefins

LAO are used as feedstocks in a variety of processes. A summary of the main uses is shown in Figure 1.1.

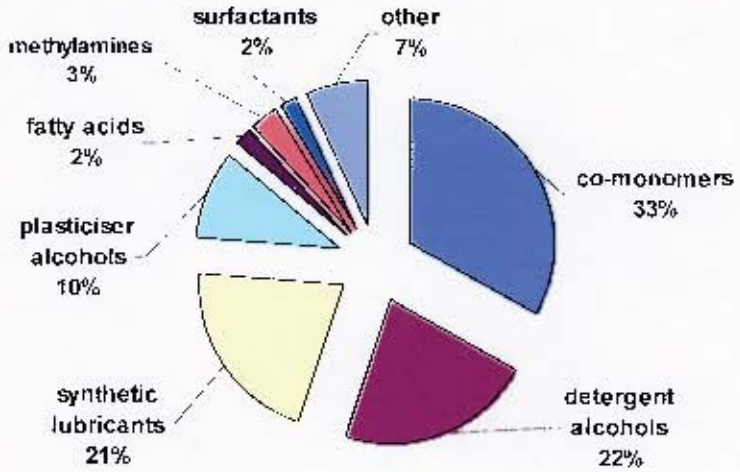


Figure 2.1: Uses of Linear Olefins in 2002
(Chemical Market Reporter – α–Olefins, 2002)

The C_4, C_6 and C_8-olefins are used as co-monomers in polymer production, while the C_{10} α-olefins are in strong demand for producing lubricants. C_{12} and C_{14} α-olefins are used mainly in the production of surfactants, and the longer chain olefins are used in synthetic lubricants, petroleum additives and oilfield chemicals.

The use of LAOs in polyethylene production is a growing market worldwide. It is predicted that 1-hexene will account for 35% of the total co-monomer consumption in polymer production in 2005 *(Chemical Market Reporter, 1999)*. However, the fastest-growing markets are those using LAOs as raw materials for synthetic lubricants and for methylamines, with these categories collectively representing about 19% of the total demand for 1-hexene.

2.1.3 The α-olefin market

The demand for LAOs produced by ethene oligomerisation was approximately 1.1 million tons per annum in the year 2000. These demand figures represent the sum of production plus the difference between imports and exports for the C_6 to C_{30} fractions, and excludes the production of 1-butene *(Chemical Market Reporter, 2002)*.

The key factors responsible for a change in the growth rate are *(http://www.colin-houston.com, 2002)*:

- Expansion of companies
- Adoption of new processes
- Catalyst technology
- Changes in market demand

Sasol concentrates mainly on 2 specific α-olefins: 1-hexene and 1-octene. They are also producing small quantities of 1-pentene. Their corresponding production capacity and world market share is shown in *Table 2.2*.

Table 2.2: Sasol α-olefins – product range (2001) (www.sasol.com)

Product	Production (tpa)	Market Share
1-pentene	5 000	90%
1-hexene	200 000	30%
1-octene	47 000	14%

The commissioning of the second 1-octene train in Secunda in 2004 is expected to increase Sasol's market share to approximately one fifth of the world's consumption *(www.sasol.com, 2004)*.

The world market for 1-hexene was 260 000 – 280 000 tpa in 1996 *(Chemical Week, 31/7/96)*, with Sasol then only occupying 16% of the market (~50 000 tpa). The world demand for 1-hexene has since increased dramatically, and with the parallel increase in Sasol's production, Sasol now retains a 30% market share. Sasol supplies 44% of their 1-hexene to North America, 19% to Europe, and the remaining amount to the Mid-East, Asia-Pacific countries and South America. Only 3% of Sasol's 1-hexene is used in South Africa itself *(www.sasol.com)*.

The current global consumption of 1-octene is approximately 450 000 tons per annum, and demand is expected to increase at a rate of 6 – 8% per annum. Using 1-octene co-monomer instead of 1-hexene results in a stronger, more

elastic, flexible and impact-resistant plastic end product (*Sasol Annual Report, 2002*).

A study by Houston & Associates found that due to the growing market for polyolefins with 1-hexene and 1-octene co-monomer, it is predicted that the growth rate of 1-hexene and 1-octene will increase to 11% and 13% respectively per annum *(Chemical Market Reporter, 1999)*.

2.2 The production of 1-hexene

1-Hexene is produced by ethene oligomerisation or by recovery from Fischer-Tropsch- derived hydrocarbon streams. BP, Shell and Chevron Phillips produce α-olefins by ethene oligomerisation. More recently, 1-hexene was selectively produced by the Phillips ethene trimerisation process over a Chromium catalyst *(Marcilly, 2003)*.

2.2.1 Ethene oligomerisation

Other routes i.e. ethene oligomerisation have been developed to produce olefins which involve the oligomerisation of the lower olefins. These lower olefins i.e. ethene and butene, are available from processes such as the pyrolysis of liquefied natural gas (LNG), naphtha and gas oil fractions *(Ullman's Encyclopaedia, 1989)*.

The ethene oligomerisation process results in a distribution of even numbered 1-olefins only, as all products will have carbon numbers which are a multiple of 2, due to the ethene feedstock. Oligomerisation is then tailored to produce a carbon number distribution which fits the market demand. Recovery from Fischer-Tropsch products gives access to both even and odd-numbered 1-olefins. Their carbon number distribution is determined by the underlying Fischer-Tropsch process.

Various types of catalysts are used in ethene oligomerisation, depending on the process employed. The following processes are more commonly applied *(Ullman's Encyclopaedia, 1989)*:

- **BP process**

A Ziegler-type catalyst (triethylaluminium) is used. This process consists of two stages – ethene is first oligomerised over the Ziegler catalyst, and the reaction products are then fractionated, yielding C_4, $C_6 - C_{10}$ and $C_{12} - C_{18}$ α-olefin fractions. This process can also be done in a single-stage process, where the growth step and elimination reactions occur simultaneously at a higher temperature (> 200°C) than the 2-stage process.

However, the 2-stage process is capable of achieving a 95% conversion of ethene into higher α-olefins. This is not possible with the single-stage process, but this disadvantage is compensated by the ability of the single-stage process to produce a purer α-olefin product, with a lower yield of internal and branched olefins than the 2-stage process *(Ullman's Encyclopaedia, 1989)*.

In general, this process is the least flexible process, as it results in a very fixed product carbon number distribution.

- **Shell process (SHOP)**

A homogenous nickel catalyst is used. This liquid phase process results in a highly pure α-olefin product, with trace amounts of dienes, aromatics and alkanes. The overall SHOP process consists of three stages – oligomerisation, isomerisation and metathesis. This combination of chain lengthening and shortening makes the SHOP process very flexible and it is possible to obtain any desired olefin cut.

The reactant, product and catalyst phases are easily separated in this process. Surplus α-olefins are recycled to an isomerisation-disproportionation system, and the catalyst is recycled repeatedly. The chain-length of the

α–olefins is controlled by varying the composition of the catalyst *(Ullman's Encyclopaedia, 1989)*.

However, a disadvantage is a significant proportion of the product being internal olefins, which are lower in value *(http://pep.sric.sri.com/public/reports/)*.

- **Phillips process**

A chromium-based catalyst is used in ethene trimerisation, which has selectivity to 1-hexene of 95%. This process involves a reaction pathway different to conventional ethene oligomerisation as the catalyst causes the formation of metallacycles i.e. the 5- and 7-membered ring structures. The latter are unstable and decompose, resulting in high selective formation of the C_6 α-olefins *(chemsystems, 2002)*.

2.2.2 Recovery from Fischer-Tropsch product

1-Hexene, together with a whole range of other α-olefins, is the major product of high temperature Fischer-Tropsch synthesis over iron-based catalysts. These α-olefins are recovered by complex separation technology.

The C_6 cut is distilled from the Fisher-Tropsch product. This stream consists mainly of 1-hexene, with smaller percentages of other hydrocarbons and oxygenates. The purified product stream (after extractive distillation) contains about 99.3% 1-hexene. The separation process is shown in Figure 2.2 below.

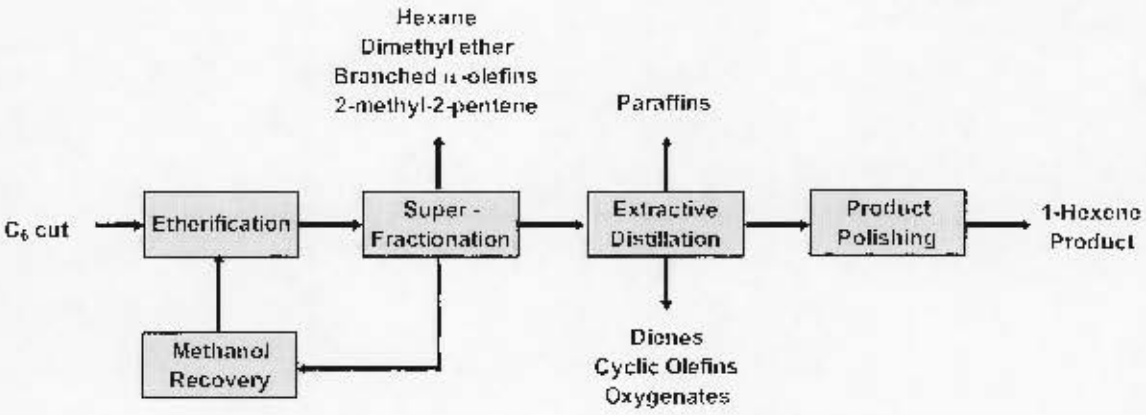
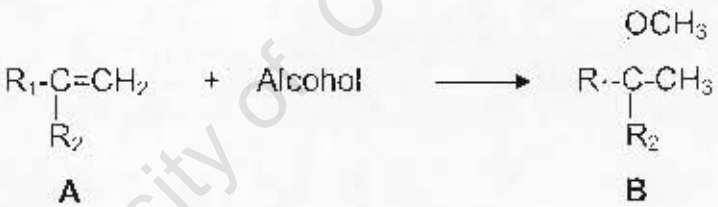


Figure 2.2: Block flow diagram of 1-hexene purification process (Sasol) (W Böhringer, 2001; P Jacobs, 2004)

Etherification: The addition of an alcohol (methanol) in the presence of an acid catalyst results in the formation of an ether, from the tertiary olefins. The etherification reaction is:



A B

The difference in boiling points between the resulting ethers and 1-hexene is large enough to now to allow distillative separation of the branched, tertiary olefins from the mixture.

Superfractionation: This highly efficient distillation separates the lower boiling branched α-olefins, and unconverted methanol and dimethyl ether as well as the higher boiling internal olefins, the n-paraffin and ethers from the desired LAO. A cut is left which still contains 1-hexene cyclic oletins, dienes and hexynes as impurities.

Extractive Distillation: The addition of a polar solvent affects the volatility of the compounds such that the iso-paraffins become more volatile than the 1-hexene and the cyclics, and the oxygenates left become less volatile, resulting in a 2-stage distillation which removes these compounds from the 1-hexene product. The solvent is worked up in a solvent recovery column and recycled.

The result is a 99.3 wt% 1-hexene final product stream, which is then polished and sold.

2.3 The need for additional purification of industrial α-olefin streams

Industrial 1-hexene is acquired on a large scale and purified. However, there are still impurities present in the product stream such as dienes, alkynes, cyclics and branched compounds, which may affect the performance of catalysis in the polymerisation process. Examples of these impurities are shown in Figure 2.3. Some are only present in the ppm range (e.g. dienes and ethynes) but may still need to be removed.

Currently, the Sasol process consists of a product polishing step to remove the impurities in the commercial 1-hexene stream before the product is transferred to storage. This stage consists of a 2-stage absorption process, which employs the use of guard beds to absorb the impurities. However, even though this process successfully removes the impurities, a significant amount of 1-hexene is lost. Another disadvantage is that the guard beds require frequent regeneration, which is costly.

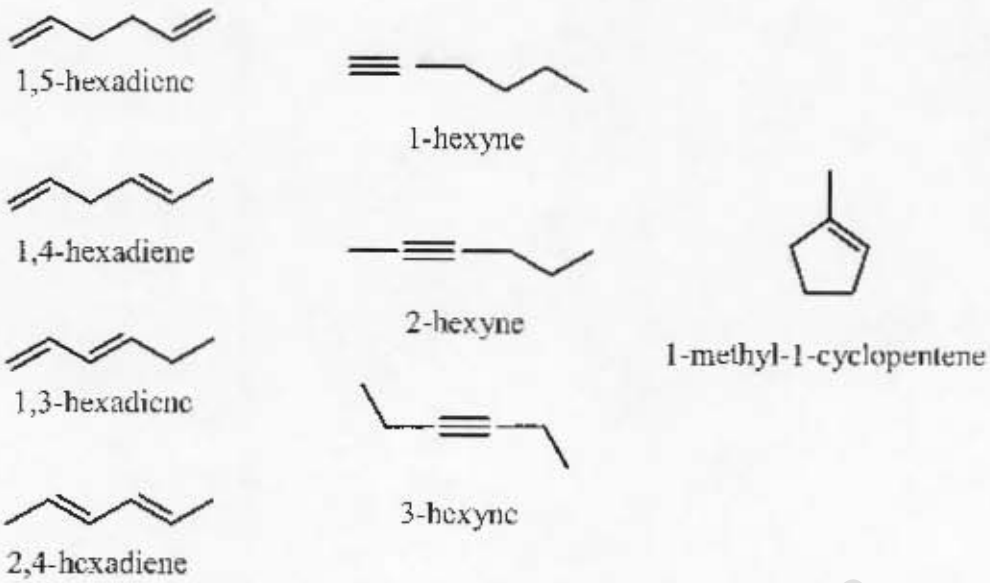


Figure 2.3: Typical impurities present in a C_6 α-olefin feedstock

An alternative purification method is proposed in this work. This SELECTIVE HYDROGENATION is currently widely applied in the case of C_2 to C_4 olefin purification and makes use of a catalyst to selectively hydrogenate the undesired impurities in the stream, in the presence of a huge excess of the respective 1-olefin.

2.4 Selective hydrogenation as a means of purification

The removal of the alkyne and diene impurities from ethene-, propene- and butene-rich streams is crucial to avoid downstream poisoning of polymerisation catalysts. Selective hydrogenation is successfully applied for the removal of the highly unsaturated impurities in the C_2 - C_4 olefin streams from the steam cracker.

The aim of this purification method is to selectively hydrogenate the impurities in the stream, while inhibiting the hydrogenation or isomerisation of the 1-olefin. This is achieved for instance in the case of C_2 olefin purification, with ethyne being reduced to levels of less than 10 ppm *(Guczi et al., 1984)*. Furthermore, it is even possible to obtain a gain in the 1-olefin yield by selective partial hydrogenation of the highly unsaturated impurities. Indeed, a gain in ethyne was obtained under optimal conditions in the selective hydrogenation of a C_2-olefin stream *(Godinez et al., 1995)*. However, in the hydrogenation of C_3 and C_4-olefin streams, a gain in 1-olefin is not typically observed.

A key issue of this reaction is the selectivity. Activity is of secondary importance. Selective hydrogenation is not industrially employed for the purification of C_{5+}-olefin streams *(Molnár et al., 2001)*. There are two possible explanations for this:

- Double bond isomerisation can take place, which is not possible with C_2- and C_3-olefins due to the structure of the molecules but double bond isomerisation is especially prevalent in higher α-olefin streams, and this results in a loss of the valuable 1-olefin.
- It has also been shown that the replacement of C-H with C-R groups results in a decrease in the adsorptive strength of the compound with the catalyst surface, thus affecting the selectivity of the reaction *(Jackson et al., 1997)*. This decrease in adsorptive strength is thought to be as a result of repulsion between the substrate and the surface. Also, it was found that certain intermediates, which are formed during the hydrogenation reaction, cannot be formed from internal alkynes such as 2- and 3-hexyne.

It is for these reasons that the technology developed for the purification of a C_2-olefin stream cannot be directly transferred for the hydrogenation of higher α-olefin streams.

2.5 Kinetics

The selective hydrogenation of higher α-olefin streams consists of a complex series of parallel reactions. The main objective of selective hydrogenation of impurities is to preserve maximum 1-olefin selectivity. A combination of factors such as choice of catalyst metals and supports, catalyst particle size, operating conditions, co-adsorbates, etc. will therefore play a major role in the selectivity of the reaction.

2.5.1 Hydrogenation of impurities

It is well known that the more unsaturated molecules adsorb more strongly on the surface of a metal catalyst than do the less unsaturated molecules. Therefore, alkynes have higher adsorption strength than alkadienes and alkadienes have higher absorption strength than the corresponding alkenes *(Ponec and Bond, 1995)*.

Originally it was thought that surface coverage by the alkyne is very high until all the alkyne has reacted, after which the diene will adsorb and react, followed by the mono-alkene. In other words, the 1-olefin will not be hydrogenated in the presence of a more unsaturated impurity such as alkynes or alkadienes. However, later experiments suggested that there are various sites present on the catalyst surface, resulting in the hydrogenation of ethene even in the presence of high concentrations of ethyne over a silica-supported palladium catalyst (T = 20°C, P_{H2} = 37.5 Torr) *(Al Ammar and Webb, 1979)*. ^{14}C-labelling also showed that there is a direct route to ethane formation from ethyne, besides a route via the hydrogenation of ethene.

The volcano relationship illustrated in Figure 2.4 is known as a "thermodynamic selectivity" and the order of reactivity of the impurities can therefore be explained by the difference in adsorption strength. More severe conditions are needed for the hydrogenation of alkynes as opposed to alkenes, as alkenes interact with the metal surface more strongly. Thus, it is expected that there will be a higher conversion of alkenes in a mixture than of alkynes due to these differences.

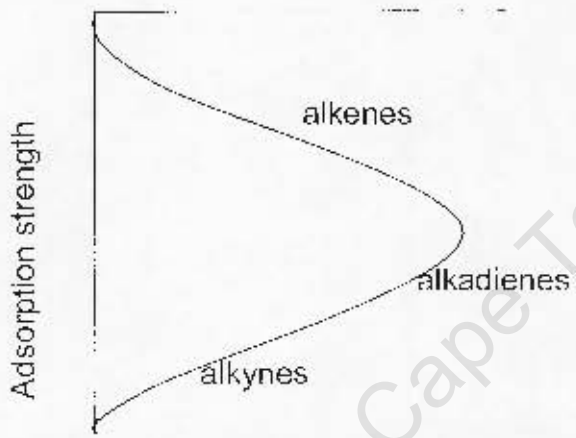


Figure 2.4: Relative Adsorption Strength
(Ponec and Bond, 1995)

The hydrogenation of non-conjugated dienes is very similar to the hydrogenation of monoenes. Dienes with a terminal double bond are slightly more reactive than dienes with internal double bonds only. They will compete with the monoene for an active site. Due to the close proximity of the double bonds in a conjugated diene, it was seen that these dienes are less reactive than the non-conjugated dienes *(Sales et al., 2000a)*.

2.5.2 Hydrogenation of alkenes

It was found that hydrogen is dissociatively adsorbed on the surface of a metal catalyst *(Stadler et al., 1984; Ponec & Bond, 1995)*. Ethene was used as a model compound to investigate the mechanism by which the dissociated hydrogen reacts with an alkene on the surface of the catalyst *(Ponec and Bond, 1985)*. This mechanism is shown in Figure 2.5.

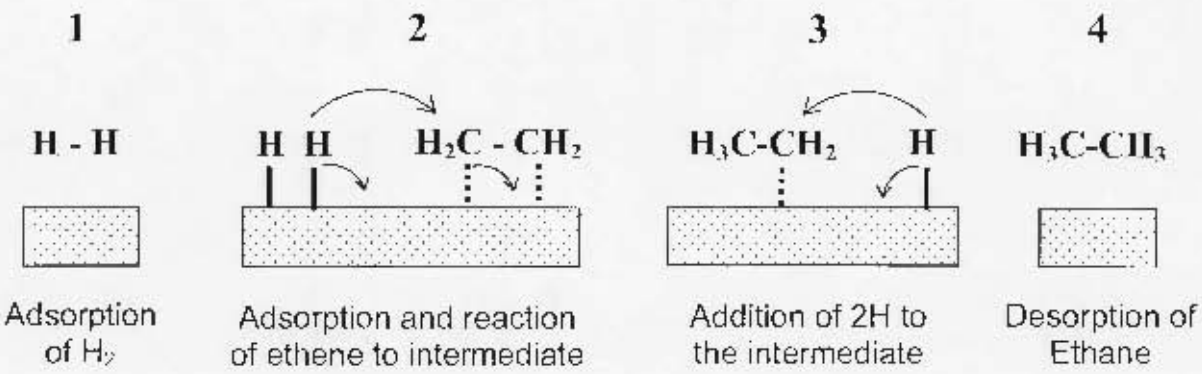


Figure 2.5: Schematic of the Horiuto-Polanyi mechanism of hydrogenation (adapted from Ponec and Bond, 1995)

Hydrogenation occurs via the consecutive addition of hydrogen atoms to an adsorbed alkene. This mechanism is the basis of all hydrogenation reactions, including the hydrogenation of higher alkenes. It is considered to be independent of the isomerisation reactions, which also occur on the catalyst surface *(Ponec and Bond, 1985)*.

2.5.3 Reaction pathway

The selective hydrogenation of more unsaturated impurities in the presence of excess amounts of 1-olefin consists of a system of consecutive and parallel reactions. Figure 2.6 shows the reaction pathway for the selective hydrogenation of a C_5-olefin stream over a palladium metal catalyst.

The impurities consist of both hexynes and hexadienes. The reaction pathway illustrated in Figure 2.6 considers the non-conjugated 1,5-hexadiene and terminal alkyne, 1-hexyne as impurities for simplicity.

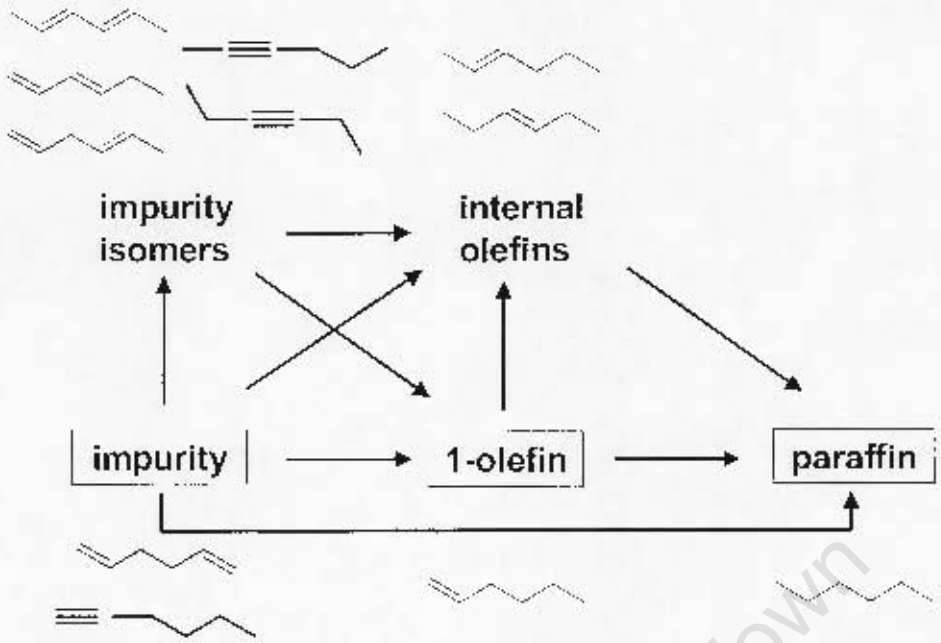


Figure 2.6: Reaction Pathways of impurity conversion (adapted from Stadler et al., 1984)

The impurity can be converted via several reactions. It can either be partially or completely hydrogenated to a 1-olefin or paraffin, or it can undergo isomerisation, forming either its own isomers or, if simultaneous with partial hydrogenation, internal olefins. It has also been shown that a route does exist for the direct formation of the paraffin from the impurity. The 1-olefin follows a very similar pattern of reactions – it is either fully hydrogenated to a paraffin or isomerises to internal olefins.

2.5.4 Simplified pseudo-parallel reaction scheme

Since the isomerisation products (impurity isomers and internal olefins) are of no value, conversion by isomerisation results in no net removal of the impurities in the stream. Additionally, the paraffin is of low commercial value. Therefore, isomerisation and full hydrogenation are undesired in this reaction scheme. The complex reaction scheme may, hence, be simplified into a system of two lumped pseudo-parallel reactions, which are the key reactions of significance, as follows:

- Removal of impurities and impurity isomers by hydrogenation (desired).
- Loss of 1-olefin via hydrogenation or isomerisation (undesired).

This simplified scheme of desired and undesired reactions is shown in Figure 2.7.

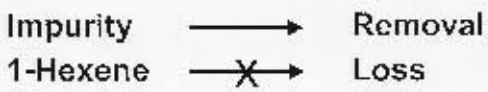


Figure 2.7: Simplified pseudo-parallel reaction scheme

The pseudo parallel reactions are assumed to be first order with respect to hydrocarbon concentration *(McPherson, 2003)*. The ratio of the desired vs. undesired reactions overall was defined as *Specificity (McPherson, 2003)*.

$$\text{Specificity} = Sp = \frac{X_{\text{impurity + impurity isomers}}}{X_{\text{1 hexene}}}$$

Since conversion is independent of initial concentration for first order reactions, the specificity term represents the relative reactivity of each component, that is that the rate constants of the respective pseudo first order reactions determine which reaction is favoured.

Specificity may be shown graphically by plotting the conversion of the impurity ($X_{\text{impurity + impurity isomers}}$) vs. the loss of 1-olefin ($X_{\text{1-olefin}}$). Based on the assumption of a pseudo first order reaction scheme, a set of idealised specificity curves can be used as a model to demonstrate 3 regions:

- $S_p = 1$: the rate of removal of the impurity is the same as the rate of removal of the 1-olefin (this is the diagonal in the graph)
- $S_p > 1$: the rate of removal of the impurity is higher than the rate of removal of the 1-olefin
- $S_p < 1$: the rate of removal of the impurity is lower than the rate of removal of the 1-olefin

For example, a specificity value of 2 indicates that the rate of impurity removal is twice the rate of 1-olefin conversion.

The idealised specificity curves are illustrated in Figure 2.8. For a series of experiments at low conversion of impurity (< 25%), the model was shown to reasonably fit the experimentally observed trends *(McPherson, 2003)*.

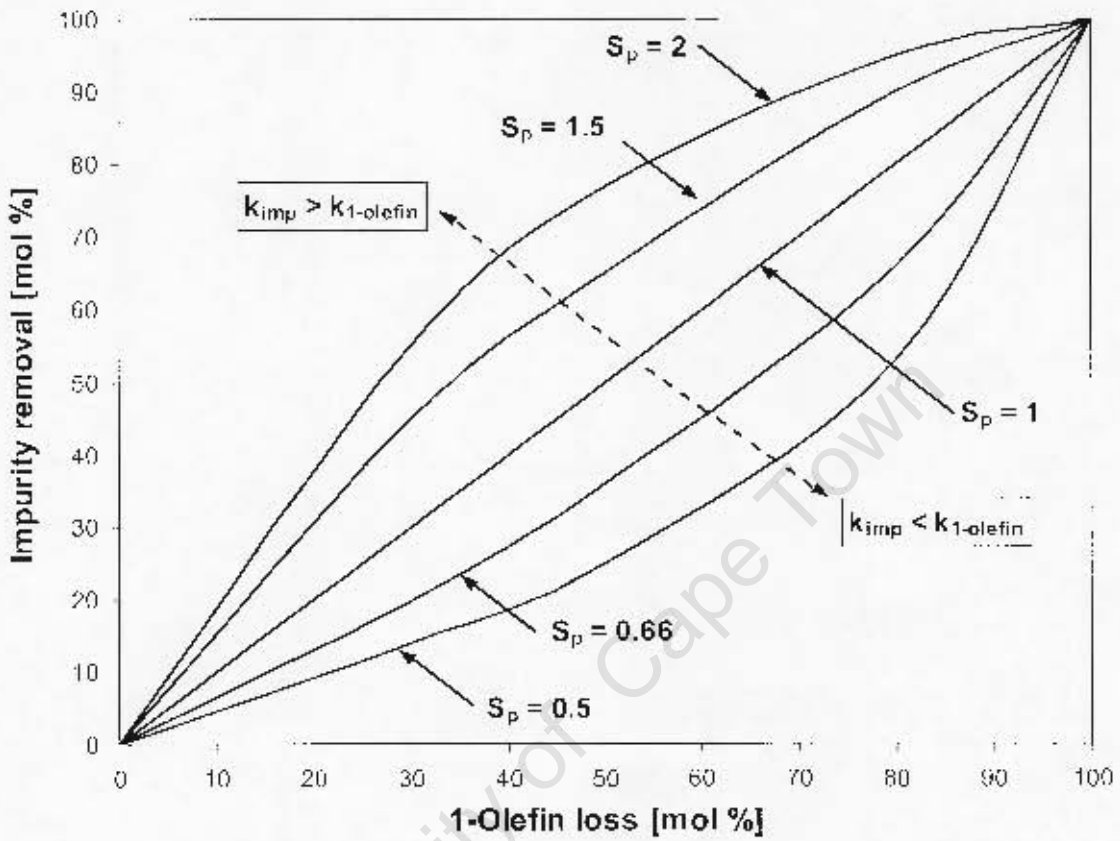


Figure 2.8: Idealised specificity plot (McPherson, 2003)

It is thus desired to operate under conditions of high specificity, where the rate of impurity removal is much higher than the loss of 1-olefin.

Selectivity was defined as the ratio of hydrogenation vs. isomerisation of the 1-olefin *(McPherson, 2003)*. Selectivity therefore quantifies the extent to which conversion happens via hydrogenation.

$$\text{Selectivity} = S = \frac{X_{\text{hydrogenation}}}{X_{\text{hydrogenation + isomerisation}}}$$

Conversion by hydrogenation is preferred as the resulting product is of more significance than the isomerisation product, i.e. it is more desirable to obtain an olefin as a product than an isomerised diene isomer. It is desirable to operate at conditions which favour high selectivity. However, specificity is the more crucial factor to consider in this reaction scheme as isomerisation activity was shown to be almost insignificant over a titania-supported bimetallic palladium-silver catalyst *(McPherson, 2003)*.

2.5.5 Rate laws

Kinetic data for selective hydrogenation are generally very scarce in literature. Usually, rate laws which are derived are applicable to a very narrow range of conditions due to several simultaneous reactions occurring on the surface of the catalyst.

- **Stadler, Schneider and Kochloefl** *(Stadler et al., 1984)*

Experiments were performed using a palladium catalyst, with a support consisting of a 50 wt% mixture of a titania and γ-alumina. The feed consisted of 8-10 mol% of 1,5-hexadiene in 1-hexene and the reaction was carried out in a flow system in trickle phase, at temperatures in the range of 40 - 75 °C, and at hydrogen pressures in the range of 5 – 30 bar *(Stadler et al., 1984)*.

Results showed that the reaction is first order with respect to the alkadiene and zeroth order with respect to hydrogen. The rate law would thus be:

$$r = k \cdot C_{alkadiene} \qquad (1)$$

- **Sales, Mendes and Bozon-Verduraz** *(Sales et al., 2000a)*

These experiments were conducted at a temperature of 40 °C and constant hydrogen pressure (~1 bar) in a well-stirred slurry reactor in the liquid phase. The feed consisted of 2 wt% hexadiene (1,5 or 1,3) in an inert n-heptane

solvent. Monometallic (Pd/Al_2O_3) and bimetallic ($Pd\text{-}Ag/Al_2O_3$) catalysts were used for the reaction *(Sales et al., 2000a)*.

A simple mechanism was proposed, involving the adsorption of the diene on the catalytic site, the surface reaction, and the desorption of products from the catalytic site. The authors took the rate-controlling step to be the *surface reaction*, with the adsorption and desorption steps in equilibrium. With the further assumptions that the reverse reaction due to approach to equilibrium can be neglected and that the alkadiene adsorbs much more strongly than all the other species, a rate expression resulted which shows a relationship which is first order with respect to hydrogen and zero order with respect to hexadiene concentration. The rate law of the alkadiene hydrogenation reaction is not conclusive, as literature sources reveal the possibility of 2 different rate laws.

There are several possible reasons which could account for the difference in rate law. Both experiments involved a palladium-based catalyst, had similar conditions of temperature and were carried out in the liquid phase. Slurry-phase and trickle-phase systems are comparable, as the catalyst is covered in liquid in both cases, hence the pores are filled and hydrogen is dissolving in the liquid phase. The only significant difference between these two experiments is the hydrogen pressure. The experiments conducted by *Sales et al. (2000a)* are carried out at lower hydrogen pressure (~ 1 bar) and feed concentration than the experiments conducted by *Stadler et al. (1984)*. This could possibly explain why Stadler's rate law is independent of alkadiene concentration.

The experiments carried out by *McPherson (2003)* confirmed Sales et al.'s result in terms of the rate law being zero order with respect to alkadiene concentration. The experiments were conducted in the liquid phase at temperatures of 55 – 65°C and a total pressure of 15 bar. The results showed that an increase in alkadiene feed concentration had no effect on the catalyst specificity.

2.6 Catalysts used for selective hydrogenation

The process of selective hydrogenation of C_2 – C_4 olefinic streams is successfully performed in industry to remove higher unsaturated impurities from the stream, with relatively good selectivity. Palladium is recognised by most authors to have the highest selectivity compared to other catalysts *(Coq et al., 2001)*.

2.6.1 Principal catalytic metals

Selective olefin hydrogenation catalysts are generally comprised of the Group VIIIa metals *(Ponec and Bond, 1995)*. Of these metals, palladium and platinum are more commonly used for the purpose of hydrogenation because they are active at room temperature and ambient pressure, making their industrial utilization advantageous.

It was observed that palladium shows the highest catalytic selectivity with respect to alkadiene hydrogenations (*Arnold et al., 1997*). Since platinum is more active than palladium and this can be a disadvantage in reactions where the product is liable to further hydrogenation. Therefore, the probability of full hydrogenation is higher over platinum catalysts than palladium catalysts (*Petro et al., 1974*). This was shown in an experiment involving the hydrogenation of 1,3-butadiene using supported palladium and platinum catalysts, under comparable conditions. The palladium catalyst resulted in 100% selectivity to 1-butene, while a more significant fraction of butane resulted with the Pt catalyst (*Webb, 1963*). This result was confirmed later by other authors *(Massardier et al, 1988; Pradier et al., 1988; Oudar et al., 1987)* and explained by a difference in the mode of absorption of the semi hydrogenated intermediate on each catalyst surface. In the case of palladium, it is assumed to be a π–allyl species. However, the reason for the difference in selectivity over palladium and platinum-based catalysts is not conclusive, as the conditions of the experiments are unknown. It would be necessary to compare each catalyst

under individually optimised conditions to be able to draw the above-mentioned conclusion.

However, palladium can result in a higher degree of double bond isomerisation probably due to a difference in the mode of adsorption of the semi hydrogenated intermediate. It is assumed to be a π-allyl species (*Boitiaux et al., 1987*). This was shown in the hydrogenation of 1,3-butadiene, where a much higher rate of double bond isomerisation (i.e. higher yields of 2-butene) was found when using a Pd catalyst.

2.6.2 Promoter metals

The selectivity to 1-hexene is known to be improved by the addition of a second metal to palladium *(Sales et al., 2000a)*. Typically, the addition of metals from the groups IB and IIB of the periodic table are considered. Examples of these metals include copper, gold, silver, zinc, mercury or cadmium.

A study conducted by *Sales et al. (2000a)* showed that selectivity of the catalyst can be enhanced by the addition of a second metal from the groups IB and IIB of the periodic table. The more common metals used are silver, tin and gold. Sales investigated the hydrogenation of 1,3- and 1,5-hexadiene in an inert solvent heptane over various bimetallic catalysts on alumina supports. The experiments were carried out at atmospheric pressure and a temperature of 40°C. High conversions of the hexadiene were obtained in these experiments. However, 1-hexene was not present in large excess, and thus the pseudo parallel reaction scheme (presented in 2.5.4) is not applicable.

Bimetallic Pd/Ag and Pd/Sn catalysts resulted in an increase in the selectivity to 1-hexene but also a loss in catalyst activity. Conversion of up to 90% of 1,5-hexadiene is achieved. Generally, more isomerisation occurs at higher conversions than at lower conversions of the diene. At 70 % conversion of 1,5-hexadiene, significant isomerisation activity (~63% yield of 2- and 3-hexene) occurs over a monometallic palladium catalyst. A decrease in

isomerisation (~46% yield of 2- and 3-hexene) was seen in the experiments involving the bimetallic Pd-Ag/Al_2O_3 catalyst under the same conditions and at the same conversion *(Sales et al., 2000a)*.

The increase in 1-hexene selectivity and decrease in isomerisation activity in the case of the bimetallic catalyst is explained by a geometric effect of dilution. The second metal (which dilutes the active metal on the catalyst surface) is thought to hinder the formation of ensembles of active sites required for the isomerisation reaction. This principle will be discussed in more detail in section 2.8.

2.6.3 Catalyst support

The most common supports used for hydrogenation catalysts are alumina, silica and carbon. Alumina is the cheapest and therefore more commonly applied to both mono and bi-metallic hydrogenation catalysts. Carbon was the most widely used support for the purpose of hydrogenation in the chemical industry as well as on a lab-scale *(Blaser et al., 2000)*.

Activated carbon supports were commonly used due to their stability in both acidic and basic media. Alumina and silica do not have this property, as they are either dissolved at high pHs or attacked at low pHs. Another advantage of carbon supports is the ability to recover and recycle the active precious metal with ease, as the carbon can be burnt off and the metal recovered *(Auer et al., 1998)*.

A study conducted by *Skotak et al. (2002)* investigated the catalytic conversion of C_6 alkenes over two palladium catalysts. It was found that the acidity of the catalyst support affects the overall activity of the catalyst.

Alumina is a mildly acidic support, which favours double bond isomerisation of the desired product, and thus decreases the selectivity, whereas titania is not. This difference in properties of alumina and titania can be explained by the difference in charge on the aluminium ion in the alumina support and the

titanium ion in the titania support. In the case of alumina, the aluminium ion has a charge of 3+, while the titanium atom carries a charge of 4+ in the titania support. Surface hydroxyl groups are therefore bonded more strongly on the alumina support than on the titania support and this results in the alumina support being more acidic than the titania support *(E van Steen, 2003)*.

Double bond isomerisation is known to occur in the presence of acidity. A less acidic support, such as titania, will not provide the close neighbourhood of acidic sites, which promotes isomerisation activity.

A comparative study of the liquid-phase hydrogenation of 1,5-hexadiene in 1-hexene over Pd/Al_2O_3 and Pd/TiO_2 catalysts revealed a marked decrease in double-bond isomerisation in the case of the titania support *(Stadler et al., 1984)*

The addition of silica to the alumina carrier resulted in an increase in double-bond isomerisation of 1,5-hexadiene at 75°C and hydrogen pressures varied between 5 – 30 bar *(Stadler et al., 1984)*.

Overall, the selectivity of the Pd/TiO_2 catalysts to 1-hexene was found to be much higher than that of the Pd/Al_2O_3 catalysts. Conversions of about 80% of 1,5-hexadiene were achieved, with a marginally small amount isomerised to 1,4- and 2,4-hexadiene. No 1,3-hexadiene was detected *(Stadler et al., 1984)*.

The amount of n-hexane formed was found to increase rapidly after all the hexadiene had been consumed. A substantial amount of 2- and 3-hexene resulted, which indicates significant isomerisation activity *(Stadler et al., 1984)*.

Another comparative investigation of alumina and titania supports in the selective hydrogenation of impurities in a commercial 1-octene feedstock showed that the alumina-supported catalyst produces significant double-bond isomerisation *(McPherson et al., 2000)*.

Overall, it has been shown that titania-supported catalysts result in a lower degree of double-bond isomerisation than alumina-supported catalysts.

2.6.4 Mass transfer effects in selective hydrogenation

Egg-shell type catalysts are commonly used for liquid-phase selective hydrogenation reactions, where a very thin layer of the active metal (<100 μm in thickness) is deposited as a thin shell on the exterior surface of the catalyst particle. As discussed before (section 2.5.1), the adsorption of olefins is suppressed by the stronger absorption of ethynes and dienes on the catalyst surface. However, a rapid decrease in concentration of the ethynes and dienes in the catalyst pore will give the olefins a chance to react. The application of an egg-shell type catalyst is thought to lessen the effect of these diffusion limitations in the sense that the thin active layer of metal will limit the reaction to the hydrogenation of the impurities mainly, and inhibit the hydrogenation of the mono-olefin *(Ardiaca et al., 2001)*.

Results from a hydrogenation of ethyne over a series of Pd/Al_2O_3 catalysts, with varying shell thickness, revealed the following relationship between the selectivity and the metal loaded shell thickness. The feed mixture consisted of 1% ethyne, 1% hydrogen in 98% ethene and the selectivity was measured at 70% conversion for all catalysts. The catalysts all contained identical amounts of palladium per mass of catalyst, but different solutions were used to impregnate the support which yielded a range of egg-shell catalysts with varying shell thicknesses.

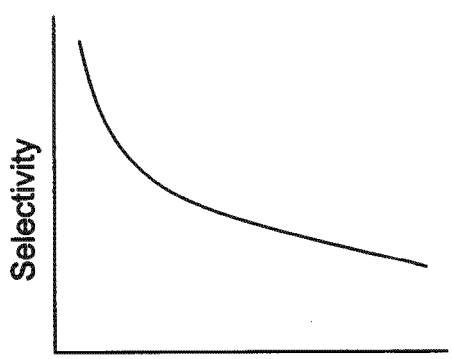


Figure 2.9: Effect of Pd-shell thickness on selectivity of ethyne to ethene conversion [Pd/Al_2O_3 egg-shell catalyst; 1% ethyne, 1% hydrogen, 98% ethene] (Gallei et al, 1999)

Figure 2.9 suggests that in the case of ethyne hydrogenation, a smaller width of the palladium shell results in higher selectivity to the desired olefinic product. There is no single interpretation for this result, as it could be explained by various factors such as *diffusion time* or *relative metal density.*

2.6.5 Hydrogen limitation

The results of a study conducted by *Ardiaca et al. (2001)* revealed that the more dominant cause of mass transfer effects is the existence of a hydrogen limitation. It was found that hydrogen in excess of the amount required to hydrogenate the impurities inside the catalyst, activates the reaction of the 1-olefin.

A comparison of the hydrogenation activity of a given catalyst bed operated in trickle mode for the selective hydrogenation of 1,5-hexadiene (5%) in 1-hexene at different space times and various temperatures showed the existence of a hydrogen mass transfer limitation from gas to liquid phase at temperatures above 60°C *(McPherson, 2003)*. The rate of hydrogen consumption was seen to decrease slightly with increasing space-time. The observed hydrogen mass transfer limitation was considered to result from a decreased gas-liquid interfacial area due to reduced turbulence in the reactor. This, in turn, limits the transfer of hydrogen from the gas to the liquid phase and therefore to the catalyst surface.

It was shown, however, that catalyst specificity i.e. the rate of impurity removal vs. rate of 1-olefin removal *(section 2.5.3)*, is unaffected by the presence of a hydrogen mass transfer limitation since the data points obtained from these experiments were seen to all fall on the same line of specificity *(figure 2.10)*. This is as expected for a pseudo-parallel first order reaction scheme.

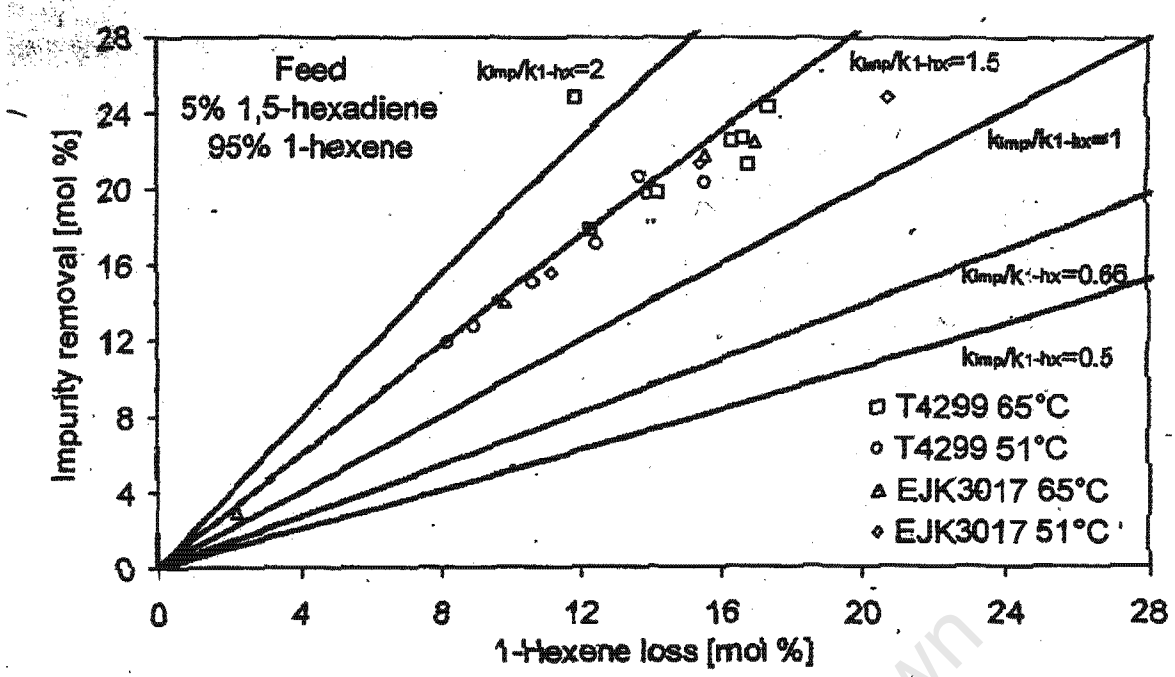


Figure 2.10: Effect of mass transfer on catalyst specificity [P = 15 barg, H_2/oil = 0.2 (molar), WHSV = 4-12 hr^{-1}] (McPherson, 2003)

2.6.6 Catalyst deactivation

Catalyst poisoning and deactivation is undesirable and can be the result of several factors or conditions. Therefore, knowledge about the reasons for loss of activity or selectivity of the catalyst is essential for the optimisation of the process conditions.

An increase in temperature can result in variation in the metal dispersion, sintering and a loss of active area of catalyst metals. However, it was found that for the catalysts of interest this effect is enhanced at temperatures around 500°C and above (*Albers et al., 2001*).

The chemical effects of poisoning on palladium catalysts are known to have an impact on the catalytic activity. This involves the deposition and accumulation of coke on the surface of the catalyst. However, sometimes the effect of selective poisoning is known to modify the adsorption properties and catalytic surface conditions, and thus affect the selectivity too. This can be a desired

affect as well and is widely applied in the selective hydrogenation of ethyne to ethene in the presence of traces of carbon monoxide (*Albers et al., 2001; Nierlich and Obenhaus, 1986*). This is discussed in more detail in *section 2.9*.

2.6.7 The proposed catalyst

For the hydrogenative purification of commercial 1-olefin streams, a catalyst must be used which will promote the hydrogenation of the impurities, inhibit the hydrogenation of the 1-alkene to the respective alkane and suppress isomerisation. With higher olefins i.e. 1-hexene, the proposed catalyst for this reaction path is a titania-supported palladium catalyst. Palladium is ideal for its low temperature activity, while the titania support is less acidic and will not favour isomerisation.

2.7 Previous findings on selective hydrogenation of C_6 - olefin streams

2.7.1 Relative reactivities of unsaturated C_6-compounds

An investigation into the use of palladium and gold catalysts for the selective hydrogenation of a model C_6-olefin feedstock provided a basis for the work which was carried out in this study. Various catalysts were investigated, including a commercial bimetallic palladium catalyst on a titania support. The experiments were carried out in a trickle-bed reactor, with an impurity feed concentration of 5 mol% and H_2/oil ratio of 0.2. The temperature range was between 50 – 65 °C and a pressure of 15 bar for all experiments over the Pd/Ag-TiO_2 catalyst. The experiments were conducted under conditions of large hydrogen excess with respect to the impurity concentration *(McPherson, 2003)*.

The simplified pseudo parallel reaction scheme presented in *section 2.5.4* assumed the two key reactions to be first order with respect to hydrocarbon concentration. The resulting specificity parameter (Sp) is used to represent the relative 'reactivity' of various impurities in a bulk 1-hexene stream compared to 1-hexene. This was confirmed by testing the effect of three different 1,5-hexadiene feed impurity concentrations on the specificity of the catalyst, while keeping all other experimental conditions constant *(McPherson, 2003)*. The three sets of data were found to lie on the same line of specificity, which proves that the catalyst specificity is independent of the initial feed ratio and therefore the assumption of a pseudo parallel scheme of first order reactions holds.

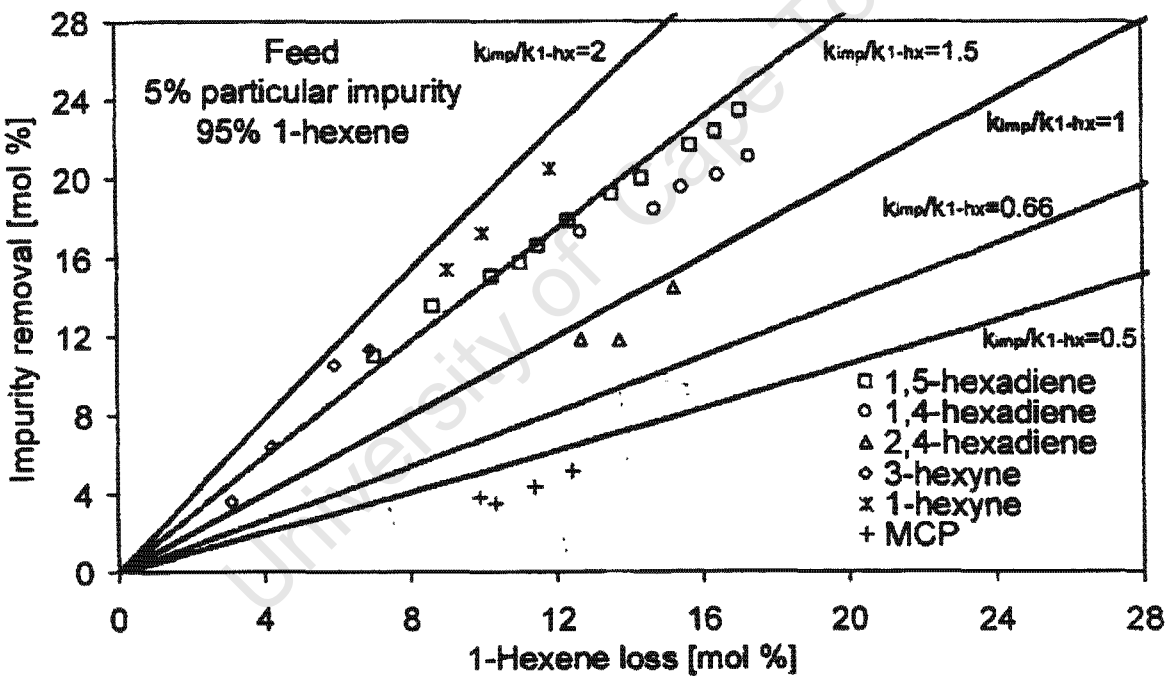


Figure 2.11: Relative reactivities of various impurities over a Pd-Ag/TiO_2 catalyst [P = 15 barg, H_2/oil = 0.2 (molar), WHSV = 4-12 hr^{-1}] (McPherson, 2003)

Various impurities were investigated to determine the relative reactivities of various dienes, hexynes and methyl cyclopentene. The results are shown in Figure 2.11.

It can be seen that in the investigated range of impurity conversions (<25%), specificity curves derived from the kinetic model (shown in Figure 2.8) fits the data reasonably with $k_{impurity}$ relative to $k_{1\text{-hexene}}$ being the only parameter fitted. The x-axis represents the effective loss of feed (1-hexene), which is undesired. Low initial slopes correspond to less reactive impurities i.e. low specificity values ($S_p < 1$), whereas high slopes correspond to more reactive impurities.

McPherson (2003) found that the hexynes generally had the highest relative reactivity, while the cyclic olefin exhibited the lowest reactivity. The cyclic olefin served as a representative of the group of substituted cyclo-alkenes. The dienes are slightly less reactive than the hexynes.

Overall, the following order of reactivity for the impurities tested was found by *McPherson*:

alkynes > alkadienes > 1-alkene >> cyclics *(McPherson, 2003)*

Furthermore, it is evident that the conjugated diene (2,4-hexadiene) is less reactive than the non-conjugated dienes (1,5- and 1,4-hexadiene).

In general, it was found that the internal triple and double bonds are slightly less reactive than the terminal triple and double bonds respectively. The tendency of a molecule with an internal unsaturated bond to be less reactive than those with terminal unsaturated bond is in agreement with literature *(Stadler et al., 1984; Molnár et al., 2001)*. It is explained by the reduced accessibility of internal unsaturated bonds to the catalytic site.

The results of *McPherson's (2003)* work with specificities ($k_{impurity}$ / $k_{1\text{-hexene}}$) of highly unsaturated impurities just somewhat above one, show the need to improve catalyst specificity to far higher values, which only make a process of selective hydrogenation industrially viable. At present, the loss of 1-hexene is too large compared to the amount of impurity which is removed.

2.8 The effect of dispersion on catalyst specificity

The theory of ensembles describes a common geometric effect in the area of catalysis, and is sometimes used to explain the changes in catalytic activity and selectivity of the selective hydrogenation of alkynes and dienes *(Molnár et al., 2001)*. It is well known that certain catalytic reactions require an 'ensemble' of adjacent sites, such as the hydrogenation of alkynes and dienes. Therefore, the regular or random replacement or coverage of a certain percentage of active catalyst surface sites hinders the formation of ensembles and thus has an influence on selectivity. There are several ways of achieving this "site dilution" on the catalyst surface, two of which will be discussed in this chapter. The first method is the application of a bimetallic catalyst. A second metal is added, which is thought to 'dilute' the pure active metal surface, and thus suppress the reactions which require ensembles of adjacent sites *(Sales et al., 2000b)*. The second method requires the introduction of an inert co-adsorbate, which has the ability to temporarily block some of the active surface sites on the catalyst, and thus also suppress the formation of ensembles *(Guczi et al., 1984)*.

2.8.1 Bimetallic catalysts

Use of bimetallic palladium catalysts has been proven by many authors to result in an increase in the selectivity to the 1-olefin in the process of selective hydrogenation of highly unsaturated impurities *(Sales et al., 2000a; Furlong et al., 1994; Ponec and Bond, 1995)*. The effect was generally explained by a geometric phenomenon.

It was shown that the addition of silver to palladium catalysts resulted in an increase in the chemisorbed CO, and thus postpones the reduction of palladium. Selectivity and activity of the catalyst is a result of the nature of the metallic phases i.e. the presence of a silver-enriched surface suppresses the formation of the β-Pd hydride phase and results in an increase in selectivity *(Sales et al., 2000b)*. The catalysts were used for the hydrogenation of hexadienes, and were also found to suppress isomerisation activity.

The type of surface bonding is influenced by the nature of the surface and the number of active sites available. The adsorption of multi-bonded compounds such as dienes (with 2 unsaturated bonds) is therefore affected. For example, if the diene normally binds onto the surface in a region where the distance between two palladium atoms is optimal for the adsorption of both the double bonds, total hydrogenation and double bond shift is possible. Dilution of the surface with atoms of a second metal will decrease this bonding probability and leave the diene bond with only one of the two double bonds, that way inhibiting immediate total saturation and double bond shift and achieving better selectivity to 1-hexene *(Ponec and Bond, 1995)*. It is expected then that bimetallic catalysts will result in an increase in catalyst specificity ($k_{impurity}$ / $k_{1\text{-hexene}}$).

This effect was further investigated by *Sales et al. (2000a)*, where the palladium to silver ratio was varied to determine the effect on selectivity to 1-hexene. When the Pd/Ag mass ratio was unity, the 1-hexene selectivity was improved but a decrease in catalytic activity was noted. When the ratio was increased to 4, the result was an increase in selectivity, with no change in catalytic activity. An increase in selectivity to 1-butene was also noted in a study conducted by *Furlong et al. (1994)* which investigated the addition of copper as a second metal to a Pd/Al_2O_3 catalyst. The feed mixture consisted of 1,3-butadiene in the presence of excess 1-butene and the experiment was carried out in a plug-flow reactor at temperatures ranging between 15 – 40°C *(Furlong et al., 1994)*.

2.8.1.1 The β-Palladium hydride phase

Hydride phases are formed by the interaction of palladium with hydrogen *(Molnár et al., 2001)*. The existence of these phases has been shown by various analytical techniques. Two surface hydride phases were identified under ambient conditions, α- and β-PdH.

Several studies, as reviewed by *Molnár et al. (2001)*, have shown the β-PdH phase to be related to the selectivity of ethene in the selective hydrogenation of ethyne in the presence of excess ethene. It was found that the presence of the

β-PdH phase increased the rate of hydrogenation of ethyne directly to ethane and decreased the selectivity to ethene. Consequently, a suppression of the β–PdH phase resulted in a significant increase in selectivity to ethene. A similar result was reported for the selective hydrogenation of 1,3-butadiene in the presence of excess 1-butene over a bimetallic Pd-Cu catalyst *(Coq et al., 2001)*.

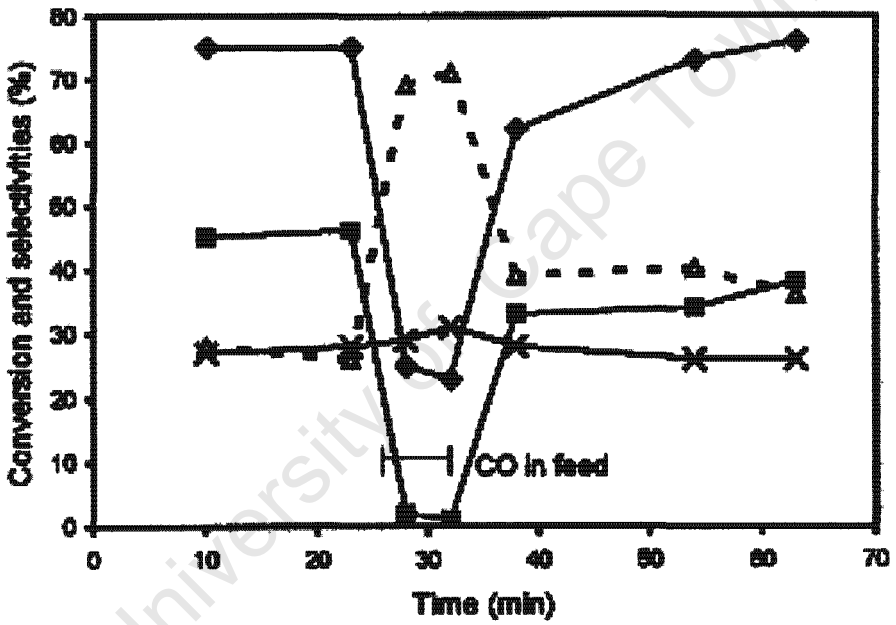
The probability of formation of the β-PdH phase is known to decrease with increasing dispersion of the metal *(Coq et al., 200; Sales et al., 2000b)*. There are two ways of achieving high dispersion - either by the use of a bimetallic catalyst which incorporates a second metal, or the use of smaller palladium crystallites. Both methods alter the electronic properties of the metal particle surface and therefore affect the relative adsorption strength of all reactants, intermediates and hydrogen *(Boudart, 1984)*. This would mean that the β-PdH phase can be avoided by either decreasing the size of palladium crystallites, or incorporating a second metal into a bulk palladium catalyst *(Coq et al., 2001)*.

The increase in selectivity to 1-hexene as a result of the addition of a second metal (such as Ag or Sn) to palladium was shown by *Sales et al. (2000b)* in a series of experiments involving the selective hydrogenation of 1,3- and 1,5-hexadiene (2 wt%) in the presence of the paraffinic solvent n-heptane. Temperature programmed reduction (TPR) confirmed the absence of the β–PdH phase in the bimetallic catalyst. The overall activity of the catalyst decreased, but this was counteracted by the significant increase in selectivity to 1-hexene.

It has also been speculated that the formation of the β-PdH phase is also related to the amount of hydrogen dissociating on the surface of the catalyst *(Molnár et al., 2001)*. However, high alkene selectivity was noted in the presence of the β-hydride phase. In a recent study, ethene selectivity was low both in the presence and absence of the β-PdH phase *(Pradier et al., 1994)*.
The above is mainly based on a recent review by *Molnár et al. (2001)* with 325 references in total. However, no conclusive relationship between the extent of a β-PdH phase and the variation of conditions was apparent.

2.8.2 Co-adsorbates

Several literature sources suggest the introduction of trace amounts of a co-adsorbate to the reaction to improve the specificity and selectivity of the catalyst *(Molnár et al., 2001; Arnold at el., 1997; Guczi et al., 1984)*. A typical co-adsorbate is carbon monoxide (CO), which is successfully applied in the selective hydrogenation of C_2- and C_4-olefinic streams to improve the selectivity to the 1-olefin (*Al-Ammar and Webb, 1977; Guczi et al., 1984*; *Nierlich and Obenhaus, 1986)*. This is explained by a temporary catalytic site-blocking effect. CO is known to behave as a reversible poison, as shown in Figure 2.12.



(♦) conversion, (▲) ethene selectivity, (■) ethane selectivity, (×) C4+ selectivity.

Figure 2.12: Reversible effect of CO concentration on ethyne conversion and selectivities (in presence of excess ethene) over a 0.04 wt% Pd-on-γ-Al_2O_3 catalyst (Guczi et al., 1984)

2.8.2.1 The effect of CO on the selective hydrogenation of ethyne

The selective hydrogenation of ethyne in the presence of excess quantities of ethene is commercially carried out in the gas phase over an alumina-supported

palladium catalyst *(Marcilly, 2002)*. In the case of the C_2-cut, ethyne is reduced to concentrations of < 10 ppm *(Guczi et al., 1984)* in the presence of CO and excess ethene. Certain operating conditions even yield a gain in ethene when ethyne is removed from ethene streams by selective hydrogenation *(Godinez et al., 1995)*.

A study which investigated the effect of introducing a selective adsorbate to enhance the selectivity of ethyne hydrogenation to ethene showed that very low concentrations of CO strongly reduced the further hydrogenation of the product ethene to ethane *(Guczi et al., 1984)*. The concentrations of CO investigated ranged from 50 – 10 000 ppm (volume). The lowest concentration of CO applied (50 ppm) resulted in only a very slight decrease in ethyne conversion (72.3 to 69.5%), but had a large effect already on the selectivities to ethene and ethane. The results of this study are summarised in Table 2.3.

Table 2.3: Effect of CO on ethyne reaction rate and product selectivities [0.27 – 0.34% ethyne in ethene, 0.04wt% Pd/Al_2O_3, 80°C, atmospheric pressure]
(Guczi et al., 1984)

CO in feed (%)	r_{ethyne} ($mol/g_{cat}s$)	X_{ethyne} (%)	S_{ethene} (%)	S_{ethane} (%)
0	3.30E-08	72.3	-4.2	76.6
0.0058	3.18E-08	69.5	38.7	27.8
0.0224	2.98E-08	65.2	52.0	15.9
0.0843	2.38E-08	52.0	65.5	5.3
0.324	1.50E-08	32.8	70.0	1.3
1.250	9.82E-08	21.5	75.2	0.5

The improvement in ethene selectivity by the addition of trace amounts of CO has two explanations. It is thought to either be a competition between the CO and ethene for active sites *(McGown et al., 1978)*, or CO blocking the sites for hydrogen adsorption and dissociation *(Al-Ammar and Webb, 1977)*.

McGown et al. (1978) explain the competition as a result of the differences in adsorption strengths. CO molecules have an adsorption strength which lies

between that of ethyne and ethene; therefore, the CO adsorbs onto the surface after all of the ethyne has reacted and blocks the sites, inhibiting the readsorption and hydrogenation of ethene to ethane.

Al Ammar and Webb (1978) explained the CO effect as a result of CO blocking hydrogen adsorption sites i.e. CO competes with hydrogen for catalytic sites on the palladium catalyst. It was shown that the presence of CO had no effect on adsorbed ethyne or ethene by comparing the adsorption of CO relative to each species on both freshly reduced catalyst surfaces and steady state catalysts. The adsorption was identical on each of the catalyst surfaces. Therefore, the partial poisoning of palladium catalysts was explained as a competition between CO and hydrogen for the available surface metal sites.

Guczi et al. (1984) supports the explanation by *Al Ammar et al. (1978)*, in that the selectivity enhancement effect is due to competitive adsorption between CO and hydrogen at the catalytic sites, thus lowering the concentration of hydrogen at the surface and inhibiting the readsorption and hydrogenation of ethene.

In both cases the CO is thought to partially cover some of the active sites, thereby being a dispersion effect. Both authors offer evidence for their explanations. *Al-Ammar and Webb (1978)* used ^{14}C tracer studies to prove that improvement in ethene selectivity is not due to a hydrocarbon site-blocking effect, but rather due to a competition between the hydrogen and CO for the active palladium sites. It was further found that the amounts of ethane produced from the hydrogenation of ethene were very small compared to the total yield of ethane. This suggests another route to the formation of ethane, possibly the direct conversion of ethyne to ethane via a series of ethylidyne intermediates. It was speculated that three types of hydrogenation sites exist:

The nature of the three different sites was not discussed. It is speculated that the enhancement in specificity of selective hydrogenation caused by the use of CO occurs by the blocking of the Type III sites.

2.8.2.2 The effect of CO on selective hydrogenation of a C_4-olefin stream

A study conducted by Nierlich and Obenhaus *(1986)* investigated the selective hydrogenation of a C_4-olefin cut over a Pd/Al_2O_3 catalyst. Alkynes and dienes were present as impurities in the stream (ca. 50 and 500 ppm respectively) and experiments were conducted at a temperature of 21°C and pressure of 13 bar. This investigation also explored the issue of gas-phase hydrogen in the system (see section 2.10).

The results of the introduction of a co-adsorbate (CO) to the process of selective hydrogenation of C_4 impurities are shown in Table 2.4.

Table 2.4: Feed and product composition (Nierlich and Obenhaus, 1986) [Pd/Al_2O_3, T = 21°C, P = 13 bar, LHSV = 35l/l]

Feed		Product (with saturator)	
		no CO	0.6 ppm CO
1-Butene (mol %)	48.2	47.1	48.4
n-Butane (mol %)	21.6	21.7	21.6
Butadienes (ppm)	5140	650	< 1
Butynes (ppm)	56	6	< 1

Firstly, the elimination of gas phase hydrogen to the reaction phase by the introduction of a saturator, results in a substantial conversion of the impurities (butynes and butadienes). This will be addressed in section 2.10. Furthermore, the addition of trace amounts of carbon monoxide improves the selectivity more in that the impurity concentrations are decreased to < 1ppm and a gain in 1-butene is obtained.

2.8.2.3 Other co-adsorbates

In very early experimental work, it was found that organic bases such as quinoline and ammonia increased the alkene selectivity in selective hydrogenation reactions over a Lindlar catalyst *(Molnár, 2001)*. This was explained by the ability of nucleophilic compounds to increase the electron density of palladium through donation of electrons, and therefore decrease the strength of interaction with electron-rich compounds such as alkynes or dienes. The mechanism of nitrogen and sulphur-based additives is apparently very complex and cannot be explained by competitive adsorption or site poisoning. The disadvantage of nitrogen-based additives is that they are often quite difficult to remove from the product stream, and therefore very costly.

It is well known that industrial product streams sometimes contain a host of ketones, aldehydes, alcohols and carboxylic acids in varying concentrations. The influence of these compounds on the hydrogenation of highly unsaturated impurities in an α-olefin stream is not known. However, it may be expected that small quantities of alcohols such as methanol and ethanol will have an influence on the selectivity of the reaction, which can be explained by the same mechanism as CO addition.

2.9 Elimination of gas phase hydrogen

The study conducted by *Nierlich and Obenhaus (1986)* into the selective hydrogenation of C_4-olefin impurities (butadiene and butyne) in the presence of excess 1-butene also investigated the absence of gas phase hydrogen to improve the selectivity of the reaction. This was achieved by the introduction of a saturator.

A saturator was added to the experimental setup, which was operated at the same conditions as the reactor, to enable the gaseous hydrogen to dissolve in the liquid hydrocarbon feed prior to reaction. A simplified diagram of the saturator and reactor is shown in figure 2.13.

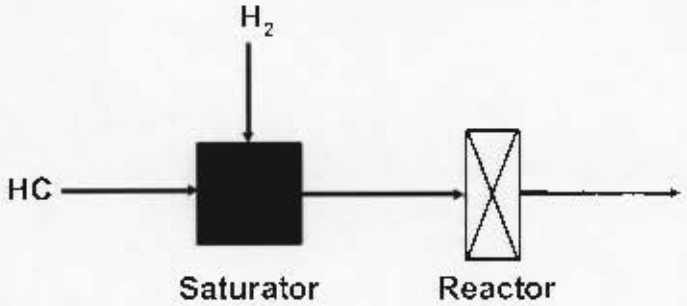


Figure 2.13: Simplified experimental setup for the elimination of gas phase hydrogen
(Nierlich and Obenhaus, 1986)

The results of the introduction of a saturator to achieve dissolved hydrogen in the liquid phase are shown in table 2.5. Trace amounts of CO were also introduced to the reaction to investigate the effect of a co-adsorbate, as discussed in section 2.9.2. The results of 2 experiments, one of which includes the presence of CO, are compared in table 2.4.

Table 2.5: Feed and product composition (Nierlich and Obenhaus, 1986)
[Pd/Al_2O_3, T = 21°C, P = 13 bar, LHSV = 35l/l]

Feed		Product	
		Saturator 0.6 ppm CO	No saturator 0.6 ppm CO
1-Butene (mol %)	48.2	48.4	35.5
n-Butane (mol %)	21.6	21.6	21.8
Butadienes (ppm)	5140	< 1	2170
Butynes (ppm)	56	< 1	27

The elimination of gas phase hydrogen by the introduction of a saturator results in significant removal of impurities. The dienes and butyne are removed from the feed almost completely, while even a slight gain in 1-butene resulted. This effect is not explained by the authors. It is thought that the presence of hydrogen in the liquid phase avoids any mass transfer limitation of hydrogen to the liquid phase, resulting in improved conversion of impurities.

2.9.1 The solubility of hydrogen in a C_6-hydrocarbon stream

The solubility of hydrogen in a C_6-olefin stream was calculated using Hysis, a chemical engineering simulation program (Appendix A). Calculations were based on the assumption of a feed consisting of pure 1-hexene since the feed concentration of 1-hexene was always > 95 mol % in all experiments and the impurities were olefinic as well. The solubility plot is shown in *figure 2.14*.

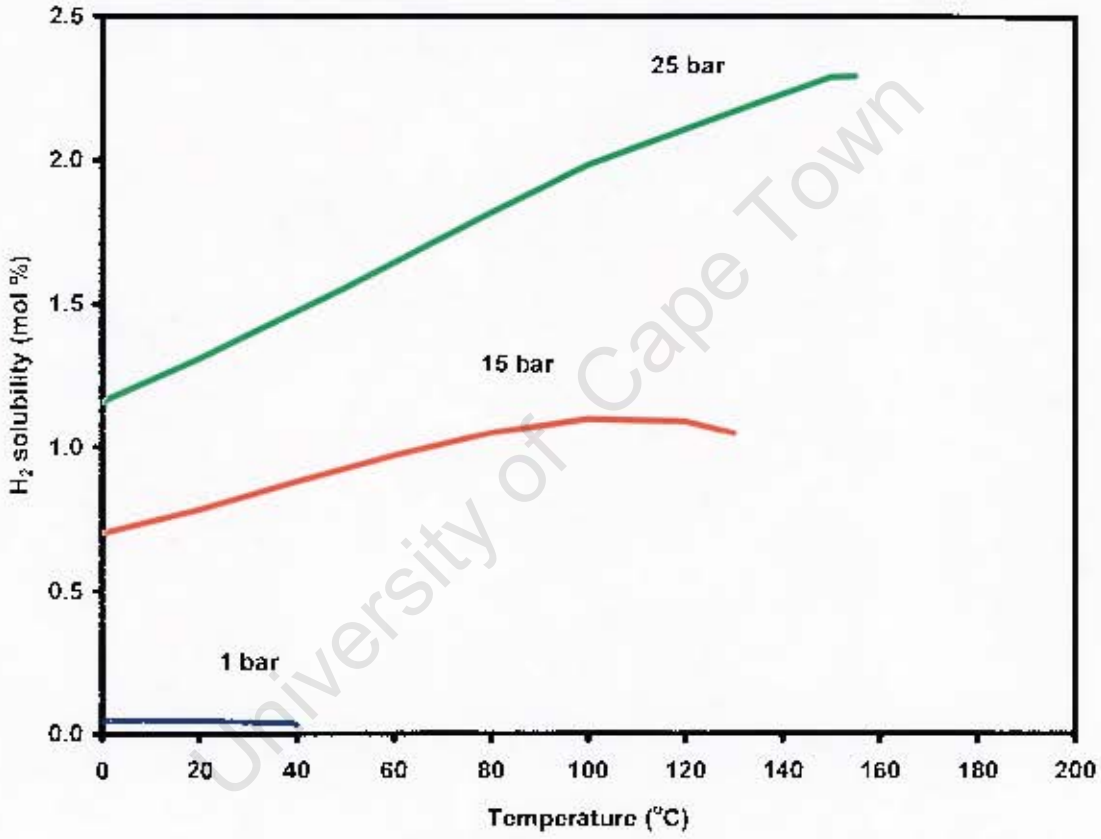


Figure 2.14: The solubility of hydrogen in 1-hexene

The plot shows the mole fraction of hydrogen which dissolves in 1-hexene as a function of temperature, at three different pressures. It can be seen that the solubility of hydrogen at atmospheric pressure is insignificant. The hydrogen solubility only starts becoming noteworthy at pressures above 10 bar. For example, at 60°C and 15 bar, the amount of hydrogen which will dissolve in the

liquid hydrocarbon feed is approximately 1 mol%. Increasing the temperature and pressure results in higher hydrogen solubility until the system becomes gaseous (temperatures > 140 °C).

In case the amount of hydrogen required for the total removal of highly unsaturated impurities must be provided in dissolved form, elevated pressure is required for the reaction *(Nierlich and Obenhaus, 1986)*.

3 OBJECTIVES OF THIS STUDY

It was shown in literature that bimetallic palladium catalysts result in improved selectivity to the 1-olefin in the process of catalytic selective hydrogenation. Also a non-acidic support, such as titania, was found to be more suitable since it limits double-bond isomerisation.

The overall objective of this work is to selectively hydrogenate the highly unsaturated impurities in a model 1-hexene feedstock, but avoid hydrogenation of the 1-hexene to n-hexane and isomerisation to internal olefins.

Several methods have been proposed to enhance the specificity of the catalyst that is increasing the removal of the impurities while reducing the loss of 1-hexene.

This study seeks to enhance the specificity of the catalyst to a commercially acceptable level by:

- Reducing the H_2/oil ratio to approximately stoichiometric and sub-stoichiometric level compared to preliminary studies.
- Eliminating gas-phase hydrogen in the reactor at these low H_2/oil ratios by introducing a pre-saturation stage, where the gas is allowed to dissolve in the liquid hydrocarbon phase prior to the catalytic reaction.
- Introducing co-adsorbents (carbon oxide and ethanol) to the system to cause a site 'diluting' effect, which may hinder the formation of ensembles of sites on the catalyst surface, which affect specificity.

4 EXPERIMENTAL PROCEDURE

An industrial bimetallic palladium catalyst, Pd-Ag/TiO_2, was employed in this study. It must be noted that this catalyst is not designed, optimized or supplied specifically for the task of C_5 purification via selective hydrogenation. It was selected, based on the results of previous studies *(McPherson, 2003)*, for its metal combination and the need for a non-acidic support.

Literature *(see chapter 2)* showed that a bimetallic palladium catalyst on a non-acidic support such as titania is the most suited catalyst for the task at hand i.e. selective hydrogenation.

4.1 Catalyst

A commercial, bimetallic palladium-silver catalyst, supported on titania was chosen for the experiments conducted in this study. It is an eggshell type catalyst in the form of tablets, in that the metals are deposited onto the geometric surface of the catalyst tablets. The specifications of the catalyst, as provided by the supplier, are listed in Table 4.1. Note that this catalyst is not designed or optimized for the task of selective hydrogenation.

Table 4.1: Composition of the catalyst employed in this study

Designation:	T4299
Source:	Süd-Chemie
Support:	TiO_2 [1]
Base metal:	0.18 wt% Pd
Promoter metal:	0.13 wt% Ag
Catalyst particles: Diameter:	4.5 mm x 4.5 mm
Shape:	cylindrical tablets
Metal crystallite size:	3 nm [2]
Metal dispersion	41%
Surface Area:	37 m^2 / g

Notes: (1) The titania support of this catalyst consists of Degussa P41 which comprises of 10 nm primary particles which are aggregated into 100 nm clusters and, finally, 10 μm agglomerates.

(2) Transmission Electron Microscopy (TEM) and CO chemisorption analyses were conducted in a previous study *(McPherson, 2003)* and indicated that T4299 has a metal particle size of between 2 – 5 nm.

4.2 Feedstocks

Sasol supplied 1-hexene of > 99.99% purity, and this was used as the bulk material for most feedstocks. n-Hexane was used as the bulk material in specific studies. Various other C_6-hydrocarbons were used to "spike" the bulk feed to represent the "impurities" likely to be present in the existing industrial streams. Compounds are listed in Table 4.2. For the most, the concentration of the impurity was maintained at 1 mol% in 1-hexene but initial experiments included impurity concentrations of 5 mol%. All experimental feeds were produced by weighing in a certain quantity of impurity, then adding the corresponding amount of bulk compound. Feed mixtures were stored in a refrigerator to prevent evaporation and stripping of the more volatile components.

Table 4.2: Feedstock constituents used

Compound	Supplier	Purity
1-Hexene	Sasol	> 99.99 %
1,5-Hexadiene	Sigma Aldrich	97%
1-Hexyne	Sigma Aldrich	97%
n-Hexane	Kimix	99%
Ethanol	Merck	99.78%

The gaseous feedstocks, hydrogen and nitrogen, were supplied by Messer Fedgas. Purities were 99.999% (< 2 ppm H_2O and < 3 ppm O_2) and 99.995% respectively. Several dilute mixtures of carbon monoxide in hydrogen were needed. These were either obtained from Air Liquide or made up in house from pure gases.

4.3 Catalyst performance test apparatus

The experimental apparatus consists of a 3-phase down-flow trickle bed reactor mounted in an oil bath, stirred with a magnetic stirrer, for isothermal operation. The flow sheet of the apparatus is shown in figure 4.1. Liquid feed is supplied via a metering pump and gaseous feed via thermal mass flow controllers. The reactor effluent proceeds via a sampling loop to a liquid knock-out vessel with gaseous effluent venting to atmosphere via a throttle valve. Pressure control is achieved by the introduction of a high pressure gas downstream between the knock-out vessel and the throttle. A detailed description of the major components of the experimental apparatus follows.

4.3.1 Feed system

Gaseous feed components (hydrogen, nitrogen and carbon monoxide or carbon monoxide/hydrogen mixtures) are supplied from cylinders, via a set of mass flow controllers. The guard catch pot located downstream the mass flow controllers are designated to provide protection against backflow of the liquid feed in case of accidental line or reactor blockage.

An HPLC metering pump (HP1100; 0.01 to 5 ml/min) supplies liquid feed to the reactor.

4.3.2 Reactor

A section drawing of the reactor is provided in figure 4.2. The reactor body consists of an 11 cm long stainless steel tube with an internal diameter of 1.6

cm. At its base, where it connects to the effluent line, the reactor is internally tapered to minimize dead volume and backmixing. Four fins, protruding 1 cm radially from the reactor body, over the full length, serve to break up the vortex formation in the oil bath and to promote heat transfer.

The top of the reactor comprises a stainless steel gasketed VCR fitting which serves to connect the reactor body to the feed line and provides access for recharging the catalyst. The top section includes an entrance point for the feed and a 1/8" axial thermowell extending the full length of the reactor. The reactor has a bed volume of approximately 14 ml and provides an effective bed volume of 1.88 ml per cm of bed depth (considering the thermowell).

4.3.3 Saturator

For some experiments a saturator is introduced upstream the reactor. The purpose of the saturator in combination with low H_2/oil ratios is to avoid the presence of gaseous feed components to the reactor. The saturator is designed to achieve complete dissolution of the gaseous components in the liquid feed prior to entering the reactor.

The body of the saturator is identical to the body of the reactor, with the exception of the fins and gasketed VCR fitting. The top of the saturator includes an entrance point for the gaseous and liquid feeds; the bottom connects to the adjacent reactor. The entire volume of the saturator is packed with inert silicon carbide particles (900μm) and maintained at the same conditions as the reactor.

4.3.4 Sampling line

A sampling line is provided downstream of the reactor so as to permit the recovery of an instantaneous liquid sample without depressurisation of the reactor and the consequent flow disturbance. It comprises of a ca. 2.5 m 1/8" stainless steel cooling coil (air-cooled) connected in parallel to the reactor effluent line via two 3-way valves. In combination with an additional valve in

the reactor effluent line, flow may be directed to either pass through or bypass the sample line. It is attached to the pressure regulating gas supply to allow for loop repressurisation independently from the rest of the system, thereby preventing pressure drops in the system after sample collection. *(See section 4.5.4.3 for the sampling procedure)*

4.3.5 Pressure control

Pressure control is achieved by the introduction of a back pressure regulating gas (nitrogen) into the effluent gas stream downstream of the liquid knockout vessel. A regulating valve is employed to throttle this combined gas stream before venting, such that the pressure in the reactor is maintained by the delivery pressure of the pressure regulating gas.

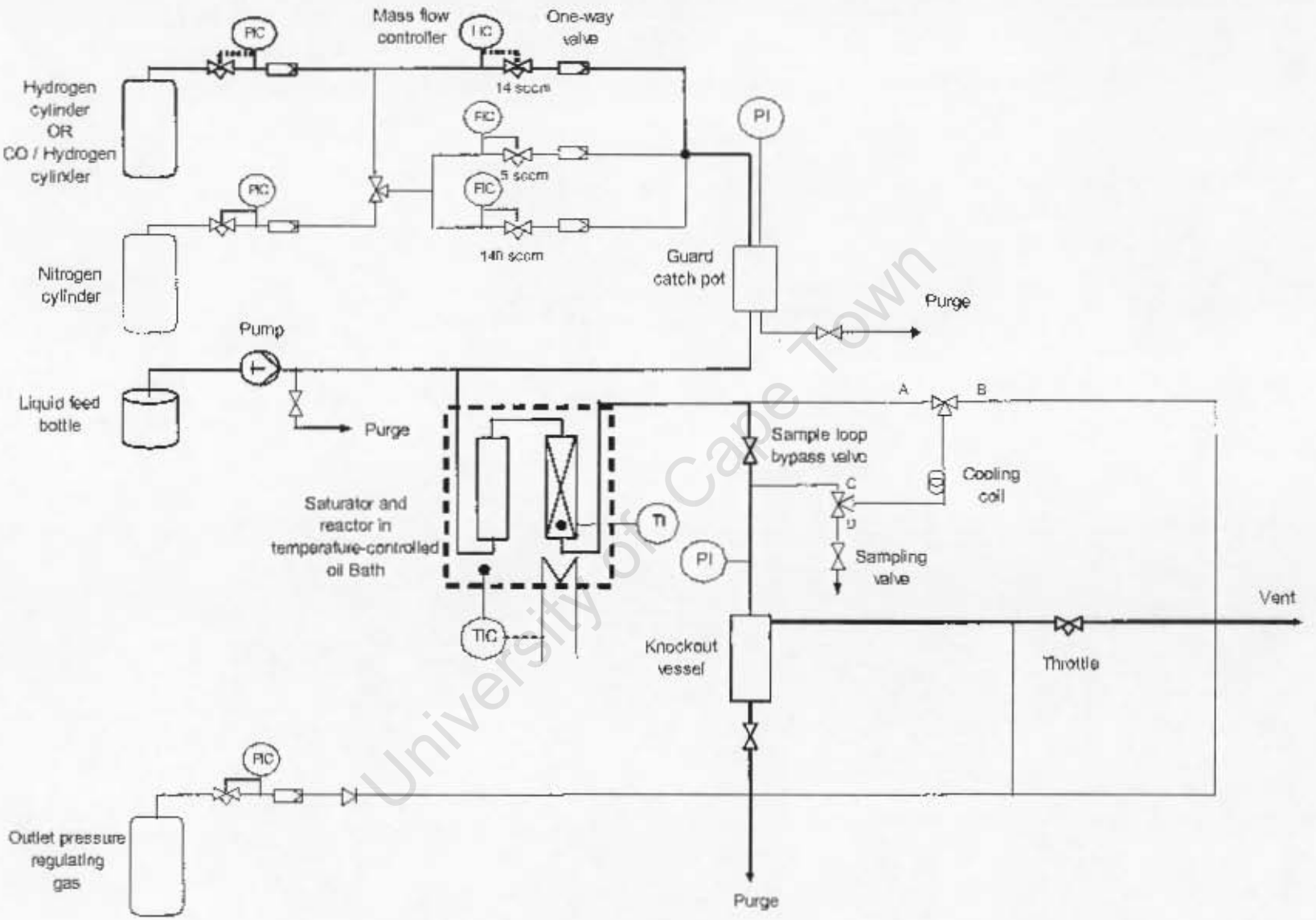


Figure 4.1: Schematic of experimental apparatus, saturator included

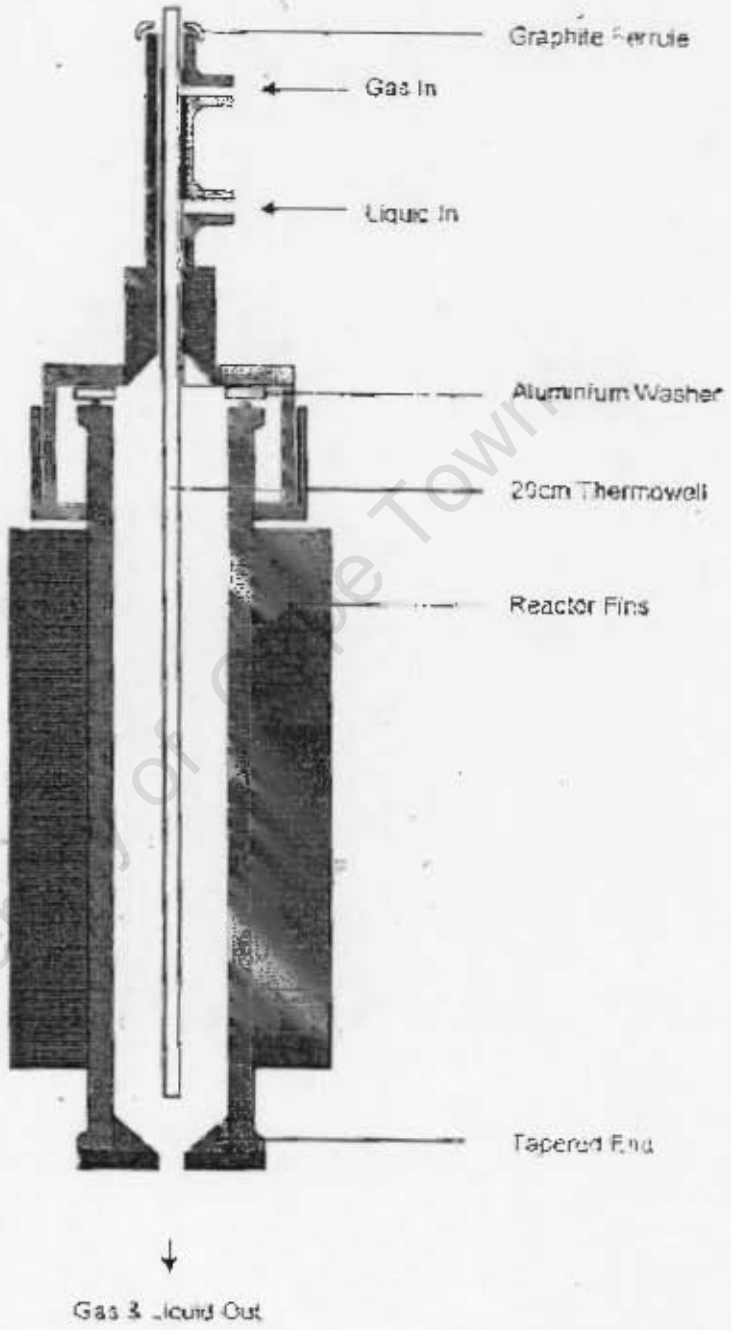


Figure 4.2: Section drawing of the reactor

4.4 Experimental operating procedures

4.4.1 Catalyst loading

A thin plug of silane treated glass wool is positioned at the bottom of the reactor to cover the reactor exit and prevent any loss of catalyst and inert diluent from the bed. The thermowell is positioned axially in the reactor and left to rest just above the glass wool.

The reactor packing comprises of 3 zones as shown in figure 4.3 *(see also section drawing, figure 4.2)*. Inert silicon carbide (SiC) granulate (900 μm) packed above and below the catalyst bed serves as preheat and flow distributor, and bed support, respectively.

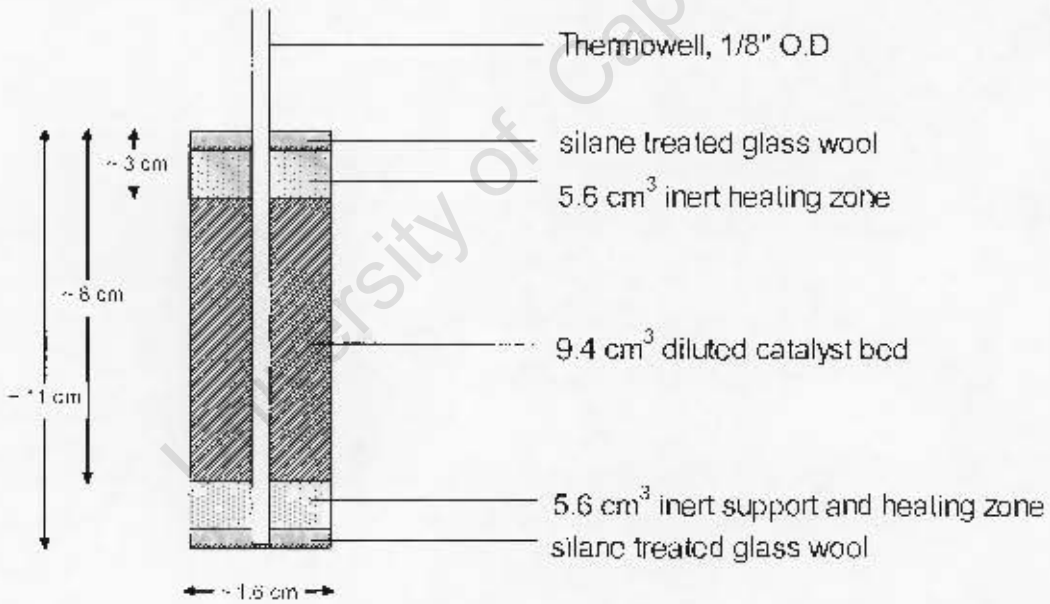


Figure 4.3: Reactor packing

The central 5 cm of the reactor length comprises a diluted catalyst bed, typically 1 gram of catalyst diluted with inert SiC granulate to a total volume of approximately 9.8 cm^3. The packing is covered with another plug of silane treated glass wool. After closing the reactor, the thermowell, which protrudes

from the top section, is sealed in-place using a graphite ferrule and standard 1/8 inch tube fitting.

4.4.2 Reactor leak test

The freshly packed reactor is leak tested by nitrogen pressurization at 25 bar. The reactor is judged leak tight when no bubbles are seen and when no pressure drop occurs.

Then the experimental apparatus is flushed with nitrogen and pressurized to 15 or 30 bar. The entire rig is judged leak tight when no pressure drop occurs. Finally the system is returned to atmospheric pressure for the activation / reduction procedure.

4.4.3 Catalyst activation / reduction

The in-situ reduction follows a procedure recommended by Süd-Chemie AG, the manufacturer of the catalysts.

A dilute reduction mixture (5 vol.% H_2 in N_2) is set to flow over the catalyst at atmospheric pressure and at the highest flowrate (124 sccm) achievable with the installed equipment. The reactor temperature is ramped at 1°C/min from ambient to 100°C. It is then maintained at 100°C for 3 hours, followed by a further hour at this temperature under pure hydrogen flow at 124 sccm.

4.4.4 Reactor operation

4.4.4.1 Start-up procedure

- After completion of the activation / reduction procedure (section 4.4.3), standard reaction temperature and pressure are set *(see Table 4.3)*.
- Pressurisation proceeds by closing the system throttle valve and adjusting the feed gas (H_2) delivery pressure under static conditions. Upon reaching

the standard pressure (16 bar) the pressure regulating gas (16 bar) is introduced and the throttle valve adjusted to maintain stable flow and system pressure.

- Once reaction temperature and pressure have stabilized, the feed pump is purged with pure 1-hexene via its own purge valve to ensure removal of air-bubbles trapped in the line or pump head.
- The apparatus is then primed with 1-hexene at a flowrate of 5 cm^3/min until liquid can be drawn at the sample valve. Thereafter the standard liquid and gas flows (Table 4.3) are set and the system is allowed to reach steady-state (typically 48 hours).

4.4.4.2 On-line procedure

Upon the alteration of experimental conditions, a period of at least one and a half residence times (usually corresponding to about 1.5 hours at the standard conditions) is allowed to elapse before sampling is initiated. Only upon obtaining 3 sequential identical samples, is the system considered to have reached steady-state operation. Standard conditions are re-set after each series of experiments. Catalyst performance was consistently monitored by running a standard condition after each series of condition settings. In the case of no change of catalyst performance, experiments were continued. In the case of a change to catalyst performance, the catalyst was recharged and the last condition setting was repeated.

If catalyst performance is not monitored for extensive periods (e.g. over weekends), the hydrocarbon feed is switched to pure 1-hexene under standard conditions so as to conserve expensive feedstock mixtures.

4.4.4.3 Sampling

- Under normal operation, reactor effluent flows via the sample line to the knockout vessel *(three-way valves in positions A and C respectively, see figure 4.1)*.

- Samples are taken by opening the sample line bypass valve and isolating the sample line switching 3-way valves to positions B and D. The sample valve is then slightly opened and the sample is ejected from the sample line under the influence of the system pressure controlling gas. The first ca. 1 ml drained is discarded. Therefore, the sample is collected in a 2 ml glass vial which is immediately sealed with an airtight cap.
- Thereafter the 3-way valves are switched back and the sample line bypass valve and sampling valve are closed. Since the sample line is pressurized to system pressure via the pressure control gas neither an empty volume nor a pressure pulse is introduced and, no flow disturbance occurs.
- All liquid samples are analysed by gas chromatography immediately after collection and then are stored in a refrigerator to prevent volatile components from evaporating.

4.4.4.4 Altering reaction variables

Procedures with respect to the alteration of specific reaction variables are as follows:

Pressure

The system pressure is increased by closing the throttle valve and the incoming feed is used to pressurize the system. Once the desired pressure is reached, the pressure control gas regulator is set to the desired value and the throttle valve is opened slightly again to re-establish flow.

To decrease the system pressure, the delivery pressure of the pressure control gas is lowered to the desired value and as a result, the system slowly depressurizes across the throttle.

Space velocity

Increasing and decreasing space velocity involves simultaneously adjusting MFC and pump setpoints to maintain constant H_2/oil ratios.

H_2 / oil ratio

A change in the H_2/oil ratio is achieved by changing only the hydrogen flow at a set liquid space velocity. The linear gas velocity through the reactor is therefore dependent on the H_2/oil ratio while the hydrogen partial pressure remains constant.

Feed

Changing hydrocarbon feed type for testing a different impurity or concentration of impurity involves exchanging a freshly prepared feed bottle with that already attached to the pump. This is undertaken with the pump switched off but the gas feed maintained. A brief pump-priming step is employed to remove air bubbles which may have been introduced into the liquid feed lines during the changeover of feed. However, a typical feed exchange procedure takes less than 3 minutes and was found to have no effect on catalyst performance *(McPherson, 2003)*.

4.4.4.5 Shut-down procedure

- In order to recharge, the feed pump is switched off, and the gas feed is changed to nitrogen at the maximum possible flowrate of 124 sccm while maintaining the temperature constant in order to strip residual hydrocarbons from the system.
- After approximately 3 hours, heating is terminated, pressure regulating gas is turned off and the system is allowed to depressurise.
- Finally, all gas flow is turned off and the oil bath and the reactor are left to cool. Then the reactor is removed from the oil bath and opened.

4.5 Operating conditions

4.5.1 Standard conditions

Preliminary experiments indicated a slight increase in catalyst activity prior to the attainment of a steady-state conversion, after which time negligible activity loss is observed with increasing time-on-stream. As a result, prior to the commencement of all catalyst performance tests, the fresh catalyst is allowed to stabilize under "standard" conditions, as provided in Table 4.3. Standard conditions are routinely reset to ascertain whether catalyst deactivation occurs during an experiment *(see section 4.4.4.2)*.

Table 4.3: Standard conditions and applied range of operating conditions

Condition	Standard value	Range	Units
Temperature	60	60	°C
Pressure	16	16 - 31	bar (absolute)
Molar H_2/oil ratio	0.2	0.01 - 0.2	$mol_{H2}/mol_{total\ hydrocarbons}$
WHSV	7.9	7.5 - 16	g_{oil} / g_{cat}.hr

The molar H_2/oil ratio of 0.2 is in large excess of what was stoichiometrically required to hydrogenate the impurities *(1 – 5 mol%, see Table 5.1)*.

4.5.2 Reaction conditions for performance evaluation

For the purpose of evaluating the influence of operating variables on the catalyst performance, pressure, space velocity (WHSV) and hydrogen/oil ratio were varied within the ranges presented in Table 4.3. Initial experiments were conducted under conditions of large hydrogen excess (with respect to impurity) to avoid the reaction being hydrogen limited. However, later runs were carried out at conditions of stochiometric hydrogen supply with respect to impurity.

4.6 Feed and product analyses

4.6.1 Gas chromatography

Liquid samples were analysed by gas chromatography with manual sample injection. Chromatographic conditions are given in Table 4.4.

Table 4.4: Gas chromatographic conditions

Gas chromatograph	Varian model 3700
Detector	Flame ionisation detector (FID)
Carrier gas	Helium
Make-up gas	Nitrogen
Column head pressure	47.2 psia
Carrier gas linear velocity	22.3 cm/s
Split ratio	40 : 1
Liquid sample volume	0.5 µl
Column temperature	Room temperature
Detector temperature	250 °C
Injector temperature	200 °C
Manufacturer	Tracer
Column type	Wall coated fused silica column
Stationary phase	Dimethylpolysiloxane (50.2 TR PONA)
Column length	50 m
Column internal diameter	0.2 mm
Film thickness	0.5 µm

The peaks observed in the chromatogram were identified by making use of all of:

- Pure model components
- Literature
- In-house data from Fischer-Tropsch product identification

Typical chromatograms are presented in figures 4.4 and 4.5, indicating each identified compound's identity, retention time and basis of identification. Although not all of the compounds are identified, the unidentified compounds are considered to be irrelevant since they are marginal, or, when feed constituents, were found to remain unchanged or change only marginally upon reaction over the catalyst.

Peaks in the region expected for cracked or hydrogenolysis products (< C_6) were not observed. Also, dimers (in the C_{12} range) were found to be insignificant, contributing < 0.01 % to the total chromatographic response.

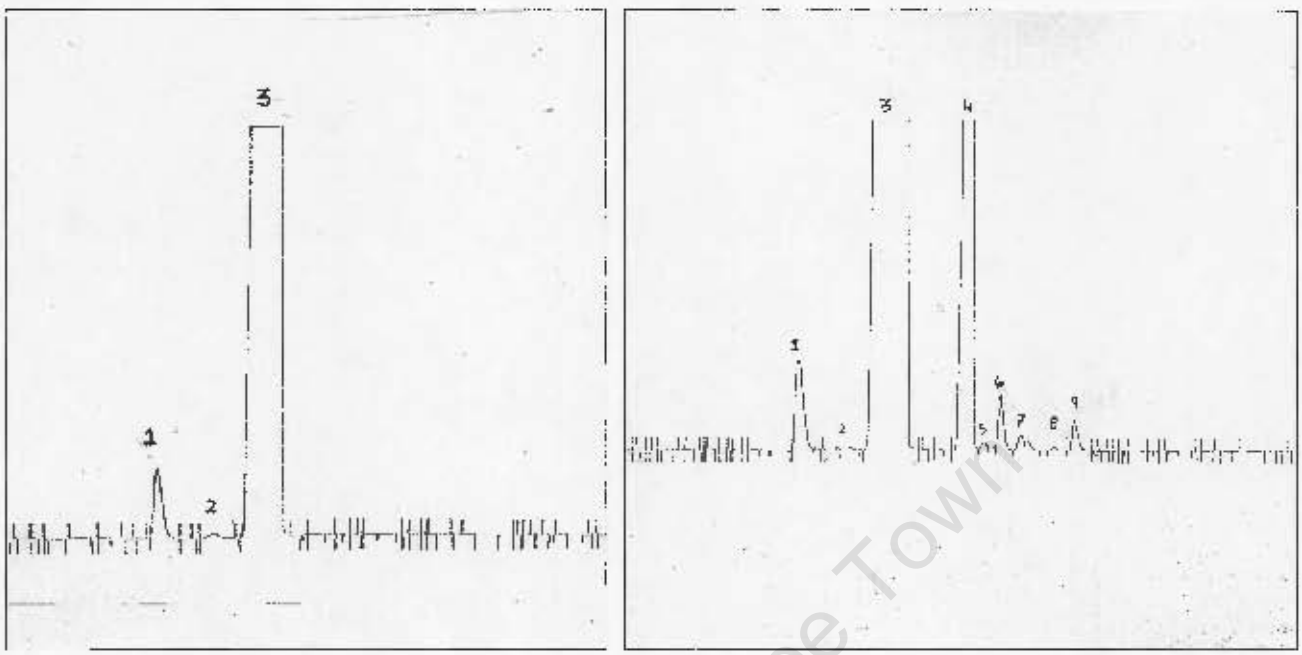
4.6.2 Data work-up

FID response factors for all components are considered to be unity. This is justified on the basis of the signal of the hydrocarbons in the flame ionization detector being proportional to the amount of carbon and on the basis of there being no evidence for relevant quantities of cracked or polymeric products (not obtained or < 0.01 %, respectively), so that the total number of moles and the number of carbon atoms per molecule is unchanged. Additionally, a carbon mass balance of 100 % is assumed as the basis for all calculations so that eventually the entire chromatogram could be evaluated simply on a peak area percent basis with mole fraction being proportional to peak area percent.

4.6.2.1 Analytical error and scatter

Reproducibility of the gas chromatographic results was proved through successive analyses of a single sample.

Feed: **Product:**



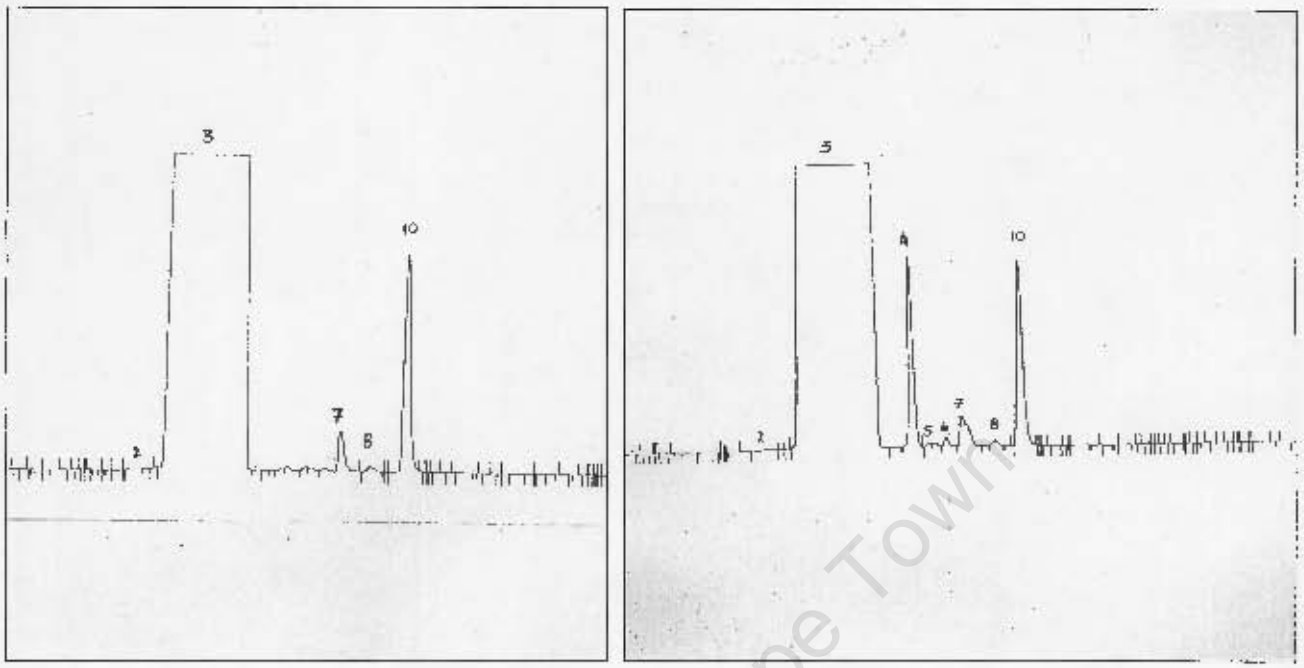
Peak number	Time (minutes)	Compound
1	10.15	1,5-hexadiene
2	10.59	3-methyl-pentane
3	11.31	1-hexene
4	12.00	n-hexane
5	12.12	3-hexene (trans and cis)
6	12.28	(trans) 2-hexene
7	12.47	2-methyl-2-pentene
8	12.82	Unknown
9	13.02	(cis) 2-hexene

Figure 4.4: A sample chromatogram and analyses for 1,5-hexadiene as a feed impurity

[1 mol% 1,5-hexadiene in 1-hexene, T = 60°C, P = 15 bar, molar H_2/oil = 0.2, WHSV = 8.7 – 15.2 hr^{-1}]

(Table 5.1: experiment 3a)

Feed: **Product:**



Peak number	Time (minutes)	Compound
2	10.59	3-methyl-pentane
3	11.31	1-hexene
4	12.00	n-hexane
5	12.12	3-hexene (trans and cis)
6	12.28	(trans) 2-hexene
7	12.47	2-methyl-2-pentene
8	12.82	Unknown
10	13.77	1-hexyne

Figure 4.5: A sample chromatogram and analyses for 1-hexyne as a feed impurity

[1 mol% 1-hexyne in 1-hexene; P = 15 bar; T = 60°C: WHSV = 7.5 – 15.8 hr^{-1}]

(Table 5.1: experiment 9)

It was found that results for species present in very low concentrations (< 1 mol %) are prone to greater scatter. Overall, the scatter is low (< 0.5 %) since the key compounds are generally present in amounts greater than 1 mol %.

4.6.2.2 Conversion

The conversion of two C_6 species, namely the impurity and 1-hexene, is of interest.

Conversion of impurity

In calculating the conversion of the impurity, only impurity hydrogenation is of interest as any double bond or skeleton isomerisation of the impurity is not considered to be a net removal. Total impurity in the product is therefore defined as the rest of the starting impurity plus any of its isomers. The conversion (removal) of impurity is then defined as follows:

$$X_{impurity} = \frac{(x_{impurity,feed} - x_{impurity,product}) + (\sum x_{impurity\ isomers,feed} - \sum x_{impurity\ isomers,product})}{(x_{impurity,feed} + x_{impurity\ isomers,feed})} \quad (1)$$

As outlined in the introduction to section 4.6.2, molar fractions are proportional to percentage peak area (A%) given in the chromatogram data records, so that

$$X_{impurity} = \frac{(A\%_{impurity,feed} - A\%_{impurity,product}) + (\sum A\%_{impurity\ isomers,feed} - \sum A\%_{impurity\ isomers,product})}{A\%_{impurity,feed} + A\%_{impurity\ isomers,feed}} \quad (2)$$

Conversion of 1-hexene

The conversion of 1-hexene is calculated by measuring the molar fraction of 1-hexene in feed and product samples as follows:

$$X_{1\ hexene} = \frac{(x_{1-hexene,feed}) - (x_{1-hexene,product})}{x_{1-hexene,feed}} \quad (3)$$

$$X_{1-hexene} = \frac{(A\%_{1-hexene,feed} - A\%_{1-hexene,product})}{A\%_{1\ hexene,feed}} \quad (4)$$

The loss of 1-hexene, via hydrogenation (to n-hexane), via isomerisation (to hexene isomers) or both, is taken into account in these equations.

Impurities, hexadienes as well as hexynes, may form 1-hexene when hydrogenated so that negative 1-hexene conversion values are possible. A negative 1-hexene conversion value would indicate a net "gain" of 1-hexene while a positive conversion value would indicate a net "loss" of 1-hexene. However, no 1-hexene gains were observed under any conditions in this study.

Hydrogen conversion

Hydrogen conversion is the result of both 1-hexene and impurity hydrogenation. Certain impurities (hexadienes and hexynes) may consecutively be hydrogenated, first to hexenes and subsequently to n-hexane. Therefore, net hydrogen consumption can be determined by considering both impurity hydrogenation and n-hexane formation. Hence hydrogen conversion is defined and determined according to equations 5 to 8.

It was found that the impurity was instantaneously saturated to n-hexane with only traces of 1-hexene being detectable (see sections 5.4 and 6.3). This means that the impurity has to be considered twice in the hydrogen balance, since two moles of hydrogen are required per mole of impurity to get complete hydrogenation to n-hexane, so that the degree of hydrogen conversion is calculated as follows:

Conventional:

$$X_{H_2} = \frac{[(x_{hexane,product} - x_{hexene,feed}) + (\sum x_{impurity+isomers,feed} - \sum x_{impurity-isomers,product})]}{\text{molar } H_2\text{/oil ratio}} \quad (5)$$

$$X_{H_2} = \frac{[(A\%_{hexane,product} - A\%_{hexane,feed}) + (\sum A\%_{impurity+isomers,feed} - \sum A\%_{impurity+isomers,product})]}{\text{molar } H_2\text{/oil ratio}} \quad (6)$$

Based on feed composition:

$$X_{H_2} = \frac{[(x_{impurity,feed} - x_{impurity,product})X2 + (x_{1-hexene,feed} - x_{1-hexene,product})]}{\text{molar } H_2/\text{oil ratio}} \quad (7)$$

$$X_{H_2} = \frac{[(A\%_{impurity,feed} - A\%_{impurity,product})X2 + (A\%_{1-hexene,feed} - A\%_{1-hexene,product})]}{\text{molar } H_2/\text{oil ratio}} \quad (8)$$

Specificity

The specificity parameter (S_p) describes the overall reaction with respect to desired and undesired reactions and is defined in equation 9.

$$Sp = \text{Specificity} = \frac{X_{impurity}}{X_{1-hexene}} = \frac{\text{impurity removal}}{\text{hexene loss}} \quad (9)$$

A specificity value of unity indicates that at low conversion, the rate of both impurity removal and loss of 1-hexene is equal, whereas specificity values of > 1 indicate that the impurity is being removed at a faster rate than the 1-hexene is lost.

5 RESULTS

5.1 Experiments carried out

5.1.1 Catalysts used

All experiments were carried out using a commercial Pd-Ag/TiO_2 catalyst (T4299) which was supplied by Süd-Chemie *(properties appear in table 4.1)*. This is one of the catalysts *McPherson (2003)* studied so that results can be compared.

5.1.2 Individual experiments and conditions

Several factors controlling the selective hydrogenation of C_6-olefinic streams were investigated. Such factors include the type of feed impurity, the pressure and temperature of the reaction and the amount of hydrogen available for reaction. The effect of pre-saturation of the feed with hydrogen and the effect of co-adsorbates on the selectivity and specificity of the reaction using CO and ethanol were also investigated. A record of all experiments is listed in table 5.1.

Catalyst performance was consistently monitored by running a standard condition after each series of condition settings. In the case of no change of catalyst performance, experiments were continued. In the case of a change to catalyst performance, the catalyst was recharged and the last condition setting was repeated.

Table 5.1: List of experimental runs

[Reaction temperature: 60°C]

Exp no.	Feed composition [mol%]	Reactor packing	Amount of catalyst [g]	Pressure [bar]	WHSV [$g_{oil}.hr^{-1}/g_{cat}$]	H_2 / oil molar ratio
NO SATURATOR						
1	100 % 1-hexene	SiC	-	15	note (1)	0.2
2	5% 1,5-hexadiene in 1-hexene	SiC	-	15	note (1)	0.2
3a	1% 1,5-hexadiene in 1-hexene	Pd-Ag/TiO_2	0.97	15	7.5 - 15	0.2
3b	5% 1,5-hexadiene in 1-hexene	Pd-Ag/TiO_2	0.97	15	7.5 - 15	0.2
4	1% 1,5-hexadiene; 1% 1-hexene in n-hexane	Pd-Ag/TiO_2	1.07	15	7.9 - 15.8	0.2
5	1% 1,5 hexadiene in n-hexane	Pd-Ag/TiO_2	1.07	15	7.9 - 15.8	0.2
6	100 % 1-hexene / 1% 1-hexyne in 1-hexene	Pd-Ag/TiO_2	1.05	15	8.0 - 17.3	0.2
7	1% 1-hexyne in 1-hexene	Pd-Ag/TiO_2	1.07	15	7.5 - 15	0.2
8	1% 1-hexyne in 1-hexene	Pd-Ag/TiO_2	1.07	15	7.9 - 15.8	0.04
SATURATOR						
9	1% 1-hexyne in 1-hexene	Pd-Ag/TiO_2	1.07	15	7.9 - 15.8	0.01
10	1% 1-hexyne in 1-hexene	Pd-Ag/TiO_2	1.07	30	7.9 - 15.8	0.01
11	1% 1-hexyne in 1-hexene (0 ppm CO) [2]	Pd-Ag/TiO_2	1.10	30	7.6 - 15.3	0.01
12	1% 1-hexyne in 1-hexene (5 ppm CO) [2]	Pd-Ag/TiO_2	1.10	30	7.6 - 15.3	0.01
13	1% 1-hexyne in 1-hexene (25 ppm CO) [2]	Pd-Ag/TiO_2	1.10	30	7.6 - 15.3	0.01
14	1% 1-hexyne in 1-hexene (50 ppm CO) [2]	Pd-Ag/TiO_2	1.10	30	7.6 - 15.3	0.01
15	1% 1-hexyne in 1-hexene (0 ppm Ethanol) [2]	Pd-Ag/TiO_2	1.09	30	7.7 - 15.5	0.01
16	1% 1-hexyne in 1-hexene (100 ppm Ethanol) [2]	Pd-Ag/TiO_2	1.09	30	7.7 - 15.5	0.01
17	1% 1-hexyne in 1-hexene (1000 ppm Ethanol) [2]	Pd-Ag/TiO_2	1.09	30	7.7 - 15.5	0.01
18	1% 1-hexyne in 1-hexene (5000 ppm Ethanol) [2]	Pd-Ag/TiO_2	1.09	30	7.7 - 15.5	0.01

Notes: 1. The pump rates for experiments 1 and 2 were equal to experiments 3 - 7.

2. Concentrations of CO and Ethanol are molar concentrations relative to liquid feed

5.2 Preliminary findings

Catalyst specificity, which was defined in previous work *(McPherson, 2003)*, is used as a basis for performance for all effects investigated *(see section 2.5.4)*.

5.2.1 Blank experiments

Blank experiments (experiments 1 and 2, table 5.1) were carried out using 100% inert catalyst diluent (SiC) to confirm the background reactions in the absence of the catalyst. No hydrogenation or isomerisation of both 100% 1-hexene feed and 5 mol% 1,5-hexadiene impurity in 1-hexene feed was found to occur at reaction conditions and reactor residence times as applied in experiments over catalyst. The catalyst diluent and the reactor walls and tubing were therefore considered to be completely inert under typical experimental conditions. Therefore, all activity observed can be attributed to the presence of the catalyst.

5.2.2 Reproducibility

The experimental reproducibility which is demonstrated in figure 1 (experiments 10, 11 and 15, table 5.1), involved three separate experimental runs over similar amounts of fresh catalyst. The figure shows the conversion of the 1-hexyne impurity as a function of the loss of 1-hexene ("specificity"). Impurity conversions range from 42 – 50% in all three experiments at various WHSVs, with all other variables kept constant.

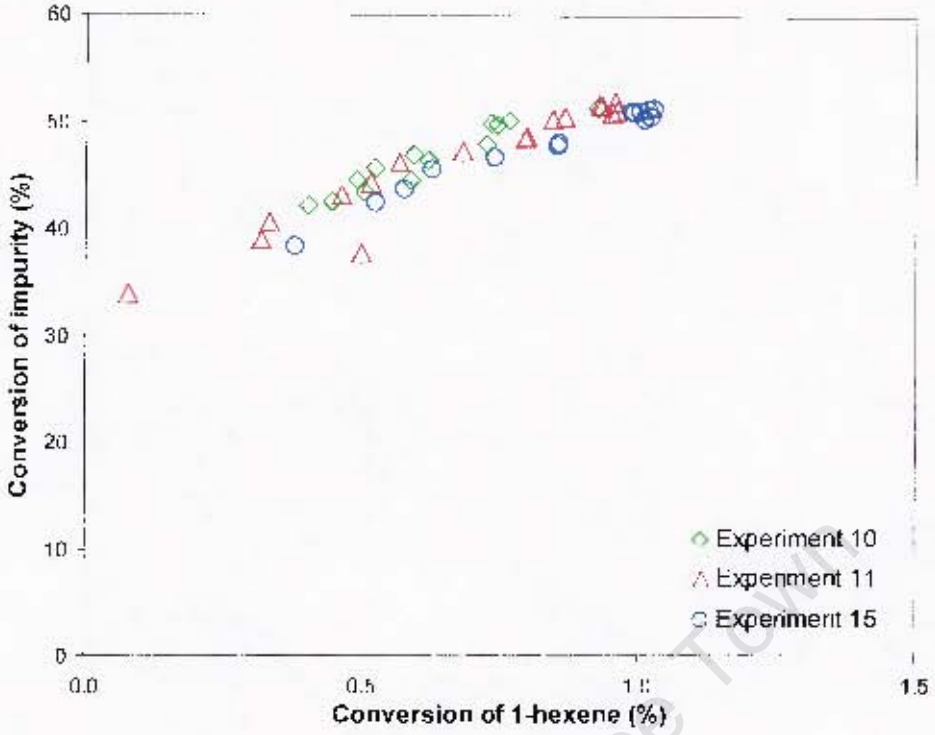


Figure 5.1: Specificity plot for experimental reproducibility (Pd-Ag/TiO_2 catalyst) [1.07 – 1.10g fresh catalyst in each of the experiments, 1 mol% 1-hexyne in 1-hexene, T = 60°C, P = 30 bar, molar H_2/oil = 0.01, WHSV = 7.9 – 15.8 hr^{-1}] (Table 5.1: experiments 10, 11 and 14)

5.2.3 Catalyst stability

Experiment 6 (table 5.1) was carried out to determine the stability of the catalyst. Initially, the catalyst was operated with pure 1-hexene at the standard condition (T = 60°C, P = 15 bar, molar H_2/oil = 0.2, WHSV = 8.0) and allowed to achieve steady state operation (0 – 7 hrs). Thereafter the feed was changed to 1-hexene containing 1 mol% 1-hexyne impurity. WHSV was varied. After 130 hours on stream, the catalyst was once again exposed to the standard condition with a 100% 1-hexene feed. It was found that conversion was unchanged vs. the initial period at these conditions.

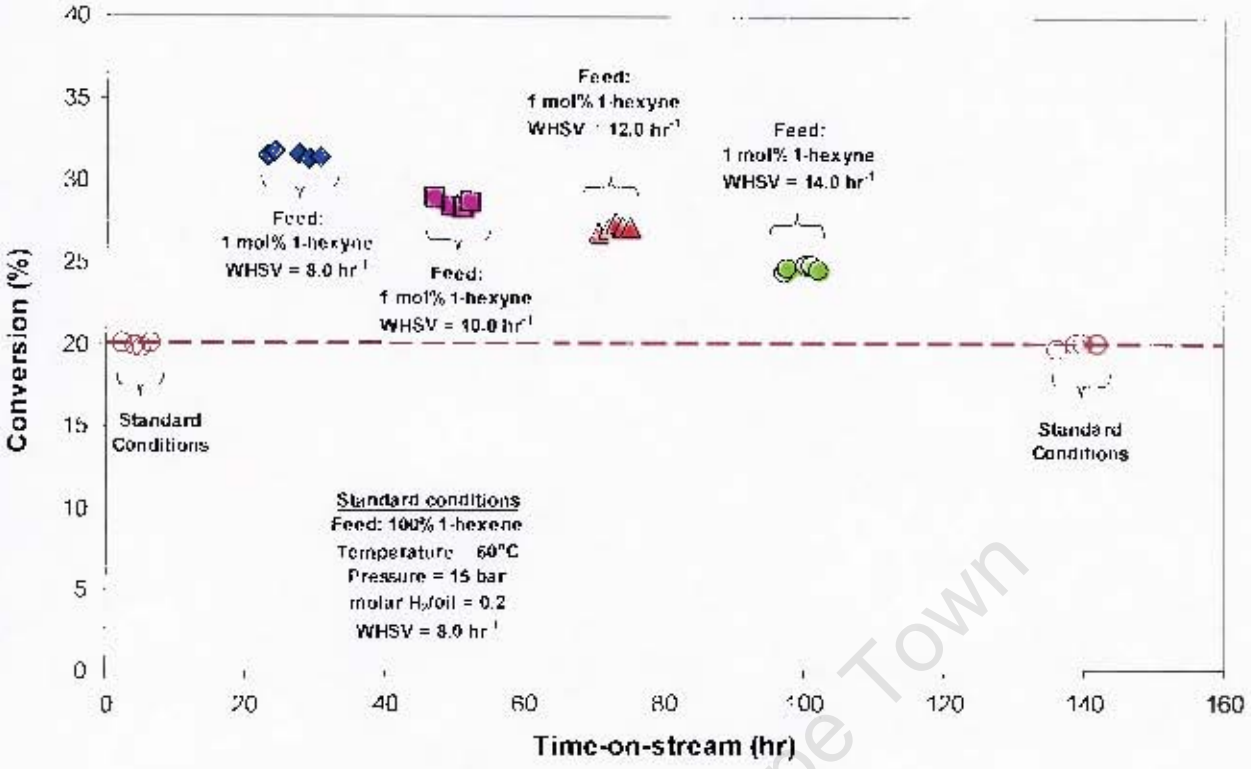


Figure 5.2: Time-on-stream performance of catalyst at standard condition and varying space velocity

(Experiment 6 – table 5.1)

As mentioned previously, standard conditions using pure 1-hexene feed were repeated after each series of condition settings to check for catalyst performance. In the case of no change of catalyst performance, experiments were continued. In the case of a change to catalyst performance, the catalyst was recharged and the last condition setting was repeated.

In other experiments (see table 5.1), individual catalyst charges were on stream for periods of up to 2 months without deactivation. All data was obtained under non-deactivating conditions.

5.2.4 Variation of Weight hourly space velocity (WHSV)

The weight hourly space velocity was altered by simultaneously changing both the gas and liquid flow in order to maintain a constant H_2/oil molar ratio (experiment 3a, table 5.1). Specificity was observed as a function of changing WHSV for all experiments in this study. WHSV was varied between 7.5 hr^{-1} to about 16 hr^{-1}. This trend is shown in figure 5.3.

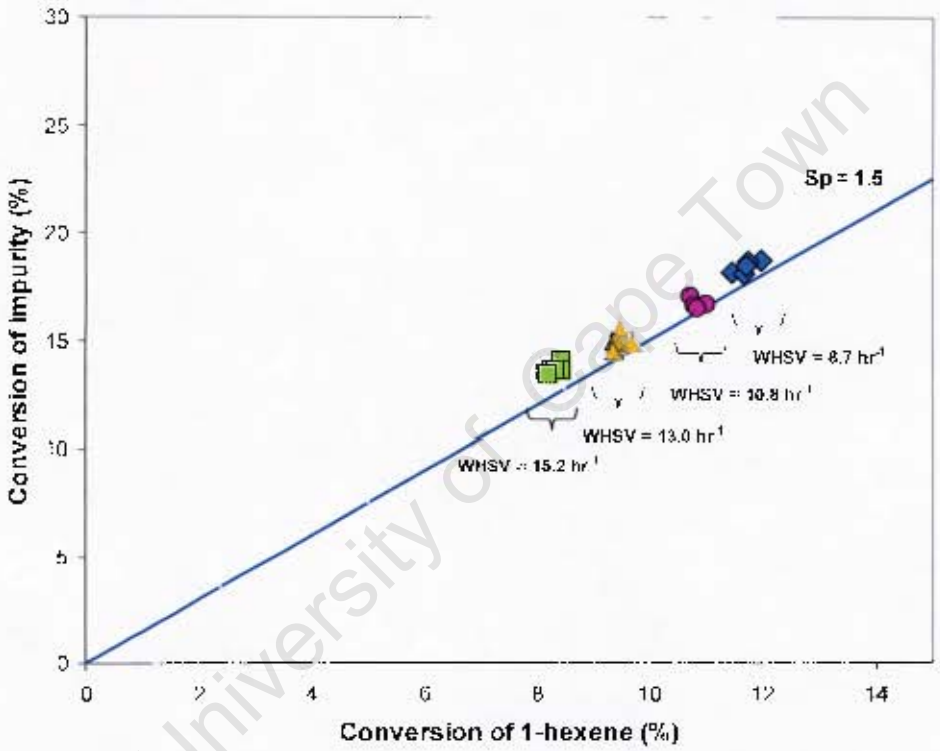


Figure 5.3: Specificity plot for the effect of varying WHSV
[1 mol% 1,5-hexadiene in 1-hexene, T = 60°C, P = 15 bar, molar H_2/oil = 0.2]
(Table 5.1: experiment 3a)

5.2.5 Variation of feed impurity concentration

The effect of varying the feed impurity concentration was investigated using 1,5-hexadiene as an impurity (experiments 3a and 3b, table 5.1). Two feed impurity concentrations (1 mol% and 5 mol%) were tested by varying the

WHSV to change the conversion, while maintaining all the other variables. This data was then compared with the results of *McPherson (2003)* (5 mol% 1,5-hexadiene in 1-hexene) for experimental reproducibility. The results are shown in figure 5.4.

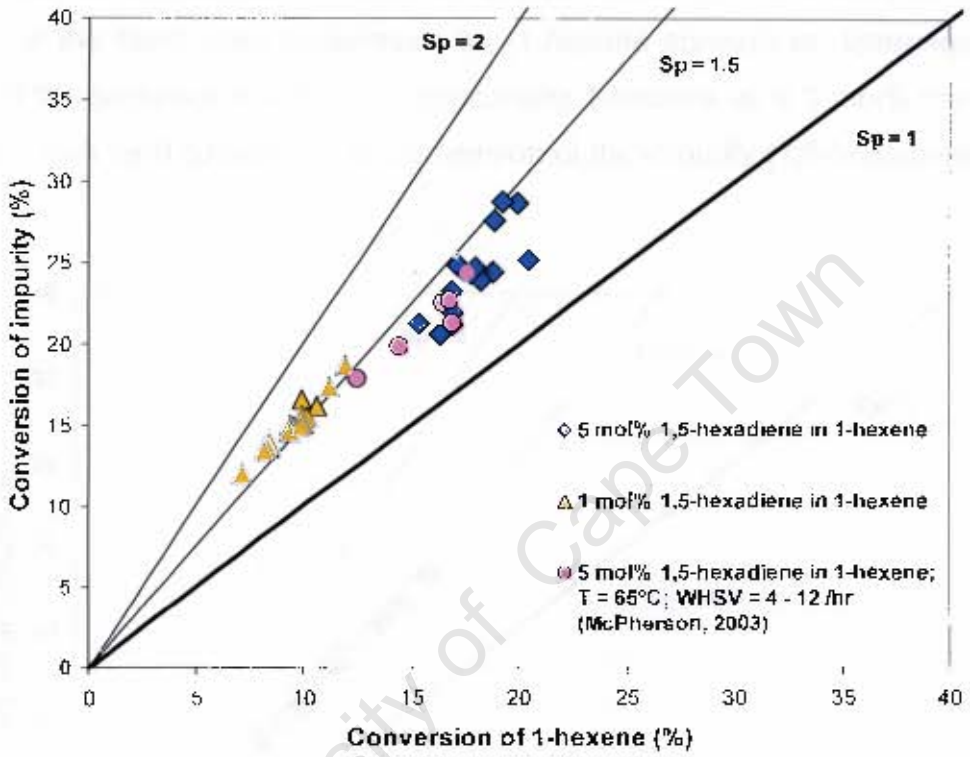


Figure 5.4: Specificity plot for the effect of varying WHSV [T = 60°C, P = 15 bar, molar H_2/oil = 0.2, WHSV = 8.7 – 15.2 hr^{-1} unless otherwise stated]

(Table 5.1: experiment 3a and 3b)

5.3 Mass transfer limitations

The experiment refers to indications of hydrogen mass transfer limitations from gas to liquid phase reported by McPherson *(2003)* (see section 2.6.5). To probe these findings an experiment was carried out using n-hexane, the n-C_6 paraffin, as the bulk phase, which cannot be converted consuming hydrogen.

5.4 Reaction pathway

In order to find out whether the impurity is hydrogenated stepwise or in one step, an experiment was carried out with 1 mol% 1,5-hexadiene in paraffinic solvent n-hexane i.e. with no 1-hexene present in the feed (experiment 5, table 5.1). Results are given in table 5.2 and compared with results from experiment 4.

Table 5.2: The effect of inert bulk component n-hexane on conversion of 1,5-hexadiene

[T = 60°C, P = 15 bar, molar H_2/oil = 0.2, WHSV = 7.9 – 15.8 hr^{-1}]

(Experiments 4 and 5 – table 5.1)

WHSV	1 mol% 1,5-hexadiene, 1 mol% 1-hexene, in n-hexane			1 mol% 1,5-hexadiene in n-hexane		
[hr^{-1}]	$X_{1,5\text{-hexadiene}}$	$X_{1\text{-hexene}}$	$X_{hydrogen}$	$X_{1,5\text{-hexadiene}}$	$Y_{1\text{-hexene}}$	$X_{hydrogen}$
7.88	~21%	~14%	2.80%	~24%	~0.04%	2.40%
9.85	~23%	~16%	3.10%	~24%	~0.04%	2.40%
11.82	~20%	~13%	2.65%	~23%	~0.03%	2.30%

Conversion of the impurity is almost the same in both experiments. The experiment which has no 1-hexene present in the feed results in very low yields of 1-hexene compared to the 1,5-hexadiene conversion.

It can be seen that more hydrogen is consumed in the case where there is 1 mol% 1-hexene present in the feed in addition.

5.5 Catalyst specificity

Catalyst specificity was shown to be affected by several process conditions in previous work on selective hydrogenation *(see section 2.8)*. Three of these variables were investigated in this study, namely the H_2/oil ratio, the presence or absence of gas phase hydrogen in the reactor and the effect of total pressure.

All results were obtained with 1 mol% 1-hexyne impurity in 1-hexene. Graphs include the "base" case H_2/oil = 0.2 (molar), 15 bar, without pre-saturation (experiment 7, table 5.1).

5.5.1 Variation of H_2/oil ratio

Previous work *(McPherson, 2003)* showed the specificity of 1-hexyne hydrogenation in 1-hexene to approach a value of 2 at conditions of high molar H_2/oil ratio of 0.2. This specificity meant that the 1-hexyne impurity was removed at a rate which was approximately two times higher than the rate of 1-hexene loss via hydrogenation or isomerisation.

Figure 5.6 shows the resulting specificity plot. The effect of H_2/oil ratio on the conversion of the impurity vs. the conversion i.e. loss of 1-hexene was studied in experiments 7 and 8 (table 5.1).

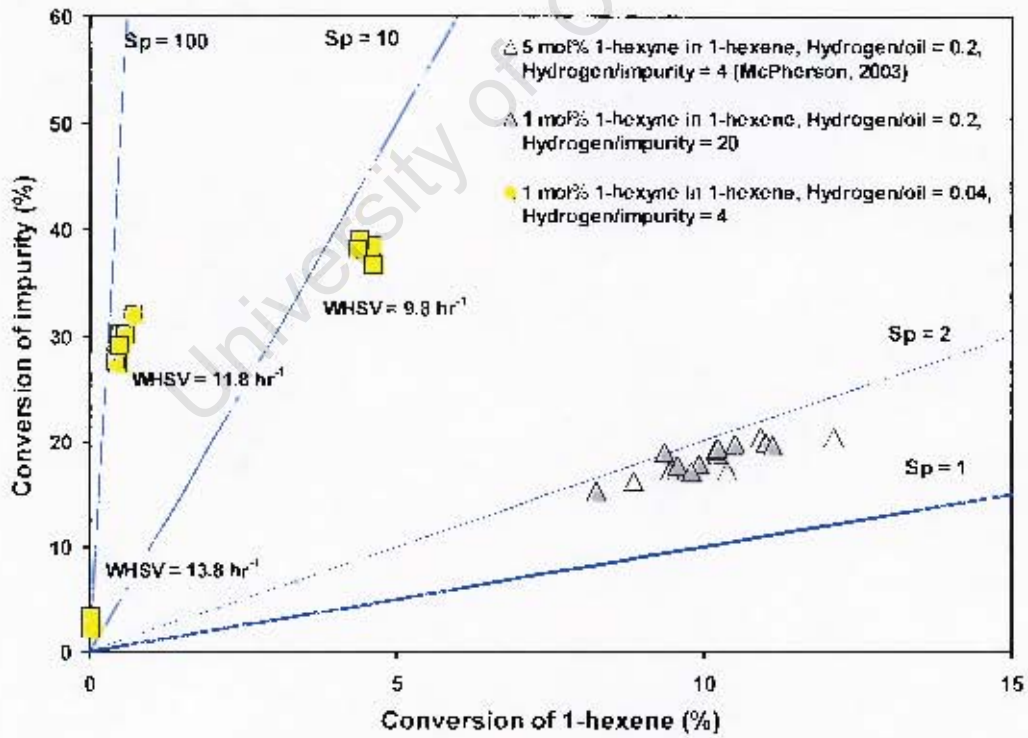


Figure 5.6: Specificity plot for the effect of molar H_2/oil ratio [1-hexyne in 1-hexene; P = 15 bar; T = 60°C; WHSV = 7.5 – 15.8 hr^{-1} unless otherwise stated]

(Table 5.1: experiments 7 and 8)

It can be seen that the decrease in the molar H_2/oil ratio from 0.2 to 0.04 resulted in an increase in the specificity values from approximately 2 to close to 100. A curvature in the data is seen at low space velocities for the experiment conducted at the lower H_2/oil ratio.

It can also be seen that the H_2/impurity ratio does not affect specificity.

5.5.2 Presence or absence of gas phase hydrogen

The influence of the absence of gas phase hydrogen in the reactor (as discussed in section 2.10) was studied in experiment 9 (table 5.1). Results are presented in figure 5.7. The elimination of gas-phase hydrogen was achieved experimentally at a H_2/oil ratio of 0.01 (as calculated in section 2.10.1 for 60°C and 15 bar total pressure). This corresponds still to a stoichiometric amount of hydrogen with respect to impurity concentration for conversion of the triple bond in 1-hexyne to a double bond i.e. 1-hexene but only to half the stoichiometric amount required for complete hydrogenation (to n-hexane). Also, a saturator was introduced upstream the reactor. The saturator allowed the complete pre-dissolution of the supplied hydrogen into the liquid hydrocarbons, prior to exposure to the catalyst in the reactor.

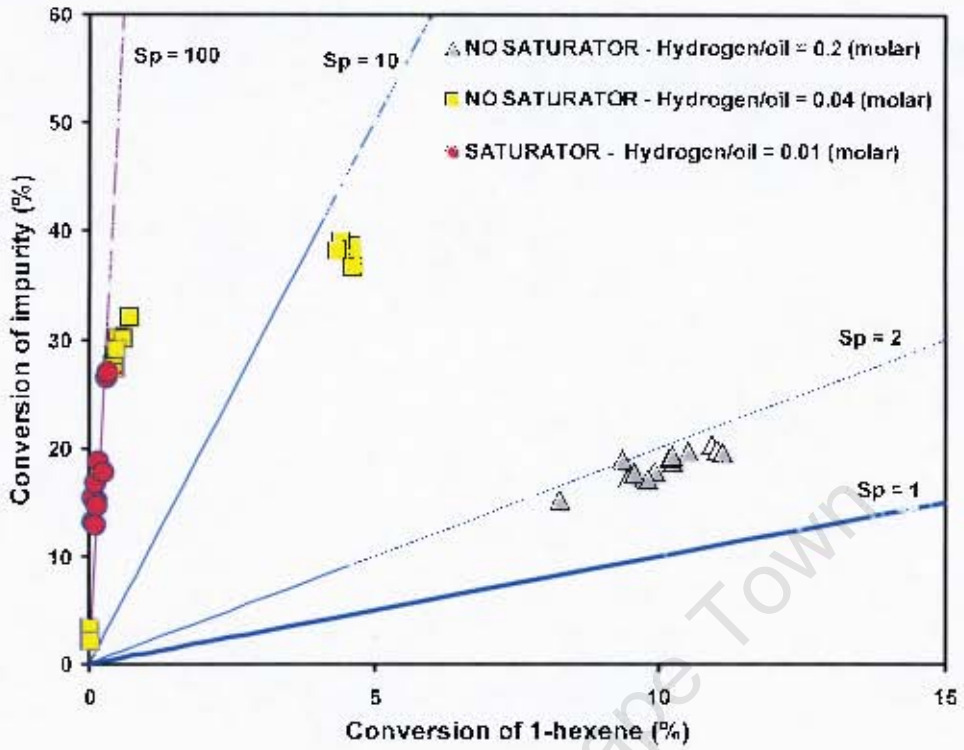


Figure 5.7: Specificity plot for the effect of the presence ("no saturator") or absence ("saturator") of gas phase hydrogen
[1 mol% 1-hexyne in 1-hexene; P = 15 bar; T = 60°C; WHSV = 7.5 – 15.8 hr^{-1}]
(Table 5.1; experiments 7, 8 and 9)

The elimination of gas phase hydrogen resulted in a further increase of specificity. The specificity is approaching values of approximately 100.

5.5.3 Pressure

While maintaining conditions of improved specificity, the pressure was increased from 15 bar to 30 bar (experiment 10, table 5.1) to ensure efficient dissolution and complete solubility of the hydrogen gas into the liquid phase (see section 2.9.1).

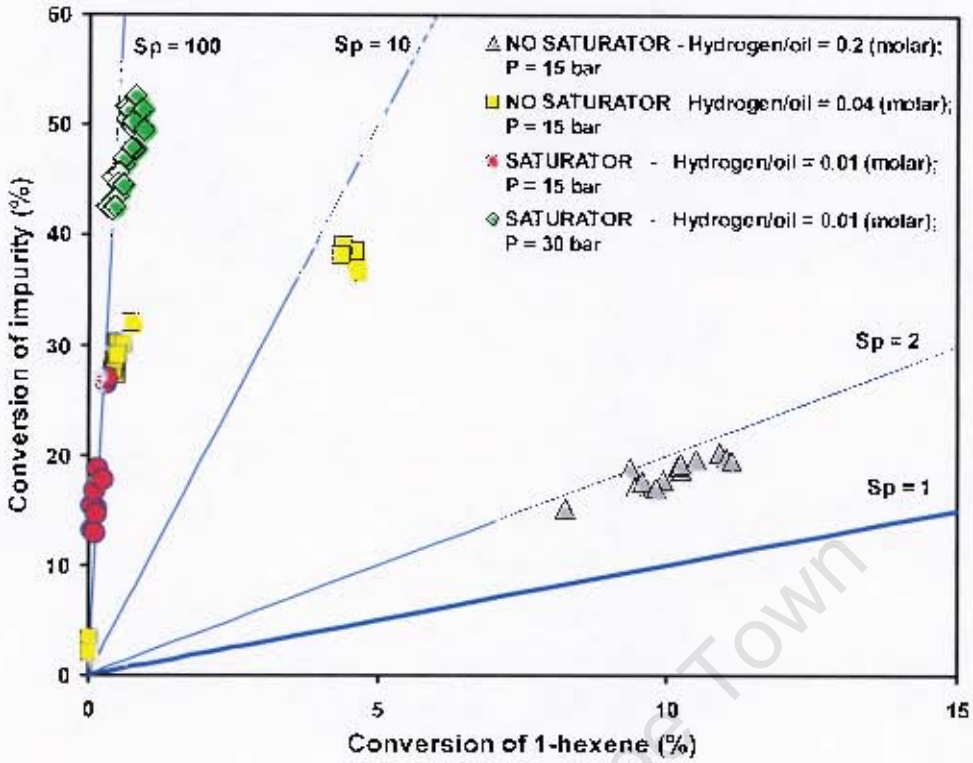


Figure 5.8: Specificity plot for the effect of pressure and saturation [1 mol% 1-hexyne in 1-hexene; T = 60°C; WHSV = 7.5 – 15.8 hr^{-1}] (Table 5.1: experiments 7 – 10)

Results are shown in figure 5.8. The conversion of the 1-hexyne impurity more than doubled with a doubling of the pressure, while the specificity was maintained at a value of approximately 100. Impurity conversions around 50% were achieved at the lowermost WHSV applied of 7.5 hr^{-1}.

5.6 The effect of co-adsorbates and potential poisons

Generally, the above results indicate that the specificity of the selective hydrogenation process can be improved to around 100, i.e. to a level where the rate of impurity removal is approximately 100 times faster than the rate of 1-hexene loss. This is achieved by operating at conditions of stoichiometric amounts of hydrogen supplied with respect to the feed impurity concentration

and at elevated pressure, where all the hydrogen is dissolved in the liquid phase.

However, literature reveals the possibility of introducing a co-adsorbate to the selective hydrogenation reaction mixture as a means of enhancing specificity (see section 2.8.2).

The effect of co-adsorbates CO and ethanol was studied. The amount of co-adsorbate in all of the experiments is given as a molar concentration with respect to moles of feed.

5.6.1 Introduction of carbon oxide

Carbon oxide was introduced to the feed at various concentrations to determine the effect on specificity. Since it was shown in previous work (see section 2.8.2) that only trace amounts of the co-adsorbate were necessary to have an effect on specificity, very low concentrations (in the ppm range) were employed. (experiments 11 – 14, table 5.1)

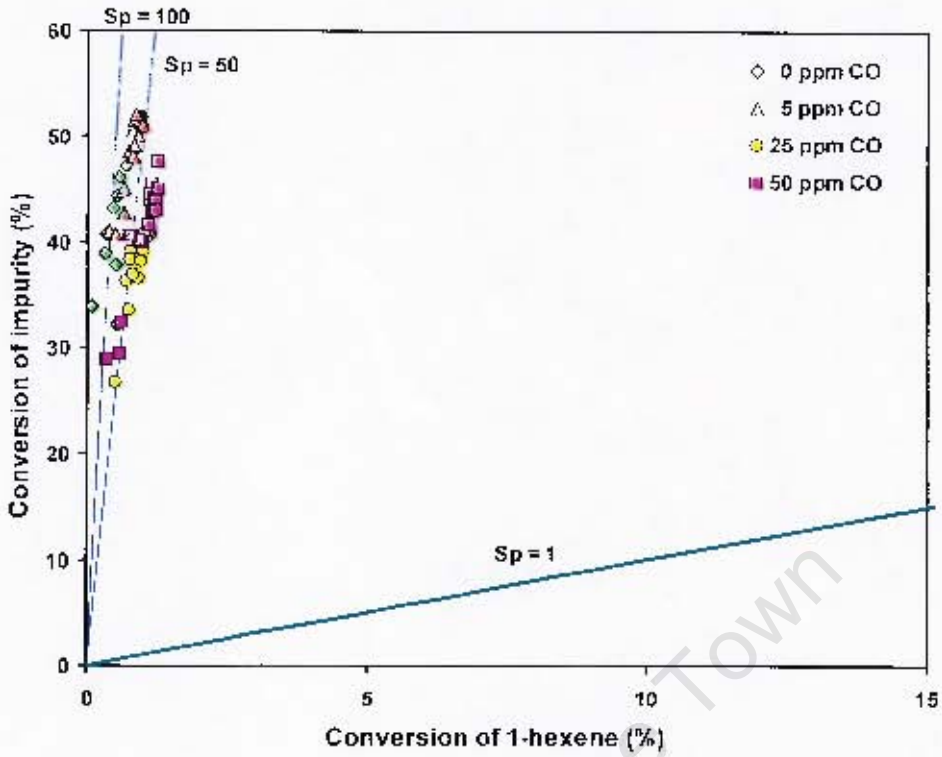


Figure 5.9: Specificity plot for the effect of carbon monoxide (molar ppm with respect to oil)

[Saturator: 1 mol% 1-hexyne in 1-hexene; molar H_2/oil = 0.01; P = 30 bar; T = 60°C; WHSV = 7.6 – 15.3 hr^{-1}]

(Table 5.1: experiments 11 – 14)

The results shown in figure 5.9 indicate that the introduction of CO results in impurity conversions and specificity values which are still in the range of the previous results where no co-adsorbate was used (0 ppm data) i.e. specificity values between 50 and 100.

Figure 5.10 shows an expansion of the data points in figure 5.9. The same trend is observed as in the other experiments, whereby an increase in WHSV is accompanied by a slight decrease in impurity conversion but a significant increase in specificity.

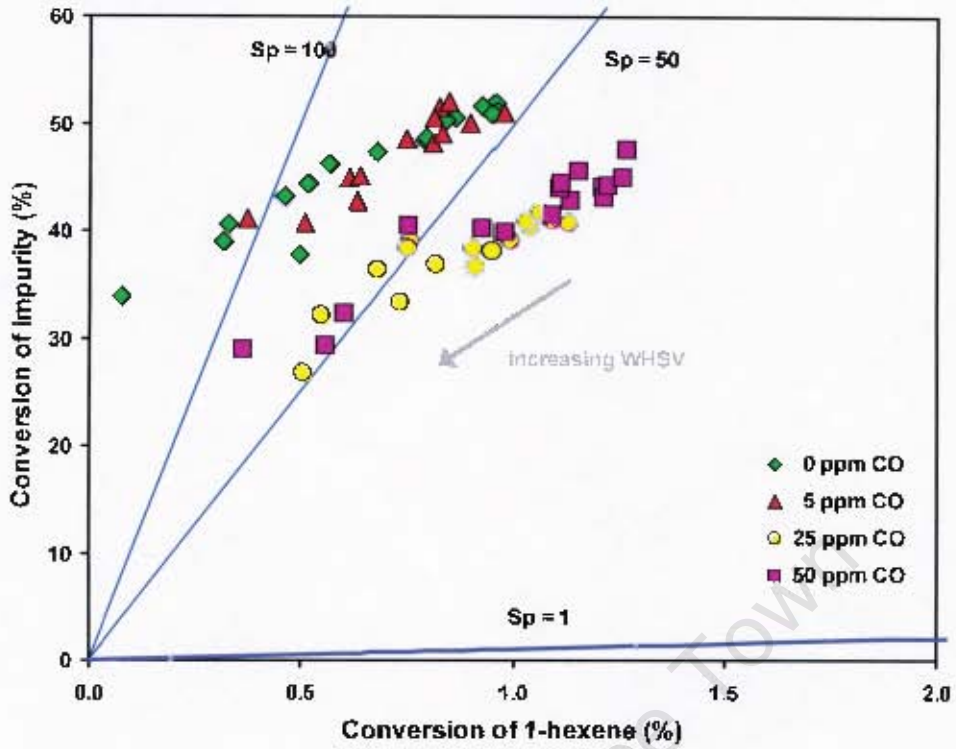


Figure 5.10: Expanded from figure 5.9 - Specificity plot for the effect of CO (molar ppm with respect to oil)
[Saturator; 1 mol% 1-hexyne in 1-hexene; molar H_2/oil = 0.01; P = 30 bar; T = 60°C; WHSV = 7.6 – 15.3 hr^{-1}]
(Table 5.1: experiments 11 – 14)

A concentration of 5 ppm CO seems to have little or no effect on specificity but the specificity appears to decrease slightly at higher concentrations of CO.

5.6.2 Introduction of ethanol

Since oxygenates are sometimes present in small quantities in industrial streams, prior to the extraction of 1-hexene as a chemical, it was decided to investigate the influence of small concentrations of oxygenates on the specificity of selective hydrogenation, using ethanol as a model compound. (experiments 15 -18, table 5.1)

It can be seen in figures 5.11 and 5.12 that the introduction of up to 5000 ppm (mol) ethanol results in a specificity which is still within the same range as the previous results where no co-adsorbate was used. Once again, the results of all experiments using ethanol as a co-adsorbate are compared to the base experiment which contains 0 ppm of ethanol for the purpose of experimental reproducibility.

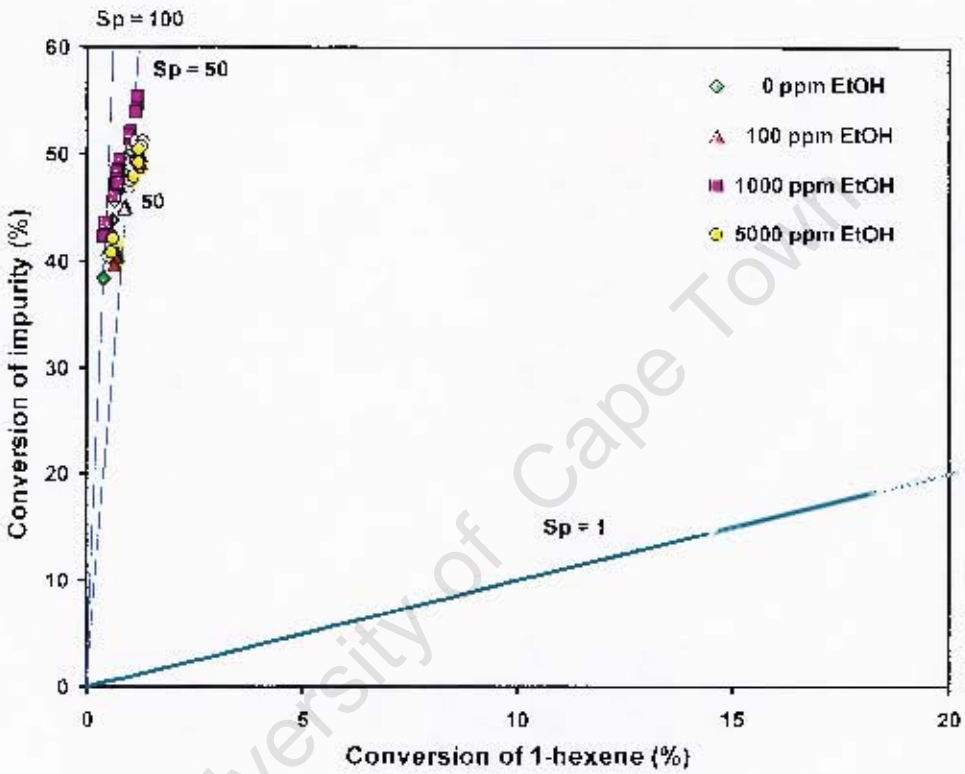


Figure 5.11: Specificity plot for the effect of ethanol (molar ppm with respect to oil)

[Saturator; 1 mol% 1-hexyne in 1-hexene; molar H_2/oil = 0.01; P = 30 bar; T = 60°C; WHSV = 7.6 – 15.3 hr^{-1}]

(Table 5.1: experiments 15 – 18)

The expansion of figure 5.11 shows that there is no effect beyond scatter.

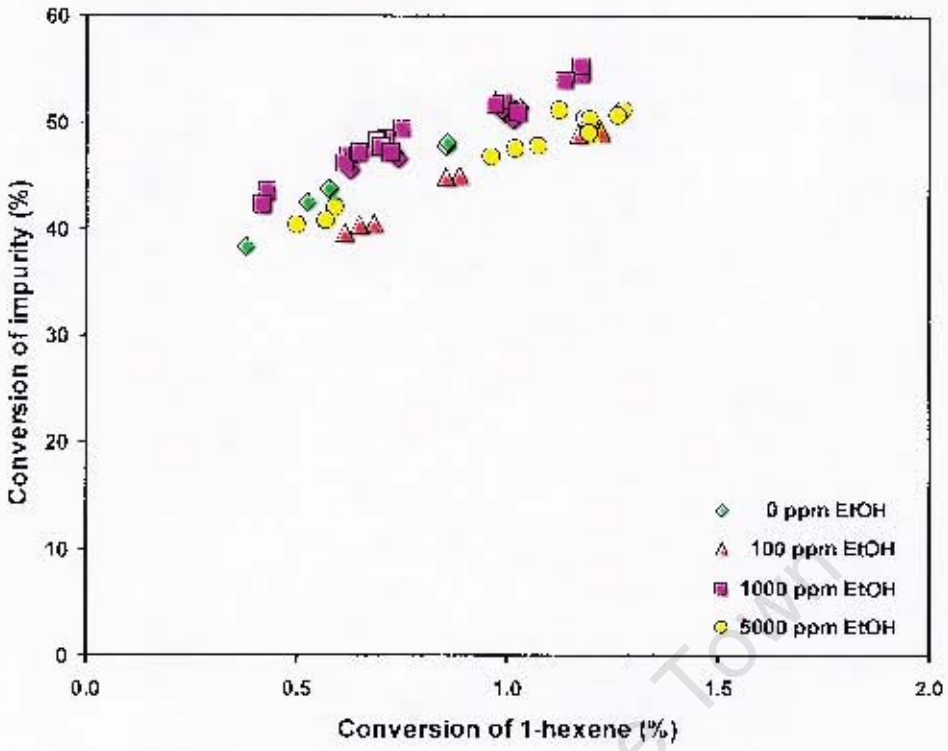


Figure 5.12: Expanded from figure 5.11 - Specificity plot for the effect of ethanol (molar ppm with respect to oil)
[Saturator; 1 mol% 1-hexyne in 1-hexene; molar H_2/oil = 0.01; P = 30 bar; T = 60°C; WHSV = 7.6 – 15.3 hr^{-1}]
(Table 5.1: experiments 15 – 18)

5.7 Hydrogen balance

Both equations 6 and 8 (see section 4.6.2.2, 'hydrogen conversion') should yield the same result for hydrogen conversion and hydrogen consumption, respectively, that is, just differ by the typical range of experimental scatter.

However, with the experiments at very low H_2/oil ratios and correspondingly low 1-hexene conversions and n-hexane yields, differences were found to be far beyond the range of experimental scatter that is typically obtained with this kind of experiment.

Consequently, no hydrogen balance can be carried out. Conversions of impurity and 1-hexene as well as the yield of n-hexane, clearly indicate that about twice as much hydrogen was available in the system than expected from the setting of the H_2/oil ratio and the hydrogen mass flow controller.

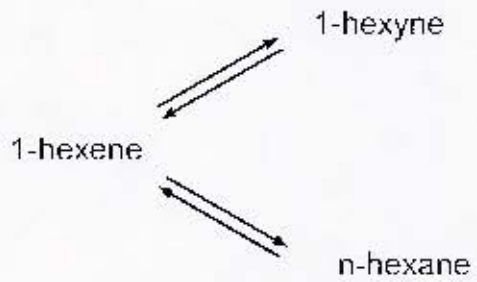
According to figures 5.8, 5.10 and 5.12 at a molar H_2/oil ratio of 0.01 (i.e. 1 mol% hydrogen in the reaction system), around 50% impurity conversion (at a feed concentration of 1 mol%) and 1% 1-hexene conversion were obtained. This requires a hydrogen consumption corresponding to around 2 mol% (note that 2 mol hydrogen are required per mole of impurity converted due to the instantaneous per-saturation to n-hexane, see sections 5.4 and 6.3).

Catalyst coking can be excluded as the source of the additional hydrogen. Coking was not observed and is very unlikely to occur at the given reaction temperature of 60°C. Also, given the space velocities applied and the long catalyst lifetimes achieved, coking cannot account for the additional hydrogen.

The observed discrepancy is probably due to operating the hydrogen mass flow controller close to its lower limit (5% of scale).

5.8 Thermodynamic equilibrium at low H_2/oil ratios

A molar H_2/oil ratio of 0.01, i.e. 1 mol% hydrogen in the system, and an impurity concentration of 1 mol% 1-hexyne in 1-hexene, correspond stoichiometrically to the complete conversion of 1-hexyne to 1-hexene. Therefore, the equilibrium distribution between 1-hexyne, 1-hexene and n-hexane can be treated in thermodynamic calculations simply as a disproportionation of 1-hexene as follows:



Note that in this system 1-hexyne and n-hexane form in equal amounts (1:1 molar ratio) with the hydrogen balance being fulfilled.

Supporting calculations of the thermodynamic equilibrium distribution are presented in Appendix B. Results show equilibrium distributions to be far on the side of 1-hexene at around 99.9 mol% at 60°C (and still 99.0 mol% at 200°C) and corresponding concentrations of n-hexane and 1-hexyne of 0.05 mol%.

6 DISCUSSION

The effects of reaction variables such as temperature, pressure, WHSV and H_2/oil ratio on hydrogenation activity and specificity were investigated thoroughly in previous studies *(McPherson, 2003)*. It was found that catalyst specificity is not affected by any reaction variables except H_2/oil ratio. Based on these results, a set of conditions (60°C, 15 bar and WHSV between 7.5 and 15 hr^{-1}) were chosen and used as a basis for this study (see table 5.1).

Preliminary studies proved the following:

- Reactor wall and tubing materials as well as the catalyst diluent (SiC) are inert with regard to the conversion of both 1-hexene and impurity (section 5.2.1).
- Results are reproducible within the range of scatter (see section 5.2.2 and Figure 5.1).
- The same amount of catalyst was used in repeating experiments and this therefore also confirms that the catalyst pellets have consistent metal loadings. The variation in conversions is generally less than 3%.
- Catalyst activity is stable with time on stream. The presence of the impurity does not cause deactivation (section 5.2.3 and Figure 5.2).
- In other experiments (see table 5.1), individual catalyst charges were on stream for periods of up to 2 months without deactivation.
- All data was obtained under non-deactivating conditions.
- Reproduction of earlier results using the same equipment *(McPherson, 2003)* was possible (Figures 5.4 and 5.6).

6.1 Effect of feed impurity concentration

It can be seen in Figure 5.4 *(section 5.2.5)* that the data obtained for different impurity concentrations in the feed roughly lie on the same line of catalyst

specificity (~1.5), and compares favorably to the results obtained by *McPherson (2003)*. Figure 5.3 shows that conversion i.e. change of concentration due to consumption, has no effect on specificity either. This confirms that the catalyst specificity is independent of the concentration of the impurity in the feed. Therefore the assumption is valid of a simplified pseudo-parallel reaction scheme (*as discussed in section 2.5.4)* and its application on determining catalyst specificity as the key parameter of interest in this study.

6.2 Absence of mass transfer limitations

Indications of hydrogen mass transfer limitations were reported to occur at temperatures above 55°C in previous studies *(McPherson, 2003)*. The aim of a respective experiment carried out in this study was to ensure that the amount of hydrogen in the bulk phase would be unchanged along the catalyst bed using a paraffinic solvent n-hexane, which cannot be hydrogenated. Therefore, a decrease in hydrogen concentration in the liquid phase and correspondingly hydrogen transfer limitations from the gas to the liquid phase could be excluded.

The results in Figure 5.5 show that the specificity is unchanged by the absence of 1-hexene as a bulk feed component, when all the other variables are kept constant. The fact that using 1-hexene as the bulk feed constituent produced the very same specificity and similar conversion to the experiment where hydrogen mass transfer control could be excluded (using n-hexane as the bulk feed constituent) proves, that in the former case mass transfer limitations do either not exist or do not have any effect on catalyst specificity.

6.3 Instantaneous per-saturation of feed impurities

In the conversion of 1 mol% 1,5-hexadiene in n-hexane at approximately 25% conversion *(table 5.2, last column)*, the potential intermediate, 1-hexene, was observed only in trace amounts. This clearly indicates that the impurity is converted on the catalyst surface straight through to the paraffin without desorption of olefinic intermediates. It can be anticipated that this conclusion holds even more for alkyne-type impurities.

This means that the stoichiometric amount of hydrogen required for complete conversion of the impurities is twice the amount of the impurities present in the feed so that 1 mol% of impurity stoichiometrically requires a molar H_2/oil ratio of 0.02.

If 1,5-hexadiene and 1-hexene were both present on impurity level concentration in n-hexane *(table 5.2, middle column)*, the conversion of the diene is almost the same as in the absence of 1-hexene *(table 5.2, last column)*.

The conversion of 1-hexene is a "true" conversion, since no 1-hexene is formed from the hydrogenation of the 1,5-hexadiene impurity. According to the specificity of 1.5 and the fact that only 1 mole of hydrogen is consumed per mole of 1-hexene converted, the result is that the total hydrogen consumption increases only moderately *(table 5.2)*.

6.4 Improvement of specificity at low H_2/oil ratio and absence of gas phase hydrogen

Catalyst specificity was defined as the ratio of the conversion of the impurity vs. the conversion of 1-hexene. The specificity plot is a measure of the

removal of the impurity relative to the simultaneous removal (loss) of 1-hexene.

Catalyst specificity increased from values of around 2 in previous work to values around 100 (as illustrated in Figure 6.1). Such high specificities are very desirable for the process of selective hydrogenation, as the impurity is removed at a rate which is approximately 100 times faster than the rate of loss of 1-hexene. The results shown in Figure 6.1 are consistent with the findings of Nierlich and Obenhaus *(1984)*, where a similar specific increase in impurity conversion was obtained with only the use of dissolved hydrogen (and absence of gas phase hydrogen) in the reactor and near-stoichiometric amounts of hydrogen.

The observed increase in specificity is the result of two improvements:

- A significant decrease in the H_2/oil ratio
- The absence of gas phase hydrogen

Based on the limited number of data available *(section 5.4.1, Figure 5.6 and section 5.4.2, Figure 5.7)*, it cannot yet be distinguished which of the two factors is controlling.

Based on the amount of hydrogen fed (molar H_2/oil ratio = 0.01 i.e. 1 mol%) limited by the hydrogen solubility level (hydrogen solubility in the feed at reaction conditions is ca. 1.7 mol%, see Figure 2.14), the available amount of hydrogen is less than the stoichiometric amount needed to hydrogenate 1 mol% of impurity in the feed. It must be taken into account that the impurity was found to react through to the paraffin immediately with only minimal formation of intermediate 1-hexene.

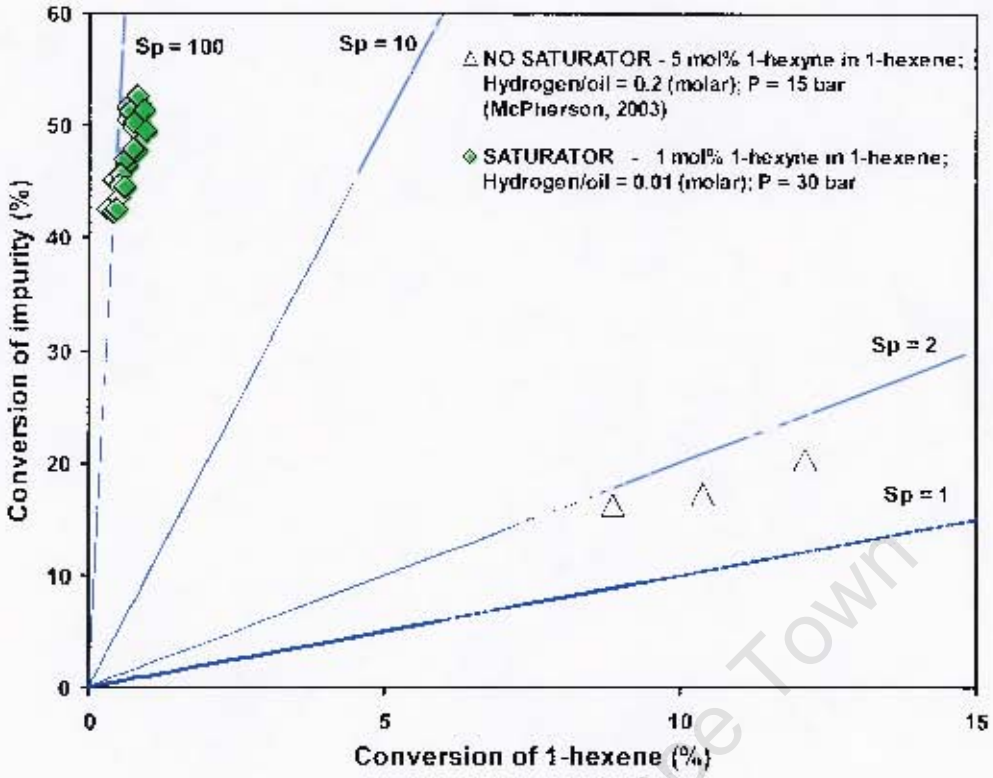


Figure 6.1: Specificity plot for the overall effect of hydrogen content and pre-saturation

[1 mol% 1-hexyne in 1-hexene; T = 60°C; WHSV = 7.5 – 15.8 hr^{-1}]

The interaction of palladium with dissociated hydrogen on the surface of the catalyst to form an α- and β-hydride phase is a well-known phenomenon *(section 2.8.1.1)*. It is thought to play a role in hydrogenation reactions. The suppression of the β-PdH phase has been shown to decrease the rate of 1-alkene hydrogenation to the respective paraffin in the case of C_2- and C_4-olefinic cuts. Therefore the increase in specificity, at low hydrogen/oil ratios and in absence of gas phase hydrogen, in the case of C_6-olefin cuts might be explained by the diminishing of the β-PdH phase.

However, literature does not present a clear relationship between reaction conditions and the presence or absence, or the concentration of the β-PdH phase hydrogen on the catalyst surface.

6.4.1 Stoichiometric limitation – hydrogen depletion

It appears from Figures 5.8, 5.10, 5.12 and 6.1 that impurity conversion at low molar H_2/oil ratio of 0.01 was limited to about 50%.

As outlined in section 5.7, the stoichiometric amount of hydrogen to completely remove the impurity would be 2 mol%. Considering the consumption of hydrogen for the simultaneous hydrogenation of 1-hexene at a specificity of 100, another 1 mol% of hydrogen, i.e. a minimum molar H_2/oil ratio of 3 would be required.

This indicates that the limitation of impurity conversion to about 50%, as observed in the low H_2/oil ratio experiments, may be an artificial effect due to hydrogen depletion.

6.4.2 Thermodynamic limitations

According to thermodynamic calculations on a mixture containing 1 mol% of 1-hexyne in 1-hexene and another mol% of hydrogen (at a molar H_2/oil ratio of 0.01), only traces of 1-hexyne should be left (0.05 mol%) and only traces of n-hexane should be formed (0.05 mol%), *see section 5.8 and Appendix B.*

From the only around 50% conversion of impurity obtained in the experiments (0.5 mol% remaining) and the fact that the hydrogen content in the system was even higher than 1 mol%, it is clear that the reaction system is still kinetically controlled.

6.5 Effect of co-adsorbates

Co-adsorbates have been shown to significantly improve the selectivity and specificity of selective hydrogenation catalysts *(see section 2.8.1)*. This is thought to be caused by altering the geometric properties of the catalyst

surface. The theory of ensembles *(see section 2.8.1)* predicts that the partial replacement or coverage (by the co-adsorbate) of a certain number of active sites, restricts the possibility of formation of ensembles of adjacent active sites which are required by certain hydrogenation reactions. Two methods of achieving this "dilution" effect were discussed in section 2.8.2 – one of which is the introduction of trace amounts of strong co-adsorbates to the reaction mixture.

In the case of feeding CO as a co-adsorbate, the results *(Figures 5.9 and 5.10)* show that trace amounts of CO (5 molar ppm in H_2) in the reaction mixture resulted in no significant change of the specificity of the reaction. In fact, even a negative effect, i.e. a slight decrease in specificity, seems to occur at higher concentrations of CO (up to 50 molar ppm in H_2). However, the observed trend is very unsteady so that this slight decrease in specificity is rather questionable. Results could still be within the experimental error range of the base experiment (0 ppm CO) so that any effect of CO in fact could not be demonstrated clearly.

An even clearer indication of the absence of an effect can be seen for the case where ethanol is used as a co-adsorbate *(Figures 5.11 and 5.12)*. There is scatter between the series but no trend of the specificity with increasing amounts of ethanol, even at ethanol concentrations of approximately 5000 molar ppm in the oil, i.e. 0.5 mol%.

It is known that the use of a bimetallic catalyst is a way to achieve surface site dilution *(see section 2.8.2)*. The replacement of some of the surface Pd atoms, i.e. catalytic sites, by a second metal geometrically hinders the formation of ensembles. Therefore the result of no effect being caused by co-adsorbates can be explained by the fact that the "dilution" effect is already present, achieved by the use of the bimetallic catalyst Pd-Ag. Thus the use of a co-adsorbate to further improve selectivity is merely redundant. It is expected that the specificity of the reaction will be enhanced by co-adsorbates when a monometallic palladium catalyst is employed, as reported in literature

for the case of ethyne hydrogenation in the presence of ethene *(see section 2.8.2)*.

6.6 Effect of reaction conditions

The amount of hydrogen available for reaction, which was controlled by manipulating the H_2/oil ratio, was observed in this study to have a significant effect on specificity *(section 5.5, Figures 5.6 – 5.8)* and therefore became a focus of this study. Small amounts of hydrogen with respect to the amount of impurity present in the feed (e.g. a molar H_2/oil ratio of 0.01 at 1 mol% impurity concentration) resulted in very high specificity values around 100, which achieve one of the objectives of this study.

Pressure has no direct effect on catalyst specificity *(see section 5.5.3, Figure 5.7, results from operating with saturator at 15 bar and 30 bar respectively)*. Higher pressure was employed to ensure complete dissolution of hydrogen in the liquid phase, according to the solubility data *(see section 2.9.1, Figure 2.14)*, since it is the issue of the absence of gas phase hydrogen at low hydrogen/oil ratios, which is seen as being responsible for the enhancement in specificity *(see section 6.4)*.

7 CONCLUDING REMARKS

This study has evaluated the feasibility of selective hydrogenation for the removal of impurities from industrial 1-hexene streams, where the impurities could be present in the ppm range. Experiments were conducted over a commercial Pd-Ag/TiO_2 catalyst.

The focus of the study was to improve the specificity of the catalyst i.e. the extent of impurity removal vs. the extent of 1-hexene loss to a commercially acceptable level by investigating the effects of H_2/oil ratio, pre-saturation of hydrogen in the liquid phase and the introduction of co-adsorbents to the reaction mixture.

Catalyst specificity proved to be an efficient catalyst evaluation tool as it was found to be insensitive to temperature, pressure and WHSV. Specificity is a direct measure of the desired vs. the undesired reaction.

From the limited findings of this study it may be deduced that operating at very low molar H_2/oil ratios so that the presence of gas phase hydrogen in the reactor could be avoided, dramatically improves the specificity from values of about 2 as observed in previous studies to values of about 100. The removal of the impurity (the desired reaction) at a rate which is one hundred times faster than the simultaneous loss of the 1-olefin (the undesired reaction), now makes the process of selective hydrogenative purification of industrial 1-hexene streams feasible.

The introduction of low concentrations of co-adsorbents (carbon monoxide and ethanol) to the reaction mixture had no effect on catalyst activity and specificity, suggesting that the expected site "dilution" effect is already achieved by the use of the bimetallic palladium-silver catalyst, and that co-adsorbents are redundant.

Undoubtedly, there is still need for a deeper understanding of the observed phenomena and there is still room for improvement in terms of approaching 100% impurity conversion while maintaining high specificity.

It is recommended that future studies include:

i) Improvement of the operation of the experimental apparatus in terms of more accurate H_2/oil ratio settings.

ii) Optimisation of design variables to achieve high impurity conversion at still high specificity values such as:
   - Application of higher pressure to increase the hydrogen content in the system in absence of gas phase hydrogen.
   - Using a multi-stage design with intermediate hydrogen supply and saturation.

iii) Lowering impurity concentrations to < 1 mol%.

iv) Clarification if the specificity enhancement is either a result of:
   - The effect of operating in absence of gas phase hydrogen (i.e. with a pre-saturated feed).
   - The effect of reduced H_2 / impurity / oil ratio.
   - The effect of total hydrogen depletion.
   - Or the effect of a combination of two or more of these factors.

v) An attempt to a better understanding of the role of the β-palladium hydride phase and, if favourable, how to avoid or minimize its formation.

vi) Investigation of the effect of other co-adsorbents such as water and ammonia.

vii) Investigation of the role of the co-adsorbents (carbon oxide and ethanol) over a monometallic palladium catalyst.

viii) Evaluation of the selective hydrogenation of a commercial 1-hexene feedstock, which contains a host of impurities of the alkadiene and alkyne-type once process design and reaction parameters have been optimised.

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Personal Communications

Walter Böhringer, Catalysis Research Unit, Dept. of Chemical Engineering, University of Cape Town (2002 - 2004)

A/Prof Jack CQ Fletcher, Catalysis Research Unit, Dept. of Chemical Engineering, University of Cape Town (2002 - 2004)

Paul Jacobs, Lead Engineer, Sasol Olefins & Surfactants SA, Secunda (2004)

Prof Eric van Steen, Catalysis Research Unit, Dept. of Chemical Engineering, University of Cape Town (2003)

Appendix A

Solubility of hydrogen in 1-hexene

Data basis for figure 2.14.

A HYSIS simulation was done, where equimolar amounts of hydrogen and 1-hexene were fed to a mixer via separate streams. The temperature of the mixer was then varied from -20 to 155°C at three different pressures with the maximum temperature limited by the boiling point of 1-hexene at the given pressure. The liquid fraction of each component in the product stream was then used to calculate the solubility of hydrogen in 1-hexene. The results of the simulation and the hydrogen solubility are tabulated.

Results from HYSYS simulation (basis: 100% 1-hexene, liquid) are the following:

Temp	H_2	1-Hexene		mol H_2 / g 1-hexene	Solubility		
					$x_{hydrogen}$		$x_{1\text{-hexene}}$
[°C]	[mol]	[mol]	[g]		[mol frac]	[mol %]	[mol frac]
Pressure: 1 bar							
-20	0.40	973.90	81966.68	4.85E-06	0.0004	0.0408	0.9996
0	0.40	913.60	76891.40	5.21E-06	0.0004	0.0438	0.9996
20	0.32	737.30	62053.46	5.11E-06	0.0004	0.0430	0.9996
30	0.21	532.95	44854.59	4.70E-06	0.0004	0.0396	0.9996
40	0.04	108.04	9092.97	3.91E-06	0.0003	0.0329	0.9997
Pressure: 15 bar							
-20	6.22	998.20	84011.34	7.40E-05	0.0062	0.6188	0.9938
-10	6.61	996.76	83889.98	7.88E-05	0.0066	0.6588	0.9934
0	7.02	994.44	83694.72	8.38E-05	0.0070	0.7005	0.9930
20	7.78	985.47	82940.36	9.38E-05	0.0078	0.7836	0.9922
40	8.59	966.53	81346.23	1.06E-04	0.0088	0.8807	0.9912
60	9.12	929.47	78226.73	1.17E-04	0.0097	0.9713	0.9903
80	9.12	859.47	72335.15	1.26E-04	0.0105	1.0502	0.9895
100	8.08	726.11	61111.85	1.32E-04	0.0110	1.1001	0.9890
120	5.02	455.12	38304.60	1.31E-04	0.0109	1.0915	0.9891
130	2.23	209.72	17650.83	1.26E-04	0.0105	1.0508	0.9895
Pressure: 25 bar							
-20	10.32	998.87	84068.23	1.23E-04	0.0102	1.0224	0.9898
0	11.68	996.57	83874.24	1.39E-04	0.0116	1.1586	0.9884
20	13.13	991.15	83418.24	1.57E-04	0.0131	1.3079	0.9869
50	15.33	970.81	81706.28	1.88E-04	0.0155	1.5547	0.9845
80	17.02	919.59	77395.12	2.20E-04	0.0182	1.8167	0.9818
100	17.21	850.51	71581.73	2.40E-04	0.0198	1.9835	0.9802
130	13.90	626.87	52759.43	2.64E-04	0.0217	2.1697	0.9783
150	6.56	279.85	23552.59	2.78E-04	0.0229	2.2901	0.9771
155	3.29	140.05	11787.20	2.79E-04	0.0229	2.2930	0.9771

The following calculations were used to calculate the solubility of each component in the mixture:

$$x_{hydrogen} = \frac{H_2(mols)}{[H_2(mols) + 1-hexene(mols)]}$$

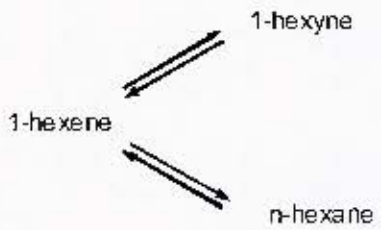
$$x_{1-hexene} = \frac{1-hexene(mols)}{[H_2(mols) + 1-hexene(mols)]}$$

Appendix B

Thermodynamic equilibrium of 1-hexyne, 1-hexene and n-hexane

Calculated as disproportionation of 1-hexene (see section 5.8).

In this system 1-hexyne and n-hexane are formed in equal amounts (1:1 molar ratio) with the hydrogen balance being fulfilled.



Defining the *equilibrium constant*:

$$K = \frac{x_{1\text{-hexyne}} \bullet x_{n\text{-hexane}}}{(x_{1\text{-hexene}})^2}$$

Where x_i : mole fraction

Solving the equation for $x_{1\text{-hexene}}$:

$$x_{1\text{-hexene}} = \sqrt{\frac{x_{1\text{-hexyne}} \bullet x_{n\text{-hexane}}}{K}}$$

Since $x_{1\text{-hexyne}} = x_{n\text{-hexane}}$ (disproportionation), it follows that:

$$x_{1\text{-hexene}} = \sqrt{\frac{(x_{1\text{-hexyne}})^2}{K}}$$

$$x_{1\text{-hexene}} = x_{1\text{-hexyne}} \bullet \sqrt{\frac{1}{K}}$$

Also:

$$x_{1\text{-hexyne}} = \frac{(1 \quad x_{1\text{-hexene}})}{2}$$

So that:

$$x_{1\text{-hexene}} = \frac{(1 - x_{1\text{-hexene}})}{2} \sqrt{\frac{1}{K}}$$

$$2x_{\text{hexene}} = \sqrt{\frac{1}{K}} \quad x_{1\text{ hexene}} \sqrt{\frac{1}{K}}$$

$$2x_{1\text{ hexene}} + x_{1\text{ hexene}} \sqrt{\frac{1}{K}} = \sqrt{\frac{1}{K}}$$

$$x_{1\text{ hexene}} (2 + \sqrt{\frac{1}{K}}) = \sqrt{\frac{1}{K}}$$

Finally:

$$x_{1\text{ hexene}} = \frac{\sqrt{\frac{1}{K}}}{(2 + \sqrt{\frac{1}{K}})}$$

Temerature		delta G_F			delta G_{R°		K	molar distribution		
		1-hexene	1-hexyne	n-hexane				1-hexene	1-hexyne	n-hexane
[K]	[°C]		[kcal/mol]		kcal/mol	kJ/mol		[mol fraction]		
298	25	20.90	52.24	-6.06	10.38	43.4	0.00000002	0.9997	0.00016	0.00016
300	27	21.09	52.37	6.18	10.37	43.3	0.00000003	0.9997	0.00017	0.00017
333	***60***	***24.62***	***54.96***	***4.73***	***10.46***	***43.71***	***0.00000054***	***0.9989***	***0.00053***	***0.00053***
400	127	31.78	60.23	13.96	10.63	44.4	0.00000158	0.9975	0.00125	0.00125
500	227	42.94	68.24	28.31	10.67	44.6	0.00002191	0.9907	0.00464	0.00464
600	327	54.41	76.89	43.02	11.09	46.4	0.00009213	0.9812	0.00942	0.00942
700	427	66.10	85.51	57.98	11.29	47.2	0.00030097	0.9665	0.01677	0.01677
800	527	77.91	94.22	73.08	11.48	48.0	0.00073595	0.9485	0.02573	0.02573

Note: ΔG_f° values at temperature = 60°C were interpolated.

Appendix C:

Tabulated hydrogenation data

The raw data was worked up according to the equations shown in section 4.6.2.

Notes:

1. The data for each experiment outlined in table 5.1 (section 5.1) is shown in the following tables, where both the feed and product is listed.

2. The most important mole fractions are listed i.e. impurity, 1-hexene and n-hexane. The values listed are all steady-state readings.

3. The conversions of impurity, 1,5-hexadiene or 1-hexyne, were determined by equations 2 and 4 respectively (section 4.6.2.2). Bear in mind that only impurity hydrogenation is considered, and thus a conversion of impurity to an impurity isomer is not considered as impurity conversion.

4. The specificity is calculated for each WHSV.

Experiment 3a

1% 1,5-hexadiene in 1-hexene, 60°C, 15 bar, H_2/oil ratio = 0.2, 0.97g Pd-Ag/TiO_2

	WHSV	mol%			$X_{impurity}$	$X_{1\text{-hexene}}$	Sp
	[$g_{oil}.hr^{-1}/g_{cat}$]	1,5-hexadiene	1-hexene	n-hexane	(%)	(%)	
Feed	-	1.085	98.661	-	-	-	-
Product	8.665	0.866	86.855	11.286	18.698	11.966	1.56
		0.866	87.079	9.351	18.662	11.739	1.59
		0.872	87.359	10.139	18.154	11.455	1.58
		0.872	87.147	10.621	18.103	11.670	1.55
		0.869	87.090	9.476	18.421	11.728	1.57
	10.831	0.884	88.086	9.698	16.993	10.718	1.59
		0.888	88.011	9.471	16.593	10.794	1.54
		0.887	87.791	9.480	16.672	11.018	1.51
		0.890	87.956	9.311	16.438	10.849	1.52
	12.998	0.906	89.289	8.997	14.936	9.498	1.57
		0.899	89.323	9.490	15.578	9.464	1.65
		0.905	89.402	8.871	14.986	9.384	1.60
		0.906	89.109	9.162	14.927	9.681	1.54
		0.910	89.425	8.789	14.549	9.361	1.55
	15.164	0.920	90.496	7.795	13.638	8.278	1.65
		0.921	90.610	6.850	13.506	8.160	1.66
		0.915	90.341	7.978	14.103	8.433	1.67
		0.920	90.344	7.908	13.588	8.429	1.61
		0.920	90.430	7.847	13.578	8.342	1.63
		0.922	90.576	7.662	13.403	8.195	1.64

Experiment 3b

5% 1,5-hexadiene in 1-hexene, 60°C, 15 bar, H_2/oil ratio = 0.2, 0.97g Pd-Ag/TiO_2

	WHSV	mol%			$X_{impurity}$	$X_{1\text{-hexene}}$	Sp
	[$g_{oil}.hr^{-1}/g_{cat}$]	1,5-hexadiene	1-hexene	n-hexane	(%)	(%)	
Feed	-	5.124	94.506	-	-	-	-
Product	8.665	3.654	75.664	19.477	28.692	19.938	1.44
		3.652	76.327	18.780	28.720	19.236	1.49
		3.711	76.659	18.452	27.574	18.885	1.46
		3.879	77.685	17.442	24.299	17.799	1.37
	10.831	3.931	78.505	16.548	23.279	16.932	1.37
		3.874	76.750	18.529	24.385	18.788	1.30
		3.999	78.520	16.583	21.951	16.916	1.30
		3.900	77.294	17.830	23.886	18.213	1.31
	12.998	4.071	79.025	16.270	20.544	16.381	1.25
		4.038	78.490	16.849	21.195	16.948	1.25
		3.850	78.293	16.900	24.868	17.156	1.45
		3.862	77.489	17.687	24.629	18.006	1.37
		4.035	79.989	15.246	21.245	15.361	1.38
		3.834	75.204	20.255	25.176	20.425	1.23

Experiment 4

1% 1,5-hexadiene, 1% 1-hexene in n-hexane, 60°C, 15 bar, H_2/oil ratio = 0.2,1.07g Pd-Ag/TiO_2

	WHSV	mol%			$X_{impurity}$	$X_{1\text{-hexene}}$	Sp
	[$g_{oil}.hr^{-1}/g_{cat}$]	1,5-hexadiene	1-hexene	n-hexane	(%)	(%)	
Feed	-	1.031	1.016	97.965	-	-	-
Product	7.878	0.812	0.868	98.322	21.289	14.545	1.46
		0.809	0.866	98.326	21.504	14.805	1.45
	9.848	0.788	0.852	98.361	23.557	16.146	1.46
		0.791	0.852	98.356	23.272	16.129	1.44
		0.792	0.853	98.353	23.191	16.064	1.44
	11.817	0.819	0.874	98.308	20.595	13.943	1.48
		0.817	0.873	98.308	20.759	14.073	1.48
		0.822	0.876	98.305	20.258	13.800	1.47
	13.787	0.847	0.899	98.253	17.888	11.536	1.55
		0.846	0.895	98.260	17.946	11.933	1.50
		0.847	0.896	98.256	17.890	11.840	1.51

Experiment 5

1% 1,5-hexadiene in n-hexane, 60°C, 15 bar, H_2/oil ratio = 0.2, 1.07g Pd-Ag/TiO_2

	WHSV	mol%			$X_{impurity}$	$Y_{1\text{-hexene}}$
	[$g_{oil}.hr^{-1}/g_{cat}$]	1,5-hexadiene	1-hexene	n-hexane	(%)	(%)
Feed	-	1.096	-	98.904	-	-
Product	7.878	0.847	0.041	99.112	22.653	0.041
		0.835	0.040	99.123	23.771	0.040
		0.830	0.039	99.131	24.223	0.039
		0.828	0.042	99.130	24.447	0.042
	9.848	0.830	0.056	99.114	24.260	0.056
		0.827	0.043	99.131	24.525	0.043
		0.826	0.045	99.130	24.590	0.045
		0.832	0.043	99.127	24.063	0.043
	11.817	0.864	0.038	99.097	21.102	0.038
		0.864	0.000	99.135	21.146	0.000
		0.836	0.037	99.126	23.690	0.037

Experiment 6

100% 1-hexene / 1% 1-hexyne in 1-hexene, 60°C, 15 bar, H_2/oil ratio = 0.2, 1.05g Pd-Ag/TiO_2

	WHSV	mol%		$X_{impurity}$	$X_{1\text{-hexene}}$	TOS
	[$g_{oil}.hr^{-1}/g_{cat}$]	1-hexyne	1-hexene	(%)	(%)	(hrs)
Feed 1	-	-	100	-	-	-
Feed 2	-	1.088	98.379	-	-	-
Product	7.996 (feed 1)		79.996	-	20.004	2.18
			80.154	-	19.846	4.06
			80.208	-	19.792	5.24
			79.936	-	20.064	6.35
	7.996 (feed 2)	0.745	90.205	31.535	8.309	23.02
		0.743	89.988	31.755	8.529	24.02
		0.744	90.202	31.639	8.312	27.55
		0.747	90.108	31.313	8.408	29.03
		0.746	90.004	31.391	8.513	30.57
	9.995	0.773	91.239	28.973	7.267	47.13
		0.779	90.427	28.434	8.083	49.54
		0.780	90.384	28.336	8.127	51.19
		0.776	90.109	28.664	8.406	52.27
	11.994	0.796	86.871	26.819	11.698	70.56
		0.793	86.812	27.104	11.757	72.06
		0.789	86.749	27.486	11.821	73.04
		0.793	86.616	27.154	11.956	74.00
		0.792	86.658	27.206	11.914	75.00
	13.990	0.823	91.048	24.369	7.452	97.11
		0.820	90.934	24.670	7.567	97.57
		0.818	90.577	24.784	7.931	100.14
		0.818	90.586	24.834	7.921	101.00
		0.821	90.705	24.570	7.800	102.00
	7.996 (feed 1)		80.303	-	19.697	136.16
			79.971	-	20.029	138.81
			79.945	-	20.055	139.87
			79.939	-	20.061	141.82

Experiment 7

1% 1-hexyne in 1-hexene, 60°C, 15 bar, H_2/oil ratio = 0.2, 1.07g Pd-Ag/TiO_2

	WHSV	mol%			$X_{1\text{-hexyne}}$	$X_{1\text{-hexene}}$	Sp
	$[g_{oil}.hr^{-1}/g_{cat}]$	1-hexyne	1-hexene	n-hexane	(%)	(%)	
Feed	-	1.088	98.379	-	-	-	-
Product	7.996	0.867	87.644	8.677	20.339	10.912	1.86
		0.872	87.550	8.755	19.813	11.008	1.80
		0.875	87.446	8.884	19.591	11.113	1.76
	9.995	0.882	89.173	9.488	18.973	9.357	2.03
		0.884	88.314	10.323	18.716	10.231	1.83
		0.880	88.361	10.309	19.134	10.183	1.88
		0.878	88.318	10.358	19.336	10.227	1.89
		0.874	88.043	10.610	19.664	10.506	1.87
	11.994	0.901	89.080	10.603	17.169	9.452	1.82
		0.896	88.967	10.704	17.670	9.567	1.85
		0.895	88.609	11.040	17.784	9.931	1.79
		0.894	88.619	11.040	17.834	9.921	1.80
		0.902	88.738	10.991	17.070	9.800	1.74
	13.993	0.923	90.263	11.292	15.187	8.250	1.84

Experiment 8

1% 1-hexyne in 1-hexene, 60°C, 15 bar, H_2/oil ratio = 0.04, 1.07g Pd-Ag/TiO_2

	WHSV	mol%			$X_{1\text{-hexyne}}$	$X_{1\text{-hexene}}$	Sp
	$[g_{oil}.hr^{-1}/g_{cat}]$	1-hexyne	1-hexene	n-hexane	(%)	(%)	
Feed 1	-	1.043	98.711	-	-	-	-
Feed 2	-	1.006	98.677	-	-	-	-
Product	7.878	0.755	98.290	0.678	27.611	0.427	64.62
	(feed 1)	0.758	98.255	0.730	27.343	0.463	59.09
		0.755	98.280	0.661	27.635	0.437	63.25
		0.746	98.278	0.722	28.507	0.439	64.92
	9.848	1.008	98.684	0.079	3.388	0.028	122.11
		1.020	98.685	0.054	2.174	0.026	82.80
	11.817	0.728	98.213	0.850	30.229	0.504	59.93
		0.729	98.135	0.848	30.102	0.584	51.57
		0.709	97.998	1.009	32.048	0.723	44.34
		0.740	98.232	0.782	29.088	0.486	59.85
	13.787	0.618	94.135	4.875	38.558	4.603	8.38
	(feed 2)	0.613	94.327	4.713	39.086	4.409	8.87
		0.622	94.382	4.636	38.117	4.353	8.76
		0.637	94.119	4.880	36.636	4.619	7.93

Experiment 9

SATURATOR: 1% 1-hexyne in 1-hexene, 60°C, 15 bar, H_2/oil ratio = 0.01, 1.07g Pd-Ag/TiO_2

	WHSV	mol%			$X_{1\text{-hexyne}}$	$X_{1\text{-hexene}}$	Sp
	$[g_{oil}.hr^{-1}/g_{cat}]$	1-hexyne	1-hexene	n-hexane	(%)	(%)	
Feed 1	-	1.099	98.644	-	-	-	-
Feed 2	-	1.072	98.660	-	-	-	-
Product	7.869	0.801	98.346	0.591	26.461	0.302	87.60
	(feed 1)	0.796	98.309	0.630	26.946	0.340	79.29
	9.837	0.910	98.517	0.330	15.108	0.145	104.33
	(feed 2)	0.931	98.595	0.226	13.137	0.066	198.42
		0.907	98.578	0.268	15.328	0.083	185.06
		0.893	98.533	0.307	16.710	0.129	129.38
		0.872	98.498	0.366	18.654	0.165	113.27
		0.915	98.509	0.303	14.618	0.153	95.46
	11.804	0.935	98.549	0.256	12.789	0.113	113.61
		0.882	98.393	0.457	17.729	0.271	65.45

Experiment 10

SATURATOR: 1% 1-hexyne in 1-hexene, 60°C, 30 bar, H_2/oil ratio = 0.01, 1.07g Pd-Ag/TiO_2

	WHSV	mol%			$X_{impurity}$	$X_{1\text{-hexene}}$	Sp
	$[g_{oil}.hr^{-1}/g_{cat}]$	1-hexyne	1-hexene	n-hexane	(%)	(%)	
Feed	-	1.077	98.189	-	-	-	-
Product	7.869	0.533	97.571	1.590	50.473	0.630	80.09
		0.521	97.557	1.626	51.584	0.644	80.06
		0.577	97.581	1.528	46.400	0.620	74.84
		0.572	97.607	1.543	46.913	0.594	79.04
		0.525	97.519	1.683	51.280	0.683	75.09
	9.837	0.590	97.792	1.329	45.168	0.405	111.56
		0.538	97.469	1.652	50.000	0.734	68.15
		0.509	97.401	1.793	52.696	0.803	65.65
		0.540	97.458	1.703	49.827	0.745	66.87
		0.523	97.281	1.899	51.408	0.925	55.56
		0.536	97.436	1.735	50.226	0.767	65.47
	11.804	0.619	97.884	1.221	42.553	0.311	136.96
		0.585	97.675	1.453	45.701	0.524	87.18
		0.544	97.251	1.885	49.512	0.956	51.79
		0.562	97.406	1.731	47.776	0.798	59.87
		0.561	97.477	1.664	47.898	0.725	66.03
		0.596	97.707	1.413	44.614	0.491	90.78
	13.771	0.622	97.794	1.306	42.249	0.402	104.98
		0.608	97.693	1.417	43.485	0.506	85.97
		0.618	97.752	1.353	42.554	0.445	95.62
		0.597	97.611	1.486	44.567	0.589	75.61

Experiment 11

SATURATOR: 1% 1-hexyne in 1-hexene (0 ppm CO), 60°C, 30 bar, H_2/oil ratio = 0.01, 1.10g Pd-Ag/TiO_2

	WHSV	mol%		$X_{impurity}$	$X_{1\text{-hexene}}$	Sp
	$[g_{oil}.hr^{-1}/g_{cat}]$	1-hexyne	1-hexene	(%)	(%)	
Feed	-	1.050	98.885	-	-	-
Product	7.648	0.509	97.745	51.547	0.933	55.27
		0.505	97.720	51.890	0.957	54.20
		0.519	97.810	50.602	0.867	58.37
		0.521	97.831	50.362	0.845	59.61
		0.507	97.749	51.733	0.928	55.72
		0.512	97.716	51.206	0.962	53.24
	9.560	0.585	98.106	48.186	0.567	81.47
		0.541	97.881	48.445	0.794	60.98
		0.515	97.726	50.915	0.952	53.48
		0.640	98.351	39.005	0.319	122.42
		0.693	98.589	33.963	0.077	440.91
		0.553	97.993	47.297	0.681	69.47
		0.538	97.879	48.716	0.797	61.15
	11.473	0.584	98.156	44.380	0.516	85.98
		0.597	98.207	43.175	0.464	93.06
		0.623	98.337	40.655	0.332	122.46
		0.653	98.174	37.793	0.498	75.91

Experiment 12

SATURATOR: 1% 1-hexyne in 1-hexene (5 ppm CO), 60°C, 30 bar, H_2/oil ratio = 0.01, 1.10g Pd-Ag/TiO_2

	WHSV	mol%			$X_{impurity}$	$X_{1\text{-hexene}}$	Sp
	$[g_{oil}.hr^{-1}/g_{cat}]$	1-hexyne	1-hexene	n-hexane	(%)	(%)	
Feed	-	1.07	98.682	-	-	-	-
Product	7.648	0.590	98.074	1.019	44.918	0.615	72.98
		0.518	97.864	1.337	51.571	0.829	62.23
		0.513	97.842	1.317	52.031	0.851	61.16
		0.529	97.877	1.259	50.585	0.815	62.04
		0.550	97.942	1.165	48.594	0.749	64.85
	9.560	0.630	98.310	0.792	41.144	0.376	109.34
		0.588	98.051	1.069	45.092	0.639	70.58
		0.555	97.880	1.286	48.180	0.812	59.31
		0.524	97.719	1.454	51.019	0.975	52.32
	11.473	0.535	97.792	1.321	50.003	0.901	55.48
		0.614	98.058	1.044	42.676	0.632	67.51
		0.634	98.180	0.921	40.747	0.509	80.11
		0.544	97.857	1.319	49.130	0.836	58.80

Experiment 10

SATURATOR: 1% 1-hexyne in 1-hexene, 60°C, 30 bar, H_2/oil ratio = 0.01, 1.07g Pd-Ag/TiO_2

	WHSV	mol%			$X_{impurity}$	$X_{1\text{-hexene}}$	Sp
	$[g_{oil}.hr^{-1}/g_{cat}]$	1-hexyne	1-hexene	n-hexane	(%)	(%)	
Feed	-	1.077	98.189	-	-	-	-
Product	7.869	0.533	97.571	1.590	50.473	0.630	80.09
		0.521	97.557	1.626	51.584	0.644	80.06
		0.577	97.581	1.528	46.400	0.620	74.84
		0.572	97.607	1.543	46.913	0.594	79.04
		0.525	97.519	1.683	51.280	0.683	75.09
	9.837	0.590	97.792	1.329	45.168	0.405	111.56
		0.538	97.469	1.652	50.000	0.734	68.15
		0.509	97.401	1.793	52.696	0.803	65.65
		0.540	97.458	1.703	49.827	0.745	66.87
		0.523	97.281	1.899	51.408	0.925	55.56
		0.536	97.436	1.735	50.226	0.767	65.47
	11.804	0.619	97.884	1.221	42.553	0.311	136.96
		0.585	97.675	1.453	45.701	0.524	87.18
		0.544	97.251	1.885	49.512	0.956	51.79
		0.562	97.406	1.731	47.776	0.798	59.87
		0.561	97.477	1.664	47.898	0.725	66.03
		0.596	97.707	1.413	44.614	0.491	90.78
	13.771	0.622	97.794	1.306	42.249	0.402	104.98
		0.608	97.693	1.417	43.485	0.506	85.97
		0.618	97.752	1.353	42.554	0.445	95.62
		0.597	97.611	1.486	44.567	0.589	75.61

Experiment 11

SATURATOR: 1% 1-hexyne in 1-hexene (0 ppm CO), 60°C, 30 bar, H_2/oil ratio = 0.01, 1.10g Pd-Ag/TiO_2

	WHSV	mol%		$X_{impurity}$	$X_{1\text{-hexene}}$	Sp
	$[g_{oil}.hr^{-1}/g_{cat}]$	1-hexyne	1-hexene	(%)	(%)	
Feed	-	1.050	98.665	-	-	-
Product	7.648	0.509	97.745	51.547	0.933	55.27
		0.505	97.720	51.890	0.957	54.20
		0.519	97.810	50.602	0.867	58.37
		0.521	97.831	50.362	0.845	59.61
		0.507	97.749	51.733	0.928	55.72
		0.512	97.716	51.206	0.962	53.24
	9.560	0.565	98.106	46.186	0.567	81.47
		0.541	97.881	48.445	0.794	60.98
		0.515	97.726	50.915	0.952	53.48
		0.640	98.351	39.005	0.319	122.42
		0.693	98.589	33.963	0.077	440.91
		0.553	97.993	47.297	0.681	69.47
		0.538	97.879	48.716	0.797	61.15
	11.473	0.584	98.156	44.380	0.516	85.98
		0.597	98.207	43.175	0.464	93.06
		0.623	98.337	40.655	0.332	122.46
		0.653	98.174	37.793	0.498	75.91

Experiment 12

SATURATOR: 1% 1-hexyne in 1-hexene (5 ppm CO), 60°C, 30 bar, H_2/oil ratio = 0.01, 1.10g Pd-Ag/TiO_2

	WHSV	mol%			$X_{impurity}$	$X_{1\text{-hexene}}$	Sp
	$[g_{oil}.hr^{-1}/g_{cat}]$	1-hexyne	1-hexene	n-hexane	(%)	(%)	
Feed	-	1.07	98.682	-	-	-	-
Product	7.648	0.590	98.074	1.019	44.918	0.615	72.98
		0.518	97.864	1.337	51.571	0.829	62.23
		0.513	97.842	1.317	52.031	0.851	61.16
		0.529	97.877	1.259	50.585	0.815	62.04
		0.550	97.942	1.165	48.594	0.749	64.85
	9.560	0.630	98.310	0.792	41.144	0.376	109.34
		0.588	98.051	1.069	45.092	0.639	70.58
		0.555	97.880	1.286	48.180	0.812	59.31
		0.524	97.719	1.454	51.019	0.975	52.32
	11.473	0.535	97.792	1.321	50.003	0.901	55.48
		0.614	98.058	1.044	42.676	0.632	67.51
		0.634	98.180	0.921	40.747	0.509	80.11
		0.544	97.857	1.319	49.130	0.836	58.80

Experiment 13

SATURATOR: 1% 1-hexyne in 1-hexene (25 ppm CO), 60°C, 30 bar, H_2/oil ratio = 0.01, 1.10g Pd-Ag/TiO_2

	WHSV	mol%			$X_{impurity}$	$X_{1\text{-hexene}}$	Sp
	$[g_{oil}.hr^{-1}/g_{cat}]$	1-hexyne	1-hexene	n-hexane	(%)	(%)	
Feed	-			-	-	-	-
Product	7.648	0.661	98.007	1.150	36.344	0.679	53.49
		0.638	98.000	1.363	39.025	0.759	51.43
		0.620	97.634	1.411	40.735	1.129	36.07
		0.617	97.673	1.429	40.998	1.091	37.59
		0.709	98.210	0.822	32.183	0.547	58.85
		0.644	97.855	1.232	38.431	0.906	42.42
		0.610	97.701	1.450	41.724	1.062	39.28
	9.560	0.663	97.848	1.152	36.616	0.913	40.10
		0.660	97.942	1.140	36.937	0.818	45.17
		0.624	97.723	1.351	40.318	1.040	38.78
		0.619	97.732	1.366	40.851	1.030	39.65
	11.473	0.645	98.007	1.146	38.363	0.752	51.03
		0.696	98.026	0.990	33.470	0.732	45.70
		0.766	98.251	0.713	26.773	0.505	53.03
		0.637	97.770	1.283	39.087	0.992	39.38
		0.647	97.810	1.212	38.135	0.952	40.07

Experiment 14

SATURATOR: 1% 1-hexyne in 1-hexene (50 ppm CO), 60°C, 30 bar, H_2/oil ratio = 0.01, 1.10g Pd-Ag/TiO_2

	WHSV	mol%			$X_{impurity}$	$X_{1\text{-hexene}}$	Sp
	$[g_{oil}.hr^{-1}/g_{cat}]$	1-hexyne	1-hexene	n-hexane	(%)	(%)	
Feed	-	1.066	98.607	-	-	-	-
Product	7.648	0.609	97.488	1.593	42.851	1.135	37.76
		0.596	97.414	1.636	44.099	1.210	36.44
		0.580	97.471	1.662	45.538	1.152	39.51
		0.558	97.359	1.782	47.624	1.265	37.63
		0.607	97.413	1.616	43.044	1.211	35.54
		0.597	97.512	1.577	44.014	1.110	39.65
		0.591	97.511	1.590	44.520	1.111	40.06
		0.595	97.403	1.639	44.180	1.221	36.19
		0.586	97.369	1.686	45.009	1.255	35.85
	9.560	0.640	97.641	1.437	39.900	0.979	40.74
		0.623	97.533	1.487	41.542	1.090	38.12
		0.637	97.691	1.360	40.213	0.929	43.28
		0.633	97.862	1.201	40.549	0.755	53.70
	11.473	0.753	98.054	0.894	29.348	0.560	52.37
		0.757	98.247	0.784	28.920	0.365	79.16
		0.721	98.011	0.974	32.358	0.605	53.51

Experiment 15

SATURATOR: 1% 1-hexyne in 1-hexene (0 ppm Ethanol), 60°C, 30 bar, H_2/oil ratio = 0.01, 1.09g Pd-Ag/TiO_2

	WHSV	mol%			$X_{impurity}$	$X_{1\text{-hexene}}$	Sp
	$[g_{oil}.hr^{-1}/g_{cat}]$	1-hexyne	1-hexene	n-hexane	(%)	(%)	
Feed	-	1.048	98.670	-	-	-	-
Product	7.729	0.515	97.691	1.639	50.897	0.993	51.28
		0.511	97.666	1.673	51.240	1.017	50.36
		0.510	97.657	1.673	51.352	1.027	50.01
		0.512	97.678	1.654	51.112	1.005	50.86
		0.513	97.695	1.648	51.083	0.988	51.68
		0.518	97.662	1.612	50.556	1.022	49.48
	9.661	0.571	98.051	1.238	45.536	0.627	72.63
		0.547	97.827	1.481	47.795	0.854	55.94
		0.521	97.671	1.658	50.265	1.012	49.67
		0.646	98.296	0.928	38.355	0.379	101.31
		0.559	97.939	1.339	46.647	0.741	62.97
		0.544	97.825	1.491	48.066	0.857	56.11
	11.593	0.590	98.101	1.173	43.730	0.576	75.90
		0.602	98.153	1.104	42.525	0.524	81.16

Experiment 16

SATURATOR: 1% 1-hexyne in 1-hexene (100 ppm Ethanol), 60°C, 30 bar, H_2/oil ratio = 0.01, 1.09g Pd-Ag/TiO_2

	WHSV	mol%			$X_{impurity}$	$X_{1\text{-hexene}}$	Sp
	$[g_{oil}.hr^{-1}/g_{cat}]$	1-hexyne	1-hexene	n-hexane	(%)	(%)	
Feed	-	1.041	98.648	-	-	-	-
Product	7.729	0.532	97.496	1.642	48.869	1.168	41.86
		0.522	97.454	1.714	49.850	1.211	41.17
		0.522	97.469	1.700	49.893	1.195	41.75
		0.529	97.444	1.703	49.174	1.221	40.29
	9.661	0.572	97.774	1.372	45.056	0.886	50.84
		0.574	97.804	1.343	44.846	0.855	52.43
	11.593	0.619	97.975	1.077	40.542	0.682	59.42
		0.621	98.007	1.097	40.364	0.650	62.13
		0.629	98.042	1.051	39.607	0.614	64.51

Experiment 17

SATURATOR: 1% 1-hexyne in 1-hexene (1000 ppm Ethanol), 60°C, 30 bar, H_2/oil ratio = 0.01, 1.09g Pd-Ag/TiO_2

	WHSV	mol%			$X_{impurity}$	$X_{1\text{-hexene}}$	Sp
	$[g_{oil}.hr^{-1}/g_{cat}]$	1-hexyne	1-hexene	n-hexane	(%)	(%)	
Feed	-	1.019	98.674	-	-	-	-
Product	7.729	0.575	98.250	0.873	43.561	0.430	101.28
		0.589	98.261	0.835	42.258	0.419	100.97
		0.463	97.512	1.664	54.575	1.177	46.35
		0.456	97.515	1.690	55.249	1.174	47.05
		0.470	97.552	1.642	53.877	1.137	47.39
		0.516	97.935	1.248	49.384	0.749	65.93
		0.526	97.973	1.171	48.422	0.711	68.11
		0.528	97.994	1.159	48.227	0.689	70.03
	9.661	0.541	98.059	1.096	46.903	0.624	75.20
		0.550	98.067	1.073	46.083	0.615	74.95
		0.540	98.034	1.121	47.070	0.649	72.53
		0.489	97.696	1.484	51.997	0.991	52.48
		0.493	97.716	1.539	51.630	0.971	53.18
		0.534	97.982	1.184	47.580	0.701	67.87
		0.539	97.958	1.148	47.146	0.726	64.94
	11.593	0.502	97.630	1.348	50.760	1.058	47.98
		0.501	97.661	1.523	50.843	1.026	49.54

Experiment 18

SATURATOR: 1% 1-hexyne in 1-hexene (5000 ppm Ethanol), 60°C, 30 bar, H_2/oil ratio = 0.01, 1.09g Pd-Ag/TiO_2

	WHSV	mol%			$X_{impurity}$	$X_{1\text{-hexene}}$	Sp
	$[g_{oil}.hr^{-1}/g_{cat}]$	1-hexyne	1-hexene	n-hexane	(%)	(%)	
Feed	-	1.05	98.563	-	-	-	-
Product	7.729	0.513	97.456	1.629	51.152	1.123	45.55
		0.514	97.306	1.740	51.066	1.276	40.03
		0.518	97.317	1.688	50.661	1.264	40.07
		0.521	97.397	1.680	50.415	1.183	42.63
		0.522	97.384	1.688	50.306	1.196	42.05
	9.661	0.559	97.616	1.425	46.797	0.961	48.68
		0.551	97.559	1.487	47.482	1.019	46.60
		0.548	97.507	1.526	47.782	1.071	44.59
		0.535	97.387	1.671	49.058	1.193	41.12
		0.609	97.980	1.022	41.989	0.591	71.03
		0.627	98.070	0.914	40.324	0.500	80.67
	11.593	0.622	98.002	1.012	40.729	0.569	71.58
		0.624	98.078	1.030	40.560	0.492	82.44