CHAPTER 1. INTRODUCTION

1.1 GENERAL

Ever since hydrocarbons have been used as fuel for the internal combustion engine, an anti-knock additive to ensure uniform combustion of the fuel/air mixture, was sought. A large variety of materials were tested until in 1921, tetra ethyl lead was discovered. This compound was found to be a powerful anti-knock additive and has since been used extensively to increase the octane of the base fuels. In the late 1960s and early 1970s the environmentally polluting effects of auto emissions such as carbon monoxide, hydrocarbons, NO_x and poly-nuclear aromatics were recognised. This source of pollution was to be prevented by converting these compounds to CO_2, N_2 and H_2O by placing a suitable catalyst in the vehicle's exhaust system. As lead is a poison for these catalysts, the search for a suitable anti-knock compound was resumed. Amongst the materials that received attention were organic oxygen compounds such as alcohols and ethers. These oxygenate compounds, in addition to having octane-enhancing properties, represent avenues for the conversion of coal and biomass to liquid fuels. Hence, not only is an increase in the octane of the un-leaded base fuel achieved, but an increase in the availability as well. In the case of the alcohols, it was found that as the molecular mass increased, the octane number decreased. Hence, the lighter alcohols, such as methanol (RON = 133) and ethanol (RON = 130), were initially favoured. Methanol, however, is not soluble in gasoline at all concentrations and if the blend adsorbed even small amounts of water, as little as 500 to 700 ppm, phase separation occurs thus depriving the fuel of its anti-knock additive. To mitigate the effect of water on the blends, a co-solvent was required. Iso and tertiary butyl alcohol were eventually identified as suitable materials. Other problems associated with the alcohol fuel blends were not as easily overcome. It was found that when alcohols were blended with gasoline, changes occurred in the intake mixture stoichiometry and fuel properties. These changes altered the driveability, emission and reliability of existing motor vehicles and required the re-design of the existing fuel systems. Furthermore, the lower heat of combustion of the blends results in decreased fuel efficiency, of between 10 and 14 %. In addition, starting problems due to vapour lock caused by an increase in the Reid vapour pressure (RVP), and corrosion of the material used in the construction of fuel systems, were reported. An alternative anti-knock additive was thus sought.

The next group of compounds that were studied was the ethers. As was the case in the alcohols, it was found that for the ether to be effective as an anti-knock additive it had to have a low molecular mass, and more importantly, contain a tertiary carbon atom. Hence, methyl tertiary butyl ether (MTBE), RON = 118, ethyl tertiary butyl ether (ETBE), RON = 118, and methyl tertiary pentyl ether (TAME), RON = 111, are predominantly being used.

Using ethers as anti-knock additives increases the capability of the fuel blend to adsorb n-butane and other light hydrocarbons used to adjust the front-end octane of the fuel, without effecting the RVP or the ASTM distillation characteristics of the fuel. This property of the blend is just as important to the refinery industry, as is the increase in the anti-knock quality and the elimination of lead. Furthermore, ethers do not exhibit any of the negative properties that the alcohols do. They are completely miscible with gasoline at all concentration levels and the blend is not water sensitive. Also, since the mixture is not corrosive, it can be used in existing vehicles without any major modifications to their fuel systems being required, and it enhances engine efficiency during low speed acceleration. Furthermore, the ethers are no more toxic or anaesthetizing than ordinary un-leaded gasoline, and cause the emission levels of pollutants, in particular CO, to decrease.

To produce the desired tertiary ether, such as MTBE, is a relatively easy process and involves the condensation of isobutene with methanol. A variety of catalysts can be used, which include various porous crystalline silicates as well as the zeolites such as ZSM-5 and ZSM-11. Other suitable catalysts include Lewis acids such as aluminium trichloride and boron trifluoride, mineral acids such as sulphuric and hydrochloric acid, heteropoly acids of various metals and phosphoric acid. Furthermore, organic acids such as alkyl and aryl sulphonic acids and ion exchange resins, particularly macroreticular resins, are suitable. Ion exchange resins, namely Amberlyst 15 and Lewatit SPC 118 are used in most commercial applications for the manufacture of MTBE. The ion exchange resins are typically operated at temperatures below 100°C, above which the reverse reaction is favoured, and at pressures sufficient to maintain the reactants in the liquid phase. Under these conditions, only alkenes containing an olefinic carbon atom, one to which two alkyl groups are attached, will react with the alcohol while di-, alpha- and beta- olefins are inert. Hence, when using a mixture of alkenes high selectivities to the tertiary ether are obtained with the yield characteristically being in excess of 99 %. The limiting factor in the production of suitable tertiary ether such as MTBE or ETBE is the availability of the reactive alkenes, in particular isobutene. A detailed study of the availability and sources of isobutene is thus required.

1.2 SCOPE AND OBJECTIVES OF THIS INVESTIGATION

A detailed review of the literature was conducted. From this it became apparent that a number of industrial sources and multi-step processes, using a variety of feeds, for the production of isobutene were already available. One process which had not been commercialised was the single step skeletal isomerisation of the linear butenes to isobutene as part of a closed loop isomerisation/etherification plant. A more detailed study of the feasibility of this process was thus required.

After examining the thermodynamics of the skeletal isomerisation of the n-butenes to isobutene and briefly looking at possible side reactions, it was concluded that the process was indeed feasible, although the yield of isobutene per pass would be low. The reaction of the four isomers of butene for simple electrophilic addition type reactions such as etherification are vastly different, with isobutene being the only reactive isomer. Hence, the hydrocarbon products from an isomerisation reactor are suitable for use as feed to the etherification unit without extensive purification being required. The un-reacted butenes may again be recycled to the isomerisation reactor to ensure a high overall conversion and hence a high yield of the desired tertiary ether. In this way, although the conversion and yield of isobutene per pass through the skeletal isomerisation reactor may be low, a high yield of the desired tertiary ether can still be achieved. A detailed review of the literature showed that a number of catalytic systems had been studied, but that these and the information for use in the rigorous design of a skeletal isomerisation reactor, were not available. Against this background, the scope of the investigation may be defined.

Hence, the objective of this work was to identify, from a review of the literature, a catalyst suitable for the skeletal isomerisation of the n-butene to isobutene. This was done, and a sample of a proprietary, experimental catalyst obtained from a supplier of refinery technology. Next, using this material and a C4 stream produced via the Fischer Tropsch process, an operating procedure suitable for commercialisation was to be developed. The effects of the operating conditions and feed contaminants on the performance of the system were also to be quantified. The latter was to include an investigation as to the effects of recycling various components, as would be done in a closed loop isomerisation/etherification plant. The long-term stability of the system, when using a commercially representative feed, was also to be determined.

Using a fixed bed reactor system, a detailed kinetic investigation in an attempt to identify the reaction mechanism and to develop the intrinsic kinetic equation suitable for use in the rigorous design of the skeletal isomerisation reactor, was to be performed. The kinetic models required to describe both single step and multiple steps controlling the overall reaction rate were to be considered. The suitability of the fixed bed reactor system for the measurement of the intrinsic kinetics, and hence the complexity of the reactor model required, was to be investigated in detail. Of course, the necessary FORTRAN fixed bed reactor model was also to be developed.