

ETHERIFICATION OF SOME C₈-ALKENES TO FUEL ETHERS

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Abstract

Tertiary ethers are formed in a reaction between alcohols and alkenes. They are used in gasoline to enhance its burning and to reduce harmful exhaust emissions. They also have high octane rating, which is beneficial for gasoline blending. Regulations in regard to fuel composition and exhaust emissions are tightening and new, cleaner burning high octane gasoline components are of wide interest.

This work concerns the etherification of C₈-alkenes. Several C₈-alkenes were screened for their reactivity. Study of the properties of the resulting ethers showed that some of them are potential for gasoline blending. 2,4,4-Trimethyl pentenes were chosen for more detailed study in view of the availability of the feed stock in industrial scale and the promising properties of the resulting ether.

The reactivity of 2,4,4-trimethyl pentenes was tested with various alcohols. The marked effect of the alcohol on the reaction rate was attributed primarily to the polarity of the alcohol, which affects the adsorption of the components and the catalyst.

Compared with the ethers currently in commercial production, the C₈-alkenes are etherified rather slowly. A new catalyst was sought to enhance the reaction rate. Traditionally, etherification is catalysed by strong cation exchange resin beads, such as Amberlyst resins, but a novel fibrous Smopex-101 catalyst was found to be more active in the etherification of 2,4,4-trimethyl pentenes with methanol, evidently because diffusional limitations were less.

A kinetic model was developed for the etherification of 2,4,4-trimethyl pentenes with methanol for purposes of reactor design. Kinetic experiments were performed with Smopex-101 as catalyst. Before the kinetic studies, thermodynamic parameters were derived for the etherification reactions and for the isomerisation reaction between 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene.

The results of the kinetic modelling indicated that the adsorption of the alkenes was minor. The best models to describe the data were the Langmuir-Hinshelwood type model where the adsorption of alkenes is assumed to be negligible compared to other reactive components and the Eley-Rideal type model where alkenes are not adsorbed. Adsorption behaviour was different on the fibrous catalyst than on the ion exchange resins: ether was better adsorbed than alcohol on the fibrous catalyst, whereas alcohol is known to better adsorb than ether on the traditional ion exchange resin catalyst. The better adsorption of ether on the fibrous catalyst was attributed to the greater hydrophobicity of this catalyst.

Preface

The work for this thesis was carried out in the Laboratory of Industrial Chemistry, Helsinki University of Technology, and was funded by Fortum Oil and Gas Oy, formerly Neste Corp.

I wish to express my warmest thanks to Professor Outi Krause for her advice and continual support. The project members at Fortum Oil and Gas Oy, Smoptech Ltd. and the University of Joensuu are thanked for their co-operation. And many, many thanks to all colleagues in the laboratory for creating a pleasant working atmosphere and good team spirit. A special debt of gratitude is owed to Dr. Juha Linnekoski for practical advice that helped to get the work started and for his assistance in troublesome situations.

And finally, loving thanks to Kimmo and Katja for help and “help” and thanks for being there...

Espoo, March 2002,

Reetta Karinen

List of publications

This thesis is based on the following publications (Appendices I-VII), which are referred to in the text by their roman numerals.

- I R. S. Karinen, A. O. I. Krause, Reactivity of some C₈-olefins in etherification with methanol, *Appl. Catal. A* **188** (1999) 249-256.
- II R. S. Karinen, A. O. I. Krause, E. Y. O. Tikkanen, T. T. Pakkanen, Catalytic synthesis of a novel tertiary ether, 3-methoxy-3-methyl heptane from 1-butene, *J. Mol. Catal. A* **152** (2000) No 1-2, 253-255.
- III R. S. Karinen, A. O. I. Krause, A novel tertiary ether. Synthesis of 3-methoxy-3-methyl heptane from 2-ethyl-1-hexene and methanol, *Catal. Lett.* **67** (2000) 73-79.
- IV R. S. Karinen, A. O. I. Krause, K. Ekman, M. Sundell, R. Peltonen, Etherification over a novel acid catalyst, *Stud. Surf. Sci. Catal.* **130** (2000) 3411-3416.
- V R. S. Karinen, M. S. Lylykangas, A. O. I. Krause, Reaction equilibrium of the isomerisation of 2,4,4-trimethyl pentenes, *Ind. Eng. Chem. Res.* **40** (2001) 1011-1015.
- VI R. S. Karinen, J. A. Linnekoski, A. O. I. Krause, Etherification of C₅- and C₈-alkenes with C₁- to C₄-alcohols, *Catal. Lett.* **76** (2001) 81-87.
- VII R. S. Karinen, A. O. I. Krause, Kinetic model for the etherification of 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene with methanol, *Ind Eng. Chem. Res.* **40** (2001) 6073-6080.

Reetta Karinen's contribution to the appended publications:

- I, III, IV The author defined the research plan, carried out the experiments, interpreted the results and wrote the manuscript.
- II The author defined the research plan for the etherification part, carried out the etherification experiments and interpreted the results. She wrote the manuscript together with the co-authors.
- V The author defined the research plan, carried out some of the experiments and was the major contributor in the interpretation of the results and writing of the manuscript.
- VI The author defined the research plan, interpreted the results and wrote the manuscript together with the co-authors.
- VII The author defined the research plan, carried out some of the experiments, performed the modellings, interpreted the results and wrote the manuscript.

ETHERIFICATION OF SOME C₈-ALKENES TO FUEL ETHERS

ABSTRACT

PREFACE

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Publications I-VII

1. Introduction

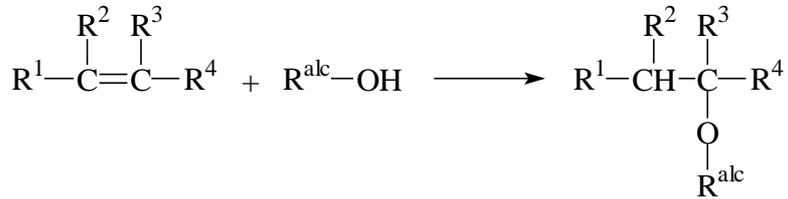
Our consciousness of the environment has been awakened in a dramatic way during the last few decades. In the case of road traffic, this has led to a focus on exhaust emissions and, in particular, on reducing them. The industrialised world has established regulations for the composition of fuel and harmful exhaust emissions as a means of ensuring reduced load to the environment.

The composition of fuel has changed tremendously, and also engine technology has played an important role in improvements related to combustion. At the same time the number of motor vehicles has increased rapidly world-wide and the cut-backs on harmful emissions have become of utmost importance. One of the major changes in gasoline composition has been the development of reformulated gasoline and the introduction of high-octane oxygen-containing compounds, known as oxygenates, into the gasoline pool. Oxygenates reduce the emissions of carbon monoxide and hydrocarbons by improving the combustion of the fuel. The first oxygenate, *tert*-butyl alcohol (TBA), was incorporated in gasoline in 1969, and the blending of the first tertiary ether, methyl *tert*-butyl ether (MTBE) was first commercialised in the United States in 1979 [1]. Oxygenates have been key components of reformulated gasoline, with MTBE and ethanol the two most widely used. The next step in the regulation of gasoline composition will be the reduction of the total aromatic and olefin (i.e. alkene) content to improve the gasoline quality and to further reduce harmful emissions.

1.1 Preparation and properties of tertiary ethers

Tertiary ethers are typically produced in liquid phase reaction under mild conditions with acid catalysts, mainly with strong cation exchange resins. Alcohol and alkene react to ether according to Scheme 1. The double bond in the alkene must be attached to a tertiary carbon atom. Elevated pressure is used to ensure that the reactants remain in the liquid phase at typical reaction temperatures, i.e. below 100°C. Tertiary ethers currently finding commercial use as gasoline components are MTBE produced from

isobutene and methanol, TAME (*tert*-amyl methyl ether) produced from isoamylenes and methanol, and ETBE (ethyl *tert*-butyl ether) produced from isobutene and ethanol.



Scheme 1. Formation of tertiary ether from alkene and alcohol. R¹, R² and R^{alc} are alkyl groups, R³ and R⁴ alkyl groups or hydrogen atoms.

One of the most useful properties of oxygenates is their high octane rating. Oxygenates are one of the few high octane alternatives to aromatics in gasoline [1]. Octane numbers, which represent the antiknock properties of components, are presented in Table 1 for the most common oxygenates.

Table 1. Octane numbers, blending vapour pressures, and water solubilities of the most important oxygenates [1-3]. RON = research octane number, MON = motor octane number

	RON	MON	Blending vapour pressure, bar	Water solubility, wt-%
methanol	133	99	5.2	miscible
ethanol	130	96	1.5	miscible
TBA	105	95	1.0	miscible
MTBE	117	101	0.55	4.3
ETBE	118	101	0.28	1.2
TAME	112	98	0.14	2.0

The vapour pressure, also included in Table 1, affects the volatility of the gasoline: the lower the vapour pressure the lower the emissions caused by evaporation of the gasoline. In this respect, tertiary ethers are far more suitable oxygenates for gasoline

than are alcohols. Ethers are also photochemically much less reactive than most gasoline hydrocarbons [4]. Water solubility is an important property where storage of the fuel is of concern.

1.2 Fuel oxygenates

1.2.1 MTBE

The use of MTBE has grown tremendously over the last decades, but the future is uncertain. Recently MTBE has gained considerable negative publicity. After it was detected in ground water in California, the state government passed legislation [5] that prohibits its use in California by the end of the year 2002. California presently accounts for over one third of the MTBE consumption in the United States [6]. Attempts are now being made to replace MTBE with ethanol in order to maintain the oxygen level in the gasoline. No plans exist to eliminate the use of MTBE in Europe [7]. Instead, Europe is moving to reduce aromatics in gasoline from 45 to 35% by volume in 2005, which may even increase MTBE consumption [8].

Unlike other gasoline components, MTBE is highly soluble in water. With a solubility of 4.3 wt-% [1], it is tens of times more water-soluble than any non-oxygenate component of gasoline. Once it gets into the ground, MTBE travels through the soil into ground water, where it is easily detected even at very low concentrations owing to its distinctive taste and odour. Leaking storage tanks were the main source of the MTBE in soil and ground water in California. The poor condition of the tanks was known earlier, but MTBE was the first major disaster to arise due to the leaking tanks. The situation is better in Europe because double-walled storage tanks are common [9].

MTBE degrades in sunlight, but very slowly or scarcely at all in soil or ground water [9]. As MTBE is a relatively new component in the ecosystem, microorganisms have not yet developed the capability to break it down. Recently, however, a microbe was

developed [10] which is able to eliminate MTBE from soil and ground water on laboratory scale, and encouraging results have also been obtained on larger scale [11].

The US Environmental Protection Agency, EPA, has examined MTBE as a potential carcinogen, but recently it was decided that MTBE should not be classified as a human carcinogen [12]. The health effects of MTBE continue to be somewhat obscure. However, we must bear in mind that some other components of gasoline have been proven far more toxic than MTBE is even suspected of being. For example, MTBE has replaced lead components and, in part, benzene, both of which are known to be toxic and hazardous for human health.

1.2.2 Ethanol

In some parts of the world ethanol is being used in the gasoline pool, either as fuel, as in Brazil, or as a fuel component, as in some parts of the United States. Ethanol can also be exploited in gasoline in the form of tertiary ethers. ETBE, which is produced from ethanol and isobutene, is already commercially used as a gasoline component [13].

Ethanol can be produced from biomass, such as corn, grain and even agricultural waste [14], and renewable stock can thus be introduced into fuels. In renewable fuels the carbon originates from biomass and does not add to carbon dioxide emissions in the way that fossil fuels do. Since carbon dioxide is a greenhouse gas, this carbon cycle of renewable fuels helps in preventing the accumulation of CO₂ in the atmosphere that leads to the greenhouse effect.

The blending vapour pressure of ethanol is quite high, however (see Table 1). Hence, increasing the ethanol content in gasoline without other modifications of the gasoline composition leads to greater hydrocarbon emissions and higher ozone-forming potential [15]. Furthermore, ethanol in gasoline has a strong tendency to pick up water and any contaminants suspended in the water, which creates difficulties in blending and

storing the gasoline [15]. Furthermore, at low temperature the separation of the organic and water phases poses a risk [2]. The infinite water solubility of ethanol could create a similar problem that created by MTBE if it were to leak from underground gasoline storages.

1.2.3 Other tertiary ethers

When the molecular size of tertiary ethers increases, the water solubility decreases [1], as can be seen from Table 1. Thus when moving from MTBE to higher ethers, the problem with water solubility becomes less serious. At this moment, TAME and ETBE are the largest ethers incorporated in gasoline.

Many larger ether molecules have been studied, e.g. the ethanol-based tertiary ethers *tert*-amyl ethyl ether (TAEE) and *tert*-hexyl ethyl ethers (THEE) [16-21]. The etherification of C₄- and C₅-alkenes with higher alcohols has also been studied, mainly with propanols and butanols [22-27] but also with C₅- to C₁₄-alcohols [28]. Some ether compounds have been tested for their antiknock properties and found suitable for gasoline blending in this respect; these include methyl *tert*-hexyl ether and methyl *tert*-heptyl ether [29], and methyl *tert*-octyl ether and 3-methoxy-camphene [30].

1.2.4 Other compounds

Although ethers and alcohols are the only oxygenates currently used in gasoline, several other oxygen-containing components have been screened, and also some non-oxygen-containing components have been tested, for their potential use in gasoline. Furan derivatives and *p*-cresol have been found to exhibit enhanced antiknock properties and to reduce emissions of hydrocarbons and carbon monoxide [31]. As well, amines, phenols, formamides and terpenes have been tested for their octane numbers [30]. In particular, dipentene and *N-tert*-butylfurfurylamine are regarded as

promising gasoline components because of their high octane rating and reduced exhaust emissions.

1.3 Aim of this work

This work involved the etherification of C₈-alkenes which, to the best of our knowledge, had not earlier been studied in detail. The properties of the ethers were investigated to determine whether they would be suitable components for gasoline. The aim was to produce ether compounds with high boiling point and octane rating, which could be used in the gasoline pool to replace aromatics and olefins whose amounts will be limited by new regulations [32]. The primary goal was to study the ethers with the view to their use as fuel components, but these components have also been proposed for use as low volatility solvents in paints, inks and lacquers [33].

Etherification of the C₈-alkenes is described in detail in the appended papers: the reactivity of 2,4,4-trimethyl pentenes and 2-methyl heptenes in etherification with methanol is described in paper I and the reactivity of 2-ethyl-1-hexene in etherification, which is reported for the first time in the literature, in papers II and III. The 2,4,4-trimethyl pentenes were chosen for more detailed study, because the ether obtained from them has properties that make it suitable as a gasoline component. The isobutene feed stock used for the now threatened MTBE production could be diverted to the production of these alkenes.

Paper V presents thermodynamics of the isomerisation between 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene, and paper VI compares the role of various alcohols in etherification. To enhance the etherification rate a novel fibrous etherification catalyst is introduced in paper IV and its performance is compared with that of a traditional etherification catalyst, Amberlyst 35 ion exchange resin. A kinetic model for the etherification of 2,4,4-trimethyl pentenes with methanol, presented in paper VII, was developed with the fibrous Smopex-101 catalyst. The model can be exploited in the design of a suitable reactor configuration.

2. Experimental

2.1 Reactor

The experiments were carried out in an 80-cm³ stainless steel batch reactor equipped with a magnetic stirrer and a mixing baffle. The reactor was placed in a water or oil bath to adjust the temperature of the reactor to 50–110°C. Reaction pressure was maintained at 0.8 MPa with nitrogen to ensure that the reaction mixture remained in the liquid phase. Liquid samples were taken manually via a cooled sample valve.

Samples were analysed with a Hewlett-Packard 5890 Series III gas chromatograph equipped with a capillary column DB-1 (J&W Scientific, length 60 m, film thickness 1.00 µm, diameter 0.250 mm) and a flame ionisation detector. The products were quantified by the internal standard method.

2.2 Chemicals and catalysts

The alkenes used in this work were a mixture of 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene (diisobutylene, Fluka Chemica AG, 95%, molar ratio of isomers was approximately 3.5), 2,4,4-trimethyl-1-pentene (Fluka Chemica AG, >98%), 2,4,4-trimethyl-2-pentene (Fluka Chemica AG, >98%), 2-methyl-1-heptene (Aldrich, 99%), 2-methyl-2-heptene (Aldrich, 98%), a mixture of 2-methyl-2-butene and 2-methyl-1-butene (Fluka Chemica AG, 90.5% 2-methyl-2-butene), 2-methyl-1-butene (Aldrich, >99%) and 2-ethyl-1-hexene, which was synthesised at the University of Joensuu, Finland. 2-Methoxy-2,4,4-trimethyl pentane for the ether decomposition experiments was supplied by Fortum Oil and Gas Oy, Finland.

In most of the etherification experiments the alcohol was methanol (Riedel-de Haën, >99.8%). In study [VI] also ethanol (99.5%, Primalco Oy), 1-propanol (99.5%, Riedel-de Haën), 2-propanol (99.99%, Fisher Scientific), 1-butanol (99.5%, Riedel-de Haën),

isobutanol (2-methyl-1-propanol, 99%, Riedel-de Haën), and 2-butanol (>99%, Riedel-de Haën) were used.

Isooctane (2,2,4-trimethyl pentane, Merck, >99.5%) was used to dilute the reaction mixtures. In addition, toluene (Riedel-de Haën, >99.7%) was used in the 2-ethyl-1-hexene experiments as a solvent.

The catalysts were commercial ion exchange resins Amberlyst 35Wet (Rohm & Haas, in I-VI), Amberlyst 15 (Rohm & Haas, in VI) and fibrous Smopex-101 (Smopetech Ltd., in IV and VII). Amberlyst catalysts were placed in the reactor in a metal gauze basket and Smopex-101 was used as slurry. In experiments with the fibrous Smopex-101 catalyst, a filter was placed in the sample line of the reactor to keep the fibres in the reaction mixture. The acid capacities of Amberlyst 35 and 15 were 5.2 and 4.7 mmol/g, respectively, and various capacities (1.0-4.0 mmol/g) were used with Smopex-101.

2.3 Experiments

Two kinds of experiments were performed within this study. Etherification experiments were carried out between alkene and alcohol and separate alkene isomerisation experiments were carried out where no alcohol was present. All the C₈-alkenes were tested with Amberlyst 35 ion exchange resin catalyst. The fibrous Smopex-101 catalyst was used with the 2,4,4-trimethyl pentenes. The experiments performed with the different reactants are presented in Table 2.

Table 2. Experiments performed with the various reactants

Reactants	Experiments		Catalyst	
	etherification	isomerisation	Amberlyst 35	Smopex-101
2,4,4-trimethyl-1-pentene (TMP1)	x	x	x	x
2,4,4-trimethyl-2-pentene (TMP2)	x	x	x	x
mixture of TMP1 and TMP2	x		x	x
2-methyl-1-heptene (2M1H)	x	x	x	
2-methyl-2-heptene (2M2H)	x		x	
2-ethyl-1-hexene (2E1H)	x	x	x	
2-methoxy-2,4,4-trimethyl pentane (ether)	x			x

2.4 Calculations

Conversions, selectivities and reaction rates were calculated on a molar basis. The conversions were calculated with respect to alkenes. “Isomerisation” means the double bond isomerisation of alkenes unless otherwise stated. Contact time, which is defined as time multiplied by the mass of dry catalyst in the experiment, was used to eliminate the variation in results originating from the slightly different amounts of catalyst in each experiment.

The properties of the Amberlyst 35 and Smopex-101 catalysts differ, as will be explained in section 5. Thus, in order to obtain comparable results, the time was scaled with the acid capacity of the catalyst. This capacity-based contact time is defined as

time multiplied by the total amount of acid equivalents in the catalyst, as explained in paper IV.

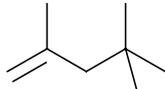
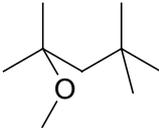
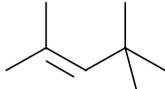
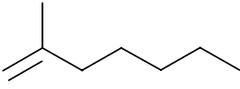
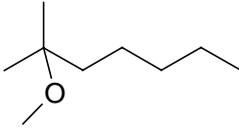
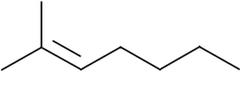
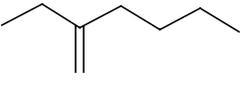
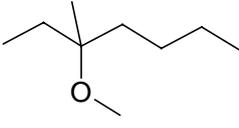
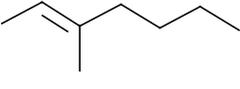
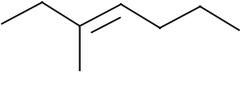
Initial rates are interpolated from the curves of molar amount of ether or alkene formed as a function of contact time. Activation energies are calculated from the initial rates according to the Arrhenius' equation.

Owing to the high non-ideality of the reaction mixture activities were used instead of concentrations in the thermodynamic calculations and in the estimation of the kinetic parameters. Activities were calculated by the UNIFAC method [34].

3. Reactivity of C₈-alkenes in etherification with methanol

The alkenes whose reactivities were tested are listed in Table 3. The table also presents the respective methyl ether products. Alkenes were pure components and, in addition, the thermodynamic equilibrium mixture of alkenes was used in the case of 2,4,4-trimethyl pentenes and 2-ethyl-1-hexene isomers.

Table 3. Alkenes and the respective methyl ethers

Alkenes	Ether
 2,4,4-trimethyl-1-pentene (TMP1)	 2-methoxy-2,4,4-trimethyl pentane
 2,4,4-trimethyl-2-pentene (TMP2)	
 2-methyl-1-heptene (2M1H)	 2-methoxy-2-methyl heptane
 2-methyl-2-heptene (2M2H)	
 2-ethyl-1-hexene (2E1H)	 3-methoxy-3-methyl heptane
<i>and the following isomerisation products:</i>	
 3-methyl-2-heptene (E- and Z-isomers)	
 3-methyl-3-heptene (E- and Z-isomers)	

3.1 Comparison of reaction rates

The two main reactions observed in the experiments were the etherification and isomerisation of alkenes. Double bond isomerisation was detected with all alkenes of Table 3, but isomerisation could not be detected in the experiments with the thermodynamic mixtures of 2,4,4-trimethyl pentenes and 2-ethyl-1-hexene isomers. Some isomerisation, which re-established the ratio of the alkenes, can nevertheless be presumed to have occurred; for the etherification probably did not consume the isomers in the same proportion and the equilibrium ratio of the alkenes was re-established through isomerisation [I]. Hydration of alkene to tertiary alcohol and dehydration of methanol to dimethyl ether were detected as side reactions.

3.1.1 Etherification

Etherification and isomerisation are competing parallel reactions and in most cases etherification was the main reaction. Table 4 presents the initial rates of etherification and isomerisation of the individual alkenes in experiments carried out with stoichiometric feed of alkene and methanol. Isomerisation was faster than etherification only with TMP2 and 2E1H. When the methanol:alkene ratio was increased in the 2E1H experiments, etherification overtook isomerisation [III].

Table 4. Initial rates in etherification experiments at 80°C with stoichiometric feed

Alkene	Initial rate, mmol/(s kg _{cat})	
	etherification	isomerisation
2,4,4-trimethyl-1-pentene	0.24	0.06
2,4,4-trimethyl-2-pentene	0.76	1.32
2-methyl-1-heptene	0.82	0.49
2-methyl-2-heptene	0.13	0.03
2-ethyl-1-hexene	1.77	1.92

As can be seen from Table 4 the total reaction rate was highest for 2E1H. Among the 2,4,4-trimethyl pentenes the reaction of the β -alkene (TMP2) was faster, and among the 2-methyl heptenes the α -alkene (2M1H). Typically in reactions of this kind of alkene the α -form is more reactive [35]; the higher reactivity of the β -form of 2,4,4-trimethyl pentenes can be attributed to the highly branched and sterically hindered structure [I, V], as will be explained in section 6.1.

3.1.2 Isomerisation

When no methanol was present in the reaction mixture isomerisation was the only main reaction and the total alkene consumption was faster than in the presence of methanol. Table 5 compares the initial rates of total alkene consumption in the etherification and isomerisation experiments, i.e. in experiments with and without methanol.

Table 5. Comparison of initial consumption rates of reactant alkenes with methanol (etherification experiments) and without methanol (isomerisation experiments) at 80°C

Alkene	Initial rate of alkene consumption, mmol/(s kg _{cat})	
	with methanol	without methanol
2,4,4-trimethyl-1-pentene	0.3	4.1
2,4,4-trimethyl-2-pentene	2.0	7.0
2-methyl-1-heptene	1.3	10.3
2-methyl-2-heptene	0.2	not measured
2-ethyl-1-hexene	4.0 *	39.2

*) includes formation of tertiary alcohol and is therefore higher than the sum of rates in Table 4

In the experiments where methanol was present the alkene was consumed mainly in etherification and isomerisation. Where methanol was not present, oligomerisation of the alkenes occurred in addition to isomerisation, but the initial reaction rate was due to isomerisation alone. Methanol inhibits the reactions of alkenes [36, 37] and, indeed, the

total reaction rate of the alkenes was very much slower in the presence of methanol, as clearly observed in Table 5, and furthermore, oligomerisation was not observed in any experiment where methanol was present. This inhibitory effect of methanol on the reactivity of alkenes is discussed in detail in section 4.

The isomerisation of the alkenes in the absence of methanol is compared in Figure 1. In each case, isomerisation was the main reaction until the thermodynamic composition was approached. As the isomerisation began to slow down, the rate of oligomerisation increased, but the oligomerisation reaction was slow compared with the isomerisation. In the case of trimethyl pentenes, as the reaction proceeded, isomerisation of methyl substituents occurred as well, but this reaction was slow compared to double bond isomerisation. Evidently, among the C₈-alkenes studied the more branched molecules (2,4,4-trimethyl pentenes) react more slowly in isomerisation than do the more linear molecules, but the reason is not purely structural. Thermodynamics also plays a limiting role: the last data points of Figure 1 approach the thermodynamic equilibrium conversion of each alkene, and in the case of 2E1H and 2M1H the equilibrium conversion is higher than with the trimethyl pentenes.

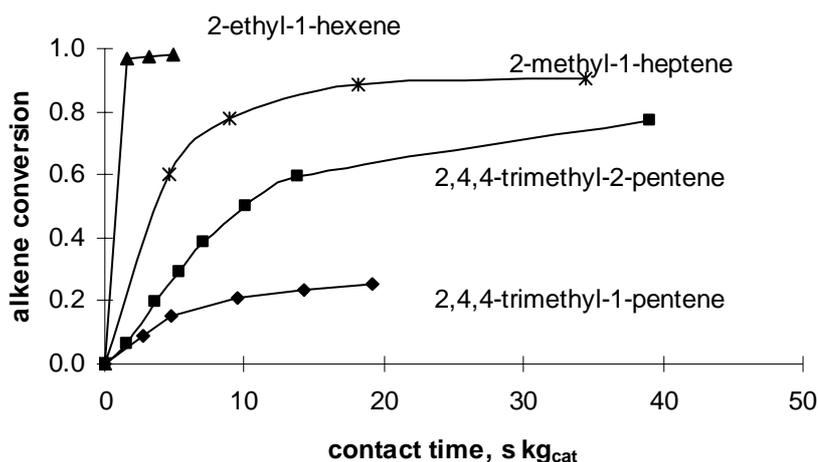


Figure 1. Comparison of conversions of alkenes in isomerisation experiments at 80°C.

The considerable difference between the reactivities of TMP1 and TMP2 is due, at least in part, to thermodynamics: the equilibrium between the isomers favours the α -form (TMP1) and thus the equilibrium conversion is much lower for the isomerisation of the α -alkene than the β -alkene (TMP2) [I, V]. The isomerisation of α -alkene thus ceases at quite an early stage of the reaction, and thereafter the conversion is mainly due to oligomerisation.

3.2 Activation energies of the etherification reactions

Apparent activation energies, which describe the temperature dependency of the etherification reaction, were determined for the formation of the methyl ethers [I, III]. Activation energy can also be used as a measure of the internal diffusion resistances: the apparent activation energy is lower when diffusion is limiting the reaction than it is in a diffusion-free situation [38]. The calculated values for the apparent activation energies of the studied alkenes are presented in Table 6.

Table 6. *Apparent activation energies for the ether formation and isomerisation with Amberlyst 35 catalyst*

Alkene	$E_{a, \text{ etherification}}$ kJ/mol	$E_{a, \text{ isomerisation}}$ kJ/mol
2,4,4-trimethyl pentenes [I]	60-65	not applicable
2-methyl-1-heptene [I]	90	108
2-ethyl-1-hexene [III]	85	88

As seen in Table 6, the activation energies for the ether formation vary significantly. The values obtained for the etherification of 2M1H and 2E1H correspond well with the values obtained for the formation of other tertiary ethers (see Table 7), but the values for the etherification of 2,4,4-trimethyl pentenes are clearly lower, indicating the existence of diffusional limitations. Indeed, a comparison of the structures of the alkenes shows that 2,4,4-trimethyl pentenes are the most highly branched alkenes of the

study and, owing to their structure, one would expect them to encounter mass transfer limitations (see Table 3 for structures). The activation energies for the isomerisation, in turn, are in very good agreement with the values presented for similar kinds of isomerisation reactions in Table 7.

Table 7. Activation energies of similar kind of reaction systems

	Reaction	Activation energy, kJ/mol
Etherification reactions	Formation of ETBE [39]	82
	Formation of TAME [40]	84-92
	Formation of THEE [20]	93-109
Isomerisation reactions	C ₅ -alkenes [41]	91
	C ₆ -alkenes [20, 21]	89-96

3.3 Properties of the ethers

The ethers were distilled at atmospheric pressure to determine their boiling points. The results presented in Table 8 show that the boiling point range of the ethers is similar to that of heavy aromatic compounds in gasoline. If the amount of aromatics in gasoline is reduced as required by the new regulations, these ethers could become useful additives to the gasoline pool, to maintain the boiling point distribution of the gasoline [29].

Table 8. Boiling points of the ethers

	Boiling point, °C
2-methoxy-2,4,4-trimethyl pentane	148
2-methoxy-2-methyl heptane	162
3-methoxy-3-methyl heptane	156

Water solubility and blending octane numbers were determined for 2-methoxy-2,4,4-trimethyl pentane. Water solubility was 0.014 wt-%, which is very low compared with

that of MTBE (4.3 wt-%), and even lower than that of toluene and benzene (0.05 and 0.18 wt-%, respectively [42]). Thus the problems encountered with MTBE are not expected with this ether. The blending motor octane number was 99 and the blending research octane number 110 [VII]. These values are very similar to those of commercially produced TAME, so that in this respect the compound is highly suitable for incorporation in gasoline.

3.4 Components for further study

With the problems being encountered with MTBE and the decision to cut down its production in the USA, a new use needs to be found for the existing MTBE plants and isobutene feed stock. A number of alternatives exists for producing gasoline components from isobutene as presented in Figure 2.

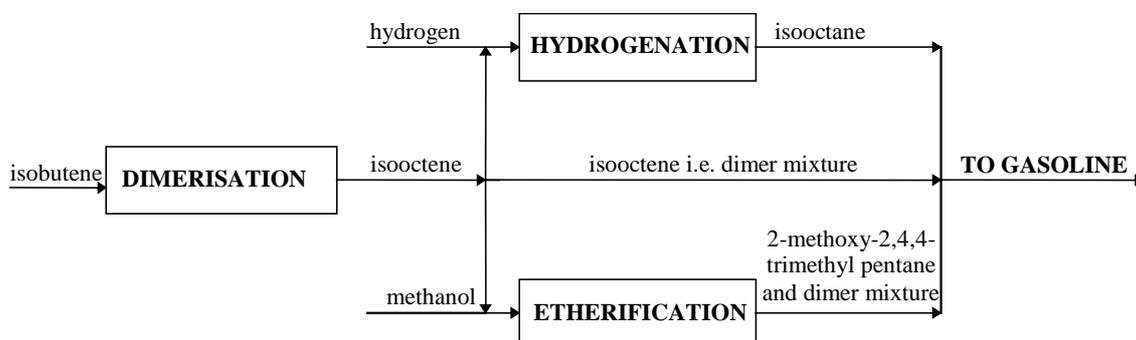


Figure 2. Scheme for producing high octane gasoline components from isobutene via dimerisation.

Some companies have already announced plans for processes to produce isooctane from isobutene [43-45]. The isobutene is first dimerised to isooctene, which is thereafter hydrogenated to isooctane. The main isomers of isooctene are TMP1 and TMP2. With its high octane rating (RON 100, MON 89), the dimeric stream itself is suitable for the gasoline pool [46], as long as the upper limits for the olefin (alkene) content are not exceeded. The third alternative, illustrated in Figure 2, is the

etherification of the dimeric stream, TMP1 and TMP2, to the corresponding ether. All three product streams have octane ratings that make them suitable for blending in the gasoline pool.

The availability of suitable isobutene feed stock to produce trimethyl pentenes and the suitable properties of the methyl ether suggested the choice of trimethyl pentenes for further testing.

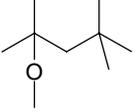
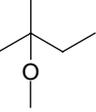
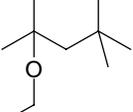
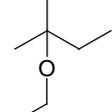
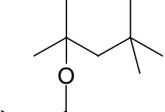
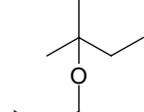
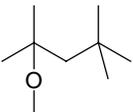
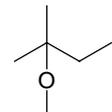
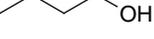
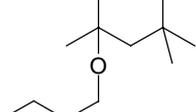
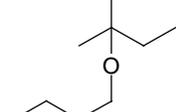
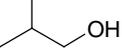
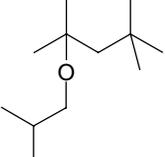
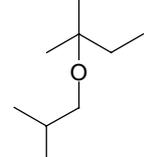
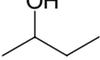
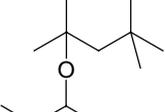
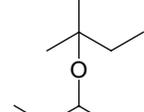
4. Etherification with various alcohols

The reactivity tests of the various alkenes were carried out with methanol. In addition, the reactivity of 2,4,4-trimethyl pentene was tested with other alcohols. Pure 2,4,4-trimethyl-2-pentene was chosen as a reactant for this study instead of the alkene mixture to allow study of the isomerisation. Altogether seven alcohols – methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol and isobutanol – were tested. For comparison, study was made of the reaction of 2-methyl-1-butene (2M1B) with these same alcohols [VI]. Table 9 shows the ether molecules formed from TMP2 and 2M1B and the various alcohols.

The etherification and isomerisation results were compared as a function of carbon number, acidity and polarity of the alcohols. These properties were chosen because they are thought to affect the etherification mechanisms and the reactivity of the alcohols and ion exchange resin catalysts [24, 47, 48]. It was observed that these properties could be used to predict the reactivities of alcohols.

Among the primary alcohols, both etherification and isomerisation rate increased as a function of increasing carbon number and acidity and decreasing polarity. The ratio of isomerisation to etherification (I/E ratio) increased with the same trends. The I/E ratios were much greater with the secondary alcohols than the primary ones. Since the isomerisation rate was in the same order of magnitude with the primary alcohols of the same size, this was caused by the almost total absence of etherification. It was concluded that the etherification reactivity of alcohols decreases sharply in the order primary > secondary > tertiary. The smallest tertiary alcohol, *tert*-butanol (2-methyl-2-propanol) is unreactive in etherification under the studied conditions [28].

Table 9. Ether molecules formed from TMP2 and 2M1B with various alcohols

Alcohol	Ether from TMP2	Ether from 2M1B
 methanol	 2-methoxy-2,4,4-trimethyl pentane	 2-methoxy-2-methyl butane (TAME)
 ethanol	 2-ethoxy-2,4,4-trimethyl pentane	 2-ethoxy-2-methyl butane (TAEE)
 1-propanol	 2,4,4-trimethyl 2-propoxy pentane	 2-methyl-2-propoxy butane
 2-propanol	 2-isopropoxy-2,4,4-trimethyl pentane	 2-isopropoxy-2-methyl butane
 1-butanol	 2-butoxy-2,4,4-trimethyl pentane	 2-butoxy-2-methyl butane
 iso-butanol	 2-isobutoxy-2,4,4-trimethyl pentane	 2-isobutoxy-2-methyl butane
 2-butanol	 2,4,4-trimethyl-2-(1-methylpropoxy) pentane	 2-methyl-2-(1-methylpropoxy) butane

The alcohol was observed to have a strong effect on the isomerisation, although it did not directly react in the isomerisation reaction. A possible reason for this effect is that the reaction mechanism includes an interaction between alkene and alcohol, and the alcohol is needed to activate the alkene towards reaction. However, isomerisation of alkenes also occurs in the absence of alcohols [e.g. V], and alcohol has been observed to inhibit the reaction rate of alkene [e.g. I, V, 36]. Thus, the effect of alcohol on the isomerisation rate more probably is related to its polarity: more polar components adsorb more strongly on the ion exchange resin catalysts [49] and this limits the adsorption of less polar components. Thus, in the presence of more polar alcohols the reaction rate of alkenes is suppressed because fewer alkene molecules are able to adsorb on the catalyst. As the polarity of the reaction mixture decreases more alkene molecules reach the catalyst and the etherification rate and especially the isomerisation rate increase. The limiting case is a reaction mixture where no alcohol is present, and it was observed that in shifting towards alcohols of lower polarity, the total reaction rate approached the rate in the total absence of polar components, i.e. pure isomerisation [V]. The effect of polarity is illustrated in Figure 3, where the total reaction rate of TMP2 is plotted as a function of the dielectric constant of the alcohol, which is a measure of polarity. The same trend was observed with isoamylenes [VI].

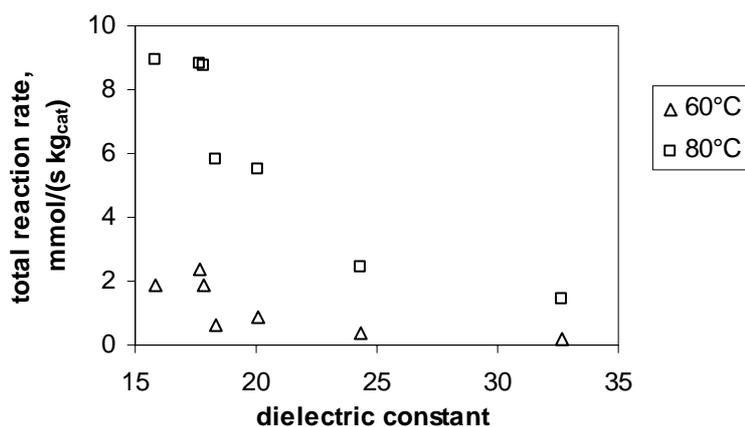


Figure 3. Reaction rate of TMP2 as a function of polarity of the alcohol.

It has been suggested that polarity of the reaction medium may determine the activity of the catalyst by influencing the number of accessible sites and their acidity [50]. In the ion exchange resin the sulfonic acid groups are linked by a network of hydrogen bonds [51]. A network of acid groups solvated by hydrogen-bonded alcohol has been observed to be catalytically much less effective than the original network of acid groups themselves, because the polar components break into the strong hydrogen bonded network, cause the protons of the acid groups to be dissociated, and reduce the proton donor-acceptor strength of the network [51]. The accessibility and number of active sites are influenced by the swelling of the ion exchange resin matrix, which is favoured by higher polarity of the reaction mixture [52]. A certain degree of swelling is required to open the catalyst pores. In our experiments the total rate increased as a function of decreasing polarity (see Figure 3) and thus it can be concluded that the accessibility of the active sites was not limiting on the reaction rate.

5. Comparison of catalysts

The etherification of C₈-alkenes with Amberlyst 35 ion exchange resin was slow compared with the etherification of smaller alkenes, such as isoamylenes [I]. A novel catalyst, Smopex-101 (Smoptech Ltd.), was tested in an attempt to increase the reaction rate of the C₈-alkenes [IV].

Studies with 2,4,4-trimethyl pentenes, which were chosen as model components for the more detailed study, indicated internal diffusional limitations on Amberlyst 35 [I]. It was expected that elimination of these limitations on the novel catalyst might enhance the reaction rate.

5.1 Properties of Amberlyst 35 and Smopex-101

Conventionally, the etherification of alkenes has been catalysed by strong cationic ion exchange resins. Structurally these commercial resins are sulfonated copolymers of styrene and divinyl benzene [53]. The catalyst particles are spherical beads and the active sulfonic acid groups are distributed throughout the catalyst. Crosslinking makes the structure of the particles stiff but limits the mobility of the molecules inside the catalyst particles.

Internal diffusion in the pores of beads, especially in the case of larger molecules, is not very well understood. The diffusion paths may become quite long in spherical porous particles. Furthermore, alcohol swells the resin matrix and changes the nature and accessibility of the active sites [53], and thus the availability of the active sites of the catalyst is often somewhat obscure.

Smopex-101 is a novel ion exchange fibre. Because of the dimensions of the fibre (see Table 10) the diffusion paths are shorter in the fibrous catalyst and the mass transfer of the reactants is substantially easier than it is in the pores of traditional catalyst beads.

The Smopex-101 catalyst is a polyethylene-based fibre that is grafted with styrene which are sulfonated with chloro sulfonic acid [54]. As in the Amberlyst resins, the active group in Smopex-101 is sulfonic acid. The properties of Amberlyst 35 and Smopex-101 are compared in Table 10.

Table 10. Properties of Amberlyst 35 and Smopex-101

	Amberlyst 35	Smopex-101
shape	beads	fibres
matrix	styrene-divinyl benzene	polyethylene
size	diameter 700-950 μm	length 0.25-4 mm diameter appr. 30 μm
capacity, mmol/g	5.2	up to appr. 4.0 (tested 1.0; 3.0; 3.6; 3.75; 4.0)
active group	sulfonic acid	sulfonic acid

Although Smopex-101 is a relatively new catalyst, some studies on its activity have already been published [55]. In the esterification reaction of acetic acid with methanol, Smopex-101 was considerably more active than Amberlyst 15.

5.2 Etherification rates

Smopex-101 and Amberlyst 35 were compared in the reaction between 2,4,4-trimethyl pentene mixture and methanol, and also in the etherification reaction of isoamylenes (mixture of 2-methyl-1-butene and 2-methyl-2-butene) to produce TAME. The Smopex-101 catalyst (capacity 3.0 mmol/g) was more active in the etherification of 2,4,4-trimethyl pentenes, and Amberlyst 35 was more active in the case of the isoamylenes [IV]. The etherifications with the catalysts at 80°C are compared in Figure 4.

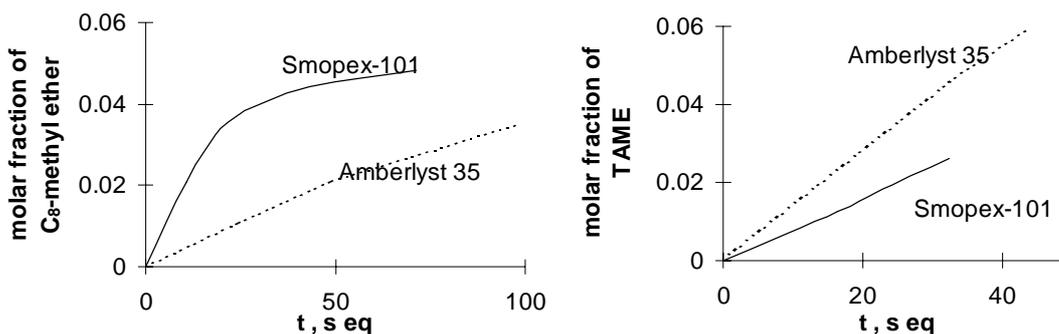


Figure 4. Comparison of formation of *C*₈-methyl ether (2-methoxy-2,4,4-trimethyl pentane, on left) and TAME (on right) with Amberlyst 35 and Smopex-101 catalysts.

The activation energy for the ether formation from 2,4,4-trimethyl pentenes with Smopex-101 catalyst was 90 kJ/mol [IV], a typical value for the formation of tertiary ethers (see Table 7). Comparison of this value with the value of 60-65 kJ/mol obtained with Amberlyst 35 (see Table 6), allows the conclusion that, indeed, internal diffusion plays an important role in the reaction of 2,4,4-trimethyl pentenes with Amberlyst 35. On the other hand, activation energies for the formation of the other two *C*₈-methyl ethers on Amberlyst 35 included in Table 6 are very similar to the value obtained for 2,4,4-trimethyl pentenes with the fibrous catalyst. This suggests that the diffusional limitations on Amberlyst 35 are caused by the branched and bulky structure of the trimethyl pentenes.

Comparison of the etherification results of 2,4,4-trimethyl pentenes and isoamylenes indicates that, in general, Amberlyst 35 is a very active catalyst in etherification. However, in the case of larger and branched molecules such as 2,4,4-trimethyl pentenes the diffusion in Amberlyst 35 has a noticeable depressing effect on the reaction rates, and use of the fibrous Smopex-101 catalyst with its minor diffusional resistance becomes advantageous [IV]. However, the activity of the Amberlyst 35 increased when it was crushed, but the rate did not reach that of Smopex-101. When the particle size of Amberlyst 35 was decreased from 700 μm to 200 μm the etherification rate of 2,4,4-trimethyl pentenes increased 18%.

The structure of the fibre strongly affects the activity of the catalyst. For example, the acid capacity of the fibre plays an important role: fibres with low acid capacity are relatively less active, and a certain minimum capacity is needed to ensure proper activity [IV]. The relationship between the reaction rate and acid capacity of the catalyst has also been observed in MTBE synthesis with various ion exchange resins as catalysts [56].

It has been suggested that the reactive component occupies more than one active site on the catalyst in accomplishing an etherification reaction [e.g. 48, 57-58]. The different behaviour of 2,4,4-trimethyl pentenes and isoamylenes may thus also mean that the active sites are more favourably situated on the fibre to bring about the reaction with 2,4,4-trimethyl pentenes, and those on the beads are more favourably situated for isoamylenes.

5.3 Effect of water

Water has a marked decreasing effect on the initial rate of etherification. Water present in the reaction mixture as impurity reacts quickly with alkene to form tertiary alcohol. Thus the initial formation of tertiary alcohol is a good indication of the presence of water in the reaction mixture. In addition to consuming the alkene in an undesired reaction, water also produces two different effects on the resin because of its polarity [50]. First, as a very polar compound water competes with the reactants for the active centres and adsorbs strongly on the ion exchange resin [49]. Second, water solvates the acidic protons of sulfonic groups by breaking the hydrogen bond network, with the result that more catalytic centres become accessible to the reactants. However, the solvated protons are less acidic, which generally yields a lower reaction rate [59]. Alcohols have the same effects, but as water is much more polar than the alcohols the effect is stronger (dielectric constant of water 78 and methanol 32.6).

As seen in Figure 5 the reaction rate decreased more rapidly as a function of water content and the effect of water on the reaction rate was stronger with Amberlyst 35

than Smopex-101. Most of the water originated from the catalyst. Thus proper handling and storage of the catalyst and reactants are of utmost importance to keep the system as dry as possible. When water-containing reactants, such as azeotropic mixture of ethanol and water, are used the water present in the mixture tends to react first [37, 60].

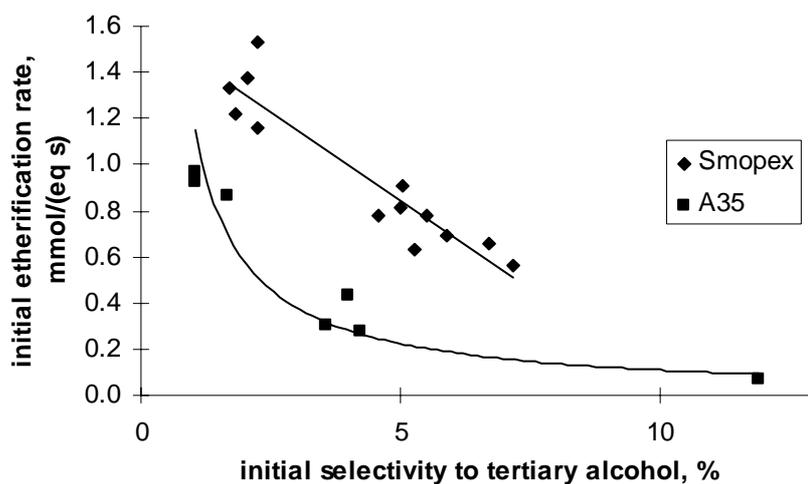


Figure 5. Effect of water: influence of initial formation of tertiary alcohol on the etherification rate with Smopex-101 and Amberlyst 35 catalysts.

6. Kinetic model for the etherification of 2,4,4-trimethyl pentenes with methanol

A kinetic model for the etherification of 2,4,4-trimethyl pentenes with methanol was derived for the purposes of reactor design. The model was derived for the temperature range 60–90°C and Smopex-101 was used as the catalyst because of lower internal diffusion limitations [IV].

The kinetics of etherification of C₄- to C₆-alkenes has been studied fairly widely, and Eley-Rideal type (e.g. MTBE [61], ETBE [39], TAME [62] and TAEI [17]) and Langmuir-Hinshelwood type (e.g. ETBE [63], TAME [64], TAEI [18], THEE [19]) reaction mechanisms have generally been proposed. To our knowledge, no kinetic studies on the etherification of C₈-alkenes have been published.

Experiments were performed with four different feeds – the mixture of 2,4,4-trimethyl pentenes, pure TMP1, pure TMP2 and ether (2-methoxy-2,4,4-trimethyl pentane) – and molar fractions of reactants were varied. Since both the isomerisation and etherification reactions are limited by thermodynamic equilibrium, the thermodynamic parameters for the isomerisation and etherification reactions were determined prior to the kinetic modelling.

6.1 Thermodynamic parameters of isomerisation

The isomerisation reaction of TMP1 to TMP2 was studied separately without alcohol [V]. In the absence of alcohol the reaction was substantially faster, and the equilibrium state was reached quicker than the respective equilibrium state in the etherification experiments. Furthermore, oligomerisation and isomerisation of methyl substituents were observed as side reactions, which did not occur in the presence of methanol. On the basis of these observations, and additionally because the reaction was too fast for reliable measurement of the initial isomerisation rate in differential conditions at higher

temperatures, kinetic analysis was not performed for the isomerisation reaction of alkenes based on these experiments.

The thermodynamic parameters were determined at 50–110°C. Although the etherification kinetics was determined with Smopex-101 catalyst, the isomerisation experiments were catalysed with Amberlyst 35, as the catalyst does not contribute to the thermodynamics. Reference runs with Smopex-101 confirmed that the equilibrium composition was the same as with Amberlyst 35. Pure alkenes, TMP1 and TMP2, were used as reagents, which means that the equilibrium composition was approached from both directions. The final compositions of the reaction mixture (see Figure 6 at 80°C) were the same within experimental error for the two feeds at each temperature, and thus the thermodynamic equilibrium constants for this isomerisation reaction can reliably be calculated from the results.

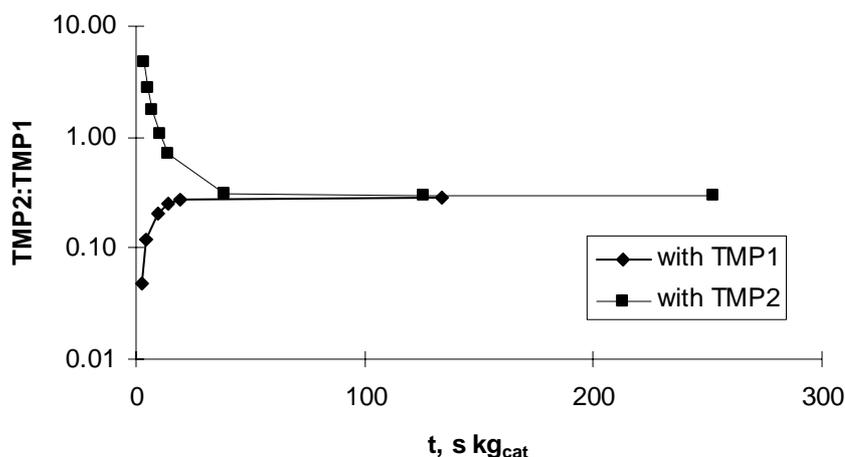
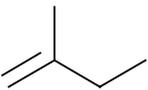
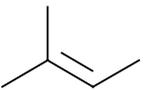
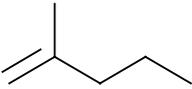
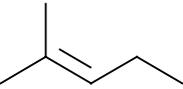
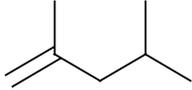
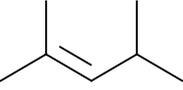


Figure 6. The molar ratio of TMP2:TMP1 as a function of contact time in isomerisation reactions at 80°C.

Equilibrium constants were calculated on both molar and activity basis. Although the values did not differ significantly, the reaction mixture in etherification is highly non-ideal and activity values must be used in the kinetic model of etherification. Reaction enthalpy and entropy were calculated from the equilibrium constants and a reaction enthalpy of $3.51 \pm 0.03 \text{ kJ mol}^{-1}$ and entropy of $-0.47 \pm 0.10 \text{ J mol}^{-1} \text{ K}^{-1}$ were obtained

[V]. Compared with the isomerisation of similar alkenes the reaction enthalpy differs substantially: here the isomerisation reaction of TMP1 to TMP2 is endothermic, whereas most reported isomerisations of α -alkene to β -alkene have been exothermic. Another distinct deviation is the excess of α -alkene in the thermodynamic equilibrium, rather than β -alkene as is usually reported (see Table 11). The reason for this behaviour lies in the molecular structure of the branched trimethyl pentenes.

Table 11. Alkene isomers structurally similar to 2,4,4-trimethyl pentenes, where the general rule of alkene stability is obeyed [65]

Less stable, less substituted	More stable, more substituted	$\Delta_R H^0$ (273K), kJ/mol [65]	
	\rightleftharpoons		-7.6
	\rightleftharpoons		-20.3
	\rightleftharpoons		-6.1

The general rule for the stability of alkene isomers states that the more substituted isomer is more stable [66]. Thus, in our case TMP2, as a trisubstituted alkene, should be more stable than the disubstituted TMP1. But here we encounter an exception to the rule: the more highly substituted alkene (TMP2) has considerable internal repulsion arising from the large *tert*-butyl group located in *cis*-position to the methyl group, and the less substituted TMP1 is the major product in the thermodynamic equilibrium.

The cause of the internal tension can be explained as follows. The double bond is rigid and shorter than a single bond. The neighbouring atoms form a plane around the double bond and in the case of TMP1, in addition to the two carbons attached to the double

bond, there are two carbon atoms and two hydrogen atoms in the plane. In TMP2, three carbon atoms and one hydrogen atom form the plane. TMP2 is trisubstituted and the largest substituent – the *tert*-butyl group – and one methyl group lie on the same side of the double bond, i.e., in *cis*-position with each other. The *tert*-butyl group is highly branched, which means that this side of the double bond becomes highly crowded, creating repulsion forces between the *tert*-butyl and methyl substituents. In the case of TMP1, the largest substituent is in *cis*-position with a hydrogen, which occupies much less space. Also, in TMP1 the bulky *tert*-butyl group is further away in the β -position to the double bond.

6.2 Thermodynamic parameters of etherification

The thermodynamics of etherification of trimethyl pentenes was determined at 50–110°C. Again, the equilibrium composition was approached from two directions: by the formation of ether from alkenes and methanol and by decomposition of ether. The equilibrium constants were determined with the compositions at equilibrium state, and the reaction enthalpies and entropies, which are presented in Table 12, were determined from the equilibrium constants. Both ether formation reactions were exothermic, as has been reported for similar ethers, e.g. MTBE ($\Delta_R H^0 = -37.3$ kJ/mol [67]), ETBE ($\Delta_R H^0 = -34.8$ kJ/mol [67]) and TAME ($\Delta_R H^0 = -26.8\dots-33.6$ kJ/mol [16]).

Table 12. Thermodynamic parameters for the reactions of 2,4,4-trimethyl pentenes

	$\Delta_R H^0$, kJ/mol	$\Delta_R S^0$, J/(mol·K)
etherification of TMP1	-18.9 ± 1.2	-71.5 ± 3.5
etherification of TMP2	-22.8 ± 1.7	-72.6 ± 4.9
isomerisation TMP1 \leftrightarrow TMP2	3.5 ± 0.1	0.47 ± 0.1

Since the two etherification reactions and the isomerisation reaction constitute a reaction triangle, their thermodynamic properties are not independent of each other. Thus, to minimise the error in the kinetic modelling, parameters of two of the reactions

were chosen to define the parameters of the third reaction. The reliability of the results was evaluated by studying the mass balances and by repeating the experiments, and it was concluded that the methanol analysis was the least reliable, and the equilibrium constant for the isomerisation reaction (K_3) was the most reliable. Since the numerical value of the equilibrium constant of the etherification of TMP1 (K_1) is smaller than that of TMP2 (K_2), the numerical error in the modelling is smaller when the equilibrium constant of the etherification of TMP1 is determined through the other two reactions, and the final equilibrium constants for the kinetic model are

$$K_1 = K_2 \cdot K_3$$

$$K_2 = \exp\left(2740.7 \frac{1}{T} - 8.74\right)$$

$$K_3 = \exp\left(421.67 \frac{1}{T} - 0.056\right)$$

6.3 Kinetic model

Eley-Rideal type and Langmuir-Hinshelwood type kinetic models were tested to describe the etherification of the trimethyl pentenes [VII]. Because of the high non-ideality of the reaction mixture, the models were derived in terms of activity.

The results showed only minor differences between the models and all models resulted in physically meaningful parameters. The best models to describe the data were the Langmuir-Hinshelwood type model in which the adsorption of alkenes was assumed to be weak compared to methanol and ether, and the Eley-Rideal type model according to which the alkenes reacted without adsorption. Activation energies of 86-94 kJ/mol and 80-90 kJ/mol were obtained for the etherification of TMP1 and TMP2, respectively, and 101-137 kJ/mol for the isomerisation reaction. These values are in good agreement with published values for similar kinds of reaction systems (see Table 7). This indicates that internal diffusion, which would lower the activation energies, is not relevant in our system. Inspection of the activation energies of the C₈-methyl ethers listed in Table 6 suggests that diffusional limitations are present when 2,4,4-trimethyl pentenes are

reacted on Amberlyst 35, but the reactions of more linear C₈-alkenes on Amberlyst are not affected by internal diffusion.

Adsorption constants were not modelled as such, but instead the ratios of constants. The adsorption constant ratio of ether to methanol, $K_{\text{eth}}/K_{\text{MeOH}}$, was modelled to be approximately 2.5, which means that more ether than methanol is adsorbed on the catalyst. With the traditional etherification catalysts, ion exchange resin beads, more methanol is adsorbed. Ion exchange resin and fibre were compared earlier in section 5.1 and the different behaviour of the catalysts could be explained in terms of their hydrophilic properties. Both the polyethylene (fibre) and styrene-divinyl benzene (beads) matrices are hydrophobic, but the sulfonic acid, which is present in both, has hydrophilic properties. Some parts of the polyethylene matrix are amorphous and some parts crystalline, and it has been demonstrated that the grafting reaction occurs in the amorphous region [68]. Thus when the grafted styrene is sulfonated, the sulfonic acid sites are located solely in the amorphous region. Although the catalyst is heated during the sulfonation, and the crystalline parts become amorphous, this has no effect on the sulfonic acid distribution because only the grafted styrene is sulfonated. Thus, the parts of the polyethylene matrix that originally were crystalline remain hydrophobic, while the sulfonated parts are hydrophilic. In the resin matrix, in turn, no differences should exist between the various parts of the matrix. Another difference between the fibre and the resin is how the sulfonic acid is attached to the matrix: in the fibre the polyethylene is grafted with styrene and the grafts are sulfonated, but in the resin the styrene-divinyl benzene matrix itself is sulfonated. For these reasons the surface of the resin is likely to be more hydrophilic, but the fibre contains more hydrophobic parts, and ether, which is less polar, reaches the fibre more easily than the more polar methanol. Thus the ether adsorbs more readily on the fibre and the ratio of the adsorption constants, $K_{\text{eth}}/K_{\text{MeOH}}$, obtains a value greater than one.

The adsorption constant ratio of alkene to methanol, $K_{\text{TMP}}/K_{\text{MeOH}}$, was included only in the Langmuir-Hinshelwood type models. Since the estimations indicated that the ratio was relatively small (appr. 0.1), the adsorption term of the alkenes was omitted from

the model, and the best fit was then obtained. The improvement in the statistics of the fit most probably was due to the decrease in the number of fitted parameters because the numerical values of the other parameters remained more or less the same. It can be concluded that, according to this model, the alkenes are adsorbed on the catalyst, but since the adsorption is weaker than the adsorption of other reactive components, it can be omitted from the model.

All of the kinetic models predicted the measured data in equal manner, as can be seen in Figure 1 of paper VII. The data points follow the same trends in each model. A similar observation was made in MTBE synthesis, and it has been suggested that one way to improve the fit of the kinetic model of the etherification is to introduce a solubility parameter [48, 50], which takes into account the reaction medium polarity, variations in the resin structure and acidity of the active sites. However, this parameter was not used in our modelling.

7. Conclusions

C₈-Alkenes were screened for their reactivity in etherification. 2,4,4-Trimethyl pentenes, 2-methyl heptenes and 2-ethyl-1-hexene were etherified with methanol and with Amberlyst 35 as catalyst. All alkenes reacted to the respective methyl ether and, at the same time, double bond isomerisation of alkenes occurred. Determination of selected properties of the ethers indicated their potential as gasoline components. 2-Ethyl-1-hexene produced a novel tertiary ether whose synthesis has not been reported in the literature prior to our studies.

The etherification of trimethyl pentenes was of particular interest. Trimethyl pentenes can be produced from isobutene, and if the production of MTBE in the United States is reduced, as currently seems possible, the isobutene feed stock could be used instead for dimerisation to trimethyl pentenes. In view of this, a kinetic model for etherification of the 2,4,4-trimethyl pentenes was developed for purposes of reactor design.

In addition to etherification, also the isomerisation reaction of 2,4,4-trimethyl-1-pentene to 2,4,4-trimethyl-2-pentene was studied and the reaction was proved to be endothermic. The α -alkene, 2,4,4-trimethyl-1-pentene, was in excess in the thermodynamic equilibrium composition, contrary to the general rule of alkene stability, which states that the more substituted alkene should predominate in the thermodynamic equilibrium state. This behaviour is due to the highly branched and bulky structure of the trimethyl pentenes, which creates internal repulsion forces in the molecule.

The reaction rate of the alkenes was markedly affected by methanol: the reaction rates were about ten times as fast when no methanol was present in the reaction mixture as when methanol was present in stoichiometric ratio. The effect of alcohol was studied further when trimethyl pentenes were etherified with seven C₁- to C₄-alcohols. The rates of both etherification and isomerisation increased as a function of decreasing polarity. Alcohol thus affected the isomerisation reaction of the alkenes, even though it

did not take part in it. The effect of polarity can be explained by the stronger adsorption of more polar components on the catalyst, which hinders the reactions of other components.

The reaction rate was clearly slower in the etherification of C₈-alkenes than for the commercially produced ethers. The relatively slow reaction rate was enhanced with use of a novel Smopex-101 catalyst. The fibrous structure of Smopex-101 suggests the existence of less diffusional resistance than with the traditional ion exchange resins. Indeed, the etherification rate of the branched C₈-alkenes was clearly faster, and the activation energies for the etherification of 2,4,4-trimethyl pentenes were higher with Smopex-101 than with Amberlyst 35, which again indicates the more severe mass transfer limitations with Amberlyst 35. Accordingly, the kinetic model for the etherification of 2,4,4-trimethyl pentenes with methanol was developed with Smopex-101 as catalyst.

The kinetic models that best described the etherification reaction of 2,4,4-trimethyl pentenes with methanol were the Langmuir-Hinshelwood type model in which the adsorption of alkenes is assumed to be small relative to methanol and ether and the Eley-Rideal type model according to which the alkenes react without adsorption. The activation energies for the formation of ether were 86-94 and 80-90 kJ/mol from TMP1 and TMP2, respectively. The estimated adsorption constants indicate that ether is adsorbed more on the catalyst than methanol. This can be explained by the hydrophobic properties of the Smopex catalyst.

The formed ether, 2-methoxy-2,4,4-trimethyl pentane, proved to have high octane values. Also other properties must be taken into account when using the component in fuel, but in this respect 2-methoxy-2,4,4-trimethyl pentane is highly suitable to be used as gasoline component.

Abbreviations and IUPAC names

ETBE	ethyl <i>tert</i> -butyl ether (2-ethoxy-2-methyl propane)
eth	ether
isoamylenes	2-methyl-1-butene, 2-methyl-2-butene
isobutanol	2-methyl-1-propanol
isooctane	2,2,4-trimethyl pentane
MeOH	methanol
MON	motor octane number
MTBE	methyl <i>tert</i> -butyl ether (2-methoxy-2-methyl propane)
RON	research octane number
TAAE	<i>tert</i> -amyl ethyl ether (2-ethoxy-2-methyl butane)
TAME	<i>tert</i> -amyl methyl ether (2-methoxy-2-methyl butane)
TBA	<i>tert</i> -butyl alcohol (2-methyl-2-propanol)
THEE	<i>tert</i> -hexyl ethyl ethers (2-ethoxy-2-methyl pentane, 3-ethoxy-3-methyl pentane and 2,3-dimethyl-2-ethoxy butane)
TMP	2,4,4-trimethyl pentenes (2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene)
TMP1	2,4,4-trimethyl-1-pentene
TMP2	2,4,4-trimethyl-2-pentene
2E1H	2-ethyl-1-hexene
2M1B	2-methyl-1-butene
2M1H	2-methyl-1-heptene
2M2H	2-methyl-2-heptene

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