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HIGH-OCTANE FUEL PRODUCTION BY UPGRADING LOW-TEMPERATURE FISCHER–TROPSCH PARAFFINS

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OF
CHEMICAL AND METALLURGICAL ENGINEERING

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High-Octane Fuel Production by Upgrading Low-Temperature Fischer–Tropsch Paraffins

MSc (50/50) RESEARCH REPORT

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Submitted to

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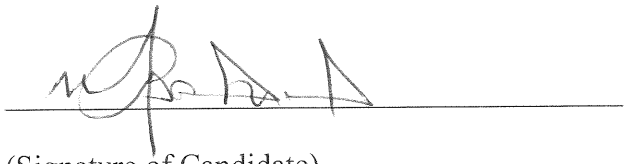
20 January, 2019

DECLARATION

I declare that this research report is my own, unaided work. It is being submitted for the Degree of Master of Science at the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination at any other University. Sasol holds the licence to Fischer-Tropsch (FT) catalyst used at its GTL and CTL facilities. This report does not include any process information which is not in the public domain. The plant specific information is sourced from information available in the public domain. The research to be undertaken did not involve animal experimentation or human participants, as defined in A.4 of the Senate Standing Orders on Higher degrees.



(Signature of Candidate)

20th day of January 2019 at Sasolburg

ABSTRACT

The octane upgrade of low temperature Fischer Tropsch paraffins provides an opportunity to add value to a low grade chemical. The addition of C_5-C_6 paraffins to the fuel mix would contribute to satisfying the increasing petrol demand. The research aim is to produce high octane fuels from low temperature Fischer Tropsch paraffins. A kinetic study was done to investigate the activation energy and rate constant of the isomerisation reaction, for the conversion of straight chain low temperature Fischer Tropsch paraffins to branched paraffins. The investigation showed that the activation energy for the conversion of C_5 paraffin is greater than that of C_6 paraffin. It was observed that the product rate constant decreased as the temperature increased. This indicated that isomerate concentration in the product stream is sensitive to the reaction temperatures. The C_5-C_6 paraffins from the low temperature Fischer Tropsch process, proved to be a suitable feed for isomerisation. The choice of isomerisation catalyst and process configuration affected the overall conversion and the resulting octane number of the isomerate. The process configuration, which includes a de-isohexaniser and de-isopentaniser, provided the optimum production of isomerate. The Fischer Tropsch process allows for paraffins to be produced without the presence of aromatics. It was found that operating the reactor at 150°C provides optimum overall conversion from normal paraffins to iso-paraffins. A 20 ton per day isomerisation unit, available from Honeywell UOP will be able to deliver the required throughput of isomerate. The isomerate modelled from C_5-C_6 paraffins was compliant with the Euro V emissions standard. The pending "Clean Fuels 2" regulations, favours the isomerisation of paraffins. The investigation showed that existing process chemistry supports the production of high octane fuels from low temperature Fischer Tropsch paraffins, and that the production process is economically feasible.

In memory of my parents

Violet Gabriel

1944 – 2017

And

Patrick Gabriel

1942 – 2017

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NOMENCLATURE

2,2-DMB	2,2-Dimethylbutane
2,3-DMB	2,3-Dimethylbutane
ADU	Atmospheric distillation unit
ATR	Auto-thermal reformer
Bottoms	Heavy product exiting the bottom of the distillation column
brCn	Branched paraffin
BTL	Biomass to liquids
BZ	Benzene
C_5-C_6	Paraffins, containing a mixture of hydrocarbon lengths of 5 and 6 carbons.
C_A	Outlet stream concentration
C_{A0}	Inlet stream concentration
C_{ISO}	Concentration of iso-paraffins
CH	Cyclohexane
CTL	Coal to liquids
DIH	De-isohexaniser
DIP	De-isopentaniser
Distillate	Light overhead product exiting distillation column
DPC	Dew-point correction
Ea_1	Activation energy for reaction: n-paraffins $\xrightarrow{K1}$ olefins
Ea_2	Activation energy for reaction olefins $\xrightarrow{K2}$ i-paraffins
EPA	Environmental protection agency
ETBE	Ethyl tert-butyl ether

F_{A0}	Inlet flow rate
F_A	Outlet flow rate
FT	Fischer-Tropsch
GTL	Gas to liquids
HT-FT	High temperature Fischer-Tropsch
iC_5	Iso-pentane
IEA	International Energy Agency
IM	Information management department
IMF	International Monetary Fund
K_1	Rate constant for paraffins (hr^{-1})
K_2	Rate constant for olefins (hr^{-1})
K_0	Frequency factor
LHSV	Liquid hourly space velocity
LT-FT	Low temperature Fischer-Tropsch
M	Module
Mb/d	Mega-barrels per day
MCP	Methyl-cyclopentane
MON	Motor octane number
MONC	Motor octane number clear (unleaded)
MSAT	Mobile source air toxics
MTBE	Methyl tert-butyl ether
Naphtha	Intermediate product in the refining of crude oil and natural gas condensate
nC_5	Normal pentane
nC_6	Normal hexane

nC6*	nC6 ⇋ 2, 2-Dimethylbutane at X=0.35
nC6**	nC6 ⇋ 2, 3-Dimethylbutane at X=0.1
OECD	Organisation for Economic Co-operation and Development
OT	Once through
PCP	Protonated cyclo-propane
Pt/Al_2O_3-Cl	Chlorinated alumina catalyst
R	Ribblett ratio
RON	Research octane number
RONC	Research octane number clear (unleaded)
RVP	Reid vapour pressure
SDU	Single distillation unit
SN	Stoichiometric number
SO	Sasolburg Operations
SSBP	Sasol slurry bed process
SSO	Sasol Synfuels Operations (Secunda)
t	Residence time
T	Outlet temperature (K)
T_0	Initial temperature (K)
TAME	Ter-amyl-methyl-ether
TEL	Tetra-ethyl-lead
V	Volume of reactor
X	Reaction conversion
Z	Length of tube
ε	Voidage

Chapter 1: Introduction

A strong world economy is expected to drive increases in oil demand, according to the International Energy Agency (IEA, 2015). Data quoted from the International Monetary Fund showed global economic growth at 3.9%, with all regions of the world expecting to perform well. Strong economies will, in turn, use more oil. Demand is expected to grow at an average rate of 1.2Mb/day (IMF, 2015). Oil demand is expected to reach 104.7Mb/d, by 2023. This would be 6.9Mb/day higher than demand in 2017 (Offshore Energy Today, 2018). China and India together will contribute to nearly half of global demand, as was the case for some years now.

World transportation energy consumption has doubled over the past 30 years, according to the International Energy Agency in its Global Transport Outlook to 2050. Light duty vehicles continue to drive growth, while road freight and air travel also increased rapidly over the past decade (OECD, 2010). Historic trends are shown in Figure 1 (IEA, 2018).

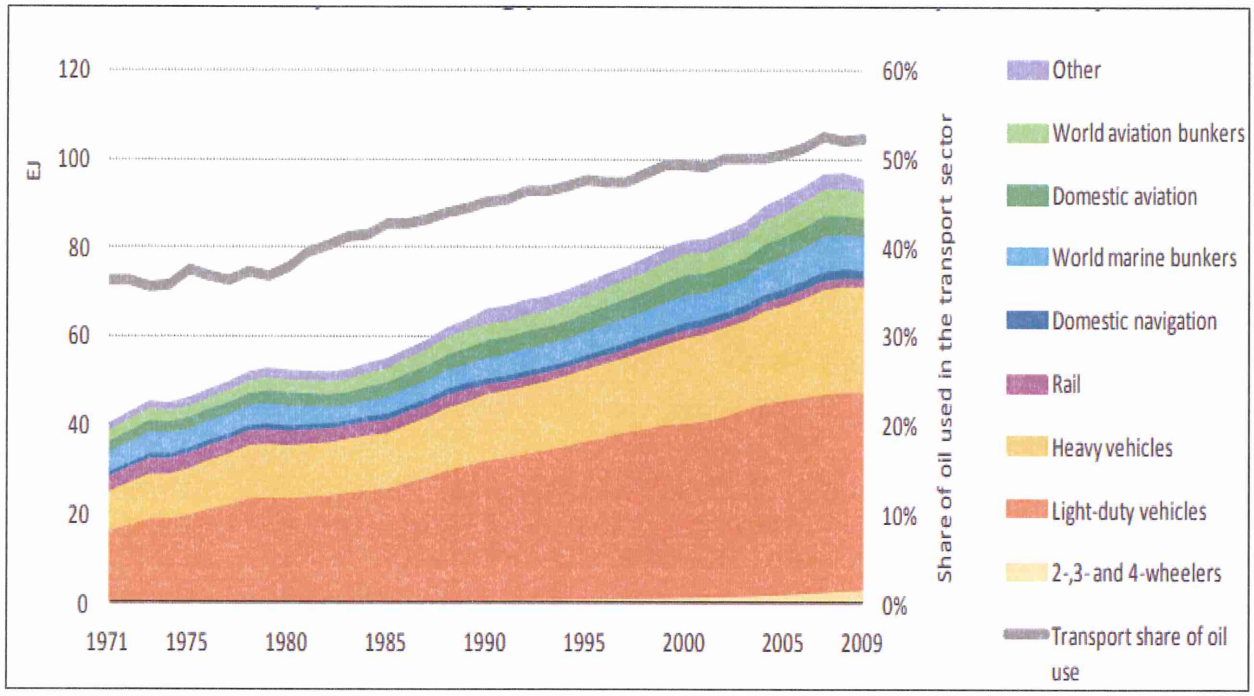

Figure 1: Transport Energy Mix (IEA, 2018).

The petrochemical sector is seen as the fastest growing source of global oil demand growth, particularly in the United States and China (Reuters, 2018). The shale gas revolution in the United States has been a source of cheap domestic feedstock. Off the forecasted growth in global oil demand to 2023, 25% of this growth in will be for the production of Ethane and Naphtha. Many more people are entering the middle class in developing countries, on the back of global economic growth. Higher incomes tend to translate to a sharp rise in demand for consumer goods and services. Chemicals derived from oil and gas, are crucial to meeting the manufacturing requirements of consumer goods. Products include personal care items, food preservatives, fertilisers, furnishings, paints and lubricants for automotive and industrial purposes (Market Watch, 2018).

The International Energy Agency developed a transport outlook to 2050, in its Energy Technology Perspectives 2012 report. With no dedicated policies, road travel is likely to double by 2050, with most growth coming from passenger light duty vehicles in developing countries. A forecast of passenger and freight travel by mode is shown in Figure 2 (IEA, 2013).

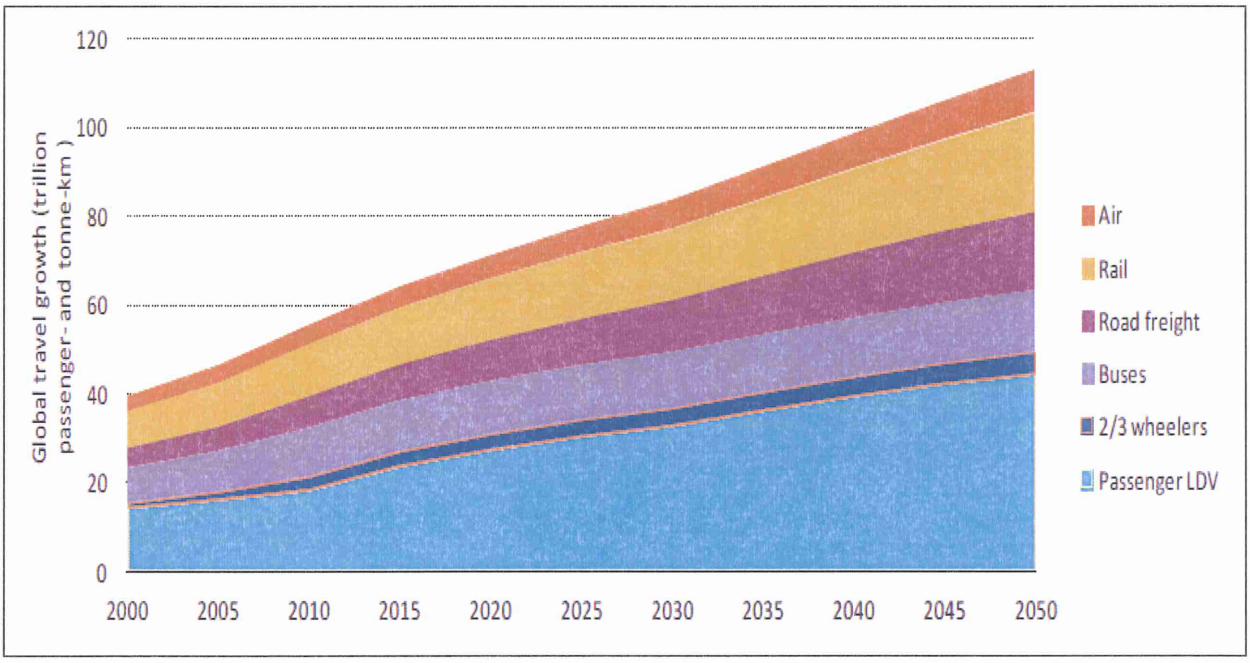

Figure 2: Mode of Travel (IEA, 2013).

The adoption of more stringent measures in curtailing emissions from motor vehicle exhaust fumes resulted in a drive for cleaner burning fuels. This has become the focus of governments and action groups, highlighting the impact on the environment and public health. The first clean fuels initiative in South Africa sought to remove Lead additives in petrol and reduce the Sulphur content in Diesel. The intention of the South African government is to implement Clean Fuels 2, which would further tighten the specifications of automotive fuels. These specifications will be in line with European fuel specifications, and would make the fuel compatible with the latest engine technology from European vehicle manufacturers. The new specifications will see a further reduction in Sulphur, olefins and aromatics. Current refineries will have to be retrofitted with further refining capacity to meet the new specifications (Nema Consulting, 2012).

1.1. Fischer-Tropsch Synthetic Crude

The composition of crude oil feed to a refinery plays a significant role in the design of the refinery to meet the required fuel specifications. Synthetic crude (Syncrude), derived from the Fischer-Tropsch (FT) process is virtually sulphur free, due to its reaction mechanism and catalyst sensitivity. The FT catalyst preparation and use will not be discussed here. Syncrude can be differentiated into a high temperature (HT-FT) and low temperature (LT-FT) product, based on the operating temperature of the FT process. Syncrude and crude oil are rich in paraffins. The difference is that syncrude is rich in olefins and oxygenates, while crude oil is rich in aromatics, with sulphur, nitrogen and oxygen as heteroatoms. Syncrude can be derived from coal, natural gas or biomass (De Klerk, 2008).

The FT process is based on the reaction of carbon monoxide with hydrogen over iron catalyst, to produce synthetic crude. Coal to liquid (CTL) and biomass to liquid (BTL) involves gasification of the feed material. The raw gas produced is washed to remove sulphur and carbon dioxide. The pure gas produced, is rich in carbon monoxide and hydrogen. The gas to liquid (GTL) process involves reforming natural gas to produce a gas stream rich in carbon monoxide and hydrogen. The syngas mixture of carbon monoxide and hydrogen is fed to FT reactors to produce syncrude. The syncrude is worked up to a range of fuels and chemicals. Due to the syngas containing

basically the elements of carbon, oxygen and hydrogen, the corresponding FT products are either hydrocarbons or oxygenates (De Klerk, 2008).

The list of FT products includes paraffins, olefins, aromatics, alcohols, aldehydes, carboxylic acids and ketones. The LT-FT process yields mainly n-paraffins, like waxes, compared to the HT-FT process which yields more branched paraffins. Like paraffins, the olefins formed are mainly n-olefins. Aromatics are almost devoid in LT-FT products but are present in HT-FT products as benzene and toluene. The same can be said about alcohols, aldehydes, carboxylic acids, esters and ketones (De Klerk, 2008).

1.2. The Sasol Process

Sasol Synfuels Operations (SSO), in Secunda, employs the HT-FT process. SSO operates on a combination of natural gas and coal feed, thus integrating CTL and GTL into the FT process. On the other hand, Sasolburg Operations (SO) employs the LT-FT process, making use of only natural gas feed. Originally SO FT process was the same as SSO.

This report will focus on the paraffins produced in the Sasolburg LT-FT process. The focus of the LT-FT operations in Sasolburg is the production of hard waxes. Syngas is fed to Sasol slurry bed process (SSBP) reactors, from which waxy crude is produced. Reactor wax is drawn off from the reactor. The rest of the waxy crude is recovered from the entrained outlet stream of the reactor. Hot condensate, a light wax and in a liquid state at high temperatures, is separated from the reactor outlet stream in a quench tower. The cold condensate, which is in a liquid state at room temperature, is separated after cooling of the stream leaving the quench tower. Reaction water is recovered after further cooling and the remaining FT tail gas exits the plant. The gas is treated at the dew point correction plant (Rectisol DPC). Carbon dioxide and any hydrocarbon condensate remains are removed, by washing with chilled methanol. The DPC tail gas from the SSBP reactors is used to produce methanol, hydrogen and ammonia. The reaction water is sent to chemical work-up to recover trace amounts of alcohol. The reactor wax and hot condensate is fed into a distillation unit (SDU), yielding separate streams of paraffins, waxy oil (waksol), medium wax and hard wax. The cold condensate is fed to the atmospheric distillation unit (ADU). ADU separates the cold

condensate into paraffins and waxy oil (waksol). The hard wax is solidified into pastilles and powders for the market. A portion of the medium wax is solidified and the rest is blended and sold in a liquid form together with Waksol, according to customers' needs (De Klerk, 2008).

1.3. Paraffins Production

The paraffins feed is received from ADU and SDU's overheads and fed to the paraffins plant. The aim of the paraffins plant is to produce pure paraffins products with a low aromatic content. The feed is first hydrogenated in two reactors and is then fractionated (distilled) in 5 distillation units to produce various product streams of specific qualities. Hydrogenation is the process where-by unsaturated hydrocarbons are reacted with hydrogen over a catalyst bed to produce saturated hydrocarbons (paraffins). The compound classes in the paraffins fraction of SSBP is shown in Table 1.

Table 1: Compound classes in Paraffins (De Klerk, 2011).

Compound Class	C_5-C_{12}	C_{13}-C_{18}
n-Alkanes	28	42
i-Alkanes	1	2
Alkenes	64	50
Aromatics	0	0
Oxygenates	7	6

Unsaturated hydrocarbons not only include alkenes and alkynes (the alkenes generally referred to as olefins), but also hydrocarbons containing oxygen bonds. Oxygen atoms double bond with carbon and therefore these compounds are also referred to as unsaturated hydrocarbons. These include oxygenates, such as acids, alcohols, esters and, carbonyls. The paraffins specifications, as shown in Table 2.

Table 2: Characteristics of paraffins cuts (Sasol, 2019).

Product Data Sheets	n-Paraffins (Mass %)	Iso-Paraffins (Mass %)
C5-C6	87 - 89	11 -13
C7-C8	89 -90	9 - 11
C9-C11	> 89	< 11
C10-C13	> 92.3	
C14-C20	> 93.1	

Substantial work has been done on the FT process, with many publications being available. Recent publications including, Fischer-Tropsch synthesis, catalyst and catalysis can be found in work done by Davis and Occelli (2016) and Aresta et al. (2015). The refining of FT products hasn't enjoyed the same focus. Refinery technology has been limited to crude oil feed, as expected, due to the sheer number of oil refineries as opposed to FT derived fuels. Sasol is the only commercial producer of FT derived fuels, with the exception of PetroSA, the national oil company of South Africa, based in Mossel Bay. Further to this, there is even less work available about FT paraffins. The paraffins light end of the FT process is the low value by-product, sold in the chemicals market, as seen in the Table 3.

Table 3: Application of Paraffins (Sasol, 2019).

C5-C6	Tyres, adhesives, seed oil extraction
C7-C8	Polymerization solvents
C9-C11	Paints, thinners
C10-C13 / C12-C13	Household aerosols
C14-C20	Chlorination
C14-C17	Foil industry
C10-C20	Drilling mud, stove fuels

An investigation carried out into refining practice for both crude oil and FT syncrude, identified fundamental differences in their refining focus and conversion behaviour (De Klerk, 2008). A critical evaluation was made of the compatibility of syncrudes from both HT-FT and LT-FT with the chemistry and catalysis of various conversion processes. Refinery designs were developed to determine configurations that would maximize the specification production of petrol, jet fuel and diesel respectively. The study illustrated the advantage of considering fundamentals in developing refineries specifically for Fischer-Tropsch syncrude, rather than imposing crude oil design practices on FT syncrude refinery designs. Thus, the scope is huge for intensification in the integration of FT synthesis to refining (De Klerk, 2008).

1.4. Problem Statement

Paraffins are a low value product, in the chemicals market, which reduces the profitability of the overall refining process, such as Sasol LTFT wax business. Branched paraffins are desirable as a fuel component, but not for applications in the chemicals market.

The impending Clean Fuels legislation will put pressure on the capital spend in upgrading the refinery products. Paraffins are mostly straight chain hydrocarbons, with a low octane number. The paraffins need to be processed in order to increase its octane number. This work seeks to explore the options that are available to increase the octane number of paraffins. The most cost effective and feasible method needs to be chosen in selecting an appropriate solution.

1.5. Research Aim

The main aim of this project is to investigate the value in upgrading paraffins from a base chemical to a higher value fuel product. The project also intends to demonstrate the suitability of paraffins as a cleaner burning fuel, which satisfies the impending clean fuels specifications.

The process of converting LT-FT paraffins into a fuel should be examined. A mass balance will be developed, based on modelled conversion. The operating margin will also be considered.

Chapter 2: Literature Review

2.1. Introduction

The growth in demand for petroleum and petrochemical products, over the past 10 years, has seen an increase in the commercial applications of upgrading light hydrocarbons in refineries. Lawmakers around the world are increasingly looking towards clean fuels to limit air pollution. Increasingly stringent regulations are being enacted to favour cleaner burning fuels. These regulations include clean fuel initiatives, such as lead phase-out, minimisation of benzene, aromatics and olefin content, and the addition of oxygenates to fuel. Isomerisation of C_5-C_6 paraffins plays a key role in meeting octane demands in the clean fuels mix which results from tighter regulations and increasing market share of premium fuels.

The conversion of normal hydrocarbon chains to branched chains has significant benefits to petrochemical production. According to Folger, branched chain hydrocarbons have a higher fuel octane number than normal hydrocarbon chains. It has been found that the conversion of normal paraffins to iso-paraffins is easiest when both acid sites and hydrogenation sites are present. Such is the case with Pt and Al_2O_3 catalysts (Folger, 2006). The representative catalysts for isomerisation include $AlCl_3$, Pt/Al_2O_3 and zeolites. Octane numbers between 80 and 93 (RON) can be achieved through the isomerisation of low octane paraffins, depending on the process configuration, catalyst type and operating conditions. The process involves the skeletal isomerisation of a straight-chained paraffins to a more highly branched paraffins with the same carbon number. Isomerisation may also affect some of the naphthene components and will also saturate aromatics. Isomerisation is one of the most economic means available for reducing benzene content in fuel (Pujadó et al., 2015).

2.2. History of Isomerisation

A variety of isomerisation technology licensors offer various commercialised processes, using fixed bed process units, which employ high-activity catalysts. The reaction conditions in these process units promote isomerisation and minimise hydrocracking. Technology companies, which have introduced various isomerisation catalysts over the years, include Akzo Nobel (now

Albemarle), Axens, NPP Neftekhim, Süd-Chemie AG (now Clariant), Shell Chemicals LP and UOP (now Honeywell UOP LLC). The first commercial isomerisation process of normal butane to isobutane dates back to the 1930's. Universal Oil Products (UOP) developed the Butamer^{TM} process for the isomerisation of normal butane to isobutane. It began with Vladimir Ipatief and his team from UOP discovering the ability to transform normal butane molecules in fuel to isobutane, using an aluminium chloride catalyst with hydrogen chloride as a co-catalyst. The use of isobutane in fuel was not popular with refiners, due to its high volatility. It eventually found favour as aviation fuel, contributing to the war effort, during World War 2. The predominant process then, as it is today, for normal butane isomerisation was the UOP Butamer^{TM} process. Isobutane was converted to isobutylene, using the UOP Oleflex^{TM} process. Isobutylene is used to produce MTBE and ETBE, for fuel blending, and butyl rubber for the petrochemical industry. Alkylation of isobutane with isobutylene formed a highly branched isooctane, with eight carbon atoms (Sullivan et al., 2014).

Hydrofluoric (HF) alkylation was subsequently used to produce a high octane and clean burning fuel, for automobiles. In the late 1950's, isomerisation of C_5-C_6 paraffins for motor fuel blending was introduced. The demand for high octane motor fuel increased in the late 1950's and 1960's, during the post-war economic expansion period. The blending of straight chain paraffins in the fuel pool had a negative effect on fuel quality. UOP scientists applied an isomerisation catalyst, similar to the Butamer process, to pentane and hexane rich naphtha and found out that the octane number can be increased by 12 to 20 numbers. Thus the UOP Penex^{TM} process was born. This process was soon being used in nearly all refineries (Sullivan et al., 2014).

There has been flow scheme improvements, to C_5-C_6 isomerisation, including the use of a recycle loop to circulate unreacted hydrocarbons exiting the reactor to the reactor inlet and the use of fractionators such as de-isopentanisers (DIP) and de-isohexanisers (DIH). Further yield improvements were achieved by installing a process section which separates normal and iso-paraffins, via a molecular sieve, rerouting the normal paraffins back to the reaction section. The octane number of isomerate is shown for various configurations in Figure 3 (Sullivan et al., 2014).

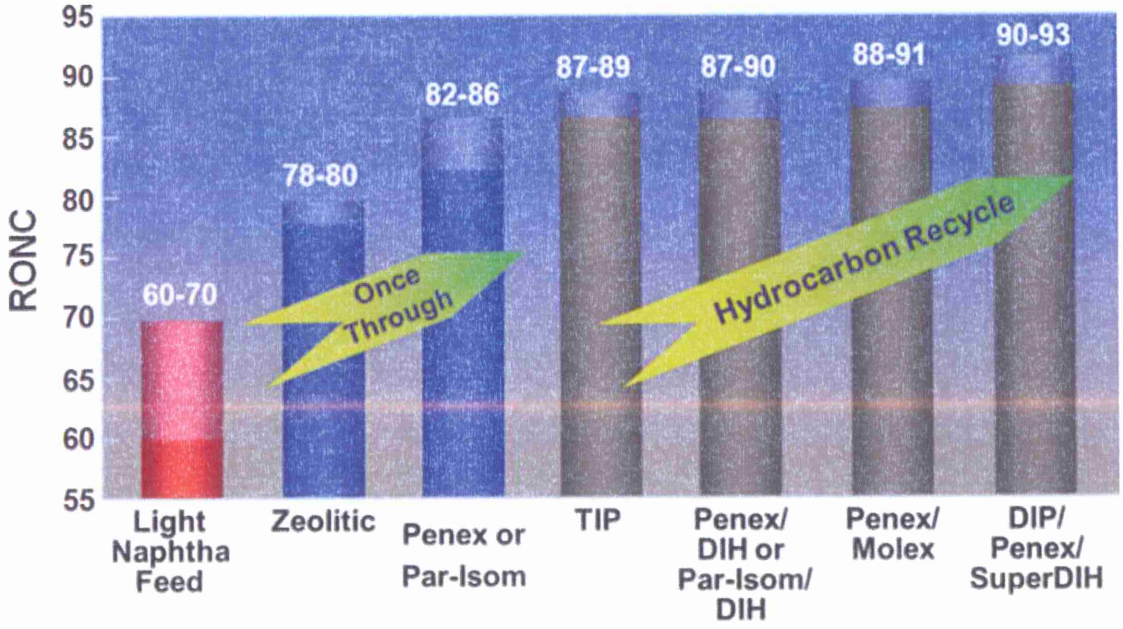

Figure 3: Isomerisation Process Configurations and Octane Values (Sullivan et al., 2014)

Increased activity, selectivity and life of chlorided alumina type catalysts were achieved through the use of new materials and base formulations. Other catalyst technologies that did not require the continuous use of a chloriding agent during production to maintain catalyst activity was developed. Catalysts which became re-generable include older generation zeolitic types, as well as more recent mixed metal oxide types (zirconia) (Sullivan et al., 2014).

2.3. Market Trends

Five percent of the total worldwide petrol pool consists of isomerate. The remaining fraction of the petrol pool consists of n-paraffins (unprocessed fraction), alkylate, reformate, polymer, and FCC fractions. Petrol also contains additives, to boost octane number and lower emissions, such as ethanol. The use of ethanol provides a twofold benefit. Ethanol blending, first and foremost, is a means of oxygenate addition to improve combustion. It, secondly, provides an additional market for maize and sugarcane farmers. Ethanol, derived maize and sugarcane, improves the green credentials of blended fuel as the consumer market becomes more environmentally conscious (Sullivan et al., 2014).

The particulate emissions from diesel engines has come under the spotlight in Europe recently. Due to health concerns, the various authorities in European countries have increased tax levies on diesel fuelled vehicles. The recent diesel emissions testing scandal has also not helped the reputation of diesel powered vehicles. Petrol powered vehicles is becoming the more economical option to price savvy consumers. As a consequence, vehicle manufactures have started reducing the diesel engine options available to consumers. This has sparked an increase in demand for petrol, and more especially clean fuels, in the market. Global oil demand growth, as forecasted by the IEA, is shown in Figure 4 (IEA, 2016). The road transport and petrochemicals sectors make the largest contributions to the demand. Strong demand growth, for transport fuel, is seen in non-OECD countries (Reuters, 2018).

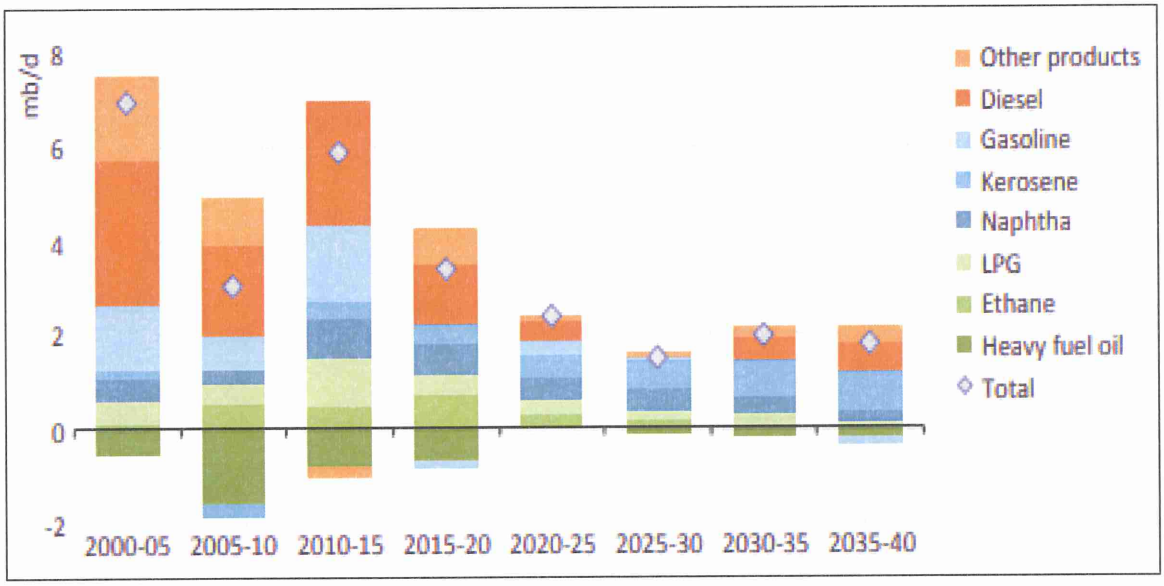

Figure 4: Change in Global Oil Product Demand in the New Policies Scenario (Reuters, 2018).

Battery powered vehicles are making a comeback in the transport scene. The infrastructure needed to support these market entrants is, unfortunately, lacking and not a priority in developing countries. Market forces have prompted the search for more efficiently burning petrol engines, as consumers look to trim back on fuel expenditure.

2.4. Fuel Regulations

Fuel quality is, to varying extents, subject to many international, regional and even local regulations. Most regulations are based on an increasing demand for clean fuels, as lawmakers focus on air quality. These regulations cover a phasing out of lead, Reid vapour pressure (RVP), limits on Sulphur, Benzene, aromatics and olefin content, including addition of oxygenates. Regulations have progressively become more stringent. Table 4, illustrates the changing specifications in Euro standards, which guide regulations in many countries. Many non-EU countries, including South Africa, are still in the planning phases of implementing either Euro IV or Euro V specifications (Sullivan et al., 2014).

Table 4: Euro Fuel Specifications (Sullivan et al., 2014).

Euro Fuel Specifications		Directive	EN 228	DIR 98/70	DIR 98/70	DIR 98/70	DIR 98/70
		Year	1993	1996	2000	2005	2009
		Class	Euro 1	Euro 2	Euro 3	Euro 4	Euro 5
Aromatics	Vol %	Max	No limit	No limit	42	35	35
Olefins	Vol %	Max	No limit	No limit	18	18	18
Benzene	Vol %	Max	5	5	1	1	1
Oxygen	Wt %	Max	3	3	3	3	3
Sulphur	ppm	Max	1,000	500	150	50	10
RON		Min	91	92	93	94	95
RVP	kPa		35-100	35-100	60-70	60-70	60-70
Lead	g/lt	Max	0	0	None	None	None

The Environmental Protection Agency (EPA) in the USA sets fuel standards. There are some variations between states, with California being the most stringent. The California Air Resources Board's (CARB) fuel specifications are similar to Euro V standards. Benzene content in petrol is one component which is broadly regulated, amongst various authorities. The EPA has implemented a Mobile Source Air Toxics (MSAT) rule to reduce hazardous air pollutants. These regulations are applied to US refiners, as well as petrol imported to the US. The overall growth of

isomerate, which is more than double the growth of petrol, is attributed to the increased focus on clean fuels. (Pujadó et al., 2015)

2.5. Overall Process Chemistry of Paraffins Isomerisation

Catalytic reforming processes provide high octane products from the heavier end fuel fractions. The lighter ends, however, suffer from low octane numbers. The conversion of fuel fractions in this lower boiling range to their respective isomers yields petrol components of high octane rating. Isomerisation serves two important functions within the petroleum refinery. The first process of significance is the conversion n-butane to iso-butane, which can be alkylated to liquid fuel in the petrol boiling range. Secondly, the process can be used to convert n-paraffins to iso-paraffins. The resultant iso-paraffins product has an increased octane number, which lies within the boiling range of petrol.

Conversion is achieved in the presence of a catalyst. It is essential to inhibit side reactions, such as cracking and olefin formation. Side reactions decrease yield of isomer production. Products from these side reactions combine with the catalyst and thus shorten its lifespan. Side reactions, where carbon-carbon bonds are broken, during the isomerisation of C_{5+} paraffins generally occur when aluminium halide catalysts are used. The use of un-promoted aluminium halide catalyst leads to disproportionation reactions. These undesired reactions can be controlled, with the addition of inhibitors with the paraffins feed or carrying out the reaction in the presence of Hydrogen. Increasing the hydrogen pressure above the operations pressure also inhibits side reactions. Isomerisation of paraffins and disproportionation reactions proceed more easily as the molecular weight of paraffins increase (Speight, 2007).

The isomerisation reaction is said to occur through the formation and re-arrangement of carbonium ions. A proton from the acid catalyst is added to an olefin molecule, forming the carbonium ion. The olefin may be formed by the dehydrogenation of the paraffins. The olefin would undergo either a movement of the position of the double bond, where a hydrogen atom shifts position, or a skeletal change, where a methyl group shifts position (Pujadó, et al., 2015). The mechanism is summarised in Figure 5 (Hsu & Robinson, 2006).

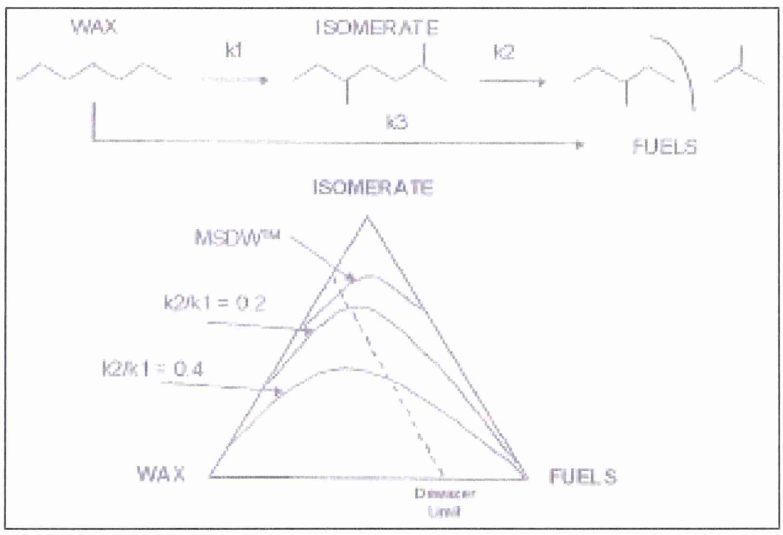

Figure 5: Hydro-isomerisation Kinetics (Hsu & Robinson, 2006).

The most highly branched C_5-C_6 paraffins have the highest octane numbers. The octane number is an indication of the anti-knock property of a given fuel. The C_5-C_6 paraffins isomers' research octane number (RON), are shown in Table 5. It is clearly seen, from Table 5, that branched iso-paraffins and more especially multi-branched iso-paraffins have octane numbers suitable for petrol production (Pujadó et al., 2015).

Table 5: Hydrocarbon Octane Values (Pujadó et al., 2015).

Component	Research Octane by ASTM 2699
n-Butane	93.8
i-Butane	100.4
n-Penatane	61.7
i-Pentane	92.3
n-Hexane	24.8
2-Methyl-Pentane	73.4
3-Methyl-Pentane	74.5
2,2-Dimethyl-Butane	91.8
2,3-Dimethyl-Butane	101.0

2.6. Isomerisation Primary Reaction Pathways

The development of new, more active and stable catalysts paves the way for advances in paraffins isomerisation. In order to maximise isomerate yields, and thus achieving a favourable economic result, specialised catalytic materials are needed. The skeletal isomerisation of paraffins is promoted by an acid catalyst and often by a metal function. The primary function of a paraffins isomerisation catalyst is to protonate a secondary Carbon atom. Combining isomerisation with reforming further enhances octane numbers, as illustrated in Table 6 (Nelson, 1964).

Table 6: Octane numbers for Platforming and Isomerization (Nelson, 1964).

	Total Yield, per cent	Octane numbers (F-1)			
		Catalytic Reforming (Platforming)		Catalytic Reforming plus isomerisation (Penex)	
		Clear	With 3 cc TEL	Clear	With 3 cc TEL
Natural Gasoline	93.5	76.5	95.0	86.5	100
Arabian Straight-run	81.5	85.5	96.5	91.0	100
Wyoming Straight-run	84.5	84.5	96.5	91.5	100

Etherification of C_5 cuts provides an additional pathway for octane improvement. Petrochemical Processes Volume 1 looked at etherification of C_5 olefinic components to Ter Amyl Methyl Ether (TAME), as shown in Table 7 (Chauvel and Lefebvre, 1989). Practical Advances in Petroleum Processing Volume 2 (Hsu and Robinson, 2006) also highlights the need for specialized catalysts in the conversion of paraffins at a refinery.

Practical Advances in Petroleum Processing Volume 2 (Hsu and Robinson, 2006) supports the notion that catalytic hydrocracking is a flexible process for the conversion of heavy, Hydrogen deficient oils into lighter and more valuable products. Part of this flexibility is its ability to handle a wide range of feeds, from heavy aromatics to paraffinic crudes and cycle stocks.

Table 7: Treatment of Steam Cracked C_5 cut (Economic Data) (Chauvel & Lefebvre, 1989).

Separation or transformation	Isopropene extraction with N-methylpyrrolidone	Selective hydrogenation	Etherification of a steam-cracked C_5 cut	
Processes	BASF	-	IFP	
Product	Isopropene	Dedienized C_5 cut	Gasoline without methanol (1)	Gasoline with methanol (2)
Capacity (t/year)	30,000	100,000	60,000	60,000
Battery limits investments (10^6 US$)	24	1.4	1.4	0.45
Initial catalyst loads (10^6 US$)	-	0.12	0.02	0.02
Consumption per ton of product				
Raw materials				
C_5 cut (t)	5.88	-	0.915	0.851
Methanol (t)	-	-	0.085	0.149
Net hydrogen (kg)	-	10	-	-
Products				
Raffinate (t)	3.71	-	-	-
Light compounds (t)	0.31	-	-	-
Piperylene (t)	0.71	-	-	-
Cyclopentadiene (t)	0.12	-	-	-
2-butyne (t)	0.03	-	-	-
Utilities				
Steam (t)	9	-	0.2	3
Electricity (kWh)	190	25	4	3
Fuel (10^6 kJ)	-	2	-	-
Cooling water (m^3)	440	(3)	10	3
Solvent: N-methylpyrrolidene (kg)	2.5	-	-	-
Catalyst and miscellaneous (US$)	1.8	0.4	0.4	0.4
Labour (opeators per shift)	4	3	1	0.5

(1) Etherified gasoline containing 27% Wt of TAME.

(2) Etherified gasoline containing 25% Wt of TAME and 7% Wt of methanol.

(3) Use of air coolers.

This motivated the interest in a heavy paraffins hydrocracking kinetics model. It was shown that C_{80} cracking models can be developed from C_{16} models. The complexity is reduced to several protonated cyclo-propane (PCP) isomerisation (normal 1, 2, 3 branch) and cracking (type A and type B) reactions. This captured all the key observations from the paraffins hydrocracking reaction mechanism: paraffins go through isomerizations before cracking, PCP isomerization always leads to branching, A-type cracking always leads to branched isomers, and B-type cracking always leads to normal or branched isomers; all the products actually come from A-type cracking of tri-branched isomers or B-type cracking of di-branched isomers, and the C-type cracking can be neglected. Figure 6 (Hsu and Robinson, 2006) summarizes the essence of this model at carbon and branch number level.

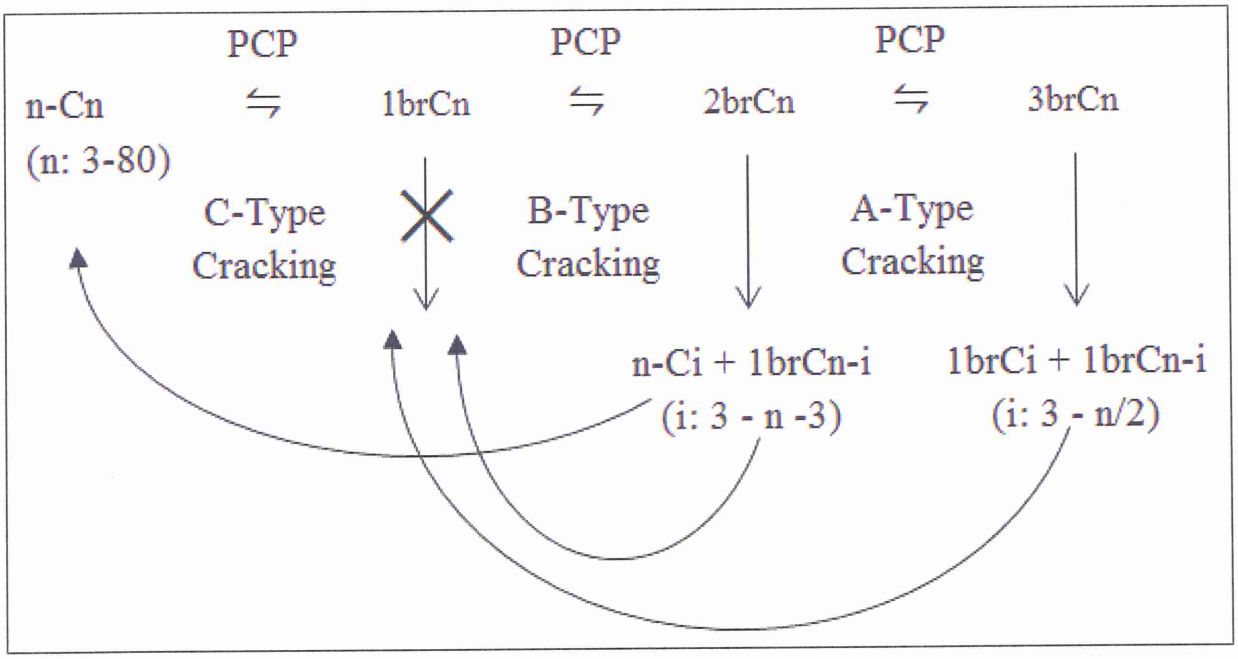

Figure 6: Mechanism Deduced Reaction Pathways at the Carbon Number and Branch Paraffins Hydrocracking Reaction Number Level (Hsu & Robinson, 2006).

2.7. Catalyst Selection

2.7.1. Isomerisation Catalysts

The economics of an operation are favourable when utilising a catalyst with the highest activity while operating the reactor at the lowest temperature. Varying levels of protonation activity are exhibited by isomerisation catalysts, having strong Lewis and Brønsted acid sites. Isomerisation catalysts must be capable of hydrogenolysis, in addition to a strong acid function. This assists in the protonation step and also serves to saturate olefin intermediates and aromatic hydrocarbons, and assisting in ring opening of naphthenes. This ability supports activity stability to the catalyst, and hereby improving the process economics (Pujadó et al, 2015).

2.7.2. Chlorided Alumina-Type Catalysts

The C_5+ yield from chlorided alumina catalysts is the highest from any commercial catalyst, with it being the highest activity paraffins isomerisation catalyst available. Chlorided alumina type catalysts are popular, having a high selectivity and low operating temperature. The octane of a typical light paraffins can be increased from approximately 70 RON to 83 RON, in a once through configuration. Up to 93 RON can be achieved by recycling low octane hydrocarbons back to the feed. This catalyst is not economically regenerable and would need to be totally replaced. It remains the most economical choice of catalyst, nonetheless (Sullivan et al., 2014).

2.7.3. Zeolitic Type Catalysts

Zeolitic isomerisation catalysts operate at higher temperatures than chlorided alumina catalysts, resulting in lower product yields. Yields are also negatively affected by the less selective characteristics of zeolitic catalysts. Paraffins octane number is typically upgraded from approximately 70 RON to 79 RON, in a once through configuration. Up to 88 RON can be achieved with separation and recycle of normal paraffins. The biggest benefit of utilising zeolitic type catalysts is that they are fully regenerable. Even so, none of the new isomerisation process units are adopting this technology due to unfavourable economics (Sullivan et al., 2014).

2.7.4. Sulphated Metal Oxide Type Catalysts

A sulphated metal oxide catalyst has higher activity than zeolitic type catalysts. These metal oxides form the base of a more recent generation of isomerisation catalysts, namely Tin Oxide (SnO_2), Zirconium Oxide (ZrO_2), Titanium Oxide (TiO_2), tungstated Zirconia, or Ferric Oxide (Fe_2O_3), which has been sulphated. Sulphated Alumina is not an active catalyst for reactions involving hydrocarbons. This increased activity, compared to zeolitic catalysts, allow an advantage of about 80°C lower operating temperature. Up to 82 RON can be achieved, for a typical feed, in a once through configuration. These catalysts, similar to zeolitic catalysts, are also fully regenerable. The

high activity of the metal oxide catalyst makes it an appropriate choice for new installations, where the full performance advantage of chlorided Alumina catalysts is not required or where contaminants in the feedstock is not a concern (Sullivan et al., 2014).

2.7.5. Comparison of Catalyst Types

The performance of well-established catalysts are shown in Figure 7 (Sullivan et al., 2014). The octane number improvement over zeolitic catalysts is illustrated, for all catalysts as a function of average reactor bed temperature.

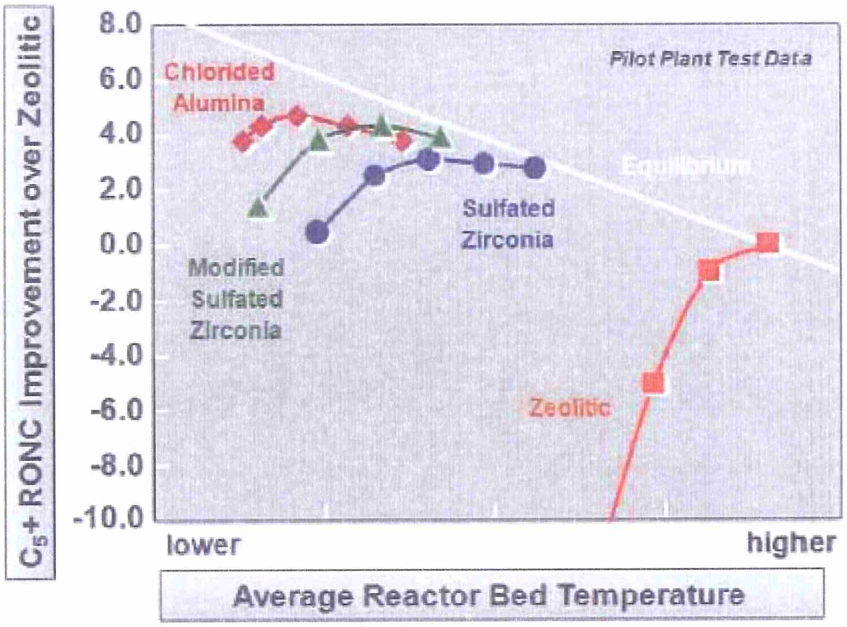

Figure 7: Octane/Activity Curve for various Isomerisation Catalysts (Sullivan et al., 2014).

The advantage of chlorided Alumina type catalyst activity over zeolitic type catalysts, clearly shows up as an improvement in octane number of their respective isomerate product. This proves helpful for existing fixed bed reactors, when considering reloading reactors. It should be noted for

unconstrained new unit designs, additional catalyst volume can be added to attain lower temperature operation and higher octane (Sullivan et al., 2014).

2.8. Process Options

The objective of present day C_4 hydrocarbon isomerisation applications, according to Speight (2007), is to provide additional feedstock for alkylation units or high octane constituents for fuel blending. Various companies have developed isomerisation processes which have increased the octane number from about 70 to more than 80. Naphtha is passed over an aluminium chloride catalyst at 120°C and a pressure of about 55bar, in a typical isomerisation process, to produce the isomerate (IEA, 2016).

2.8.1. Butamer Process

N-Butane is converted to iso-butane, over a platinum catalyst, under mild operating conditions. The operation, using a fixed bed reactor, can be designed for once through or recycle operation. The product stream would normally feed an alkylation unit de-isobutaniser to recover butane feed for the isomerisation unit (Speight, 2007).

2.8.2. Butomerate Process

The purpose of this process is to produce iso-Butane for alkylation. The feedstock is required to be dry and comparatively free of sulphur. The catalyst contains a small amount of non-noble hydrogenation metal on a high surface area support. Coke deposition on the catalyst is eliminated by a hydrogen recycle. The liquid product is stripped of light material (Speight, 2007).

2.8.3. Hysomer Process

This process uses hydrotreated pentane and hexane feedstock, without further pre-treatment. Feedstock having saturated water, say 50 ppm, can be processed without any negative effects on catalyst stability or conversion. A minimum quantity of water is essential for the activity of Zeolite catalyst, in this application. Sulphur has a minimal effect on catalyst activity. The catalyst is robust enough to handle a permanent sulphur level of 10 ppm in the feedstock. Higher concentrations, up to 35 ppm, are harmful. Operating pressure is controlled between 27 bar and 31 bar. Operating temperature is set at 290°C. The zeolite catalyst has a lifespan of approximately 2 years (Speight, 2007).

2.8.4. Iso-Kel Process

A wide variety of feedstock can be processed, including natural gas condensate, pentane and hexane cuts. A fixed bed reactor is used for this process, operating at temperatures between 345°C and 455°C. Operating pressures are between 24bar and 41bar. The vapour phase isomerisation reaction proceeds over a precious metal catalyst in the presence of hydrogen (Speight, 2007).

2.8.5. Isomate Process

A continuous, non-regenerative process for isomerising C_5 to C_8 normal paraffins, catalysed by aluminium tri-chloride and hydrogen chloride. Catalyst activity is retained by maintaining hydrogen partial pressure, which also suppresses cracking and disproportionation. The feed is saturated with anhydrous hydrogen chloride in an absorber and mixed with hydrogen before being fed into the reactor. Catalyst is added separately to the reactor. The reaction takes place in a liquid phase, at a temperature of 115°C and a pressure of 48bar. The product is acid stripped, by way of a caustic wash (Speight, 2007).

2.8.6. Isomerate Process

It is a continuous isomerisation process, designed to convert normal pentanes and hexanes into highly branched isomers. Hydrogen is co-fed with the normal paraffins to a fixed bed reactor system. Operating conditions are mild, with the operating pressure not more than 51bar and a temperature of 400°C. Normal paraffins are recycled to the feed, with complete conversion being achieved. The catalyst does not contain a noble metal (Speight, 2007).

2.8.7. Penex Process

The process where normal C_5 & C_6 paraffins are isomerised in a fixed bed reactor, using a platinum catalyst in the presence of Hydrogen. Operating temperatures are between 260°C and 480°C. Operating pressures range between 21bar and 68bar. In order to increase conversion, recycle streams can be added. A de-isohexaniser and de-isopentaniser separates normal C_6 and C_5 paraffins respectively, from the product stream, for recycle (Speight, 2007).

2.8.8. Pentafining Process

A process for isomerising pentane using a platinum catalyst, in the presence of hydrogen. The operating pressure of the isomerisation unit is between 21bar and 27bar, while the operating temperature is controlled between 425°C and 480°C. Hydrogen and n-pentane is recovered from the product stream, and recycled to the reactor feed. Catalyst can be regenerated, using a steam/air mixture. Two process options, according to Pujadó, are commercially available via, either chlorided alumina-type catalyst or sulphated zirconia catalyst. Both processes provide high product yield and octane numbers (Speight, 2007).

2.9. Isomerisation Process Flow Schemes

The C_5-C_6 paraffins isomerisation unit would typically form part of a naphtha processing or oil refinery complex, as shown in Figure 8, producing petroleum products. The paraffins feed stream is usually hydrotreated to remove contaminants, which are harmful to downstream processes. The paraffins feed is divided into lighter and heavier fractions, using a splitter. The lighter C_5-C_6 paraffins stream would then be sent to an isomerisation unit. The heavier, C_{7+} paraffins, would be sent to a catalytic reforming unit. A platformer, which is a reformer using a platinum containing acidic catalyst at elevated temperatures and pressures, converts the C_{7+} paraffins and naphthenes into a product of high octane number and rich in aromatic hydrocarbons (Hsu and Robinson, 2006).

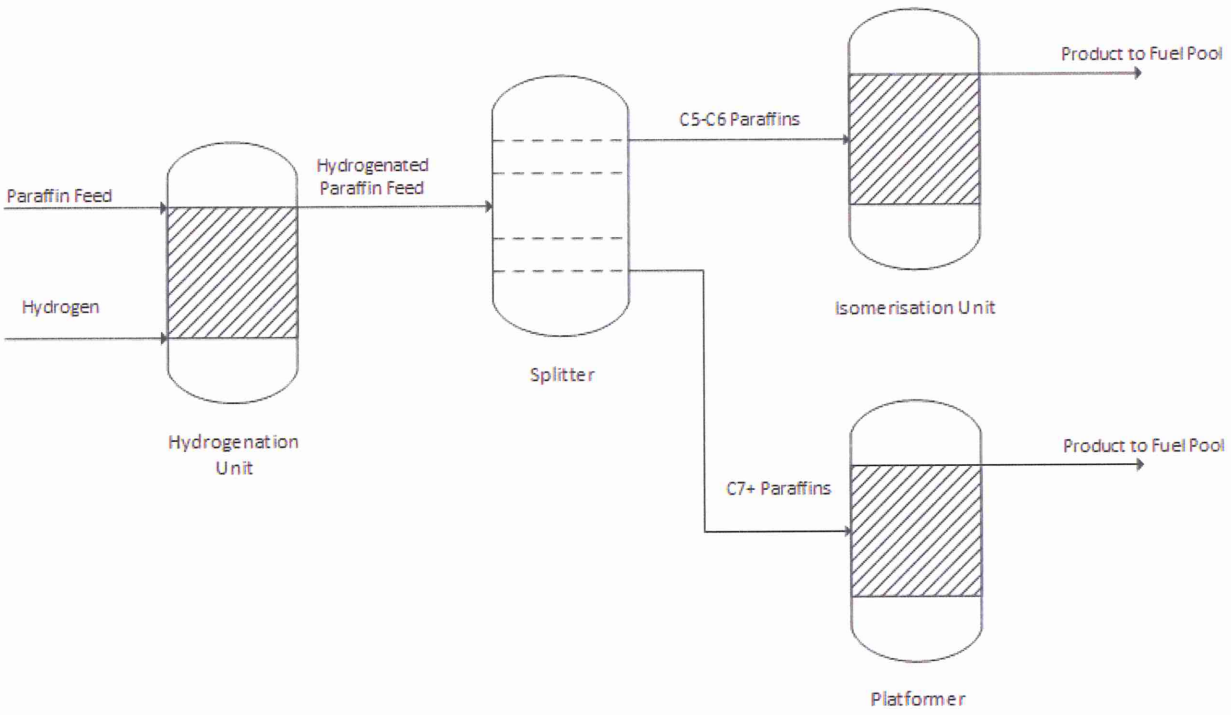

Figure 8: Typical Isomerisation Flow Scheme (Hsu & Robinson, 2006).

Constituents of the fuel blend are shown below, in Table 8 (Speight, 2007). Straight chain paraffins are converted to their respective iso-compounds continuous catalytic processes. Light straight-run

petrol is first fractionated, as a feed preparation step. High volumetric yields, of greater than 95%, with 40% to 60% conversion per pass are characteristic of the isomerisation process.

Table 8: Component Streams for Petrol Pool (Speight, 2007).

Stream	Producing Process	Boiling Range °C
Paraffinic		
Butane	Distillation	0
	Conversion	
Iso-pentane	Distillation	27
	Conversion	
	Isomerisation	
Alkylate	Alkylation	40-150
Isomerate	Isomerisation	40-70
Naphtha	Distillation	30-100
Hydrocrackate	Hydrocracking	40-200
Olefinic		
Catalytic Naphtha	Catalytic Cracking	40-200
Cracked Naphtha	Steam Cracking	40-200
Polymer	Polymerisation	60-200
Aromatic		
Catalytic Reformate	Catalytic Reforming	40-200

2.9.1. Penex Hexane Isomerisation Process Scheme

The development of new process technologies, with new catalyst systems, fully utilise the characteristics of the catalyst. The Penex process units, using chlorided Alumina-type catalysts, are the most prevalent in industry. The processes can be arranged as a once through (OT) configuration or a recycle loop. The recycle loop configuration is shown in Figure 9. The process requires continuous Chlorine addition to maintain catalyst activity. The off-gas would need a caustic scrubber, to neutralise HCl which has carried over. In order to prolong catalyst life, gas

driers need to be installed on the feed and make-up gas streams for moisture removal. The sulphated zirconia, on the other hand, does not require chloride or caustic but has to have a recycle gas compressor loop (Sullivan et al., 2014).

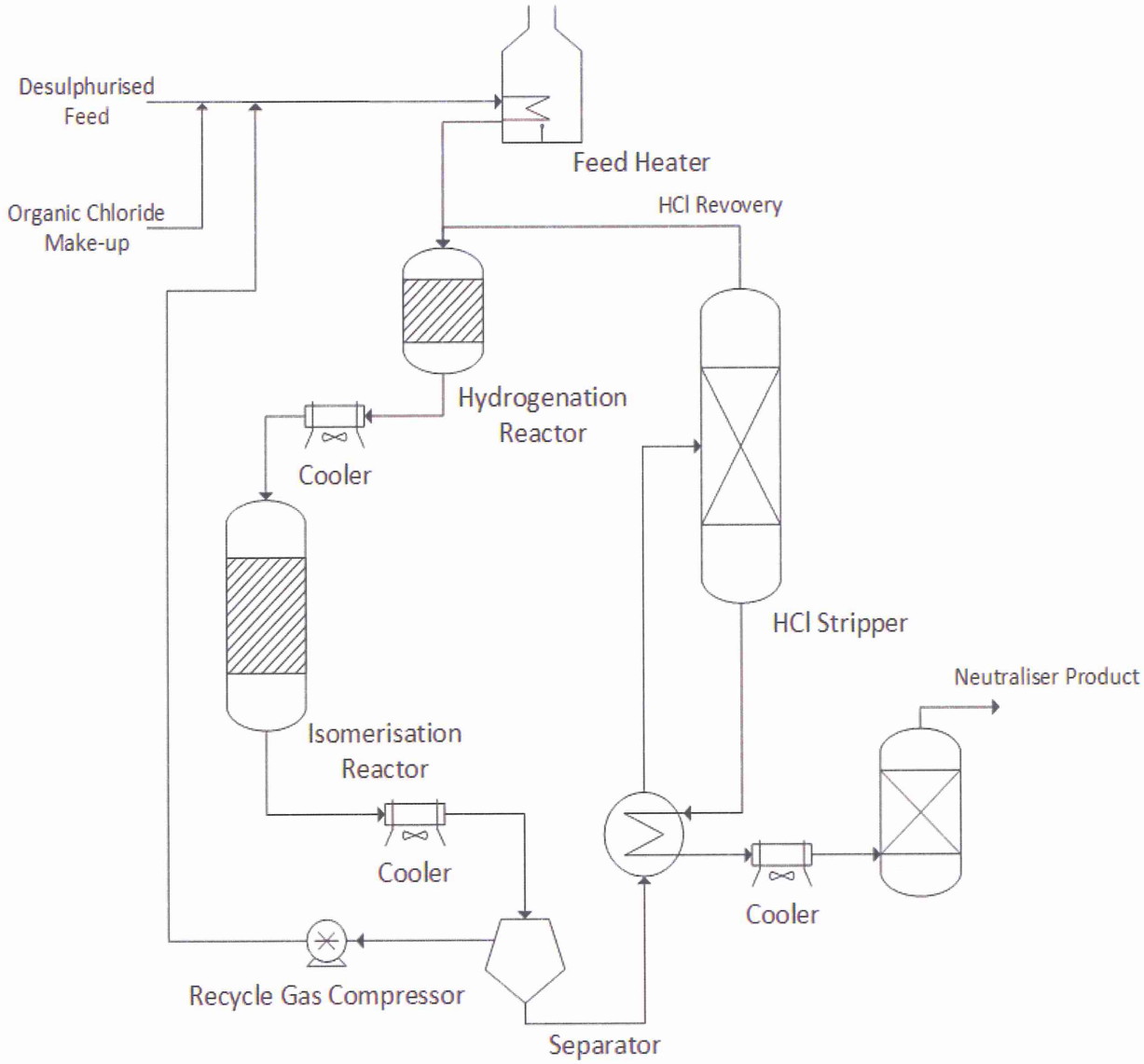

Figure 9: Pentane-Hexane Isomerisation (Sullivan et al., 2014).

2.9.2. De-isopentaniser Configuration

A limited octane gain is achieved in a simple once through isomerisation scheme, according to Axens, even with the most active isomerisation catalyst. The RON of isomerate is in the region of 83 to 84. A de-isopentaniser can be added upstream of the isomerisation unit, to improve the octane number of the isomerate, as illustrated in Figure 10. The high octane isopentane is separated from the isomerisation feed and combined with the isomerate stream. The reaction equilibrium is improved while the isomerisation feed flow rate is reduced (Sullivan et al., 2014).

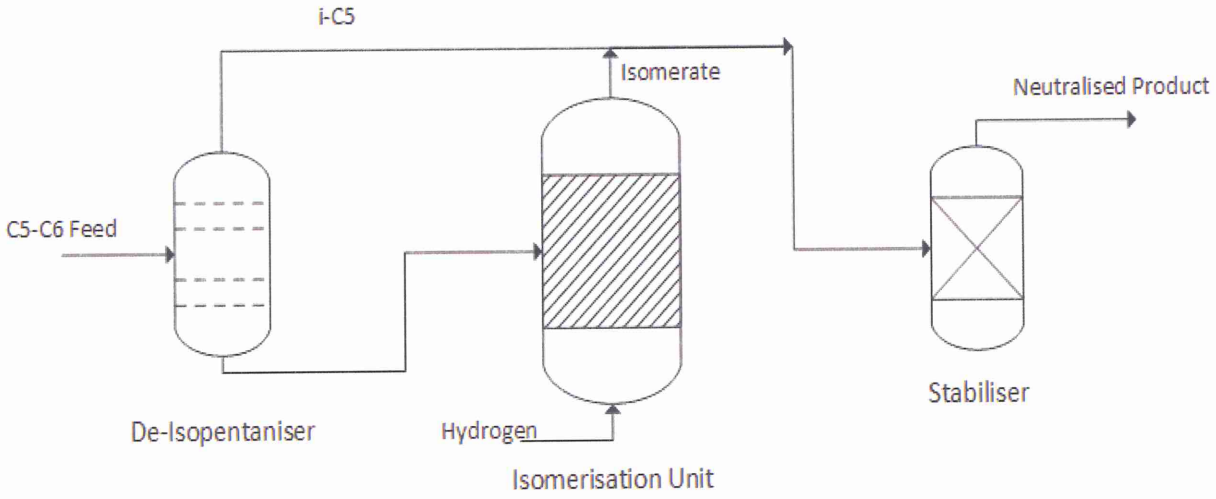

Figure 10: De-isopentaniser Application (Sullivan et al., 2014).

2.9.3. De-isohexaniser Configuration

To further improve overall conversion of n-paraffins to i-paraffins, and remove the limitations of the once-through configuration, a recycle stream of unreacted paraffins is needed. The lower octane paraffins can be separated from the isomerate, with the use of a de-isohexaniser (DIH). The higher octane iso-hexanes and C_5's are distilled and combined with the DIH bottoms to form the final isomerate product. Unconverted n-hexanes are removed as a side stream and recycled to the

isomerisation feed, as shown in Figure 11. A RON of up to 88 can be expected, with the use of a de-isohexaniser process configuration (Domergue and Watripont, 2005).

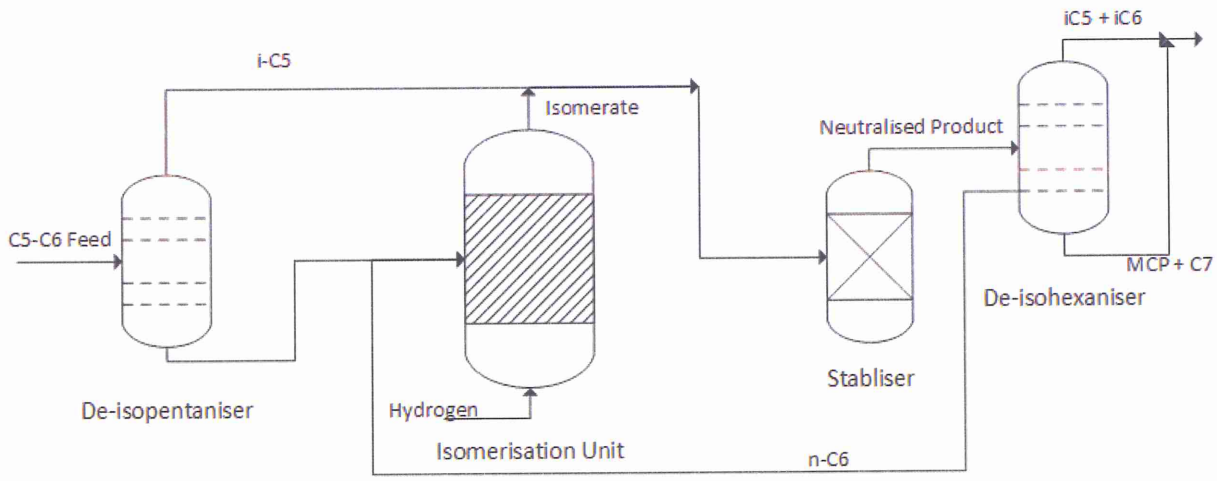

Figure 11: De-isohexaniser Application (Sullivan et al., 2014).

2.9.4. Axens Ipsorb Process Scheme

The de-isohexaniser scheme, however, does not improve the C_5 stream. The unconverted normal pentane exits the de-isohexaniser with the isomerate stream, thus having a negative effect on the final isomerate RON. In order to achieve full conversion, all of the normal paraffins in the isomerate need to be recycled to the isomerisation reactor feed. The normal paraffins can be separated from the isomerate stream by making use of modern molecular sieve adsorption technology. The application of this separation technique in the isomerisation flow scheme is shown in Figure 12. A low pressure conventional de-isopentaniser column upstream of the isomerisation unit forms an integral part of the separation scheme in the Ipsorb process. Normal paraffins are selectively adsorbed, due to their smaller molecular diameter. The normal paraffins are recovered in the desorption step, making use of hydrogen as a desorption fluid (Leprince, 2001).

The drawback of this process flow scheme is the degradation in the adsorption unit when using chlorided alumina catalyst. The adsorption system, in the Ipsorb process, is located downstream

from the isomerate stabiliser. The cyclic adsorption and desorption steps take place in the vapour phase. An isopentane-rich vapour stream is employed in a novel desorption step, to recycle normal paraffins to the upstream de-isopentaniser column. This column not only separates an Isopentane stream from the fresh feed to improve the efficiency of the isomerisation unit, but also provides an Isopentane stream for the desorption step. The Axens patented Ipsorb molecular sieve system enables product RON of up to 90. The first Ipsorb isomerisation process scheme was commissioned in Italy, in 1994 (Domergue and Watripont, 2005).

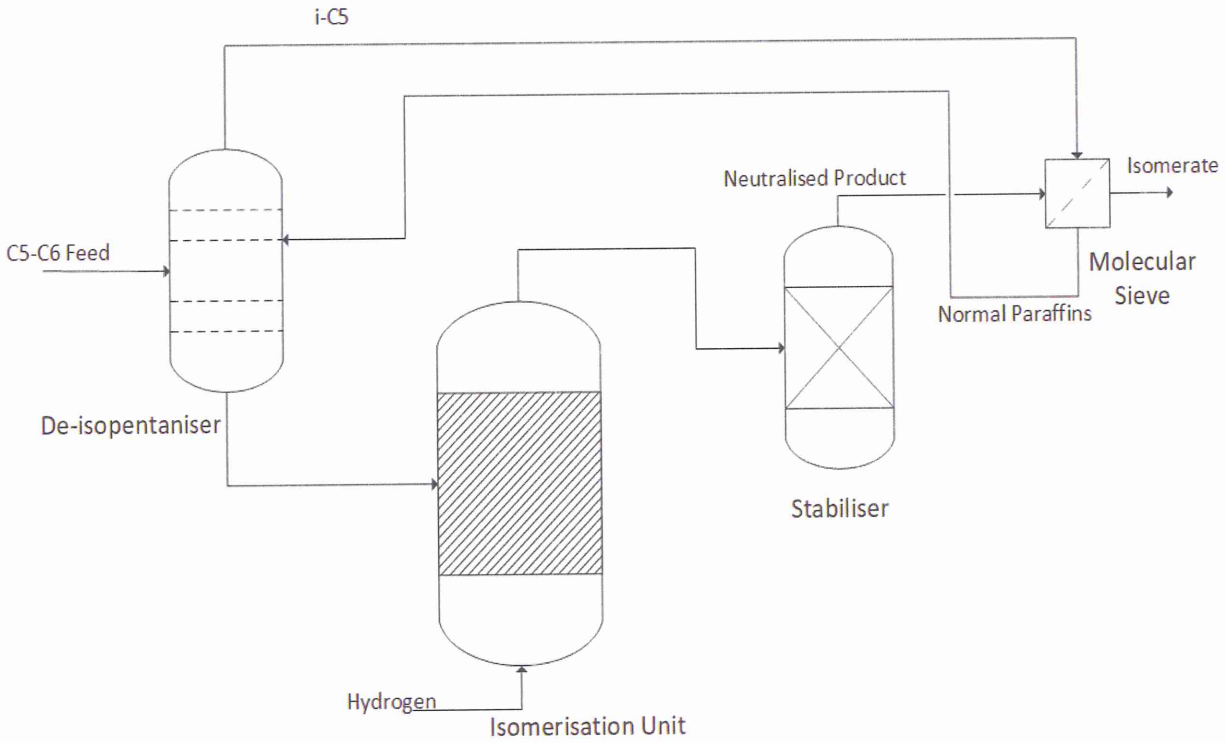

Figure 12: Ipsorb Process (Domergue & Watripont, 2005).

2.9.5. Axens Hexorb Process Scheme

In order to exceed the 90 RON threshold achieved, using the Ipsorb system, almost complete conversion of the methylpentanes is required. This can be achieved by integrating the Axens patented Hexorb separation process with the reaction section. The Hexorb process combines a de-isohexaniser on the downstream side of the molecular sieve, as shown in Figure 13. The de-

isopentaniser separates its feed into an isomerate overhead stream rich in isopentane and a bottoms purge stream, rich in C_6 naphthenes and C_{7+} hydrocarbons. A side stream from the de-isohexaniser is drawn, containing essentially all of the methyl-paraffins. The bottoms purge stream is combined with the final isomerate stream and not recycled to the isomerisation reactor. This protects the isomerisation catalyst against inhibition, caused by naphthenes and hydrocracking of C_7's.

A further improvement on the process flow scheme would be to direct the isomerisation feed to a molecular sieve adsorption unit, together with the isomerate, prior to charging the isomerisation unit. This method would ensure that only the n-paraffins and methylpentane (MCP) portion of the combined fresh feed and isomerate streams are fed to the isomerisation unit. Even though the load on the molecular sieve adsorption unit will be increased, the conversion over the isomerisation unit will increase, given that the feed to the isomerisation unit is almost only normal paraffins (Domergue and Watripont, 2005).

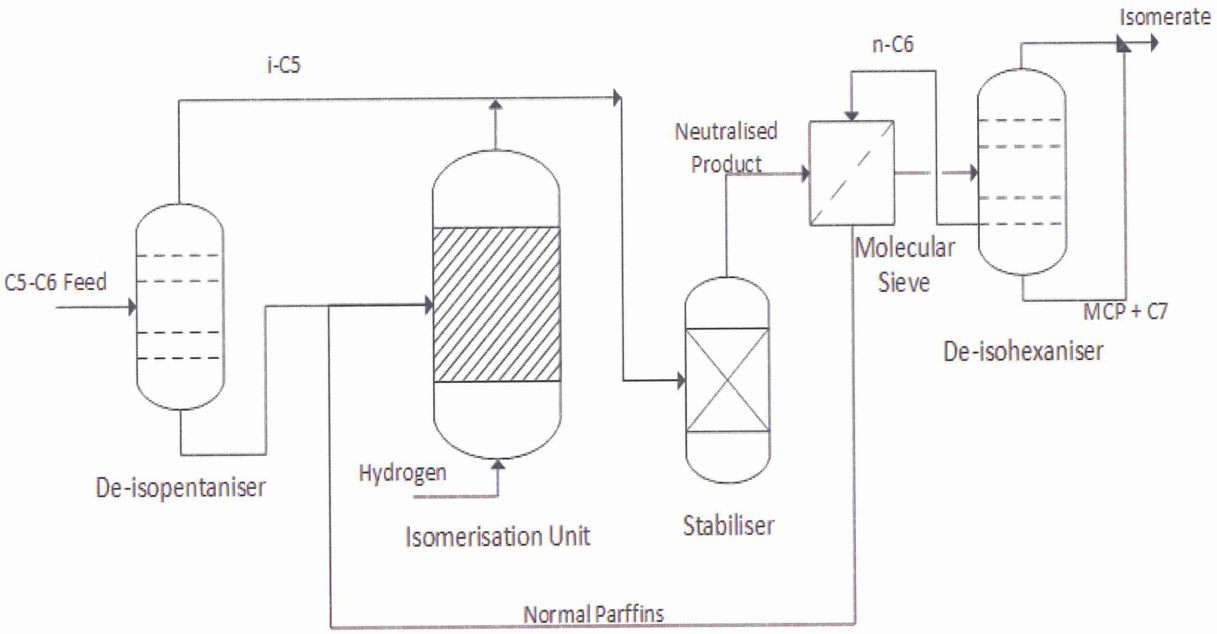

Figure 13: Hexorb Process (Domergue & Watripont, 2005).

2.10. Summary

According to the Nelson (1964), it is obvious that isomerisation of pentane and hexane, plus catalytic reforming of the heptane plus fraction of naphtha, leads to higher motor fuel octane. The major challenge faced by researchers in processing paraffins is the nature of the feed material. The presence of undesirable components in paraffins requires complex separation processes prior to conversion. Majority of literature, including Bagajewicz, suggest that paraffins should be processed making use of the following technologies to upgrade value (Bagajewicz, 2007):

a. Isomerization for a C_5-C_6 mix.
b. Platforming for C_7+ paraffins.
c. Hydrocracking for C_{16} to C_{80} paraffins.

The light ends of the LT-FT paraffins stream is still viewed as a by-product destined for a fire-sale, as opposed to being upgraded to a higher value fuel. The extensive work done by researchers on refinery units provides a backbone to bring together refinery requirements for FT syncrude.

Chapter 3: Process description and mass balance analysis

The production of paraffins, via the LT-FT process, was investigated. The C_5-C_6 cut of the final paraffins product was modelled, using excel, to evaluate the octane upgrade of LT-FT paraffins. The margin between the direct sales of paraffins to the chemicals market, and the sales price of isomerised paraffins, to the fuels market, was determined. This margin would contribute to the economics of determining the best market placement of paraffins product, notably C_5-C_6 paraffins cut. The mass balance and economics study are the main focus of this study. The LT-FT synthesis process, integrated into an overall GTL process, was diligently investigated. The process description and mass balancing, of natural gas derived paraffins, were done in this study.

3.1. Natural Gas to Chemicals

Natural gas processed in Sasolburg Operations is used as a building block in the preparation of chemicals. Chemicals and intermediates are prepared from methane, contained in natural gas. Natural gas is processed through several operating units, prior to storage of final chemical products. The stages of production represented in this chapter was based on the configuration described by Steynberg (2006).

Natural gas is converted to Syngas by a reforming process. Syngas is fed into the LT-FT process, producing a waxy Syncrude and tail gasses. Syngas is also used in the production of alcohols. The Syncrude is separated into its various grades of paraffinic hydrocarbons, from light paraffins to a heavy hard wax. Ammonia is also produced from the process, which is used to produce nitric acid and ammonium nitrate as well. The LT-FT process, in the production of C_5-C_6 paraffins, was separated into three stages, viz. syngas preparation, FT synthesis and product work-up.

3.2. **Syngas Preparation**

3.2.1. Natural Gas Feedstock

Natural gas feedstock, as a source for hydrocarbons production, was produced from petroliferous (petroleum containing) geological formations. Natural gas contains a high proportion of methane. Higher hydrocarbons of up to 6 Carbon atoms can be found in small amounts. Carbon dioxide, nitrogen and helium are often minor components in natural gas, and are regarded as containments. Trace amounts of sulphur compounds assist with leak detection, and is dosed into the natural gas line, as part of regulatory requirements.

The composition of the natural gas is dependent on the formation of the gas well. Different wells, from various locations, will exhibit different compositions. Hence, there is no single composition of components which may be referred to as typical natural gas. The reference gas for this report is a dry and lean gas, which methane is the major constituent and negligible amounts of higher molecular weight paraffins (Speight, 2007).

3.2.2. Synthesis Gas Generation Unit

Syngas preparation is an important part of the GTL process. It is the most energy intensive part of the process and is the most expensive of the three stages of the LT-FT process, and critical for the economics of the GTL process.

A purification unit is needed to remove H_2S and other Sulphur compounds, since these compounds are poisons for downstream catalysts. The desulphurisation of natural gas is a two-step process. The process involves the hydrogenation of organic sulphur compounds and subsequent absorption of H_2S. The feedstock was mixed with hydrogen, preheated and passed to a first reactor, containing a hydrogenation catalyst. The gas passes to sulphur absorbers in series, after hydrogenation, which absorbs the H_2S formed in the hydrogenation reactor (Steynberg and Dry, 2006).

The hydrogenation of organic sulphur compounds occur by reactions such as:

$$R\text{-}SH + H_2 \rightarrow RH + H_2S \quad (1)$$

$$R\text{-}S\text{-}R_1 + 2H_2 \rightarrow RH + R_1H + H_2S \quad (2)$$

$$R\text{-}S\text{-}S\text{-}R_1 + 3H_2 \rightarrow RH + R_1H + 2H_2S \quad (3)$$

$$C_4H_8S \text{ (Tetrahydrothiophene)} + 2H_2 \rightarrow C_4H_{10} + H_2S \quad (4)$$

$$C_4H_4S \text{ (Thiophene)} + 4H_2 \rightarrow C_4H_{10} + H_2S \quad (5)$$

As seen in the reactions (1) to (5), sulphur in the gas is removed in the form of H_2S. And finally, H_2S reacts with zinc oxide in the adsorption vessel according to the reaction below (Steynberg and Dry, 2006).

$$ZnO + H_2S \rightarrow ZnS + H_2O \quad (6)$$

The purified natural gas went through the adiabatic pre-reformer, where the higher hydrocarbons are converted into a mixture of methane, steam, carbon oxides and hydrogen. The adiabatic pre-reformer feed is made up of a mixture of natural gas and steam, with a small amount of Hydrogen. The effluent from the pre-reformer is pre-heated and fed to the auto-thermal reformer (ATR) (Steynberg and Dry, 2006).

The adiabatic pre-reformer is a key element in an optimised syngas generation unit. The adiabatic pre-reformer enabled the increased feed temperature to the auto-thermal reformer, without the risk of thermal cracking and carbon formation. Increasing the auto-thermal reformer feed temperature reduced the oxygen consumption and improved the carbon efficiency. Operating the pre-reformer with a low steam/carbon ratio provided for optimal process economics, but involved the risk of formation of carbon on the catalyst of the pre-reformer. Carbon formation from higher hydrocarbons is an irreversible process. The formation of carbon is illustrated by the reactions below (Steynberg and Dry, 2006).

$$CH_4 \leftrightarrow C + 2H_2 \quad (7)$$

$$C_nH_m \rightarrow nC + \tfrac{1}{2}mH_2 \quad (8)$$

The pre-reformed gas is fed into the adiabatic oxidative reformer. Oxygen was used as the oxidant in auto-thermal reforming, where a mixture of feed gas and steam was partially converted by pressurised combustion at fuel-rich conditions and the conversion of hydrocarbons into raw synthesis gas over a fixed catalyst bed. The feed gas reacted with oxygen to form raw synthesis gas in the auto-thermal reformer, operating at an outlet temperature of approximately 1050°C and an outlet pressure of 30 – 40bar. Higher outlet pressure was possible, but not advantageous at very low steam to carbon ratio due to the resulting increase in CH_4 leakage in the raw synthesis gas. In adiabatic oxidative reformer the heat for the reforming was supplied by internal combustion. The overall reactions taking place in the ATR can be described in the set of reactions below (Steynberg and Dry, 2006).

Combustion: $2CH_4 + 3O_2 \rightarrow 2CO + 4H_2O$ $\quad -\Delta H°_{298} = +519$ kJ/mole (9)

Reforming: $CH_4 + H_2O \leftrightarrows CO + 3H_2$ $\quad -\Delta H°_{298} = -209$ kJ/mole (10)

Shift: $CO + H_2O \leftrightarrows CO_2 + H_2$ $\quad -\Delta H°_{298} = +41$ kJ/mole (11)

Heat was recovered from the raw synthesis gas by production of high pressure steam. The gas was cooled for the removal of H_2O. The ratio between hydrogen and carbon oxides is often used to describe the characteristics of raw synthesis gas. In addition, to describe stoichiometric number (SN) or 'module' (M), or ribblett ratio (R) (Steynberg and Dry, 2006).

$$SN \text{ or } M = \frac{(H_2 - CO_2)}{(CO + CO_2)} \quad (12)$$

$$R = \frac{H_2}{(2CO + 3CO_2)} \quad (13)$$

It has been shown by Chauvel and Lefebvre (1989), that it is not possible to produce synthesis gas for FT synthesis or methanol production directly, by auto-thermal reforming of purified natural gas. Feed gas for LT-FT synthesis would require addition of carbon-rich gas or removal of hydrogen, whereas the feed gas for methanol would require the removal of carbon oxides or addition of hydrogen (Chauvel and Lefebvre, 1989).

3.3. FT Synthesis

3.3.1. Wax (Syncrude) Production

There are four types of FT reactors in commercial use at the moment, namely circulating fluidised bed type, fluidised bed type, tubular fixed bed type, and slurry phase type reactors. This report is based on syngas feed to the slurry phase type reactor. A typical slurry phase reactor is represented in Figure 14 (Steynberg and Dry, 2006).

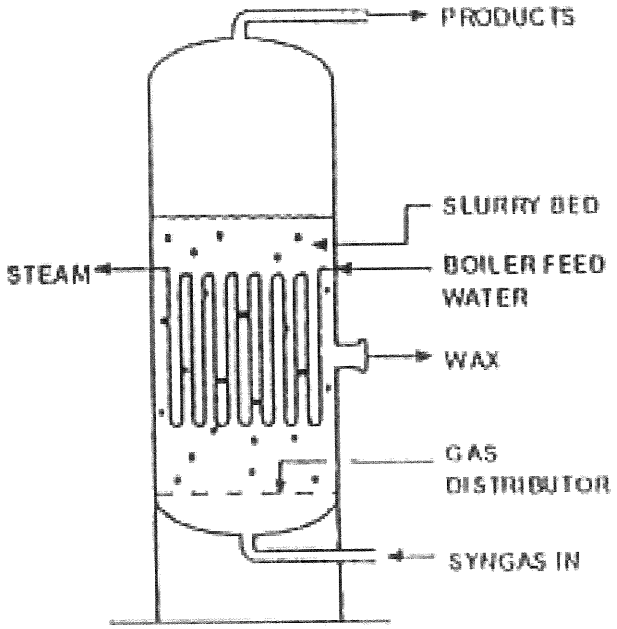

Figure 14: Slurry Phase Reactor (Steynberg & Dry, 2006).

The syngas is fed at the bottom of the reactor and bubbles through a bed of waxy slurry and catalyst. Wax is drawn out from the side of the reactor and other products are recovered from the outlet flow at the top of the reactor. Heat is recovered from the exothermic FT reactions, taking place in the slurry bed, by producing steam form boiler feed water.

The ratio of consumption of hydrogen and carbon monoxide is the primary concern of the FT stoichiometry. The syngas was fed to the SSBP wax reactors to produce syncrude using Sasol's proprietary technology catalyst. The preparation of the LT-FT catalyst has an appreciable influence on the chemistry within the reactor. The chemistry within the FT reactor is complex. It can be simplified into the following reactions:

Methane:	$CO + 3H_2 \rightarrow CH_4 + H_2O$	(14)
Heavier Hydrocarbons:	$nCO + 2nH_2 \rightarrow (-CH_2-)_n + nH_2O$	(15)
Alcohols:	$nCO + 2nH_2 \rightarrow C_nH_{(2n+2)}O + (n-1)H_2O$	(16)
Water gas shift (WGS):	$CO + H_2O \leftrightarrows CO_2 + H_2$	(17)

The desired products are the heavier hydrocarbons. The production of syngas feed, for the FT process, is a major cost factor for both capital and operating cost, depending on the complexity of the overall downstream plants. Thus it is beneficial for the conversion of syngas to hydrocarbons in the FT reactors to be as efficient and complete as possible. The operating parameters of the reactor were manipulated to favour reaction (15). The main objective is to maximize the length of the heavy hydrocarbon chain by manipulating the ratio of H_2 to CO in the syngas feed.

3.3.2. The Gas Loop

The application of Fischer-Tropsch technology involved more than syngas feed to the slurry phase reactor. The gasses and vapours leaving the FT reactor, through the overhead product stream, were further processed. This involved cooling of the product gasses and vapours, to condense hydrocarbons and reaction water, which were separated from the tail gas. The recycle of some of the gasses to the syngas feed was required for optimal operation. A portion of the tail gasses is used for fuel gas and for hydrogen production. The hydrogen produced is used to manufacture

ammonia and subsequently, nitric acid and ammonium nitrate. This gas processing scheme is known as the gas loop (Chauvel and Lefebvre, 1989).

3.4. **FT Product Work-Up**

The LT-FT products consists primarily of a light fraction, usually liquid at room temperature, and a heavy fraction, usually solid at the same conditions. The light fraction is often named hydrocarbon condensate or simply condensate. The heavy fraction, known as wax, includes the heavy paraffins. The other two product streams consist of light hydrocarbons gasses, mostly generated during the FT synthesis, and reaction water, which include some dissolved oxygenates like alcohols and organic acids. The gas stream is processed further downstream in the gas loop. The reaction water is further processed to recover valuable products (Steynberg and Dry 2006).

3.4.1. Hydrotreating FT Paraffins

The quality of the primary FT products, including condensate and wax, can be improved through hydrotreatment. The primary objective of the hydrotreatment is to saturate olefins and oxygenates to the corresponding paraffins. The hydrogenation resulted in hydrocarbon products, which remains stable, even when stored for long periods. The resulting LT-FT wax product has better colour and stability (Steynberg and Dry, 2006).

3.4.2. Paraffins Fractionation

The hydrogenated paraffins are stabilised in a depentaniser. The primary objective is to obtain the C_7-C_{20} paraffins fraction from the bottom of the column for work-up in the downstream paraffins fractionation section. The overhead stream of the depentaniser is made up of a range of hydrocarbons from methane to hexane. The depentaniser overhead stream is further stabilized in a debutaniser. The final product of the column is a pentane-hexane mix. The light overhead product

is not collected and can be flared, but is more useful as a fuel gas. Excess overhead gas produced was sent to the flare system. If there was a deficit in overhead gas production, the fuel gas to the gas fired furnace can be made up by feeding the factory fuel gas to the feed furnace (Steynberg and Dry 2006).

The fractionation section is made up of 3 units. The C_7-C_{20} bottoms of the depentaniser column was fed to the first fractionation column. The bottom C_{10}-C_{20} product is sent to storage for further fractionation in the third column. The C_7-C_{11} feed enters the second fractionator. The overhead C_7-C_8 stream drawn off from the condenser and sent to storage for export. The bottom C_9-C_{11} product is removed from the reboiler and sent to storage for export as final product. The composition of the LT-FT syncrude is shown in Table 11.

Table 9: Composition of LT-FT Syncrude (De Klerk, 2011).

Product Fraction	Carbon Range	Compound Class	Mass %
Tail Gas	C_1	Alkane	4.3
	C_2	Alkene	1.0
		Alkane	1.0
LPG	C_3-C_4	Alkene	6.0
		Alkane	1.8
Naphtha	C_5-C_{10}	Alkene	7.7
		Alkane	3.3
		Aromatic	-
		Oxygenate	1.3
Distillate	C_{11}-C_{12}	Alkene	5.7
		Alkane	13.5
		Aromatic	-
		Oxygenate	0.3
Wax	C_{22}+	Alkene	0.7
		Alkane	49.2
		Aromatic	-
		Oxygenate	-
Aqueous Product	C_1-C_5	Alcohol	3.9
		Carbonyl	-
		Carboxylic Acid	0.3

3.5. Overall Mass Balance

The mass balance over the wax value chain has excluded the LTFT synthesis reactor, in order not to infringe on Sasol IP. The overall mass balance boundary begins with the hydrocarbon product streams from the SSBP wax reactors, namely condensate, and wax. The paraffins products originate from the condensate stream. The wax stream is further processed to medium and hard waxes.

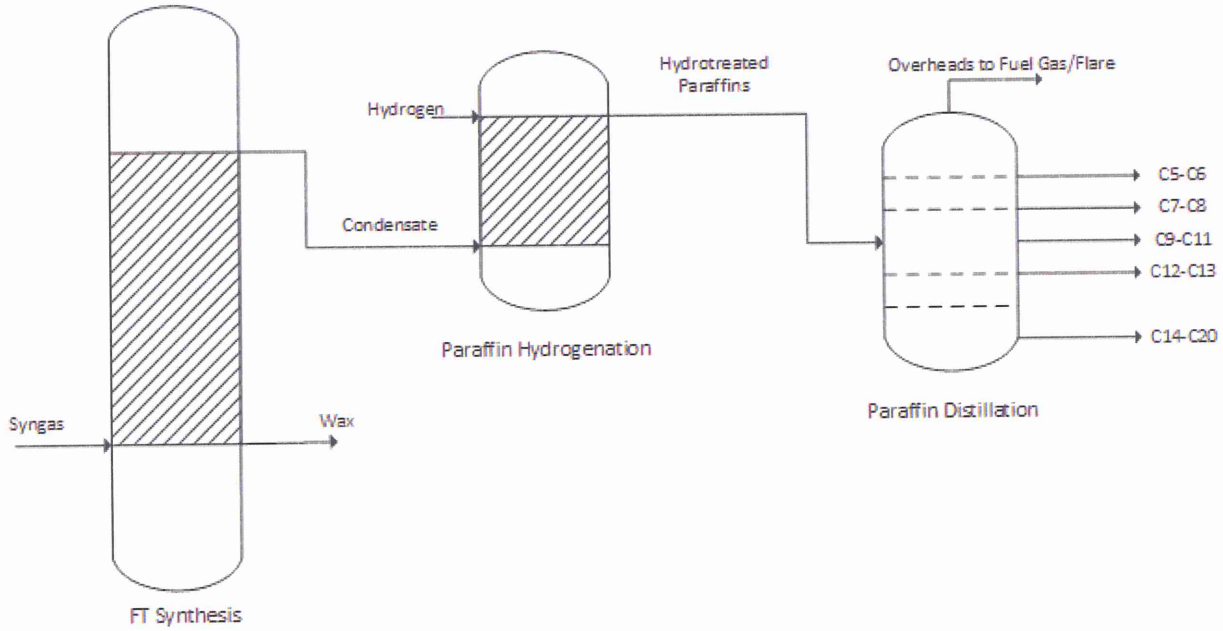

Figure 15: Wax Value Chain.

Basis:

The boundary of the system feed begins after the Slurry Bed Wax Synthesis reactors. The syncrude feed into the system is assumed to be reactor wax, hot condensate and cold condensate. Hydrogen is supplied from the ammonia plant. The outlet streams were measured individually, from sales tonnages. The products are solidified in the form of pastilles and powders. The pastille and powder products are packaged into bags, according to stock keeping unit requirements. The light ends,

which are produced at the paraffins distillation unit is consumed in the pre-heating furnace as utility fuel gas. This syncrude feed is assumed to be 1000 tons.

Total Feed Available:

Thus, Total Feed In = Total Condensate + Total FT Reactor Wax

= 1000 tons

Total Production, calculated from table 11:

Total of Streams Out = Tail Gas + LPG + Naphtha + Distillate + Wax + Aqueous Product

Total Out = 63 tons + 78 tons + 123 tons + 195 tons + 499 tons + 42 tons

= 1000 tons

Overall Balance:

Feed + Produced – Out – Reacted = Accumulation

Accumulation = 1000 tons + 0 – 1000 tons

= 0 tons

The zero accumulation signifies that there is no accumulation, thus we say the system is at steady state. Accumulation is possible due to discrepancies in flow measurement. The tolerated deviation in flow measurement is approximately 3%. The assumed deviation is within the accepted tolerances.

3.6. **Component Balance**

Paraffins feed originates from the hydrocarbon condensate stream, produced at the FT synthesis section. The condensate stream is directed to the feed storage at the paraffins plant. This forms the feed tank to the paraffins hydrogenation unit. Condensate produced, as a result of converting oxygenates in the feed stream to condensate, is transferred to the chemical sewer system. Hydrogenated paraffins are separated into various marketable components in the distillation section. The paraffins product steams are sent to storage. After the products are quality assured, it is drummed for delivery to customers.

Basis:

The straight-run C_5-C_6 paraffins cut constitutes about 40% of the total C_5-C_{10} naphtha fraction in LT-FT syncrude (De Klerk, 2011).

Component Balance:

Total Naphtha = 123 tons

C_5-C_6 paraffins = 0.4 (Naphtha fraction)
= (0.4) (123 tons)
= 49.2 tons

3.7. **Isomerisation Chemical Reaction Engineering**

3.7.1. Process Flow

The light stream paraffins were modelled as feed to an isomerization unit. Multiple reactions proceed, simultaneously, within an isomerisation reactor. They include paraffins isomerisation, naphthene hydrogenation, naphthene isomerisation, benzene saturation, hydrocracking and naphthene alkylation. The model developed by Hamadi and Kadhim (2017), is based on the Penex (DIH) de-isohexaniser configuration. The C_5-C_6 paraffins cut from the paraffins distillation section of the LT-FT value chain was used as feed to the isomerisation model. The reaction proceeds in a hydro-catalytic fixed bed tubular reactor to promote isomerisation and minimise hydrocracking. The non-converted, low octane, components from the de-isohexaniser was recycled to the reactor feed for further upgrading (Hamadi and Kadhim, 2017).

The reactors were operated using chlorinated alumina (Pt/Al_2O_3-Cl) as catalyst. This catalyst has proven to be more active at lower temperatures, ranging between 120°C and 180°C. This range is favourable to maximise iso-paraffins production. Operating at higher temperatures shifts the reaction equilibrium towards hydrocracking, which increases carbon formation on the catalyst. The UOP Penex unit modelled, consisted of 2 reactors in series. The flow-scheme of the Penex DIH process is illustrated in Figure 18.

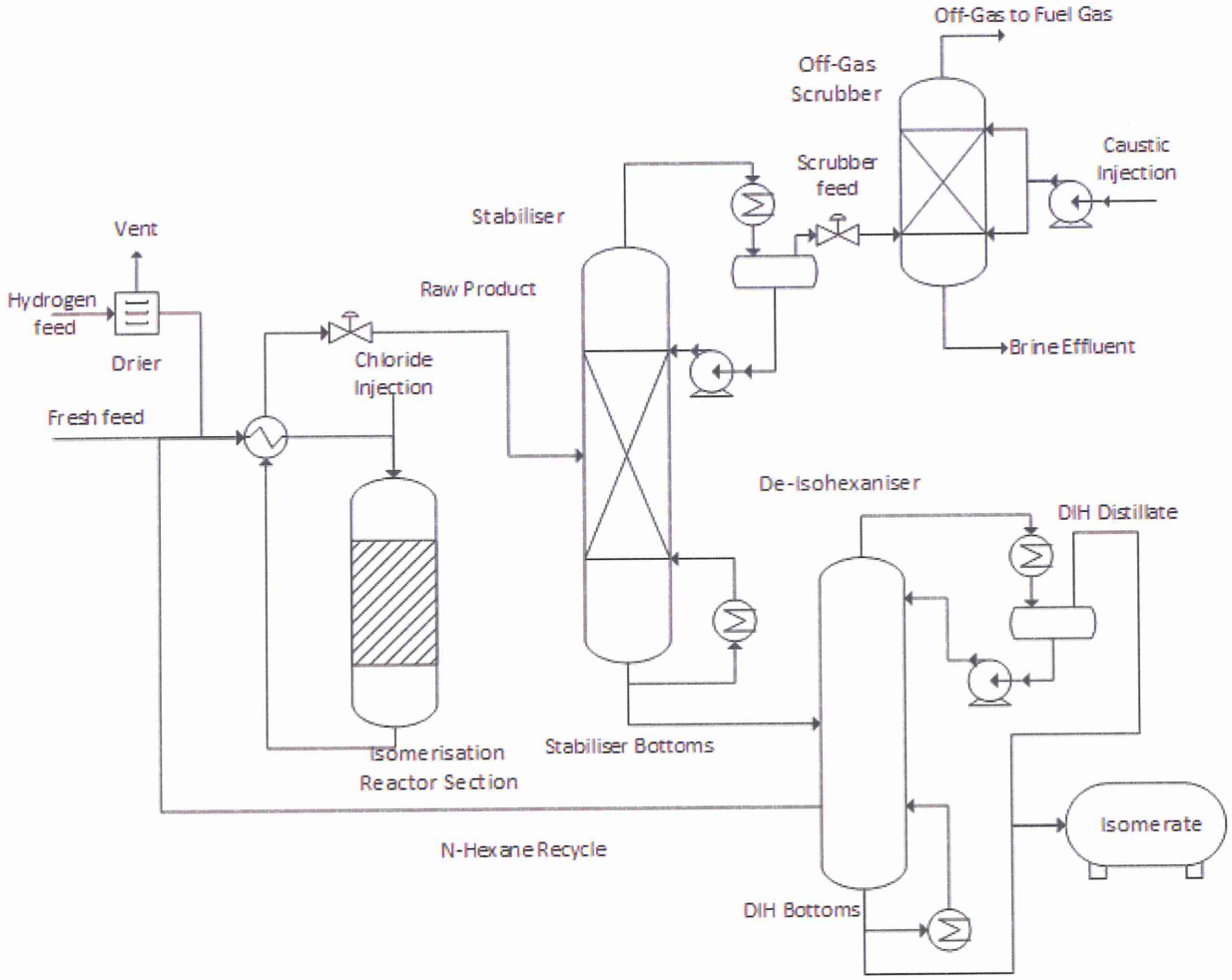

Figure 16: Flow-Scheme of Penex (DIH) Isomerisation Unit (Hamadi and Kadhim 2017).

There are three streams entering the reactor, namely the feed (C_5-C_6 paraffins), Make-up gas (H_2), and recycle from the de-isohexaniser. The product stream exits the reactor and preheats the feed, before entering the stabiliser column. Light gasses exiting the top of the stabiliser column enters the scrubber column. NaOH solution neutralises the HCl present in the gas and exits the bottom of the column as salt and water. The off-gas from the scrubber unit can be utilised as fuel gas. The stabiliser bottoms product contains the isomerate stream, including unconverted normal paraffins, which then enters the de-isohexaniser (DIH) column. The n-hexane stream is drawn out from the

side of the DIH column. The top and bottoms product of the DIH column combine to form the final product isomerate stream.

3.7.2. Reaction Mechanisms

a. Primary Reactions

The isomerisation reaction is slightly exothermic. The isomerisation reaction proceeds in a series of steps. Normal paraffins are converted to olefins in the presence of the metal catalyst, as an intermediate product, by dehydrogenation, in the first step. The n-olefins are converted to carbonium ion with the introduction of strong chloride acid, as ion initiator. This ion initiator favours the forward reaction of converting the carbonium ion into i-olefin, by hydrogenation to create a positive site for the re-arrangement of the molecules and subsequent dehydrogenation. In the last step, the iso-olefin is converted, by hydrogenation, to an iso-paraffins in the presence of the metal catalyst (Hamadi and Kadhim, 2017).

The general reaction pathway is as follows:

$$\text{n-Paraffin} \overset{\text{Pt}}{\leftrightharpoons} \text{n-Olefin} \overset{\text{acid}}{\leftrightharpoons} \text{Carbonium Ion} \overset{\text{acid}}{\leftrightharpoons} \text{i-Paraffin Carbonium Ion} \overset{\text{Pt}}{\leftrightharpoons} \text{i-Paraffin} \quad (18)$$

The isomerisation of n-pentane and n-hexane follow the same pathway. The overall reactions for n-pentane and n-hexane taking place in the isomerisation reactors is shown in reactions below.

$$\text{n-Pentane} \overset{\text{Pt}}{\leftrightharpoons} \text{2-Methylbutane} \quad (19)$$

$$\text{n-Hexane} \overset{\text{Pt}}{\leftrightharpoons} \text{2-Methylpentane} \quad (20)$$

$$\text{n-Hexane} \overset{\text{Pt}}{\leftrightharpoons} \text{3-Methylpentane} \quad (21)$$

$$\text{n-Hexane} \overset{\text{Pt}}{\leftrightharpoons} \text{2,2-Dimethylbutane} \quad (22)$$

$$\text{n-Hexane} \overset{Pt}{\leftrightharpoons} \text{2,3-Dimethylbutane} \quad (23)$$

$$\text{2-Methylpentane} \overset{Pt}{\leftrightharpoons} \text{3-Methylpentane} \quad (24)$$

$$\text{3-Methylpentane} \overset{Pt}{\leftrightharpoons} \text{2,2-Dimethylbutane + 2,3-Dimethylbutane} \quad (25)$$

The formation of 2,2-di-methyl-propane from n-pentane is not included, due to the selectivity of currently available commercial catalysts which don't favour this reaction.

b. Secondary Reactions

Chloride promoter is injected into the isomerisation reactor. The perchloroethylene (C_2Cl_4) is injected on the reactor feed line at a temperature of at least 110°C. The C_2Cl_4 reacts with the hydrogen present in the reactor, in the presence of the catalyst (Pt/Al_2O_3-Cl), to form hydrogen chloride (Hamadi and Kadhim, 2017).

$$C_2Cl_4 + 5H_2 \xrightarrow{(Pt/Al_2O_3\text{-}Cl)} 4HCl + C_2H_6 \quad (26)$$

The hydrogen chloride formed in the reactor is separated from the isomerate, in the downstream stabiliser column, as off-gas. The off-gas is scrubbed with a caustic solution to form salt and water.

$$HCl + NaOH \longrightarrow NaCl + H_2O \quad (27)$$

3.7.3. Development of the Isomerisation Model

The isomerisation model was based on the 2 step transition from n-paraffins to i-paraffins. Olefins were formed as an intermediate product (Hamadi and Kadhim, 2017).

$$\text{n-Paraffin} \xrightarrow{K_1} \text{n-Olefin} \xrightarrow{K_2} \text{i-Paraffin} \qquad (28)$$

The following assumptions were made for reactor conditions:

a. Reactions are of first order occurring at steady state.
b. The reactions take place under isothermal conditions
c. Reactions occur in a gas phase
d. Reactor is controlled to maintain constant physical properties, with a negligible gradient in respective pressure drop, temperature and concentration.

The cross section of the packed bed reactor, from where the mass balance was developed, is illustrated in Figure 19.

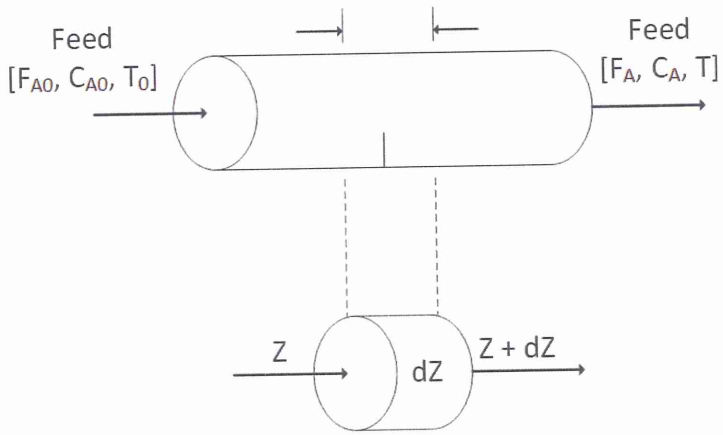

Figure 17: Packed Bed Tubular Reactor Cross Section (Folger, 2006).

Mass Balance:

$$C_{A0} = C_A + C_N + C_{ISO} \tag{29}$$

$$C_A = C_{A0}\, e^{(-K_1 t)} \tag{30}$$

$$C_N = \frac{K_1 C_{A0}}{K_2 - K_1}\left[e^{(-K_1 t)} - e^{(-K_2 t)}\right] \tag{31}$$

$$C_{ISO} = C_{A0}\left[1 - e^{(-K_1 t)} - \frac{K_1}{K_2 - K_1}\left[e^{(-K_1 t)} - e^{(-K_2 t)}\right]\right] \tag{32}$$

Design Equation for a tubular reactor:

$$V = F_{A0} \int \frac{dx}{-K_1 C_{A0}} \tag{33}$$

Reactant concentration of C_A in gas phase:

$$C_A = C_{A0} \frac{(1 - x)T_0}{(1 - \varepsilon x)T} \tag{34}$$

Where ε is the voidage in the reactor bed

Combining equation (34) into equation (33), and rearranging to solve for K_1 gives:

$$K_1 = \frac{F_{A0}}{VC_{A0}}\left[\ln\frac{1}{1 - x}(1 + \varepsilon) - \varepsilon x\right]\frac{T}{T_0} \tag{35}$$

Using the Arrhenius equation, below, the activation energy (E_{a1}) and frequency factor (K_0) was calculated.

$$\ln K_1 = \ln K_0 - \frac{E_a}{RT} \tag{36}$$

The values for K_1 were determined experimentally, at various temperatures within the operating range. The activation energy (E_{a1}) and frequency factor (K_0) was calculated graphically, by plotting $\ln K_1$ vs $\frac{1}{T}$. The reaction rate and conversion of n-paraffins to isomerate was calculated, using this data.

Chapter 4: Results and Discussion

4.1. Determination of Constants and Conversions

The results of the model, shown in equation (28), was used to calculate the isomerisation reaction rate constant. Using data from the Penex unit at the Daura Refinery in Baghdad, K_1 values was calculated for a temperature range of 120°C to 180°C, as shown in Table 10 (Hamadi & Kadhim 2017).

The conditions of the reactors investigated were as follows:

Catalyst volume per reactor = $35.66m^3$

Hold up = 75%

$\varepsilon = 0.393$

$T_0 = 50°C$

Table 10: Paraffins reaction rate constant (K_1), shown for various temperatures.

T(°C)	K_1 (h^{-1})			
	nC5	nC6*	nC6**	CH
120	0.398	0.241	0.056	0.289
135	0.413	0.25	0.058	0.3
150	0.429	0.26	0.06	0.311
165	0.444	0.269	0.062	0.322
180	0.459	0.278	0.065	0.333

Where: nC6* represents nC6 ⇋ 2, 2-Dimethylbutane at X=0.35 and
nC6** represents nC6 ⇋ 2, 3-Dimethylbutane at X=0.1

It can be seen, from table 10, that K_1 values increase as temperatures are increased. Values for ln K_1 and $\frac{1}{T}$ have been derived, using the data from Table 10, as shown in Table 19 in Appendix A.

The trend, shown in Figure 18, has been obtained from the data in Table 19, in Appendix A.

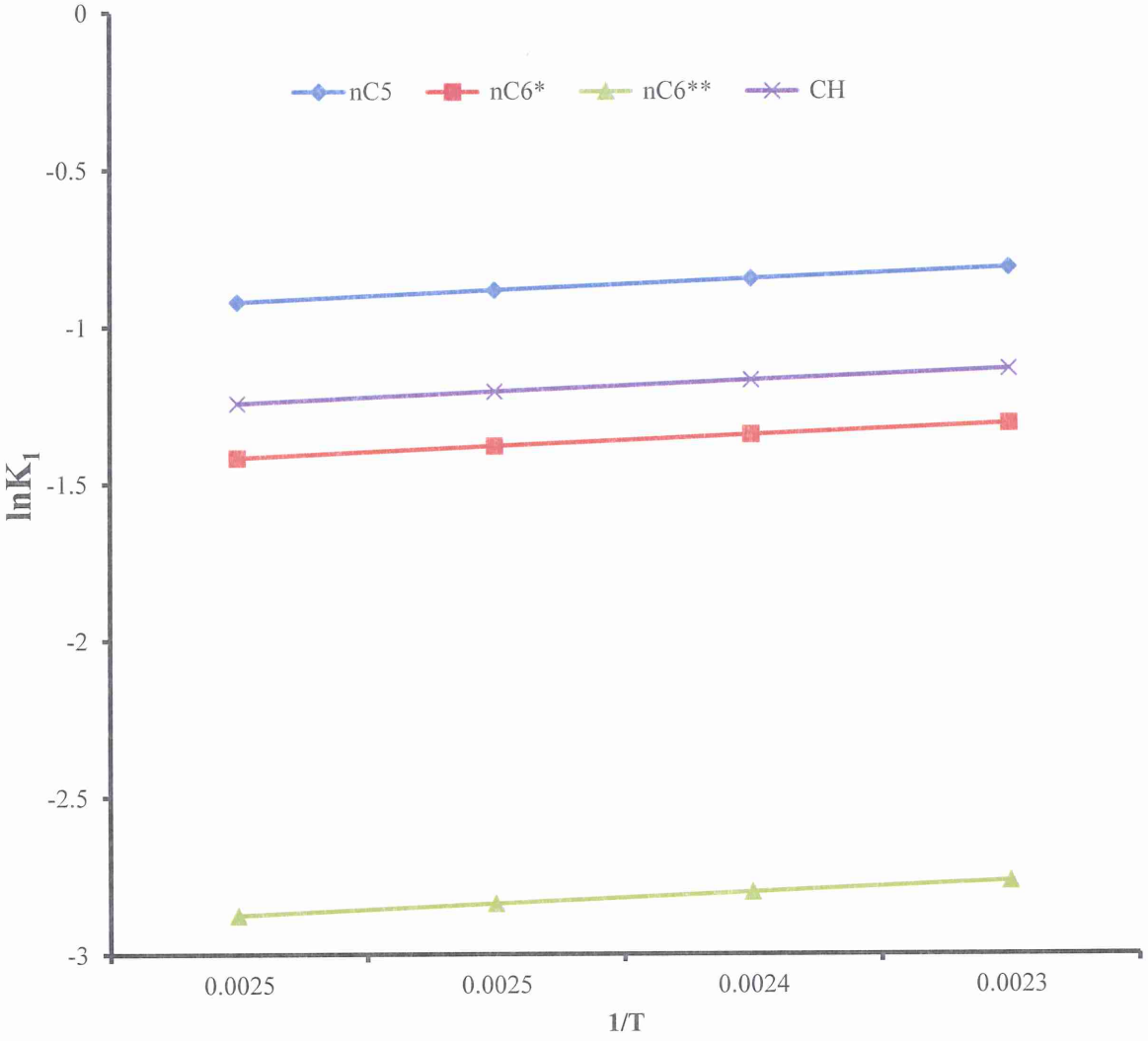

Figure 18: Relationship between reaction rate and temperature, plotted as ln K_1 vs 1/T (K^{-1}).

The activation energy (E_{a1}) and frequency factor (K_{01}) was obtained from the graph (Figure 18) and is shown in Table 11.

Table 11: Activation Energy and Ko_1 results.

Component	Ea_1 (KJ /mole)	Ko_1
nC5	2738.822	0.46
nC6*	1525.743	0.263
nC6**	1835.182	0.061
CH	2880.394	0.334

The results, from Table 11, show that: Ea_1 (nC6*) < Ea_1 (nC6**) < Ea_1 (C5) < Ea_1 (CH).

The values for rate constant K_2 were calculated, by applying equation (35). The following experimental data, from Daura Refinery in Baghdad, Iraq, was used as a basis:

LHSV = 1.5

Residence time, t = 1/LHSV = 0.667 h

The calculated values of rate constant K_2 are shown in Table 12.

Table 12: Olefins reaction rate constant (K_2), shown for various temperatures.

T(°C)	K_2 (h^{-1})			
	iC5	2,2-DMB	2,3-DMB	MCP
120	0.1547	0.2566	1.2062	0.0147
135	0.148	0.2477	1.1512	0.0124
150	0.143	0.2389	1.0998	0.0113
165	0.1384	0.2308	1.0529	0.0099
180	0.1346	0.2232	1.0099	0.0097

It can be seen from Table 12 that K_2 values decrease as the temperature increases. This indicates that isomerate concentration in the product stream is sensitive to the reaction temperatures. Values for $\ln K_2$ and $\frac{1}{T}$ have been derived, using the data from Table 12, as shown in Table 20 in Appendix A. The trend, shown in Figure 19, has been obtained from the data in Table 20 in Appendix A.

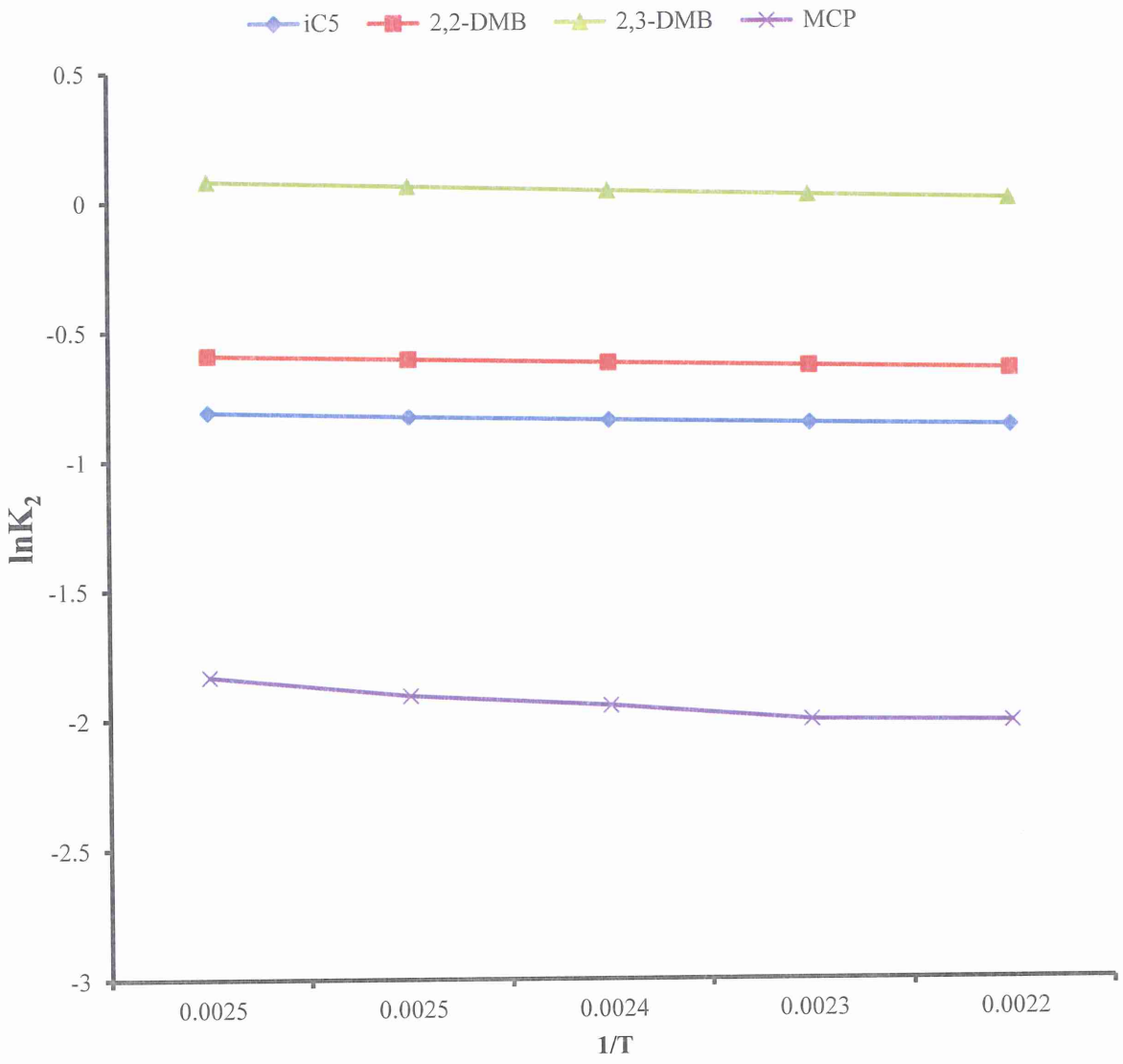

Figure 19: Relationship between reaction rate and temperature, plotted as ln K_2 vs 1/T (K^{-1}).

The activation energy (E_{a2}) and frequency factor (K_{02}) was calculated obtained from the graph (Figure 19) and is shown in Table 13.

Table 13: Activation Energy and Ko_2 results.

Component	Ea_2 (KJ/mole)	Ko_2
iC5	1.503	0.281
2,2-DMB	1.519	0.349
2,3-DMB	1.931	0.602
MCP	4.632	0.038

The results, from Table 13, show that: Ea_2 (iC5) < Ea_2 (2, 2-DMB) < Ea_2 (2, 3-DMB) < Ea_2 (MCP).

The Penex conversion for normal paraffins isomerisation, at equilibrium, is shown in Table 14.

Table 14: Penex Derived Isomerisation Conversions.

Reactions	Conversion (%)
nC5 ⇋ iC5	54
nC6 ⇋ 2,2-DMB	35
nC6 ⇋ 2,3-DMB	10
BZ+3H2 ⇋ CH	100
CH ⇋ MCP	59

4.2. Isomerisation Process Mass Balance

Honeywell UOP provided an isomerisation solution, based on required feed characteristics, of a 20tons per day unit. The performance of the quoted unit is shown in table 15.

Table 15: Process Performance of Honeywell UOP unit quotation.

Process	Isomerisation
Flowscheme	DIP / Isom / Super DIH
Isomerate RONC	90 to 92
Isomerate MONC	88 to 90
Isomerate Yield	98 to 100 LV%
Feed Requirements	Fully Hydrotreated
Catalyst Life	> 10 years

Applying the constants and resulting conversions for C5-C6 paraffins, available from the Sasolburg LT-FT process, the mass balance was determined for the Penex DIH derived isomerisation process. The results are shown in Tables 16 and 17. The total Isomerate feed was calculated from the given production rate, and is summed up from the results in the tables.

Total production = Distillate + Bottoms

= 19.58 tons/d + 0.42 tons/d

= 20.00 tons/d

Total feed required for a 20 tons/d unit = 20.15 tons/d

Table 16: Reactor and Stabiliser mass balance.

	Component	MW	Density (Kg/m3)	Reactor (tons/day) Fresh Feed	Hydrogen	Recycle	Raw Product	Stabilizer (kg/hr) Feed	Overheads	Bottoms
1	nC5	72	626	8.40	-	0.15	3.93	3.93	0.01	3.92
2	iC5	72	616	1.11	-	0.07	5.79	5.79	0.14	5.66
3	nC6	86	655	9.39	-	11.06	11.25	11.25	-	11.25
4	2,2-DMB	86	674	0.07	-	0.45	7.68	7.68	-	7.68
5	2,3-DMB	86	695	0.79	-	3.88	6.72	6.72	-	6.72
6	MCP	84	794	0.02	-	0.01	0.05	0.05	-	0.05
7	CH	84	778	0.37	-	0.10	0.45	0.45	-	0.45
8	H2	2	0.0899	-	0.000	-	0.000	0.000	0.000	-
9	HCl	36.5	1.63	-	-	-	0.005	0.005	0.005	-
10	NaOH	40	2130	-	-	-	-	-	-	-
11	NaCl	58.5	2165	-	-	-	-	-	-	-
12	H2O	18	1000	-	-	-	-	-	-	-
	Total			20.15	0.000	15.72	35.88	35.88	0.15	35.72

Table 17: Scrubber and De-isohexaniser mass balance.

	Component	MW	Density (Kg/m3)	Scrubber tons/day) Feed	Off-gas	Effluent	Deisohexanizer tons/day) Feed	Recycle	Bottoms	Distillate
1	nC5	72	626	0.01	0.01	-	3.92	0.15	-	3.77
2	iC5	72	616	0.14	0.14	-	5.66	0.07	-	5.59
3	nC6	86	655	-	-	-	11.25	11.06	0.03	0.16
4	2,2-DMB	86	674	-	-	-	7.68	0.45	-	7.23
5	2,3-DMB	86	695	-	-	-	6.72	3.88	0.00	2.84
6	MCP	84	794	-	-	-	0.05	0.01	0.04	-
7	CH	84	778	-	-	-	0.45	0.10	0.35	-
8	H2	2	0.0899	0.00	0.00	-	-	-	-	-
9	HCl	36.5	1.63	0.01	-	-	-	-	-	-
10	NaOH	40	2130	-	-	-	-	-	-	-
11	NaCl	58.5	2165	-	-	0.01	-	-	-	-
12	H2O	18	1000	-	-	0.01	-	-	-	-
	Total			0.15	0.15	0.02	35.72	15.72	0.42	19.58

4.3. Isomerisation Process Economics

The process economics of upgrading the octane number of paraffins for the fuels market was considered, in order to determine if the additional processing showed any financial benefit. This report focuses on the cost comparison of C_5-C_6 paraffins product in the chemicals market, to the cost of transforming this paraffins to a fuel. The cost of production was calculated by discounting the utility costs from the sales price of the product. Labour and maintenance costs were not included in the calculation. The price for each production process is calculated below.

4.3.1. Sales Price of Paraffins Product

The price of light naphtha (C_5-C_6 Paraffins) was accessed from Insider Incorporated. Product is valued at $ 550 per ton. (o) The price was averaged over the past year. Exchange rate of US Dollar to South African Rand is equal to R13.64/$ (SARB, 2018).

Revenue from Sale of C_5-C_6 Paraffin = Price x Production Rate

= ($550 x R13.64/$) (20.00 tons/d)

= R150 040.00 per day

4.3.2. Costing of Isomerised Paraffins

The Honeywell solution was chosen as the basis of this economic study, incorporating a de-isohexaniser (DIH) to recycle methyl-pentane and unconverted n-hexane to the reactor feed. Two reactors were used in series. As the catalyst ages the first reactor would be most affected. When the activity declines to a critical level, the catalyst would be replaced. The second reactor would be operated while the first reactor is decommissioned for the catalyst change. On returning the reactor with fresh catalyst to service, the valves are positioned so it acts as the second reactor. The former second reactor then, would be made the front reactor. The production costs, with details of

raw materials and utilities, are as noted in the PEP yearbook of 2018-Q2 (HIS Markit, 2018). The breakdown is shown in Table 18.

Table 18: Isomerisation Production Costs.

	Unit Cost	Unit Consumption per Tonne	Production Cost c/kg
Raw Materials			**64.06**
Catalyst, Isomerisation	2292.81 c/kg	0.00002 Tonne	0.05
Caustic Soda Beads	94.75 c/kg	0.00034 Tonne	0.03
Hydrogen	83.03 c/kg	0.01072 Tonne	0.89
Molecular Sieves	200.18 c/kg	0.00001 Tonne	0
Naphtha, Light (C_5-C_6)	60.35 c/kg	1.04548 Tonne	63.09
By-Product Credits			**-0.01**
Fuel Gas	9.48 c/kg	-0.00119 Tonne	-0.01
Utilities			**1.02**
Cooling Water	3.75 c/m3	2.77902 m3	0.01
Electricity	4.45 c/kWh	17.63698 kWh	0.08
Steam	1190.50 c/Tonne	0.781 Tonne	0.93
Total Cost of Production			**65.07**

Production cost of isomerisation, in Rand terms = Total cost of production x exchange rate

= (65.07c ÷ 100c/$) (R13.64/$)

= R8.88 per kg of isomerate produced

Total Cost of production = Cost per ton of production x production rate

= (R8.88/kg x 1000 kg/ton) (20.00tons/d)

= R177 600.00 per day

4.3.3. Operations Margin

The inland fuel price for 93 Octane fuel is listed as R15.24 per litre (CEF, 2018). The average density of isomerate, taken from Table 17, is equal to 653.855kg/m^3.

Therefore the volumetric production rate of isomerate = Density x production rate

$$= (653.855 kg/m^3 \div 1000 kg/ton)\ (19.73 tons/d)$$

$$= 13.077 m^3/d = 13077\ L/d$$

Thus the revenue from isomerate sale as a fuel = Fuel Price x isomerate production rate

$$= (R15.24/L)\ (13077\ L/d)$$

$$= R199\ 293.48/d$$

The operating margin is calculated as:

Operations Margin = Sales price – operating costs

$$= R199\ 293.48 - R177\ 600.00$$

$$= R21\ 693.48$$

Net gain from upgrading C_5-C_6 paraffins = Sale price of petrol – sale price of paraffins

$$= R199\ 293.48 - R150\ 040.00$$

$$= R49\ 253.48$$

4.4. Analysis of Project Outcomes

The FT wax value chain is focused primarily on hard wax production, being a highest margin product. Operating parameters of the processes within the value chain are adapted to maximise hard wax production. Paraffins are a by-product of hard wax production. The n-paraffins content, in the paraffins product, available in the market is now above 95%. Apart from hydrotreatment and fractionation, there is no other processing of paraffins to improve the purity of each fraction from the distillation section. The n-paraffins content is not enhanced within the paraffins plant. Azeotropic distillation would be needed to separate the iso-paraffins from the n-paraffins in order to improve the n-paraffins content, and thus improve the competitiveness of the product. The financial return on additional processing of paraffins for the chemicals market, may prove to be an impediment to the entire wax value chain.

This report has explored the repositioning of the paraffins product in the fuels market. Blending of paraffins in the fuel pool at refineries, is not a new concept. Refineries still blend paraffins into the fuel pool, to a limited extent. The limitation is the octane number of straight chain paraffins. It was seen, from Table 5, that the research octane numbers of n-pentane and n-hexane are 61.7 and 24.8, respectively. This is far from what is needed to meet the fuel standard. Low octane numbers in fuel leads to premature fuel ignition in the engine cylinders and thus resulting in engine knock. This phenomena is undesirable, as it may lead to engine damage and increased fuel consumption.

There are various methods available to improve the octane number of paraffins. These methods involve the rearrangement of the feed stream's molecules. These include polymerisation alkylation, isomerisation and reforming. The type of process employed will depend on the nature of the feed material. Catalytic polymerisation feedstock propylene, propene, and butylene. This feed is mainly available from the cracking process. The reaction is normally terminated to maintain liquid production for fuel. Alkylation uses similar feedstock, in combining molecules to form Octane. The advantage is that alkylation is more economical than polymerisation. Reforming is a widely used process in improving octane number. Heavy naphtha is generally fed to the reformers at refineries. Literature suggests that C_{7+} paraffins be reformed to increase its octane number. Isomerisation is the best option to improve octane number of C_5-C_6 paraffins. Isomerisation of C_{7+} paraffins lead to catalyst inhibition. This results from hydrocracking of C_{7+} molecules. The option

of diverting the C_7-C_{13} paraffins to a catalytic reformer is available. Further consideration should be given to determining a business case for directing the heavy paraffins, i.e. C_{14}-C_{20} fraction, to the catalytic cracker.

The C_5-C_6 paraffins composition is very good for isomerisation, with no heavy ends and naphthenic compounds. The average octane number of the isomerate increases as the concentration of branched paraffins increase. The main goal in designing the isomerisation process was to achieve the highest conversion of iso-paraffins from the available C_5-C_6 paraffins feed. There are many commercialised process schemes and catalyst options available, with each based on the acceptable isomerate quality. The ideal choice of catalyst would be based on its activity and operating temperature. The most favourable of the available catalyst is the chlorided alumina type. Aluminium chloride catalyst was used to isomerise Butane, Pentane and Hexane during World War II. The first application was in the production of high octane aviation fuel. Aluminium chloride combined with hydrogen chloride is widely used for low temperature processes. Aluminium chloride is volatile at commercial reaction temperatures and is somewhat soluble in hydrocarbons. Techniques must be employed to prevent its migration from the reactor. This catalyst is non-regenerable and is used either in a fixed bed or liquid contactor. The highest isomerate yield was obtained from chlorided alumina type, having highest activity while operating at the lowest reactor temperature. Active catalysts operating at high temperatures will lead to cracking. A further advantage is it being the most economical catalyst, even though the reaction system requires continuous dosing of the chloriding agent and a caustic scrubber. There are numerous reactor designs and process configurations which have been developed, as new catalysts were introduced. Fixed bed reactor technology has shown to maximise isomerisation and minimise cracking. The separation and recycle of normal paraffins to the reactor improves overall conversion to iso-paraffins. A process scheme with de-isohexaniser and de-isopentaniser produces the highest conversion to achieve higher octane numbers. Axens Ipsorb process technology provides the maximum recycle rate of unconverted paraffins, making use of a molecular sieve adsorption unit. The drawback is that the absorption material degrades with chlorided alumina catalyst.

The reaction rate for the conversion of normal paraffins to their intermediate olefins was observed to increase with temperature. However, it was also observed that the reaction rate decreased for

the conversion of the intermediate olefins to corresponding iso-paraffins. Using the observed temperature range of 120°C to 180°C, it was found that operating the reactor at 150°C provides optimum overall conversion from normal paraffins to iso-paraffins.

The octane achievable with a UOP Penex de-isopentaniser (DIP)/Super de-isopentaniser (DIH) scheme would be in the region of 91 to 91.5 octane number (RON). 92 Octane number (RON) may be possible at a push. Isomerate yields is shown to be about 99%. The isomerate produced from the n-paraffins feed, lies within the boiling range of petrol. Fuel octane can be boosted to 93 octane number (RON) with appropriate blending. The composition of the isomerate produced, shown in Table 26, is compliant with the clean fuels requirement, shown in Table 4. The positive operations margin of isomerising the C_5-C_6 paraffins fraction demonstrates the feasibility of the proposed process. The assumptions for operations margin does not include labour, maintenance and initial investment costs. The results confirm the benefits in increasing the octane number of paraffins, through isomerisation. According to available feed rates, it was deduced that a 20 ton per day isomerisation unit, available from Honeywell UOP will be able to deliver the required throughput of isomerate.

Chapter 5: Conclusion and Recommendation

8.1. Conclusion

It is concluded, that from the work done in this project that, high octane fuel production by upgrading low temperature Fischer-Tropsch paraffins is technically feasible, and is supported by a sound business case.

The nature of the paraffins feedstock, available for isomerisation, places the fuel product in a good position for compliance with the impending clean fuels legislation. FT derived paraffins, within the gas-to-liquid gas loop, are Sulphur free and contain no aromatics. The effects of toxic exhaust fumes and particulate matter on the health of populaces, have become a huge cause for concern. Vehicle exhaust emissions has been included as a major contributor to elevated greenhouse gas levels, which lead to accelerated climate change. Benzene is a known carcinogen. Most countries have regulated the composition of petrol and diesel, in one form or the other, so as to limit harmful exhaust emissions. Health concerns have guided legislation in the phase out of lead, minimisation of benzene, aromatics and olefin content in transportation fuel. The most notable environmental protection regulation, for emissions control, is the European emission standards. Oil refiners around the world are at various stages in upgrading technology, to align with the European Union (EU) Emissions Standard. South Africa is considering the implementation of the Euro V stage of the EU standard, in the near term.

Isomerised paraffins for the fuels market provides substantial returns. The value of fuel was seen to be higher than the equivalent value of paraffins. The returns, from supplying paraffins to the chemicals market, showed less value than that of the fuels market. The chemicals market requires and increased purity of n-paraffins content. Paraffins is a low value product at the tail end of the wax business. Additional installations would be needed, with increased operating costs, to increase the n-paraffins content. There would be no improvement in margins to justify the investment costs.

External factors have also favoured the use of clean burning fuels. The tax regime in many countries, by design, encourage the use of clean fuels. South African oil refineries will have to undertake major modifications to be compliant with upcoming clean fuels regulations. Vehicles with lower emissions carry a lower emissions tax, thus lowering its purchase price. Market demand

has increased for petrol powered vehicles. Emissions tax increases on diesel vehicles have discouraged potential buyers from purchasing diesel vehicles. Some vehicle manufacturers have even discontinued diesel options on certain models of cars. Engines in new model vehicles are designed with clean fuels in mind. Car maintenance service intervals are longer, for cars using clean fuels, thus increasing its economy.

Global energy demand is growing as developing countries' economies expand. India and China are the leading countries, whose economies are showing signs of robust growth. Transportation is fuelling the growth within the energy sector. The passenger vehicle market in developing countries is far from being saturated, while aviation fuel growth is also taking off. More people are joining the mainstream economy, with mobility becoming a priority to conduct business. The transportation of goods is increasing, as the belt and road initiative develops across Asia. Along with accelerated economic growth comes traffic congestion and, increased vehicle exhaust emissions. The availability of paraffins for fuels production would contribute to market demand being met. Renewable fuel technology has not developed far enough to be economically sustainable. The full business case for this technology, including the replacement cost over the lifecycle of the batteries, has not been tested as yet. Hybrid technology, using an internal combustion engine as back-up is becoming more mainstream. The infrastructure associated with recharging batteries is not fully set up, and is not a priority spending item in developing countries. The risk of running out of battery power would be limited, with an internal combustion engine used as backup. Fuel efficiency, with smaller sized engines in hybrid vehicles, has shown remarkable improvement.

The low octane number of paraffins, hinders it from being used directly as a fuel. The effect of using this directly as a fuel would be mechanical damage to vehicle engines. This report has demonstrated that this hindrance can be overcome by isomerising the produced paraffins. This work goes to show, that the paraffins produced at Sasol could be redirected from the chemicals market to the fuels market with an increase in octane number.

The work covered in this project did not cover the construction of the isomerisation unit and depreciation of assets. The costs of construction, of isomerisation unit, may seem to pose a shortfall to margins. The economics of the project, can be justified through a defined payback period.

8.1. Recommendations

I would recommend that LT-FT paraffins be upgraded for the production of high-octane fuel. Isomerisation proves to be the best method to improve the octane number of paraffins. Isomerisation is a fairly mature technology. The first commercial process of isomerisation dates back to 1930's. C_5-C_6 isomerisation was introduced in the late 1950's. As refiners optimise operations, isomerisation of light naphtha is showing improvement to sales margins. Isomerate, from C_5-C_6 paraffins, complies with Euro IV and Euro V regulations. Isomerisation of paraffins would be good a solution to satisfy premium fuel demand, in clean fuels mix. Isomerate growth has doubled as a result. Isomerisation is one of the most economic means for reducing Benzene content in fuel. Aromatics are saturated in the process.

Choosing the correct process configuration and catalyst type will enable sufficiently high octane fuel, by creating more branched paraffins. Research was conducted for the most active catalyst, highest conversion and highest RON isomerate, operating in a low temperature reactor. The C_5-C_6 fractions of paraffins, derived from the Sasol LT-FT process, is an ideal feed for isomerisation. The lack of Benzene and higher hydrocarbons enables optimum conversion in the isomerisation unit. The UOP Penex DIP/Super DIH process scheme, using chlorided Alumina catalyst, is the most appropriate option to upgrade the octane number of C_5-C_6 paraffins produced at Sasol. The results has shown the sensitivity of the isomerisation process to temperature control. I would also recommend a careful choice of operating envelope, for optimum fuel production.

The process economics underline the recommendation of transforming C_5-C_6 paraffins from a low value chemical to a high grade fuel. It would be in Sasol's interest to improve the octane number of C_5-C_6 paraffins and redirect this product into the liquid fuels market. A 20 ton per day isomerisation unit, available from Honeywell UOP will be able to deliver the required throughput of isomerate.

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APPENDIX A

RESULTS TABLES

The activation energy (E_1) would be determined by applying equation (36). The rate constant (K_1) for a range of temperatures (T), obtained from table 10, can be utilised to plot the graph of ln K_1 versus $\frac{1}{T}$. The slope of the graph would represent E_1. Table 19 shows ln K_1 values at corresponding values for $\frac{1}{T}$.

Table 19: Arrhenius plot data for paraffins conversion.

1/T	ln K_1			
	nC5	nC6*	nC6**	CH
0.0025	-0.9202	-1.4164	-2.8759	-1.2429
0.0025	-0.8828	-1.3789	-2.8385	-1.2055
0.0024	-0.8467	-1.3428	-2.8024	-1.1694
0.0023	-0.8118	-1.308	-2.7675	-1.1345

Similarly, the activation energy (E_2) can be obtained from an Arrhenius plot, using values from table 20. The K_2 values, for a range of temperatures, were extracted from table 12.

Table 200: Arrhenius plot data for paraffins conversion.

1/T	ln K_2			
	iC5	2,2-DMB	2,3-DMB	MCP
0.0025	-0.8106	-0.5907	0.0814	-1.8327
0.0025	-0.8298	-0.6062	0.0612	-1.9066
0.0024	-0.8446	-0.6218	0.0413	-1.9469
0.0023	-0.8588	-0.6368	0.0224	-2.0044
0.0022	-0.8711	-0.6513	0.0043	-2.0132