

Chapter 1

Introduction

1.1 Introduction

Living in a fast track modern world has urged societies to be highly dependent on automobile and air transportation. Most of this transportation involves the combustion of fuels such as gasoline, diesel or jet fuel to transport societies from one destination to another. During combustion, pollutants such as carbon monoxide (CO), hydrocarbons (HC) and nitrogen oxides (NO_x) are emitted [Moussavi et al., 1992] and these emissions are linked to chronic human health problems [Bleviss et al., 1990].

The environmental impact of auto emissions has led to stringent standards to improve air quality and protecting human health [Bartholomew et al., 2006].

The Euro 2, 4 and 5 international standards [SAPIA, 2008] for fuel specifications are used as a benchmark for fuel quality worldwide. South Africa has chosen to follow the European specifications of vehicle emissions legislation since Europe is an important source of vehicles for the national fleet [SAPIA, 2008]. The fuel specifications impose a restriction on the maximum allowable concentration of certain compounds in the petrol. The compounds: olefins, oxygenates and aromatics are the octane boosters of the fuel pool and play a major role in reformulating gasoline to reduce the auto emissions [Ozmen et al., 1993]. The fuel specifications, their purpose as well as their need to be controlled will be discussed in Chapter 2.

As a result, researching options for alternative components or alternative uses for existing processes are very important to continuously improve the octane number in the fuel pool. Processes such as catalytic cracking, hydrocracking, polymerization and isomerization are used to meet the demand for higher octane gasoline [Gary et al., 2004], which gives merit to the purpose of this particular study “Olefin skeletal isomerization of *n*-butene, *n*-hexene and *n*-octene using alumina-based catalysts”.

Two ways of increasing the octane numbers in the gasoline pool are the addition of oxygenates to the gasoline pool and the skeletal isomerization of olefins.

Skeletal isomerization of olefins is intended to increase the amount of feedstock used in the production of ethers, such as methyl tertiary butyl ether (MTBE), tertiary amyl methyl ether (TAME), ethyl tertiary butyl ether (ETBE) and tertiary amyl ethyl ether (TAEE) [Meyers, 1997].

Addition of oxygenates, such as ethers and alcohols, is the preferred way to add oxygen to the gasoline pool to increase the octane number of gasoline [Ozmen, 1993]. Common oxygenates added to gasoline are listed in Table 1.1.

Table 1.1
Oxygenates for Gasoline [Sheet, 2008]

Oxygenate	Formula	*MON	**RON	Oxygen Content (mass %)	Blending Vapour Pressure (kPa)
*** <i>iso</i> -octane	C ₈ H ₁₈		100		
Methanol	CH ₄ O	100	130	49.9	250
Ethanol	C ₂ H ₆ O	100	115	34.7	130
MTBE	C ₅ H ₁₂ O	100	110	18.2	55
ETBE	C ₆ H ₁₄ O	100	112	15.7	28
TAME	C ₆ H ₁₄ O	100	105	15.7	7

*MON (Motor Octane Number); **RON (Research Octane Number); ***Reference

Oxygenates are good sources of research octane number (RON) improvers as can be seen when compared to the RON of *iso*-octane (100). *iso*-octane is the standard reference point used for octane number [Gary et al., 2004] and some comparative values are shown in Table 1.1.

Methanol and ethanol have vapour pressures significantly higher than the set of ethers listed in Table 1.1. The volatile nature of ethanol causes the Reid vapour pressure (RVP) of a base fuel (with ethanol blended into it) to become too high [Gary et al., 2004]. The implication of the high RVP value is that the maximum fuel vapour pressure specification will be exceeded. The RVP specification is of utmost importance because the volatility influences the driveability index which is a measure of combustion properties and possible vapour lock formation in the vehicle fuel lines, as explained later in Chapter 2. In comparison, the vapour

pressures of MTBE, ETBE and TAME mixtures are considerably lower and make them more attractive as additives to gasoline.

The major advantages of increased amounts of ethers in the feedstock for gasoline production are [Leprince, 2001]:



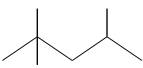
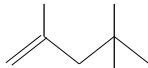
- an increase in octane number for unleaded gasoline;
- physical properties (e.g. density, energy content *etc.*) that are barely influenced by changing the hydrocarbon components (reducing benzene (aromatics) and replacing it with *iso*-olefins and ethers) of the gasoline pool which allows the blending of ethers without effecting the fuel performance;
- a decrease in the vapour pressures which allows more butane in the gasoline pool. Butane is usually added to the fuel since it is inexpensive and has a good octane quality component. Lower quantities of butane are used in the blends when alcohols are added. Thus, using a blendstock such as ethanol and methanol which raises the volatility is less attractive than using ethers [Minner, 1990]; and
- pollution control properties (less harmful to the environment) due to decreased amounts of aromatics.

The ethers are produced by reacting the *iso*-olefin with methanol. Mixtures of hydrocarbons that contain *iso*-olefins can serve as a feedstock to produce ethers [Dunning, 1953]. The amount of naturally occurring *iso*-olefins is too low to satisfy the resulting demand. To increase the *iso*-olefin content, normal olefins can be isomerized to *iso*-olefins to increase the overall yield of ether production [Meyers, 1997].

However, ethers, especially MTBE, are currently not favoured around the world since the discovery of MTBE groundwater contamination both in the United States of America (USA) and in Europe [Domokos, 2002]. MTBE was found in a number of groundwater areas, in the soil under several gasoline stations, in drinking wells, in lakes and in reservoirs. Statements were made that the MTBE leaked through damaged tanks, pipelines and it also leaked from two-stroke engines on motorboats and jet skis.

The second method through which the octane number in gasoline is increased is to skeletally isomerize the olefins to their branched isomers. Branched isomers of olefins have higher octane values and therefore increase the octane ratings of the olefin containing feedstocks [Dunning, 1953]. In Table 1.2 the relationship between Research Octane Number (RON) and hydrocarbon structure of 4 representative compounds are given as an example of Dunning's findings.

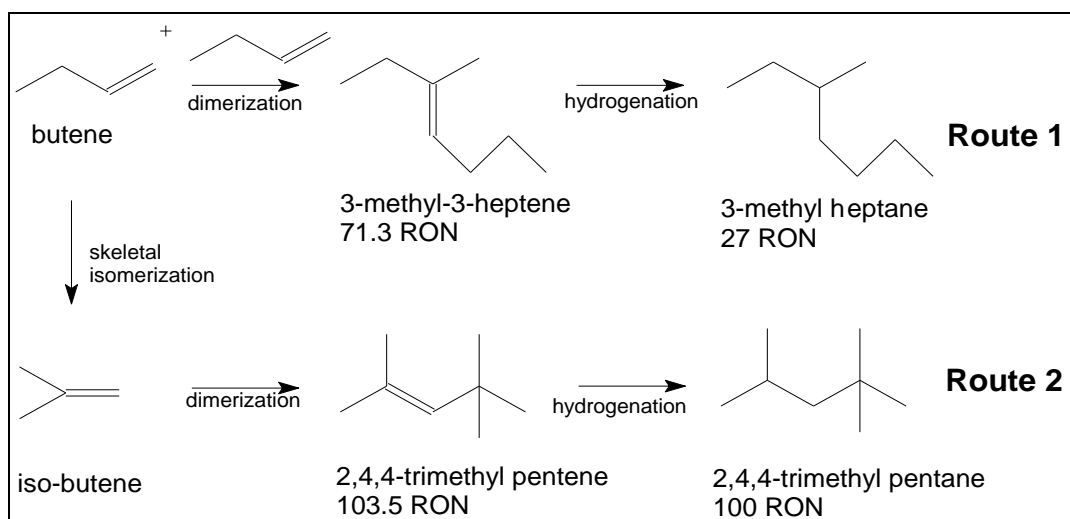
Table 1.2
Research Octane Number (RON) and structure of four hydrocarbon compounds

Research Octane Number (RON) Varies with Hydrocarbon Structure		
Compound	<i>n</i>-Octane	1-Octene
Formula	C_8H_{18}	C_8H_{16}
Structure		
RON	<0	28.7
Compound	2,2,4-Trimethyl-pentane (<i>Iso</i>-octane)	2,4,4-Trimethyl-1-pentene (<i>Iso</i>-octene)
Formula	C_8H_{18}	C_8H_{16}
Structure		
RON	100	106

Skeletal isomerization was developed to convert straight-chain hydrocarbon molecules such as octane, to branched-chain hydrocarbons such as *iso*-octane, in order to improve the octane number of a gasoline [Gary et al., 2004].

The schematic presentation, Scheme 1.1, indicates the significance of Research Octane numbers (RON) for different molecules and the reason behind the importance of skeletal isomerization.

For both routes described in Scheme 1.1, dimerization and hydrogenation occur. Hydrogenation removes the double bond. In route 2 it is shown that hydrogenation and dimerization *via* skeletal isomerization result in a RON of 100, compared to route 1 (without skeletal isomerization) which results in a RON of 27.



Scheme 1.1: Typical dimerization and hydrogenation routes with and without skeletal isomerization

Commercial technologies for butene skeletal isomerization include the Lyondell Isom Plus at Channelview, where butene olefin isomerization using a Ferrierite catalyst at temperatures between 340 °C and 440 °C was licensed by Shell [Tanabe et al., 1999]. Mobil Oil Corporation also patented a process for skeletal isomerization using medium pore zeolites, namely ZSM-23, ZSM-35 and ZSM-48 [Domokos, 2002].

No evidence of commercial technologies for the skeletal isomerization of hexene and octene could be found in literature.

1.2 Research aims

The main aim of this study is to investigate the olefin skeletal isomerization of different feedstocks, namely butene, hexene and octene into *iso*-olefins for the improvement of the RON in the refinery fuel pool.

The effects of different reaction conditions on the conversion of the selected olefins (butene, hexene and octene) over different catalysts (eta (η)-alumina, H-ZSM-5 and silicated alumina) will be investigated. All experiments will be performed at atmospheric pressure and a constant weight hourly space velocity (WHSV) of 5 h⁻¹, with temperature as the only variable (350 °C; 400 °C and 450 °C).

All the above experiments will be carried out using a fixed bed reactor. The effect of the different conditions and additions on conversion and selectivity will be determined.

1.3 Research objectives

The research objectives include:

- Setting up a suitable reactor system;
- Determination of the loading zone and the length of the catalyst bed within the reactor;
- Catalyst characterization using techniques such as thermogravimetric analysis, metal analysis, surface area analysis, pore volume analysis and surface acidity analysis;
- Product characterization using gas chromatographic analysis;
- Determination of the effectiveness of various alumina-based catalysts on the conversion and selectivity of olefin skeletal isomerization reactions of the selected compounds; and
- Reporting the influence of temperature variation (350 °C; 400 °C and 450 °C) on the performance of the different catalysts (eta (η)-alumina, H-ZSM-5 and silicated alumina).